

## Chapter 3

# Spectroscopic Technique: Near Infrared (NIR) Spectroscopy

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## 1 INTRODUCTION

*Near-infrared (NIR) spectroscopy* dates back to the early 1800s when Fredrick William Herschel, a professional musician and astronomer (Herschel, 1800; Davies, 1991, 1998), discovered the first nonvisible region in the absorption spectrum (Stark et al., 1986). The period from 1800s to the 1950s was dormant for NIR spectroscopy and it took a backseat to other analytical methods that could deliver more unambiguous results, especially regarding the explanation of molecular structures (Williams and Stevenson, 1990). It was only with the work of Karl Norris and coworkers (Butler, 1983; Norris, 1996) later in the 1950s when its potential was recognized (Day and Fearn, 1982). Today, NIR

spectroscopy has become the *quality control* method of choice in the food and feed industry because of its advantages over other analytical techniques (Woodcock et al., 2008; Manley, 2014; Baeten et al., 2015).

NIR spectroscopy was originally limited to quantitative grain analysis but today *quantitative applications* are widely used in many fields (Table 1). Spectroscopic methods with specific reference to *NIR spectroscopy* have also been shown to have potential for *discriminatory studies* to determine the *authenticity of several foodstuffs* and food ingredients (Table 2).

*Food authenticity* issues, especially in terms of *adulteration* and incorrect labeling or description, have probably been around for as long as food has been offered for sale, with an authentic product being what it claims to be. In the recent past, food adulteration has, however, become more sophisticated (Karoui and De Baerdemaeker, 2007; Lohumi et al., 2015; Sørensen et al., 2016). Foods or food ingredients that are of high value and undergo a number of processing steps are most likely to be targets for adulteration, due to the opportunities available to, for example, replace high-quality ingredients with less expensive substitutes.

In European countries, several food products owe their reputation to traditional production techniques used in defined *geographical areas*. These artisan food products are therefore differentiated from other similar products (Karoui et al., 2005a) and may be labeled according to the specific conditions which characterize their origin and the processing technology used (Bosset et al., 1997). These are referred to as products with *Protected Designation of Origin* (PDO) or *Protected Geographical Indication* (PGI) and are often associated with high production costs; they may consequently be highly priced. This makes these products prone to adulteration with cheaper alternatives for economic reasons.

Identifying adulterated food products has generally been done in terms of their chemical composition and/or physical properties (Downey, 1998a, 1998b). Monitoring these properties is, however, not always practical. In addition, foods are chiefly or exclusively composed of naturally occurring biological material, the composition of which varies depending on variety, species, geographical origin, year of production, and manufacturing process used. This complexity of the food matrix makes the task of identifying adulterated products even more complicated.

The basic idea behind the *application of NIR spectroscopy* to solve *authenticity* problems relies on the generation of a spectroscopic fingerprint of foods (Downey, 1996a; Vermeulen et al., 2010, 2017). A food product with a given chemical composition exposed to *NIR radiation* will have a characteristic spectrum which is essentially the result of the absorption by various chemical constituents although physical properties may also have an impact on the NIR absorbance values. Because of the variation present in any natural material, the exact composition of any given batch or sample will vary somewhat, depending on the variety, season, and location; therefore, a range of typical spectra for this material will exist. For this reason, a

**TABLE 1** Fields of NIR Spectroscopy Quantitative Applications

Application	References
Cereals and cereal products	Osborne (1991), Wilson et al. (1991), Windham et al. (1993), Wesley et al. (1999), Cozzolino et al. (2000), and Bao et al. (2001)
Coffee	Pizarro et al. (2004)
Confectionary	Tarkošová and Čopíková (2000)
Dairy	Rodríguez-Otero et al. (1997), Wüst and Rudzik (2003), and Blazquez et al. (2004)
Distillation industry	Gomez-Cordoves and Bartolome (1993) and Manley et al. (2003)
Essential oils	Schulz et al. (1998, 2003b)
Fats and oils	Schulz et al. (1998), Moh et al. (1999) and Armenta et al. (2010)
Fruit and vegetables	Kawano et al. (1992), Schulz et al. (1998), Goula and Adamopoulos (2003), Xing et al. (2003), Walsh et al. (2004) and Manley et al. (2007)
Grapes	Cope (2000) and Esler et al. (2002)
Herbal products	Schulz et al. (2002, 2003a), Manley et al. (2004, 2006), and Joubert et al. (2005, 2006)
Honey	García-Alvarez et al. (2000)
Meat and fish	Downey (1996b), Wold and Isaksson (1997), Pink et al. (1999), Cozzolino and Murray (2004), Realini et al. (2004), and Prieto et al. (2009)
Melamine in milk	Balabin and Smirnov (2011) and Mauer et al. (2009)
Plant species	Ren and Chen (1997), Sato et al. (1998), Ren and Chen (1999), and Velasco et al. (1999)
Spreads and condiments	Iizuka and Aishima (1999)
Tea	Grant et al. (1988), Hall et al. (1988), Osborne and Fearn (1988), Schulz et al. (1999), Luypaert et al. (2003), Schulz (2004), Zhang et al. (2004), and Ren et al. (2013)
Wine and grapes	Baumgarten (1987), Chauchard et al. (2004), and Cozzolino et al. (2004)

library of representative spectra is needed to characterize any given food and the spectrum of material under investigation may be compared with this library in order to establish its quality or authenticity. While simple in concept, this comparison is not trivial and chemometric techniques are required for its realization.

**TABLE 2** Fields of NIR Spectroscopy Qualitative Applications

Application	References
Adulteration of extra virgin olive oils with sunflower oil	<a href="#">Downey et al. (2002)</a>
Adulteration of honey	<a href="#">Downey et al. (2003)</a> , <a href="#">Chen et al. (2011)</a> , <a href="#">Kumaravelu and Gopal (2015)</a> , <a href="#">Bazar et al. (2016)</a> , and <a href="#">Guelpa et al. (2017)</a>
Adulteration of maple syrup	<a href="#">Paradkar et al. (2002)</a>
Adulteration of milk	<a href="#">Sato et al. (1990)</a> , <a href="#">Sato (1994)</a> , <a href="#">Pedretti et al. (1993)</a> , and <a href="#">Ulbert (1994)</a>
Adulteration of milk with melamine	<a href="#">Lu et al. (2009)</a> and <a href="#">Dong et al. (2009)</a>
Adulteration of orange juice	<a href="#">Scotter et al. (1992)</a> and <a href="#">Shilton et al. (1998)</a>
Adulteration of wine	<a href="#">Ferrari et al. (2011)</a>
Adulteration of ground black pepper	<a href="#">McGoverin et al. (2012)</a>
Basmati and other long-grain rice samples	<a href="#">Osborne et al. (1997)</a>
Black teas of differing qualities and geographical origin	<a href="#">Osborne and Fearn (1988)</a> and <a href="#">Ren et al. (2013)</a>
Bread baking quality of different wheat varieties	<a href="#">Downey et al. (1986)</a> and <a href="#">Devaux et al. (1987)</a>
Classification of nuts	<a href="#">Moschetti et al. (2013)</a> and <a href="#">Vitale et al. (2013)</a>
Classification of plant species	<a href="#">Laasonen et al. (2002)</a>
Classification of processing methods	<a href="#">Schulz et al. (2003a)</a>
Classification of herbal plants	<a href="#">Wang et al. (2006, 2007)</a> and <a href="#">Mao and Xu (2006)</a>
Classification of commercial teas	<a href="#">Osborne and Fearn (1988)</a> and <a href="#">Budínová et al. (1998)</a>
Classification of wines	<a href="#">Cozzolino et al. (2003)</a>
Classification between frozen and frozen-then-thawed beef	<a href="#">Downey and Beauchêne (1997a, b)</a>
Classification between Robusta and Arabica coffee	<a href="#">Downey et al. (1994, 1997)</a> , <a href="#">Downey and Spengler (1996)</a> , and <a href="#">Pizarro et al. (2007)</a>
Edible oils and fats	<a href="#">Sato (1994)</a> , <a href="#">Hourant et al. (2000)</a> and <a href="#">Nunes (2014)</a>
Virgin olive oils from different geographical origins	<a href="#">Downey and Flynn (2002)</a>

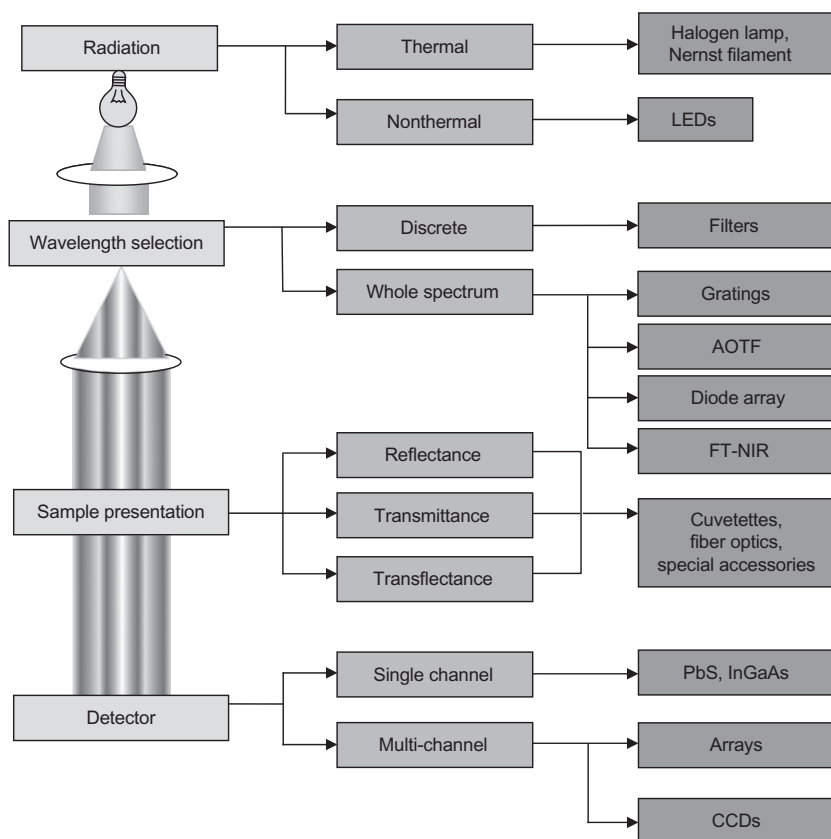
## 2 THEORY AND PRINCIPLES

The basic *principles of NIR spectroscopy* involve the production, recording, and interpretation of spectra arising from the interaction of electromagnetic radiation with matter (Osborne et al., 1993; Penner, 1994). The infrared (IR) region comprises that part of the electromagnetic spectrum in the wavelength range between 780 and 100,000 nm and is divided into near-IR, mid-IR, and far-IR subregions (Penner, 1994; Osborne, 2000); the NIR region covers the wavelength range from 780 to 2500 nm (Osborne, 2000). When compared with spectra collected in the mid-infrared (MIR) region, a NIR spectrum normally exhibits few well-defined, sharp peaks (Williams and Stevenson, 1990). *NIR spectra* of food constituents show broad bands which arise primarily from overtones and combinations of fundamental vibrations occurring in the MIR spectrum and, as a result, are one to three orders of magnitude weaker than the fundamental absorptions (Stark et al., 1986). MIR spectroscopy is typically used to determine the molecular composition of a sample.

If molecules in any given sample are illuminated by electromagnetic radiation in the NIR region, they will exhibit a large number of weak absorptions that will overlap, effectively creating broad absorption bands in the spectrum (Wetzel, 1983; Williams and Stevenson, 1990). This implies that *NIR spectra* are generated by chemically simple molecular groupings that have strong interatomic bonds; these typically are groups containing carbon (C), nitrogen (N), and oxygen (O) bonded to hydrogen (H), that is, the most common molecules found in food (Norris, 1989; Ciurczak, 1992; Downey, 1998a). A foodstuff illuminated by electromagnetic radiation will absorb radiation at certain frequencies through bonds formed between some of the atoms present in the product (Downey, 1995). By detecting this absorption, it is possible to describe the chemical composition of an unknown mixture or food product without knowing the specific molecular structure that is responsible for the vibrational energy absorption. Therefore, despite their obvious lack of observable and discriminant details, NIR spectra are rich in chemical and physical information about organic molecules and may therefore yield valuable information about the composition of a food product (Katsumoto et al., 2001). Although the differences in *NIR spectra* may often be too small to be noticeable by the naked eye, the true value of NIR spectroscopy as an analytical tool rests on the statistical and mathematical manipulation of the spectral data.

## 3 INSTRUMENTATION

During the last decade of the 20th century, great advances in *instrumentation* and data acquisition gave NIR spectroscopy a definite place among the other established analytical methods (Wetzel, 1998, 2001; Manley, 2014). When considering *NIR instrumentation*, a variety of possible configurations exist. These include discrete filter, *grating monochromator* and *acousto-optical*



**FIG. 1** Principal features of NIR spectroscopy instrumentation (AOTF, acousto-optical tunable filter; CCDs, charged-coupled devices; FT-NIR, Fourier transform near infrared; InGaAs, indium gallium arsenide; LEDs, light-emitting diodes; PbS, lead sulfide). (Reproduced with permission from Blanco, M., Villarroya, I., 2002. NIR spectroscopy: a rapid-response analytical tool. *Trends Anal. Chem.* 21 (4), 240–250. Copyright (2002) Elsevier Limited.)

tunable filter (AOTF) instruments as well as photodiode array and Fourier-transform interferometer systems (Osborne et al., 1993; Wetzels, 1998, 2001; Barton, 2002). All NIR instruments possess the same essential building blocks (Fig. 1): radiation source, wavelength selectors, sample presentation facility, and detector (Blanco and Villarroya, 2002).

### 3.1 Radiation Source

NIR radiation sources can be thermal or nonthermal. The thermal sources consist of a radiant filament producing thermal radiation, for example, the Nernst filament (a heated ceramic filament containing rare-earth oxides) or quartz-halogen lamps, and produces radiation which may span a narrow or wide range

of frequencies in the NIR region (Osborne et al., 1993). Tungsten-halogen lamps are usually employed as thermal radiation sources, while nonthermal sources consist of discharge lamps, light-emitting diodes (LEDs), laser diodes, or lasers and emit much narrower bands of radiation than the thermal sources (McClure, 2001). Nonthermal sources are the more efficient of the two types because most of the energy consumed appears as emitted radiation over a narrow range of wavelengths; they can be electronically adjusted, thus simplifying the design of the instrument and reducing its power consumption (Osborne et al., 1993).

### 3.2 Wavelength Selectors

NIR spectrophotometers can be distinguished on the basis of *wavelength selection*, that is, discrete wavelength or continuous spectrum. A discrete wavelength spectrophotometer irradiates a sample with only a few wavelengths selected using filters or LEDs (McClure, 2001; Blanco and Villarroya, 2002). *Filter instruments* are designed for specific applications in specific spectral regions; usually between six and twenty interference filters are chosen to select wavelengths that will be absorbed by certain molecular species in a specific application (Penner, 1994). These are generally the easiest to use and least expensive instruments (Osborne, 2000).

*Continuous spectrum NIR instruments* may include a diffraction grating or be of the diode array, *AOTF* or Fourier transform near infrared (FT-NIR) type. Such instruments are even more flexible than discrete wavelength instruments and can be used in a wider variety of measurements (McClure, 2001; Blanco and Villarroya, 2002).

The purpose of a *grating monochromator* is to spread out radiation according to the wavelength (McClure, 2001). Instruments incorporating a monochromator can be used in either transmittance or reflectance mode depending on sample type; such equipment is normally used in a research environment when a wide range of different applications is required or when spectral information from a wide range of wavelengths is necessary for the development of an accurate and stable calibration (Osborne, 2000).

In *diode array* technology, all wavelengths are measured simultaneously as each wavelength has a dedicated detector (McClure, 2001). This allows analysis of moving samples such as a rotating sample cell or online applications. Diode array NIR instruments do not use any moving optical parts which greatly improves instrument stability.

*AOTFs* generate discrete wavelengths across an extended range by using radio frequency signals to change the refractive index of a crystal, usually tellurium dioxide (TeO<sub>2</sub>) (McClure, 2001; Blanco and Villarroya, 2002). The crystal behaves as a longitudinal diffraction grating with a periodicity equal to the wavelength of sound across the material (Osborne, 2000). The main advantage of *AOTF instruments* over *grating instruments* is their mechanical

simplicity, that is, no moving parts, thereby ensuring more reliable, reproducible wavelength scans (Osborne, 2000; Blanco and Villarroya, 2002). This makes AOTF instruments especially suitable for applications involving hazardous or harsh conditions such as in production plants.

The *Michelson interferometer* (FT-NIR type) splits light into two beams and then recombines them after a path difference has been introduced to create the conditions for optical interference (Osborne et al., 1993; Wetzel, 2001). Simultaneous measurements of all wavelengths allow the light to be imaged onto one detector making it a multiplexing instrument. The *polarization interferometer*, unlike most instruments, works with polarized light (Ciurczak, 2005). The actual interferometer consists of a moving crystalline wedge which acts as the wavelength selector and, because only a single beam passes through the instrument, the precision alignment required for the Michelson interferometer is avoided. Fourier transform NIR instruments, with special reference to their application in authentication of agro-food products, are discussed in more detail in Chapter 4.

### 3.3 Sample Presentation Modes

One of the practical strengths of NIR spectroscopy is the wide variety of different *sample presentation* options which are readily available, making it possible to apply NIR spectroscopy to a wide range of sample types (e.g., liquids, slurries, powdered or solid samples, and gasses). These sample presentation options normally involve the use of separate, detachable accessories and include the option of using fiber-optic probes for spectral acquisition from remote sites within a large industrial complex, for example, petrol refineries and pharmaceutical production facilities (Osborne, 2000).

If the Lambert-Beer law equation (Osborne et al., 1993) is used to describe the contributing factors of the absorbance values of a spectrum at any wavelength, it will be a function of the pathlength through which the light travels and the concentration of the constituent being measured (Wetzel, 1998). For *transmittance* measurements of liquids, the pathlength is a constant determined by the thickness of the sample cuvette. This is, however, not the case for *diffuse reflectance* with changes in both pathlength, due to light scatter, and concentration.

The *scattering of light* as it passes into a granular sample is caused by interaction with a variety of angular surfaces from which the light is reflected specularly. Specularly reflected light contains no information about the composition of a sample and may be redirected back along the path of incidence to the detector; scattering increases the intensity of light returning to the detector but also increases the variability of the baseline due to the variable pathlength of individual photons of light (Wetzel, 1998). This effect describes the detection, by diffuse reflectance, of light that is a combination of both absorbed (interaction with the sample) and scattered light (no interaction with the sample)



(Wetzel, 1983). It can have a large influence on the spectrum generated since the ratio between reflected light (absorbed and scattered) and incident light determines the absorption profile. *Sample presentation* is therefore extremely important in order to minimize light scatter and, as far as possible, keep the level of *scattering* constant for each sample (Wetzel, 1983; Williams and Stevenson, 1990).

The *influence of the particle size* of granular samples on acquired spectra may be attributed to Rayleigh (elastic) scattering (Wetzel, 1983). The coarser the sample matrix, the lower the reflectance and greater the difference between the spectrum and the baseline will be. Although this effect may be of great practical value to discriminate between coarse and fine samples, it is generally a measurement complication that may be compensated for by baseline corrections which may also increase the relative size of small peaks and enlarge minor differences in large peaks (Wetzel, 1983, 1998).

### 3.3.1 Transmittance and Diffuse Transmittance Modes

In *transmittance* measurements, reflection is generally significantly reduced so that the proportion of radiation attenuated by the sample may be measured as transmittance (Osborne, 2000). Proportionality between transmittance, the concentration of the absorbing component and the sample pathlength is described by the Lambert-Beer law. Since the pathlength for the specific sample may be fixed by means of a static or flow-through sample cell or a set of fiber-optic probes, the absorbance is linearly related to the concentration of absorbing component and a calibration may be developed using standard samples. The Lambert-Beer law may only be used for clear, transparent liquid samples when there is no light scattering because scattering changes the pathlength through which the radiation passes and the amount of scattering varies from sample to sample. When a sample like liquid whole milk is used, fat globules in the milk will significantly scatter incident light (which is what makes milk appear white and opaque) and thereby cause the Lambert-Beer law to be invalid. Measurements made under these conditions are described as *diffuse transmittance* (Coventry, 1988; Osborne, 2000); the wavelength region normally used for diffuse transmittance measurements is 700–1100 nm on the basis of the greater energy (and therefore penetrating power) of NIR radiation in this wavelength range. Diffuse transmittance measurements are normally used in the analysis of liquid samples but may also be used to measure solid samples such as meat, cheese, and whole grains (Penner, 1994).

### 3.3.2 Diffuse Reflectance Mode

*Diffuse reflectance* measurements are used in the analysis of solid or granular samples (Penner, 1994; Osborne, 2000). A major complication in the analysis and interpretation of diffuse reflectance measurements, which are arguably numerically the most important NIR measurements collected, is *light scatter*.

*Scattered light* contains little or no information about the chemical composition of any given particulate sample (although it can facilitate the description of physical properties) and interferes, through baseline and intensity effects, with the spectral information collected. Attempts have been made to develop a mathematical basis to describe light scatter and to accommodate its effects on NIR spectra but no completely successful strategy has been forthcoming—this has resulted in the study of spectral pretreatment methods such as *multiplicative scatter correction* (MSC) (Geladi et al., 1985), derivatization (Osborne, 2000), and the *standard normal variate* (SNV) transform (Barnes et al., 1989) among others to address this problem.

### 3.3.3 Transflectance Mode

Reflectance and transmittance modes can be combined to form a *transflectance* mode (Osborne, 2000) which can be used to analyze liquids (turbid or clear) by placing the sample between a quartz window in a sample cell and a diffusely reflecting, for example, gold-plated metal plate. Incident radiation is transmitted through the sample, reflected from the diffusely reflecting plate, and then transmitted back through the sample. In the case of a turbid sample, some radiation will be scattered as it travels through the sample and this scattered light will then also travel back with the light reflected from the transflectance cover (Stark et al., 1986). Minimization of spectral interferences thus arising can be achieved through good instrument design as regards detector placement.

### 3.3.4 Interactance Mode

Transmittance and reflectance can also be combined to form an *interactance* mode that will illuminate and detect radiation at laterally separated points on the surface of a sample; fiber-optic probes are often used for such applications which find important applications in, for example, the analysis of large samples such as whole fruit.

## 3.4 Detectors

IR *detectors* can be differentiated according to their spectral response, their speed of response, and the minimum amount of radiant power that they can detect (McClure, 2001). There are two broad categories of IR detectors which differ in their operating principles, namely thermal detectors and photon detectors; the latter are used in NIR applications (Osborne et al., 1993). For photon detectors, it is necessary for the incident radiation to be strong enough to liberate charge carriers from either the crystal lattice (intrinsic detectors) or from impurities intentionally added to the host crystal during the manufacturing process (extrinsic detectors) (McClure, 2001).

The detection devices most widely used for NIR analysis can be divided into *single and multichannel detectors*. Single channel detectors comprise lead-salt

semiconductors. Lead sulfide (PbS) is used over the range 1100–2500 nm, epitaxially grown indium gallium arsenide (InGaAs) over 800–1700 nm and silicon detectors over 400–1100 nm (Osborne et al., 1993; Blanco and Villarroya, 2002). Multichannel detectors comprise diode arrays, in which several detection elements are arranged in rows, or charged-coupled devices (CCDs), in which several detection elements are arranged in planes (Stchur et al., 2002). Multichannel detectors can, for this reason, record many wavelengths at once and this type of detector has given rise to NIR imaging spectroscopy, a technique in which spectra are recorded using cameras that can determine composition at different points in space and record the shape and size of the object. Making measurements at different wavelengths provides a three-dimensional (3D) image that is a function of the spatial composition of the sample and the irradiation wavelength used (Blanco and Villarroya, 2002; Baeten and Dardenne, 2005).

## 4 CHEMOMETRICS

“*Chemometrics* is the chemical discipline that uses mathematics and statistics to design or select optimal experimental procedures, to provide maximum relevant chemical information by analyzing chemical data, and to obtain knowledge about chemical systems” (Massart et al., 1988).

Overlapping of the many individual absorbance bands in the NIR region results in broad bands characteristic of *NIR spectra*; a NIR spectrum cannot, therefore, be interpreted in a straightforward manner. Often, large amounts of spectral data are obtained from NIR instruments; these data contain considerable amounts of information about the physical and chemical properties of molecules that yield useful analytical information (Osborne et al., 1993; Downey, 1998a; Katsumoto et al., 2001; Blanco and Villarroya, 2002), but they also contain *noise*, uncertainties, variabilities, interactions, nonlinearities, and unrecognized features. One of the biggest challenges faced when analyzing spectral data is to eliminate or reduce the noise from the spectra. This not only eases visualization of the information contained in the spectra but also maximizes the exploitation of the useful data (Wetzel, 1998; Katsumoto et al., 2001). Chemometrics is required to extract as much relevant information from the spectral data as possible (Wold, 1995).

*Chemometrics* has a fundamental role in NIR-based calibration and method performance in deriving calibration models is an important aspect to take into account (Centner et al., 2000; Geladi, 2002). A variety of multivariate analysis techniques can be used to (a) extract analytical information contained in NIR spectra to develop models and (b) to predict relevant properties of unknown samples. There are two main groups of multivariate methods which may be distinguished by the type of analysis required, that is, qualitative and quantitative analysis.

Since the early introduction of *multivariate regression techniques* by Norris (Ben-Gera and Norris, 1968a, 1968b), the development of various mathematical procedures and the increasingly widespread availability of commercial software have contributed tremendously to the expansion and current popularity of NIR spectroscopy. Development of *calibration models for quantification* of constituents in samples is possible by relating physical or chemical properties of the investigated samples to the absorption of radiation in the NIR wavelength range. *Qualitative calibration models* depend on comparing spectra of the sample to be identified with spectra of known samples.

Owing to the vast amount of *spectral information*, the large number of samples required to build *classification and calibration models*, and the high inter-correlation within spectra, there is a need for variable-reduction methods that allow the dimensions of the original data to be reduced to a few uncorrelated variables containing only relevant information from the samples (Blanco and Villarroya, 2002). *Principal component analysis* (PCA) is such a method which searches for directions of maximum variability in spectral datasets and calculates them as new axes called principal components (Cowe and McNicol, 1985). The calculated principal components contain the spectral information in a reduced number of variables, for example,  $<20$  and these new variables can substitute the original data in subsequent calculations. The fact that these new variables are linear combinations of the original variables (absorbances at the different wavelengths) means that individual principal components may be examined graphically to reveal previously undetectable information about the role of molecular or chemical species in any given calibration model (Cowe et al., 1990). By looking at the shapes of the components, it is possible to see in which parts of the spectra the contributing absorbance bands are detected (Cowe and McNicol, 1985). PCA is an *unsupervised method*, that is, no reference to any set of analytical values is necessary to examine spectral variation and therefore provides a simple procedure for data description and compression (Devaux et al., 1988).

## 4.1 Preprocessing of Spectral Data

Maximizing the significance of any spectral differences is the main aim of using *preprocessing* algorithms (Osborne et al., 1993; Hopkins, 2001; Rinnan et al., 2009; Rinnan, 2014). Achieving this maximization becomes very difficult if the *signal-to-noise (S/N) ratio* of a given spectrum is very small. As NIR spectroscopy utilizes light of low intensity, it will necessarily produce less sensitive responses in the excited molecules (Wetzel, 1998). To compensate for this lower sensitivity, the noise levels detected by the instrument have to be kept to a minimum to create a high *S/N ratio*. *Noise* can be caused by instrument drift during scanning, sample preparation, and presentation and by the environmental conditions within which the spectra are generated (Wetzel, 1983; Katsumoto et al., 2001). Environmental conditions are especially important, as they will

affect the weakly absorbing bands of NIR spectroscopy even more significantly than those regions that produce strong absorptions. One way of *removing noise* is to collect multiple scans and average them (Katsumoto et al., 2001); although the achievement of significant noise reduction levels may necessitate large numbers of repeat scans, that is, 64 or more. If this does not reduce the noise level adequately, *smoothing techniques*, of which the *moving-average method* (Savitzky and Golay, 1964) is the most common, may be used. Other common preprocessing methods include *normalization* (Massart et al., 1988; Næs et al., 2002), *derivatives* (Massart et al., 1988; Næs et al., 2002), *MSC* (Geladi et al., 1985), and *SNV* and *de-trending* (Barnes et al., 1989). Preprocessing techniques more recently developed include *orthogonal signal correction* (OSC) (Wold et al., 1998; Sjöblom et al., 1998), *direct orthogonal signal correction* (DOSC) (Luypaert et al., 2002), and *orthogonal wavelet correction* (OWAVEC) (Esteban-Díez et al., 2004a, 2005).

#### 4.1.1 Smoothing

*Savitzky-Golay moving average* (Savitzky and Golay, 1964) and other algorithms, that is, wavelets (Katsumoto et al., 2001) can reduce the effect of noise on a spectrum by removing small variations in absorbance which are not expected to be meaningful.

#### 4.1.2 Derivatives

One of the most common preprocessing algorithms used, calculates the first or second derivatives of each spectrum (Wetzel, 1998; Næs et al., 2002). *Derivatives* are used to enhance slight spectral differences between samples and compensate for baseline shifts that have been caused by light scattering (Beebe et al., 1998). *Second derivatives* in particular can accentuate sharp spectral features and help to resolve overlapping bands. Derivatization can minimize the effects of *scattering* by removing *additive offsets* that are independent of wavelength (*first derivatives*) or by removing offsets that change linearly with wavelength (*second derivatives*).

#### 4.1.3 Normalization

*Normalization* is another method of *removing bias* from a spectrum without using derivatives (Wetzel, 1998; Næs et al., 2002). It is achieved by mean centering the spectra (subtracting the average absorbance from each spectrum) and then establishing unit variances at each wavelength by dividing the absorbance at each by the relevant standard deviation. Such normalization may, however, remove valuable information from the spectral dataset.

#### 4.1.4 Multiplicative Scatter Correction

Another normalization procedure is *MSC* (Geladi et al., 1985). This approach also mean centers the data after which the target spectrum is curve fitted to the

average and then dividing it by the curve-fit value. MSC is a very useful and powerful preprocessing method for removing additive and multiplicative differences in a spectral dataset; such differences are mainly caused by samples with inconsistent particle sizes (e.g., powders). MSC separates the chemical light absorption from the physical *light scatter* (Geladi et al., 1985).

#### 4.1.5 SNV and De-trending

SNV transforms spectral data by subtracting the mean of the spectra from the spectral values of each spectrum (Barnes et al., 1989). These centered spectra are then scaled by the standard deviation of the spectrum. SNV effectively removes the *multiplicative interferences* of *scatter* and *particle size* and is applicable to individual NIR spectra. *De-trending* accounts for the variation in *baseline shift* and *curvilinearity* (Barnes et al., 1989).

### 4.2 Quantitative Chemometric Techniques

*Quantitative NIR calibration* development involves collecting a set of calibration samples with known *reference values* (chemical constituents, physical characteristics, or other properties) covering as much as possible the range of variation expected in future or unknown samples. *Calibration development* then entails the establishment of a mathematical relationship between the NIR spectrum and the reference parameters previously determined by an independent reference analytical method. The aim is therefore to fit the NIR and reference values to a straight line and compare it statistically to a theoretically perfect line through the origin at 45 degrees to both axes. This *calibration model*, after being adequately *validated* on an *independent validation* set, can then be used to predict the properties or constituents in unknown samples on the basis of *their* NIR spectra. *Regression methods* commonly used are *multiple linear regression* (MLR) which utilizes only selected wavelengths, *principal component regression* (PCR) and *partial least-squares* (PLS) *regression*, both of which use the whole spectrum. More detail on these methods can be found in Næs et al. (2002).

### 4.3 Qualitative Chemometric Techniques

Qualitative multivariate analysis methods are being used to recognize similarities in NIR spectral data. *Qualitative analyses* are directed at extracting information about one or more important functional properties of a sample which can be used to screen samples on the basis of desired functional properties; these methods also find extensive application in the confirmation of authenticity or the detection of adulteration of food samples.

*Qualitative multivariate data analysis techniques* are known as *pattern recognition* methods (Osborne, 2000) since their application generally involves a comparison of spectra and a search for similarities or differences (Wüst and

Rudzik, 2003). In terms of *classification*, the aim is to get as many correct classifications as possible. A decisive design parameter that has to be set prior to any classification model development is the number of classes to be considered and the particular requirements that a sample has to fulfill in order to be assigned to a certain class (Esteban-Díez et al., 2007). Conventionally, a *spectral library* of known substances is built and a model developed which describes the mean spectrum and the associated variability of each sample type in multidimensional space; the spectrum of an unknown sample is then compared with the spectral library and decision rules applied to determine the likelihood of it belonging to the library or not (Wüst and Rudzik, 2003). *Qualitative applications of NIR spectroscopy* may be achieved by two different broad approaches, namely *unsupervised* and *supervised methods* (Beebe et al., 1998; Blanco and Villarroya, 2002; Pasquini, 2003). In the former, the classes of samples used for model development are known at the outset whereas, in unsupervised methods, there is no information about the class structure of the training sample set.

#### 4.3.1 Unsupervised Methods

*Unsupervised methods*, for example, PCA (Cowe and McNicol, 1985) and *hierarchical cluster analysis* (HCA), are often deployed as investigative tools in the early stages of data analysis to give indications of possible relationships between samples.

### Principal Component Analysis

*Principal component scores* for similar materials tend to cluster in multidimensional space in a similar fashion to the way the data points representing individual wavelength measurements may cluster (Mark, 1992; Downey, 1996a). PCA models are constructed using the entire data set obtained from all the measurements of the different samples to be distinguished (Mark, 1992).

### Hierarchical Cluster Analysis

*Clustering* can be defined as the process of organizing objects into groups; the members of which are similar in some way. A cluster is therefore a collection of objects, which are similar to each other and dissimilar to other objects. *HCA* is a method often used for preliminary data analysis—the process is iterative and involves assigning objects which are close to each other to a cluster, finding the closest (most similar) pair of clusters and merging them into a new, single cluster, etc., and finally computing distances (similarities) between the new cluster and each of the old clusters (Mao and Xu, 2006). The latter two steps are repeated until all items are grouped into a single cluster. An important component of a clustering procedure is the distance measure between data points; either *Mahalanobis* (Næs et al., 2002) or *Euclidean* (Næs et al., 2002) distances may be used (Mao and Xu, 2006). The most common distance measure used



is the Mahalanobis distance, which describes distance in any given direction relative to the variability along the same axis.

### 4.3.2 Supervised Methods

The more traditional *supervised methods* include *Bayes classification* or *Fisher's linear discriminant analysis* (LDA) (Næs et al., 2002). Supervised methods commonly used to solve authenticity problems are *soft independent modeling of class analogy* (SIMCA), *LDA*, *multiple discriminant analysis* (MDA), *factorial discriminant analysis* (FDA), *partial least-squares discriminant analysis* (PLS-DA), *canonical variate analysis* (CVA), *artificial neural networks* (ANNs), and *k-nearest neighbor* (*k*-NN) analysis (Downey, 1996a; Blanco and Villarroya, 2002; Stchur et al., 2002). More recent classification techniques reported include *support vector machine* (SVM) *classification* (Vapnik, 1995; Burgess, 1998), and *wavelet interface to linear modeling analysis* (WILMA) (Cocchi et al., 2003). Some of the most commonly used supervised methods are briefly described below, however, more exhaustive and detailed explanations of these methods can be found in Næs et al. (2002).

### Soft Independent Modeling of Class Analogy

Apart from problems relating to simple classification, *SIMCA* is applied to a more general class of discriminatory issues, for example, identification (Wold and Sjöström, 1977; Brereton, 2011). It is a procedure in which raw spectra are compressed by means of PCA (Downey and Beauchêne, 1997a), that is, data describing samples from each of the relevant number of classes or groups are collected and separate PCA models are calculated for each of the groups for which qualitative analysis is desired (Mark, 1992). Classes are thus modeled independently of each other and the cluster models treat new samples separately. *SIMCA* first centers and then compresses raw data by means of PCA (Mark, 1992; Downey and Beauchêne, 1997a); a multidimensional space is constructed containing the scores corresponding to each group. *Mahalanobis distances* based on the principal component scores are calculated for every sample to determine the distance from the center of the cluster in the dimensional space. Each cluster model treats new samples separately and an assessment of cluster membership is made on the basis of the distance of any given sample to the center of the cluster. An *F*-test is employed to measure the degree of similarity of an unknown sample spectrum to sample spectra in each modeled cluster, allowing an estimate of confidence to be attached to any identification decision (Downey, 1996a; Downey and Beauchêne, 1997a). The sum of squares of a residual spectrum can be compared with the variance within the class, providing a measure of certainty accompanying each identification (Downey, 1996a; Downey and Beauchêne, 1997a). The spectrum residual, which is an indication of how much of the spectrum of any given sample is not explained for by the PCA model,



provides a reliable and sensitive measure of class membership. By combining two residual distances, the critical probability of an unknown sample belonging to a specified class may be tested. *SIMCA* is claimed to have advantages in the separation of very similar materials (Downey and Beauchêne, 1997a).

### PLS Discriminant Analysis

With *PLS-DA*, or discriminant PLS (DPLS) as it is sometimes called, it is possible to build calibration models using spectral data and knowledge of the *class membership* of each sample in the training (calibration) set. In *PLS-DA1*, used for binary classification problems, each sample is given a dummy variable equal to 0 or 1; members of the class are ascribed a value of 0 and nonmembers, a value equal to 1. Unknown samples with a predicted value below 0.5 may be identified as belonging to the class being modeled; the converse applies to samples with predicted values equal to or  $>0.5$ . Cut-off values other than 0.5 may be used depending on the dispersion of predicted values and the confidence required for class identification decisions. *PLS-DA2* is used when more than two classes of material must be modeled; in this case also, the dummy variable associated with each class type is ascribed a value equal to 0 for samples belonging to the class and 1 for all other samples.

### Linear Discriminant Analysis

*LDA* is a *supervised classification* technique in which the number of categories and the samples that belong to each category are previously defined (Næs et al., 2002). The method produces a number of linear discriminant functions, equal to the number of categories  $-1$ , that allow samples to be classified in one or another category. The *Mahalanobis distances* of each object from the centroids of the categories are computed and objects are assigned to the nearest cluster.

### Factorial Discriminant Analysis

The aim of *FDA* is to predict membership of a single sample according to the other defined groups; PCA scores are used as the basis for FDA. During FDA, principal component scores calculated on mean centered spectral data are normalized and the gravity center of the score cluster for each group determined. The *Euclidean distance* of each principal component score of a given sample to each of the gravity center is calculated and the individual sample assigned to the group with the nearest gravity center, subject to a maximum membership distance of two or three times the *Euclidean distances*. The unique feature of FDA is that principal components are incorporated into the model on the basis of decreasing classification ability, not in calculation order.

### ***k*-Nearest Neighbors**

*k*-NNs are a reasonably simple method. To classify a new sample, its *Euclidean distance* from each of the samples in a training set is calculated and the *k*-nearest samples is found; *k* typically has odd, integer values. The unknown is then classified to the group that has the most members among these neighbors (Næs et al., 2002).

### **Support Vector Machine**

SVM is a two-class classifier (Vapnik, 1995; Burgess, 1998). SVM has been shown to be useful for especially nonlinear classifications. One of the benefits of SVM is that it does not need a large number of samples for model development and is not affected by the presence of outliers. With the development of least-squares-SVM (LS-SVM), which is an alternative algorithm of SVM (Suykens and Vandewalle, 1999), the more complicated calculations as in SVM are avoided.

## **4.4 Validation**

It is critically important to assess the performance of every *calibration model* on an unknown set of samples since the ultimate goal of a calibration model is to predict unknown values accurately and precisely (Geladi, 2002) and this may be best done using a test sample set which should contain a realistic representation of samples that may be encountered in the future (Osborne et al., 1993).

*Validation or prediction testing* refers to the calculated difference between *NIR spectroscopy prediction* results obtained for the constituents, properties or identification or classification, and the measurements obtained for the reference method or known identities (Næs and Isaksson, 1991). *Internal validation* involves validation of a calibration using the same sample set as that used for calibration development. An assessment based on internal validation is, therefore, not the same as prediction testing (Martens and Næs, 1989) which involves validation of a calibration using an independent sample set that was not involved in the calibration development. The two validation methods normally used include *independent or external validation* (Esbensen, 2000) and *cross-validation* which uses the calibration data set only. *External validation* requires a separate, large, and representative set of test objects in order to give relevant and reliable estimates of the future prediction ability of the model (Martens and Næs, 1989; Westerhaus, 1989; ISO, 2017). It is, however, not always possible, as multivariate calibration is often done because the traditional reference method for measuring the constituent or class of interest is too expensive, slow, or otherwise undesirable. It would be most economical to use all data available for both calibration development and for prediction testing (Martens and Næs, 1989).

*Cross-validation* is a very reliable validation method; it seeks to validate the calibration model on an independent test dataset, but contrary to external data, it

does not use samples for testing only. For cross-validation, successive samples are not included in the calibration set. In partial cross-validation, samples are removed in groups, while in full-cross validation, all samples are removed one at a time. After every deletion, a calibration is performed on the rest of the samples before being tested on the removed samples. The first sample(s) is (are) then replaced into the calibration data and the next sample(s) removed. The procedure continues until all the samples or sample groups have been deleted once (Martens and Næs, 1989; Næs and Isaksson, 1991).

The final step in NIR calibration development is statistics, which is “the art of drawing conclusions from data, and making decisions, in the presence of variability” (Wold, 1995) and is needed for interpretation of the gathered data and evaluation of the *efficiency and accuracy of the calibration model*.

The statistics most often used for *quantitative NIR analysis* are listed in Table 3, which include the *standard error of prediction* (SEP) or *standard error of cross-validation* (SECV); *bias*; *coefficient of determination* ( $R^2$ ); and *ratio of*

**TABLE 3** Equations for Statistical Calculations

Statistic	Equation	Recommendations
SD <sup>a</sup>	$\sqrt{\sum y^2 - \frac{(\sum y)^2}{n-1}}$	
SEL <sup>b</sup>	$\sqrt{\frac{\sum (y_1 - y_2)^2}{2n}}$	As small as possible
SEP <sup>c</sup> /SECV <sup>d</sup>	$\sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i - \text{BIAS})^2}{n-1}}$	As small as possible or close as possible to SEL value
V-BIAS <sup>e</sup>	$\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)$	As close to zero as possible
$R^{2f}$	$1 - \frac{\sum_i (y_i - \hat{y}_i)^2}{\sum_i (y_i - \bar{y})^2}$	See Table 4
RPD <sup>g</sup>	$\frac{SD_{\hat{y}}}{SEP} \text{ or } \frac{SD_{\hat{y}}}{SECV}$	See Table 5

<sup>a</sup>Standard deviation.

<sup>b</sup>Standard error of laboratory.

<sup>c</sup>Standard error of prediction.

<sup>d</sup>Standard error of cross validation.

<sup>e</sup>Bias of the validation set.

<sup>f</sup>Coefficient of determination.

<sup>g</sup>Ratio of standard error of performance to standard deviation.

$y$  = reference value;  $\hat{y}$  = predicted value;  $y_i$  = reference value for the  $i$ th sample;  $\hat{y}_i$  = NIR predicted values for the  $i$ th sample;  $y_1$  and  $y_2$  = duplicate reference values;  $n$  = number of samples;  $t$  = number of terms in the model.

*standard error of performance to standard deviation* (RPD) (Osborne et al., 1993; Williams, 2001; Williams et al., 2017). The SEP measures how well the calibration is going to perform in future analysis (Fearn, 2002) and should be as close as possible to the *standard error of laboratory* (SEL) for the constituent or property being measured. The SEP is used to evaluate the accuracy of a calibration by indicating the variability in deviations of the reference data from the NIR spectral data. The bias gives the average by which the results differ. Together, the SEP and the bias indicate and evaluate the overall accuracy of the prediction model. The SEP and bias should be as low as possible with a slope close to 1.0 (Williams, 2001). When cross-validation is performed, the accuracy of the calibration is indicated using the SECV. The RPD enables the evaluation of the SEP in terms of the SD of the reference data and gives an indication of the efficiency of the calibration model (Williams and Sobering, 1993; Williams, 2001). The recommended RPD value for the use of *NIR spectroscopy in quality control* is 5.0 or more (Williams, 2001). For screening purposes, a value of  $>3.1$  would be sufficient. The *coefficient of determination* ( $R^2$ ) indicates the amount of variation in the data being explained by the calibration equation (Williams, 2001). The  $R^2$  should be high ( $>0.90$ ) to indicate a good prediction capability, while with a low value ( $\leq 0.64$ ), it is not possible to obtain consistently high accuracy by NIR spectroscopy analysis.

*Qualitative calibration* results can be assessed on the basis of number of *false positive* and *false negative classifications* (Contal et al., 2002). A *false positive* occurs when a sample which does not belong to a given class is predicted by the model to be a member of that class. A *false negative* arises when a sample which does belong to a given class is not classified as such. False positives are considered the more serious of the two error types given that they represent a failure of the model to detect nonmembership or adulteration. *Accuracy of classification* results can also be expressed in terms of *sensitivity* and *specificity* (Esteban-Díez et al., 2007). *Sensitivity* is the proportion of samples belonging to a certain category correctly identified by the prediction model corresponding to that class, that is, it is a measure of the ability to correctly predict true positives. *Specificity* is the proportion of samples not belonging to a certain class classified as foreign, that is, it is a measure of the ability to discriminate against false positives. These parameters are valuable diagnostic tools for *evaluating classification and confirmation of authenticity results* since a class model should not only correctly classify samples as belonging to a specific class or category but also reject samples not belonging to that class.

## 5 ADVANTAGES AND DISADVANTAGES

*NIR spectroscopy* has several *advantages* over other analytical techniques. It is a rapid, easily used technology that is nondestructive in nature (Day and Fearn, 1982; Osborne et al., 1993; Wetzal, 1998; Manley, 2014; Baeten et al., 2015)

and required a reduced volume of chemical consumables (Downey, 1998a, b). The latter is important as the disposal requirements for hazardous waste are becoming increasingly expensive for laboratories. NIR spectroscopy requires minimal or no *sample preparation* or pretreatment (Day and Fearn, 1982; Osborne, 2000). It can record complete continuous spectra for high-moisture samples such as liquids and slurries as well as solids (Williams and Stevenson, 1990; Blanco and Villarroya, 2002) and one of the major advantages of NIR spectroscopy is that it allows several constituents or properties to be measured at the same time (Osborne, 2000).

*NIR instrumentation* is often rugged and can be used inside or outside laboratory environments (Stark et al., 1986) and measurements can be carried out online (Osborne et al., 1993; Hoyer, 1997) or in-line (Singh Sahni et al., 2004). *Portable NIR spectrophotometers* such as handheld instruments using micro-electromechanical systems (MEMS) (Crocombe, 2004; Fernández et al., 2010) technology and equipment that can be carried in a backpack or mounted on a vehicle are nowadays more freely available (Blanco and Villarroya, 2002).

The most significant advancement in instrumentation in recent years, however, is the development of miniature NIR devices (O'Brien et al., 2012). These ultra-compact spectrometers rely, for instance, on thin-film linear variable filter (LVF) technology for the light-dispersing element. The LVF ensures a high S/N for the NIR measurements (Correia et al., 2018). Handheld devices enable the instrument to be taken to the sample, thus facilitating real-time analysis, without compromising accuracy, precision, or sensitivity (Correia et al., 2018). Plants, still in the field, can now be analyzed with ease. The devices only require a connection to a laptop, tablet, or smartphone (Friedrich et al., 2014). Similarly, fruit still on the tree, can be analyzed to determine optimum harvesting time (Dos Santos Neto et al., 2017). A number of food quality control (Nascimento Marques et al., 2016; Correia et al., 2018) and authenticity applications have recently been developed using portable/minature devices (O'Brien et al., 2013; Guelpa et al., 2017; Basri et al., 2017; Grassi et al., 2018).

The most interesting advantage of NIR spectroscopy compared with other spectroscopic techniques is its ability to use longer *pathlengths* and that the optical equipment is much simpler (Karoui and De Baerdemaeker, 2007). It is possible to use optical fibers and glass for windows, sample cells, and lenses made from quartz glass. These are cheaper and easier than the alkali salts (such as KBr and KCl) typical of MIR analyses. It is also possible to create a pseudo-homogenous spectrum from a nonhomogenous sample by scanning a large area of the sample and averaging the sample's properties. The relatively deep *penetration of NIR light* into samples also permits better representation of the chemical properties. Once the method has been developed, the instrument can easily be used by technicians for process control purposes. The low absorptivity of absorption bands in NIR is compatible with moderately concentrated samples and longer pathlengths compared with MIR analyses (Osborne et al., 1993). This enables spectra to be measured by transmission through intact

materials, which allows rapid and nondestructive analysis as no sample preparation is needed. Intact, opaque, biological samples can also be analyzed by diffuse reflectance, which makes *NIR spectroscopy* a very simple technique to use and makes it the ideal application for online analyses.

The main *disadvantage* is the low sensitivity of the signal which can limit the determination of low-concentration components to be determined by the use of NIR spectroscopy (Karoui and De Baerdemaeker, 2007). This limitation of NIR absorptions, however, simplifies the spectra and restricts the information extracted to that of fundamentally strong chemical bonds between light atoms. Chemometric manipulations of the data can, however, be very revealing, if handled correctly.

The main limitation of NIR spectroscopy as an analytical technique, involves its dependence on other chemical methods of analyses that are sometimes less precise and equally empirical (Osborne et al., 1993). A large data set incorporating large variation, which is often difficult to obtain, is essential to build a robust calibration (Wetzel, 1998). *NIR spectroscopy* therefore requires an extensive *calibration and validation sample set* to produce robust prediction models. The *reference method* often requires a lot of time for sample collection, preparation, and presentation and may involve large expenses, depending upon the nature of the constituent. Effective use and development of new calibrations requires sufficient training of the operator. Furthermore, the maintenance of a *calibration set* is very difficult and this lack of sample stability over long periods of time causes problems for calibration transfer. For qualitative analysis, however, the cost of *reference method* analysis may not be a concern.

The initial high cost of the instrumentation is also an important factor when acquiring a NIR instrument for routine applications in a quality control laboratory is considered. The purchase and running costs of NIR instruments compared with the cost of consumables used in conventional chemical methods should, however, be assessed in terms of the long-term financial implications and benefits of such an investment.

## 6 APPLICATIONS IN FOOD AND BEVERAGE AUTHENTICITY

Increasing emphasis is placed on *nondestructive quality control methods* for agricultural and biological materials necessary for composition analysis (Gunasekaran and Irudayaraj, 2001; Martinez et al., 2003). *Applications of NIR spectroscopy in the food industry* were reported as early as 1938 in gelatine studies (Ellis and Bath, 1938). Nowadays, the applications of NIR in the food and beverage industries are varied and include quantification of food ingredients and composites (Williams and Stevenson, 1990; Osborne et al., 1993; Wetzel, 1998; Woodcock et al., 2008; Manley, 2014; Baeten et al., 2015); *food adulteration and authenticity* (Downey, 1995, 1996a; Lohumi et al., 2015; Sørensen et al., 2016; Vermeulen et al., 2010, 2017); the *detection of external and internal defects in foods* and crops (Osborne et al., 1993; Nicolai et al.,

2007); and qualitative and sensory determinations (Osborne et al., 1993; Downey, 1995, 1998a, b; Wetzel, 1998; Escribano et al., 2017).

In the following sections, only those applications concerning the use of *NIR spectroscopy* and appropriately combined chemometric techniques to assess *authenticity, identity, geographical origin, and detection and quantification of adulteration* in food and food products will be discussed in more detail.

## 6.1 Cereals and Cereal Products

*Wheat* used for food applications consists of mainly two species, that is, *bread wheat* (*Triticum aestivum*) and *durum wheat* (*Triticum durum*) which are characterized by different chemical and physical properties. Based on these different properties, they will differ in functional quality, nutritional contribution, and consequently commercial value. The first qualitative NIR spectroscopy analysis on wheat was performed in the 1980s and the studies reported the possibility of discriminating between wheat varieties on the basis of their *bread-baking quality* (Bertrand et al., 1985; Devaux et al., 1986, 1987; Downey et al., 1986). Using a *wheat hardness* index measured by NIR reflectance as a quality indicator, it was possible to distinguish between selected wheat samples with different bread-baking qualities on the basis of their hardness (Downey et al., 1986). NIR spectroscopy and FDA was used to identify a range of commercial white *flours*, that is, biscuit, self-raising, household, cake, bakers', and soda bread mix (Sirieix and Downey, 1993); using this approach, it was possible to correctly classify 97% of a set of 99 validation samples. Although the identification was largely due to *particle size difference* between the flours, identifications were also due to the presence of inorganic additives at different levels in some flours.

Separation of four commercial Italian bread *wheat flours* of different quality categories was attempted by means of *NIR spectroscopy* (Cocchi et al., 2005). The spectra (400–2489 nm at 2 nm intervals) were acquired in a quartz sample cell using a Foss NIRSystems 6500 spectrophotometer. The flour quality categories were defined by means of specific parameters, that is, hectolitre weight, Hagberg falling number, protein content, alveograph measurements, and farinograph stability. Despite the use of *SIMCA* and a wavelet-based feature selection/classification algorithm called WPTER, it was not possible to classify the four different categories—this was due to considerable overlap of the two intermediate quality classes. It was, however, possible to classify the two extreme classes of wheat quality with an acceptable degree of separation. Cocchi et al. (2005) found 2050–2350 nm to be the most informative part of the NIR spectrum for classifying the two categories of flour. This region corresponds to the combination bands of N—H bonds (2050–2070 nm), O—H bonds (2070–2100 nm), C—H bonds (2140–2200 and 2280–2335 nm), and C=O bonds (2140 and 2180–2000 nm). Cozzolino (2014) reviewed and provided



more detail on the use of NIR spectroscopy to discriminate between cereal samples based on functionality as reflected by their spectral properties.

In countries such as Italy (Anon, 1967), France, and Spain, the law establishes that pasta may only be made from *durum wheat* semolina and water and *durum wheat adulteration* with bread wheat is of particular interest. In north European and other countries, both bread and durum wheat are, however, often allowed. The addition of bread wheat flour is treated as adulteration in Italy as it is believed to result in a product with decreased resistance to cooking and therefore of lower quality. As accidental contamination of semolina with *bread wheat* is likely during harvesting or storage, the presence of bread wheat flour in percentages not higher than 3% is sometimes allowed (Anon, 2001). A feasibility study by Cocchi et al. (2006) showed that *PLS* and a newly developed calibration algorithm called *WILMA* (Cocchi et al., 2003), which makes use of the advantages offered by wavelet transforms, resulted in good predictive performance when the possibility of using NIR spectroscopy to quantify the degree of adulteration of durum wheat flour with bread wheat flour was explored. Using a similar instrument setup as before (Foss NIRSystems 6500 and quartz sample cell), the uncertainties associated with the developed models have been shown to be about half of the uncertainty of the current Italian official method.

Basmati, a class of *rice* grown in the Punjab region of India and Pakistan can only be grown once a year with a yield half that of other rice varieties and its eating quality cannot be duplicated by growing the same seed in other regions; there is therefore a strong incentive for its fraudulent adulteration with other long-grain rice varieties. In a preliminary attempt, NIR transmission spectroscopy was used to classify rice as basmati or nonbasmati (Osborne et al., 1997). Rice samples were analyzed using two presentation modes, that is, bulk samples or single grains using a Tecator Infratec 1225 grain analyzer over the wavelength range from 850 to 1050 nm. *Fischer LDA* was applied to the resulting datasets and a perfect discrimination between basmati and nonbasmati rice samples was achieved for the bulk samples. In the case of the single grains, the long-grain samples were, however, often misclassified as also being *basmati rice*.

## 6.2 Coffee

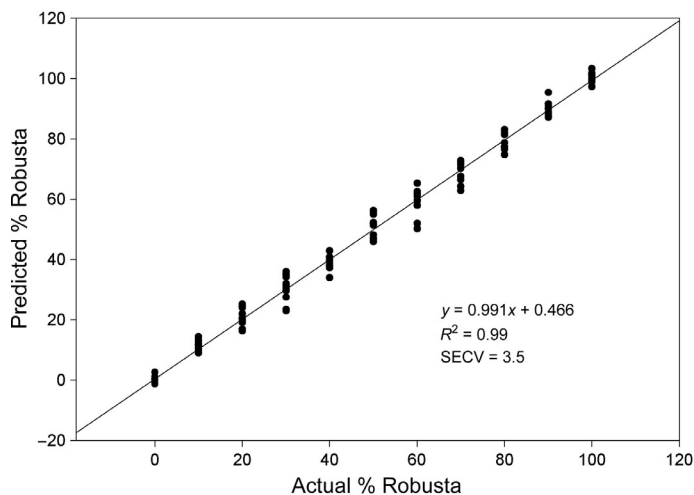
Approximately 99% of commercial *coffee* is made from *Arabica* (*Coffea arabica* Linnaeus) and *Robusta* (*Coffea canephora* Pierre ex Froehner) varieties (Downey et al., 1994; Downey and Spengler, 1996). Arabica is viewed as superior in quality to Robusta and trades at a price which is 20%–25% higher than that of Robusta (Esteban-Díez et al., 2007; Pizarro et al., 2007), thereby introducing the potential for fraud. Trained personnel can generally identify between these two coffee varieties when in bean form but this is not generally possible once the beans have been ground.

The first qualitative NIR spectroscopy work on coffee was reported by Davies and McClure (1985) who showed that it was possible to discriminate



between regular and decaffeinated coffee by use of NIR spectra without calibration against caffeine content. Downey et al. (1994) reported on the potential of NIR and FDA to discriminate between pure (green and roasted) Arabica and Robusta coffees and blends in the form of whole and ground beans. Calibration ( $n=52$ ) was performed on spectra recorded in the wavelength range of 1100–2498 nm using a Foss NIRSystems 6500 instrument and it was validated using two prediction sets ( $n=52$  and  $n=105$ , respectively). For the pure whole bean coffees, a total correct classification rate of 96.2% was achieved. From the discriminant scores, it was apparent that discriminant factor 1 separates green from roasted coffee beans while factor 2 divides Robusta coffee beans from Arabica beans. Including 50:50 blends (20 green and 20 roast samples), the classification rate was reduced to between 82.9% and 87.6%. Discrimination of 105 (52 samples for calibration and 53 for validation) ground coffee blends resulted in a correct classification rate of 83%. Downey et al. (1994) suggested that discrimination between the two varieties was on the basis of alkaloid (e.g., caffeine) content.

Using the same instrument setup as Downey et al. (1994), Downey and Spengler (1996) studied the classification of coffee blends and illustrated that PLS regression was successful in quantifying the Robusta content in Arabica bean samples blended with different levels of Robusta coffee with an accuracy that may be commercially useful. Standard errors of cross-validation of 9.21% and 3.52% were respectively obtained on second-derivative spectra of whole and ground beans (Fig. 2); the application of FDA procedures was less



**FIG. 2** Prediction of percentage Robusta content in ground bean samples by modified partial least squares regression. (Reproduced with permission from Downey, G., Spengler, B., 1996. Compositional analysis of coffee blends by near infrared spectroscopy. *Irish J. Agric. Food Res.* 35, 179–188. Copyright (1996) Irish Journal of Agricultural and Food Research.)

successful in this case. Downey and Boussion (1996) illustrated that NIR spectroscopy (NIRSystems 6500) can facilitate discrimination between beverages produced from pure Arabica, pure Robusta, and Arabica/Robusta blends with a high degree of success. Laboratory prepared coffee drinks were correctly classified at rates of 87% and 95% when using lyophilized and vacuum-dried coffee, respectively.

The use of combined NIR-MIR spectra for *coffee varietal identifications* has been demonstrated (Downey et al., 1997). This feasibility study showed that both NIR and MIR spectroscopies have the potential to discriminate between Arabica and Robusta lyophilized coffee while the combined spectral regions appear to offer advantages in terms of model robustness.

More recently, an improvement in NIR spectroscopy classification between Robusta and Arabica as well as between blends thereof was illustrated using *DOSC* method as a preprocessing technique (Esteban-Díez et al., 2007) and a potential functions method as class modeling technique (Esteban-Díez et al., 2004b). The spectra were recorded on a NIRSystems 5000 spectrophotometer in the wavelength range 1100–2500 nm at 2 nm intervals. Each recorded spectrum consisted of 32 co-added scans and 5 replicates were recorded for each sample with the samples being decompacted between each recording; an average spectrum was computed for data analysis. Five coffee categories were studied, that is, pure Arabica, three Arabica/Robusta blends, and pure Robusta; and resulted in a 100% correct classification rate of prediction samples. Subsequently, the preprocessing method *OWAVEC* (Esteban-Díez et al., 2004a) was used by Pizarro et al. (2007) to improve the detection of coffee adulteration by quantifying the actual content of Robusta variety in roasted coffee samples. The regression models developed after preprocessing first-derivative NIR spectra by *OWAVEC*, were considerably better than the models obtained from raw data; results were also an improvement over other OSC methods tested (Table 4).

### 6.3 Fruit and Fruit Products

Shilton et al. (1998) reviewed the use of NIR spectroscopy as reported by various researchers (Scotter et al., 1992; Evans et al., 1993; Scotter and Legrand, 1994, 1995; Twomey et al., 1995) to demonstrate the potential of NIR spectroscopy for detecting adulteration of *orange juices*. Based on these studies, Shilton et al. (1998) argued that the use of NIR spectroscopy as a “fingerprint” technique may be more appropriate than trying to predict specific constituent levels that may then be compared with authentic compositional databases. Subsequently, *apple juice* samples were also differentiated on the basis of apple variety using NIR spectroscopy combined with LDA and PLS (Reid et al., 2005). The results showed up to 100% correct classification of samples on the basis of apple variety.

**TABLE 4** Calibration (RMSEC) and Prediction (RMSEP) Errors and Percentages of Explained Variance Provided by the Original PLS Model (Constructed From Mean-Centered Data), the PLS Model Developed From First Derivative Spectra and the PLS Models Built After Applying OSC and DOSC Methods to NIR Spectra

	PLS-LVs	% RMSEC	% Expl. Var. (cal)	% RMSEP	% Expl. Var. (test)
Centering	10	2.13	99.67	2.98	99.38
First derivative	8	1.67	99.80	2.04	99.71
First derivative + OSC (2 O-LVs removed)	3	0.77	99.96	1.36	99.87
DOSC (5 O-PCs removed)	1	1.03	99.92	1.33	99.88

Reproduced with permission from Pizarro, C., Esteban-Díez, I., Conzález-Sáiz, J.M., 2007. Mixture resolution according to the percentage of robusta variety in order to detect adulteration in roasted coffee by near infrared spectroscopy. *Anal. Chim. Acta* 585, 266–276. Copyright (2007) Elsevier Limited.

More recently, *fruit purées* as well as fruit juices were effectively tested for adulteration using *NIR spectroscopy* (Contal et al., 2002; Léon et al., 2005). Contal et al. (2002) used a NIRSystems 6500 scanning monochromator equipped with a sample transport accessory and a short pathlength transreflectance cell (0.1-mm sample thickness) and found it to be more successful than the alternative reflectance cell (sealed with a disposable paper backing disc resulting in 0.7-mm sample thickness). Two subsamples of each purée were scanned in duplicate with the sample cell being rotated through approximately 120 degrees between duplicate scans; mean spectra were used for data analysis. It was consequently possible to quantify apple adulteration in strawberry purées rapidly and nondestructively at levels down to 20% (w/w) and in raspberry purées at a level between 10% and 20% (w/w).

## 6.4 Honey

*Honey* is a high value, completely natural product and defined in the *Codex Alimentarius* (1987) of the Food and Agriculture Organization of the United Nations as “the natural sweet substance produced by honeybees from the nectar of plants or from secretions of living parts of plants or excretions of plant sucking insects on the living parts of plants, which the bees collect, transform by combining with specific substances of their own, deposit, dehydrate, store and leave in the honeycomb to ripen and mature.” The main components

of honey are simple carbohydrates and water leading to the possibility of honey extension by cheaper, commercially available sugar syrups. Often, preparations based on cane invert sugar, which can be tailored to mimic the natural sucrose-glucose-fructose profile of honey, are added to pure honey. This makes honey an easy target for adulteration as the addition of these preparations is usually difficult to detect (Sivakesava and Irudayaraj, 2001). Detection of adulteration in honey is also difficult because of its large natural variability, arising from differences in species, maturity, environment, processing, and storage techniques. *NIR spectroscopy* has been used previously to determine the chemical composition of honey samples (Cho and Hong, 1998; Ha et al., 1998; Qui et al., 1999; García-Alvarez et al., 2000).

Downey et al. (2003) showed that *PLS-DA* can be used to detect honey that has been adulterated by the addition of fructose and glucose with a high degree of success as 99% of the adulterated honeys in this report were correctly identified. Honey spectra were collected on a Foss NIRSystems 6500 between 400 and 2498 nm with 2 nm intervals in transreflectance mode using a 0.2 mm path-length. The pure honeys were correctly identified 96% of the time. However, Downey et al. (2003) do indicate that it might be necessary to apply temperature control during performance of the NIR analysis. *SIMCA* and *k-NN* models were reported not to be able to identify *adulterated honey* samples.

Kelly et al. (2006) used a similar instrument setup but collected spectra from 1100 to 2498 nm to detect adulteration of Irish artisanal honeys by adding either beet invert syrup or high-fructose corn syrup. Applying *SIMCA* as a classification technique, all the adulterated honeys were correctly identified as not being authentic honey, while 90.0% of the authentic honeys were correctly identified. More recently, Guelpa et al. (2017) confirmed NIR spectroscopy, in combination with *PLS-DA*, as a reliable method to distinguish South African honey, from intentionally adulterated (with sugar solutions, i.e., glucose and fructose) as well as imported honey. Overall classification accuracies of between 93.3% and 99.9% were obtained. The authors evaluated different instruments and illustrated that using a portable device resulted in equally accurate classification accuracies. When proof of authenticity is required, it is always important that no false positives occur in prediction tests, that is, when selectivity is high (Downey et al., 2006).

## 6.5 Meat and Meat Products

The major *meat and meat products* authenticity issues often concern the substitution or partial substitution of high-value raw materials with less costly alternatives. This can include cheaper cuts from the same or different *animal species*, mechanically recovered meat, offal, blood, water, eggs, gluten, or other proteins of animal or vegetable origin (Hargin, 1996; Al-Jowder et al., 1997, 1999, 2002; Cordella et al., 2002). There is also a problem with differentiating meat that has been frozen-then-thawed from *fresh meat* (Al-Jowder et al., 1997).

In some countries, legislation specifically prohibits adulteration of one type of meat with that from other species and the consumption of certain meats may be proscribed for religious reasons (Al-Jowder et al., 1997).

*NIR spectroscopy* has been reported to be useful to discriminate between kangaroo and *beef* meat (Ding and Xu, 1999), fresh *pork*, *chicken*, and *turkey* (Rannou and Downey, 1997), chicken meat cuts (Ding et al., 1999; Fumière et al., 2000), lamb, and beef mixtures (McElhinney et al., 1999), between beef, pork, and chicken (Downey et al., 2000) and for identification and authentication of *raw meat species* such as pork, chicken, lamb, and beef (Cozzolino and Murray, 2004). In the latter study, based on only optical properties of the samples, an excellent differentiation of muscle species was obtained and the visible and *NIR spectroscopy* models correctly classified >85% of samples using PLS (Table 5). This therefore indicates that not only the pigments but also the composition of the muscle gives information which may be used for identification purposes. Intramuscular fat, fatty acids, and other characteristics, that is, muscle structure and type of muscle fibers, could add information to the model and allowed the discrimination between them. Cozzolino and Murray (2004) analyzed the minced meat in reflectance mode from 400 to 2500nm with 2 nm intervals using a NIRSystems 6500 in a nonrotating circular cup.

*FDA* of combined visible-NIR reflectance spectra has been shown to possess the potential to discriminate between *fresh and frozen-then-thawed samples of meat* from one bovine species using three freeze-thaw cycles (Downey and Beauchêne, 1997a). Spectra were collected between 650 and 1100nm on whole meat using a surface interactance fiber optic accessory and a NIRSystems 6500. Applying *FDA*, a four-cluster model was found to classify all frozen samples correctly. *SIMCA* did not perform as well as *FDA*; although it was possible to identify the fresh samples correctly, a large number of the

**TABLE 5** Classification for Meat Species Using PLS and PCR Regression Models

Spectra Segment (nm)	Classification of Dummy Regression			
	PCR		PLS	
	CC	IC	CC	IC
400–750	90 (81%)	21 (19%)	94 (85%)	17 (15%)
1100–2500	104 (94%)	7(6%)	104 (94%)	7 (6%)
400–2500	101 (91%)	10 (9%)	107 (96%)	4 (3%)

CC= correct classification; IC= nonclassification.

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frozen-then-thawed samples were wrongly classified as being fresh. The latter study was followed-up by an alternative approach for solving this authenticity problem based on spectral measurements of *dried meat drip juice* (Downey and Beauchêne, 1997b). Using raw spectral data, a model with six principal components correctly classified 93.4% of the validation samples set, that is, 3 of the 15 fresh meats were incorrectly identified but only 1 of the 46 frozen-then-thawed samples was wrongly classified as fresh. Again, *SIMCA* did not perform well. The fresh meat samples could be correctly identified but there was a high degree of misclassification between the samples frozen once, twice, or three times.

In an attempt to quantify the lamb content in mixtures with raw minced beef, it was reported that the accuracy of the prediction could be improved by concatenating the fingerprint region of the MIR to the corresponding NIR spectra and a SEP of 4.1% (w/w) was obtained (McElhinney et al., 1999).

Many of these studies are, however, preliminary or feasibility studies often due to the difficulty of obtaining an adequate number of samples including the required level of variation. Appropriate validations should therefore be performed before commercial implementation of any such method.

More recent uses of NIR spectroscopy in the meat industry have been comprehensively reviewed by Prieto et al. (2017). They foresee the use of NIR spectroscopy in combination with other nondestructive technologies as well as increasing implementation of portable devices.

## 6.6 Milk and Dairy Products

Adulteration of *milk products*, by either substituting a more expensive ingredient with one of lower cost or by removing a valuable component, with the hope that the authorities or consumers will not detect the adulterated product, often takes place to maximize profit (Arvanitoyannis and Tzouros, 2005). *Adulteration of milk and dairy products* can be categorized as either not complying with the legal requirements, erroneous addition of specific ingredients, and material not of dairy origin or noncompliance in terms of technological processes (Ulbert, 2003). The addition of water is one of the oldest and most obvious ways that milk can be adulterated (Arvanitoyannis and Tzouros, 2005). Another common problem is the addition of sugar to milk.

With the outbreak of the milk powder scandal in China in 2008 (Schoder, 2012), when milk and infant formula were adulterated with melamine (which gives a false indication of increased protein content) NIR spectroscopy was evaluated as a potential method of detection (Abbas et al., 2013; Domingo et al., 2014). NIR spectroscopy was considered as the Kjeldahl method fails to distinguish between protein-based nitrogen and nonprotein nitrogen (derived from small organic molecules such as melamine). Similarly, the Dumas method also cannot eliminate the negative influence of nonprotein nitrogen on the determination of protein levels. Domingo et al. (2014) reviewed the use of (together

with MIR) NIR spectroscopy to detect melamine in milk. The challenge, however, of detecting and quantifying melamine using NIR spectroscopy is the very low levels (often present only in ppm). NIR hyperspectral imaging and chemometrics were used to detect melamine in milk powder (Fu et al., 2014). Fu et al. (2014) used NIR hyperspectral imaging (990–1700 nm) and spectral similarity analyses were used to detect different concentrations of melamine adulteration (from 0.025% to 1%) in milk powders. The benefit of NIR hyperspectral imaging is the larger surface area being analyzed. Improvement in accuracy to even lower levels (<0.02% or 200 ppm) was thus suggested by means of spreading the sample mixtures in a thin layer in larger containers to increase the surface area presented for NIR hyperspectral imaging.

NIR spectroscopy is widely used in the dairy industry (Cattaneo and Holroyd, 2013; Holroyd, 2013). It was utilized for monitoring rennet coagulation in cow's milk (Laporte et al., 1998; O'Callaghan et al., 1999); reconstituted skim milk powder (Giardina et al., 2004); and the modifications that occurred in delactosated milk during storage (Giardina et al., 2003). It has also been extensively used to determine the physicochemical parameters of cheeses (Adamopoulos et al., 2001) and butter (Hermida et al., 2001). Purnomoadi et al. (1999) studied the effect of different feed sources on the accuracy of NIR prediction of milk fat and proteins. Filho and Volery (2005) used NIR spectroscopy to quantify solids content using a broad-based calibration that included five different fresh cheeses with low, medium, and high solids contents. This was done to show that the problem of narrow concentration ranges for total solids content in *fresh cheese* often found in a production environment can be overcome. Blazquez et al. (2004) carried out a similar study for moisture, fat, and inorganic salts contents in experimentally produced *processed cheeses*.

Cattaneo et al. (2005) successfully discriminated between *cheeses* (Italian fresh Crescenza cheese) according to their storage time using FT-NIR and PCA (refer to Chapter 4 for more detailed discussion).

The suitability of NIR spectroscopy for routine analysis of quality control to detect vegetable proteins in milk powder has been suggested by Maraboli et al. (2002), who developed calibrations to detect and quantify accurately the addition of nondairy protein isolates to milk powder. After having analyzed 111 samples (11 being genuine milk powder samples and the rest prepared by mixing with soy, pea, and wheat isolates) on a Bran+Luebbe InfraAnalyzer 500 from 1100 to 2500 nm at 4 nm intervals, the best relationship between NIR data and the quantifiable sample property was obtained by applying MLR to the first-derivative NIR absorbance values. The five most important wavelengths included in the calibration were 1708, 2076, 2108, 2132, and 2300 nm and it resulted in a SEP of 0.21% after analysis of 20 unknown milk powder samples.

Sato et al. (1990) showed that *fat adulteration* with as little as 3% foreign fat, that is, margarine in butter and soy milk in milk, could be detected using the limited wavelength range of 2110–2160 nm or only the two wavelengths 2124 and 2144 nm. If only the latter two wavelengths are, however, to be used



for screening samples for foreign fat adulteration, it will be necessary to check normal variation of the difference of the absorbance values of these two wavelengths due to feed, season, and stage of lactation.

Karoui and De Baerdemaeker (2007) reviewed the use of destructive and *nondestructive techniques* to determine quality and/or authenticity of dairy products including *NIR spectroscopy*. The principles of spectroscopic techniques coupled with chemometrics have been reviewed by Karoui et al. (2003).

The potential of NIR spectroscopy to predict maturity and sensory attributes of 24 Cheddar cheeses produced using five different renneting enzymes and stored at 4°C for up to 9 months has been investigated using a Foss NIRSystems 6500 instrument (Downey et al., 2005). These results still need to be validated on a larger sample set. A similar approach was followed by Blazquez et al. (2006) after which they recommended the use of NIR spectroscopy for routine quality assessment of processed cheese. Sensory attributes and instrumental texture measurements were predicted with sufficient accuracy to be commercial useful.

Most recently, the potential of FT-NIR spectroscopy for use in combination with chemometrics to discriminate between Emmental *cheeses* of various *geographic origins* was demonstrated (Pillonel et al., 2003; Karoui et al., 2005b; Karoui and Baerdemaeker, 2007).

## 6.7 Tea

*Tea*, made from the processed leaves of *Camellia sinensis*, is among the most popular beverages worldwide and is of great interest due to its beneficial health properties. Green and black teas are the two most popular categories. Drying, after light steaming and roasting the leaves produced green tea while for black tea the leaves are additionally fermented (chemically oxidized). If this fermentation is only partially carried out, Oolong tea is obtained. Due to these different processing techniques, the different tea categories will vary in their chemical structure (Chen et al., 2007).

One of the first discriminant studies on tea was reported by Osborne and Fearn (1988) and at the time, they concluded that there is a reasonable chance of successful discrimination between black teas of differing *sensory profiles* on the basis of wavelengths corresponding to absorption bands in the spectra of teas. Grant et al. (1988) revealed that six teas differing in origins and taste could be reliably distinguished from one another using CVA. During this investigation, Osborne and Fearn (1988) illustrated the effect of the grinding method used to prepare the samples to be much larger than those of sample temperature or rotation of the sample during analysis.

Using FT-NIR spectroscopy and *SIMCA*, it was possible to identify four different tea varieties (Chen et al., 2006) and the potential of FT-NIR spectroscopy combined with SVM methods to identify each of three tea categories (green tea, black tea, and Oolong tea), was demonstrated (Zhao et al., 2006; Chen et al., 2007).



## 6.8 Vegetable Oils

In 1956, NIR chemical assignments for several chemical groups characteristic of lipids were determined by investigating the spectra of synthetic fatty acids (Holman and Edmondson, 1956). The earliest application of NIR analysis of *fats and oils* was published in 1991 (Sato et al., 1991). The fatty acid composition of fats extracted from commercially available butter and pig milk, using the Röse-Gottlieb method (IDF, 1983) as well as that of soybean oil and palm oil was determined by gas chromatography after methyl or isopropyl-esterification. NIR transmittance spectra were measured between 1600 and 2300 nm on a Bran and Luebbe InfraAnalyzer 500 and the data used to examine the fatty acid composition from a qualitative point of view. Sato et al. (1991) suggested that NIR spectroscopy could be used to set up a library of spectra of various fats and oils with this then being used to detect a spectral match for an unknown sample. Other qualitative NIR studies applied discriminant (Bewig et al., 1994) and principal component (Sato, 1994) analysis to distinguish between different vegetable oils. Sato (1994) classified nine varieties of *vegetable oils* successfully from their PCA scores using the InfraAnalyzer 500 as before. Also using a Bran and Luebbe InfraAnalyzer 500 to collect the spectra, Bewig et al. (1994) derived a four wavelength equation to separate *cottonseed*, *peanut*, *soybean*, and *canola oils* successfully. The soybean oil group was, however, more dispersed than the other three groups.

Hourant et al. (2000) using a Foss NIRSystems 6500 instrument have shown the potential of NIR spectroscopy for the discrimination of fats and oil. They studied 104 edible oil and fat samples from 18 different sources, either vegetable (brazil nut, coconut, corn, sunflower, walnut, *virgin olive*, peanut, palm, canola, soybean, and sunflower) or animal (tallow and hydrogenated fish). The samples were analyzed by high-performance gas chromatography (HPGC) and NIR spectroscopy. In this work, the NIR spectral features of the most noteworthy bands were studied and discussed to design a filter-type NIR instrument. An arborescent structure, based on stepwise linear discriminant analysis (SLDA), was built to classify the samples according to their sources. Seven discriminant functions permitted a successive discrimination of saturated fats, corn, soybean, sunflower, canola, peanut, high oleic sunflower, and virgin olive oils. The discriminant functions were based on the absorbance values, between three and five, from the 1700 to 1800 and 2100 to 2400 nm wavelength regions. Chemical explanations were given in support of the selected wavelengths and the arborescent structure was then validated with a test set and 90% of the samples were correctly classified.

The increasing consumer interest in *olive oil* due to its nutritional and sensory properties and the economic value of olive oil compared with other vegetable oils makes this product prone to adulteration by cheaper oils. Consequently, the *adulteration of olive oil* is a serious problem in the modern olive oil industry and is not only a crisis in major olive producing countries, but

also is affecting small olive oil suppliers and consumers in countries such as South Africa (McKenzie and Koch, 2004). Since the South African market is flooded with olive oil imports from the Mediterranean, it has experienced local incidents of fraud (Cilliers, 2001).

*Olive oil adulteration* can be divided into two types namely, the blending of virgin olive oils with inferior quality olive oils such as refined olive oil or pomace oil and, second, the addition of other vegetable oils to olive oil (Dourtoglou et al., 2003). The former mainly occurs in major olive oil producing countries such as Greece, Italy, and Spain while the addition of other vegetable oils (e.g., sunflower, canola, and rapeseed) is mostly a problem in countries importing olive oil (e.g., the United States and Canada) and where seed oils are locally produced and are less expensive (Li-Chan, 1994). The fatty acid composition of olive oil is the most important indicator of adulteration by other oils and is mostly determined by gas chromatography. Since the International Olive Oil Commission (IOOC) and other official bodies have established specific limits for the percentage of distinct fatty acids in genuine olive oil, this method can be applied to distinguish pure from adulterated oils (Christopoulou et al., 2004). The maximum limits of fatty acids in olive oils and olive pomace oils are as follows (% m/m methyl esters): oleic 55.0–83.0, stearic 0.5–5.0, palmitic 7.5–20.0, palmitoleic 0.3–3.5, linoleic 3.5–21.0, myristic  $\leq 0.03$ , linolenic  $\leq 1.0$ , arachidic  $\leq 0.6$ , gadoleic (eicosenoic)  $\leq 0.5$ , behenic  $\leq 0.2$  ( $\leq 0.3$  for olive pomace oils), heptadecanoic  $\leq 0.4$ , heptadecenoic  $\leq 0.6$ , and lignoceric  $\leq 0.2$  (IOC, 2016). Any fatty acid present in amounts exceeding the above-mentioned limits will be indicative of adulteration with seed oil. However, the fatty acid composition is not in all cases successful in detecting fraud (Christopoulou et al., 2004).

Although several studies evaluated *NIR spectroscopy* as an alternative *quality control* tool for other *vegetable oils*, the application of NIR spectroscopy to olive oil quality control is a relatively new development (Armenta et al., 2010). PCA was used to detect and quantify adulterants in virgin olive oil (Wesley et al., 1995). It was possible to predict the type of adulterant with 75% accuracy. Wesley et al. (1996) improved on this prediction by developing a discriminant analysis equation that could identify correctly the type of adulterant in extra virgin oil in 90% of the cases. It was also possible to measure the level of adulteration to an accuracy of  $\pm 0.9\%$  (w/w).

Downey et al. (2002) demonstrated the potential of NIR spectroscopy and SIMCA to discriminate between authentic *extra virgin olive oils* and the same oils adulterated by the addition of a single *sunflower oil* sample at levels as low as 1% (w/w). They also quantified the level of sunflower oil adulterant present using PLS with a SECV equal to 0.8% (w/w) which is suitable for industrial use. The adulteration of olive oils with a variety of common adulterants was detected using FT-NIR spectroscopy analysis with very low error limits (Christy et al., 2004; Kasemsumran et al., 2005).

## 6.9 Wine and Distilled Alcoholic Beverages

An *alcoholic beverage* is a complex mixture of components presenting volatile compounds, responsible for aroma and flavor, and fixed compounds consisting of a large variety of substances with different characteristics (Arvanitoyannis et al., 1999). The *authenticity of wine* is strictly controlled by the respective national authorities (Arvanitoyannis et al., 1999). This can include official sensory evaluation, chemical analysis, and examination of the records kept by the wine producer. Various analytical techniques are being used to determine a wine's authenticity as reviewed by Arvanitoyannis et al. (1999). These techniques are often coupled with appropriate chemometric techniques, that is, PCA, LDA CVA, and cluster linear analysis (CLA) (Arvanitoyannis et al., 1999).

As was the case for other food products, the ideal is to detect adulteration or verify authenticity of an alcoholic beverage on the sample as is. In the *wine industry*, *NIR spectroscopy* has found considerable use in various applications concerning wine analysis (Kaffka and Norris, 1976; Baumgarten, 1987; Van de Voort, 1992; Sneyd et al., 1989; Van den Berg et al., 1997). NIR reflectance spectroscopy proved to be very successful in the simultaneous determination of ethanol, fructose, and residual sugars in botrytized-grape sweet wines (Garcia-Jares and Médina, 1997). In 1994, Burns (1994) proposed the employment of NIR spectroscopy as a future analytical technique for determinations of total phenolics in wines. Subsequently, Cozzolino et al. (2004) illustrated the simultaneous prediction of various phenolic compounds in fermenting must and red wine.

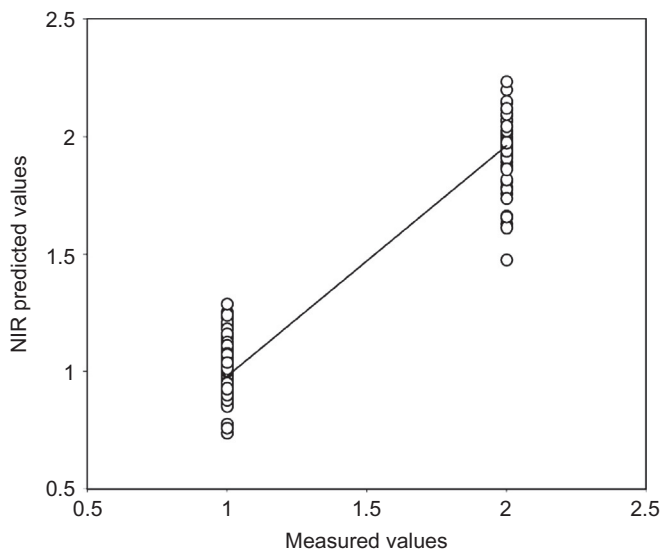
One of the main risks for the consumer of *distilled alcoholic beverages* of unknown origin is that the drinks may contain high levels of methanol which is present in alcoholic beverages in small amounts (Pontes et al., 2006). The compositional quality of *grape*, *wine*, and *spirits* determined by means of scanning NIR spectroscopy were investigated by the Australian Wine Research Institute (Gishen and Dambergs, 1998; Cope, 2000). This preliminary evaluation of the applicability of *NIR spectroscopy* to determine compositional quality showed considerable promise with potential for immediate application in the wine industry.

*NIR spectroscopy* combined with multivariate analysis, that is, PCA, PLS-DA, and LDA showed promise as a rapid method to monitor the progress of red *wine fermentation* (Cozzolino et al., 2006). In this study, visible and NIR spectroscopy were used as a qualitative technique, that is, no quantification of any compositional variable was made. Cozzolino et al. (2006) illustrated that it was possible to detect changes that occur during fermentation and to classify the progression stage of fermentation independent of variables such as grape variety, yeast strain, and temperature.

Dambergs et al. (2001) and Cozzolino et al. (2005) explored the potential of NIR spectroscopy as a tool to predict *wine sensory quality*. FT-NIR spectroscopy was used to measure the percentage of sugar in grape must and to

discriminate between different must samples in terms of their free amino nitrogen (FAN) values (Manley et al., 2001). It was also shown by Manley et al. (2001) that FT-NIR could discriminate between Chardonnay wine samples in terms of their *malolactic fermentation status* using SIMCA; table wines were successfully discriminated on the basis of their *ethyl carbamate content*.

Confirmation of *wine authenticity*, mainly in terms of *vintage*, *wine age*, *variety*, and *geographical origin*, has received increasing attention in the recent past. Chemometric models based on visible and NIR spectroscopy data were used to determine the origin of two different varieties of Australian white wine samples, that is, Riesling and Chardonnay (Cozzolino et al., 2003). No obvious differences were detected from a visual observation of the spectra between the two white wine varieties in either the visible or NIR region (Cozzolino et al., 2003). Both varieties have absorption bands at 1450 nm related to the O—H second overtone of water and ethanol, at 1690 nm related with either C—H<sub>3</sub> stretch first overtone or compounds containing C—H aromatic groups, at 1790 nm related with C—H stretch first overtone, and at 1950 nm with O—H stretch first overtone of water and ethanol. The models were constructed using PCA, PCR, and DPLS on spectra collected from 400 to 2500 using a Foss NIRSystems 6500 and a 1 mm pathlength cuvette. The PLS-DA models were able to accurately classify 100% of the Riesling and 96% of the Chardonnay wines (Fig. 3).



**FIG. 3** Prediction of commercial white wine varieties using *partial least squares* discriminant analysis (PLS-DA) (400–1100 nm) and second derivative (validation set). (Reproduced with permission from Cozzolino, D., Smyth, H.E., Gishen, M., 2003. Feasibility study on the use of visible and near-infrared spectroscopy together with chemometrics to discriminate between commercial white wines of different varietal origins. *J. Agric. Food Chem.* 51, 7703–7708. Copyright (2003) American Chemical Society.)

Manley et al. (2003) illustrated the potential of FT-NIR to categorize four different classes of *rebate brandy* and Pontes et al. (2006) proposed a strategy in which FT-NIR spectroscopy and chemometric methods, that is, PCA and SIMCA can be used in the classification and verification of adulteration in *whiskeys, brandies, rums, and vodkas* (refer to Chapter 4 for more detailed discussion).

Yu et al. (2006, 2007a) used FT-NIR to discriminate *Chinese rice wine* of different *geographical origins* and to classify Chinese rice wine with different marked *age*, respectively. Yu et al. (2007b) evaluated the potential of visible and FT-NIR to predict *vintage year* (five vintages) of Chinese rice wine in 600 mL square brown glass bottles (refer to Chapter 4 for more detailed discussion). The possibility of using NIR spectroscopy to discriminate between *wine vinegar* and *alcohol vinegar* was also illustrated using SIMCA after OSC was applied to the NIR spectral data (Saiz-Abajo et al., 2004). NIR spectra were collected from 1100 to 2500 using a Foss NIRSystems 5000 spectrometer equipped with a liquid flow cell. Each spectrum was based on 32 co-added scans at 2 nm intervals. Three replicates of each sample were taken and the mean value was subsequently calculated. Clear separation between the classes was observed when tartaric acid as used as a discriminating descriptor.

## 7 CONCLUSIONS

NIR spectroscopy, with its unsurpassed combination of speed, accuracy, and simplicity, has found its own niche in the *quality control laboratories* of *food and beverage manufacturers* worldwide. Advances in technologies such as optics, electronics, computer hardware and software, and especially chemometrics, have allowed for more powerful NIR spectroscopy instrumentation to be developed and manufactured and consequently more powerful spectral analyses. Similar to other analytical methods, it has limitations but the capabilities of NIR spectroscopy instrumentation are continually improving to maximize the performance of this very exciting technology. There is therefore no doubt that NIR spectroscopy does have the capability and potential to solve many food authentication and adulteration problems.

Many of the reported studies, investigating the use of NIR spectroscopy to confirm *authentication*, or detect and/or quantify *adulteration of food*, food products, and beverages, however, remains preliminary or only feasibility studies and performed on a limited number of samples. This is mainly due to the cost and complexity of obtaining an adequate number of samples with sufficient variation within the sample collection. Appropriate *validation* should therefore always be performed before commercial implementation of any such method is considered.

An exiting new technique which plays an important role in food authentication problems in the future is *NIR chemical imaging (NIR hyperspectral imaging)*. This nondestructive technique combines conventional NIR spectroscopy

with digital imaging. As a NIR spectrum is collected for each pixel in the image, a 3D cube consisting of both spatially resolved spectra and wavelength dependent images is created. The ability to not only quantify a chemical component but also to identify as well as locate these components within a specific sample is invaluable to understand a sample and will surely play a huge role in future to investigate issues of adulteration.

## REFERENCES

- Abbas, O., Lecler, B., Dardenne, P., Baeten, V., 2013. Detection of melamine in feed ingredients by near infrared spectroscopy and chemometrics. *J. Near Infrared Spectrosc.* 21 (3), 183–194.
- Adamopoulos, K.G., Goula, A.M., Petropakis, H.J., 2001. Quality control during processing of feta cheese-NIR application. *J. Food Compos. Anal.* 14, 431–440.
- Al-Jowder, O., Kemsley, E.K., Wilson, R.H., 1997. Mid-infrared spectroscopy and authenticity problems in selected meats: a feasibility study. *Food Chem.* 59 (2), 195–201.
- Al-Jowder, O., Defernez, M., Kemsley, E.K., Wilson, R.H., 1999. Mid-infrared spectroscopy and chemometrics for the authentication of meat products. *J. Agric. Food Chem.* 47, 3210–3218.
- Al-Jowder, O., Kemsley, E.K., Wilson, R.H., 2002. Detection of adulteration in cooked meat products by mid-infrared spectroscopy. *J. Agric. Food Chem.* 50, 1325–1329.
- Anonymous, 1967. Legge 580, 4 luglio 1967. Disciplina per la lavorazione e il commercio dei cereali, degli sfarinati, del pane e delle paste alimentari (as cited by Cocchi et al., 2006).
- Anonymous, 2001. Decreto del President della Repubblica No 187, 9 febbraio 2001. Regolamento per la revisione della normativa sulla produzione e commercializzazione di sfarinati e paste alimentari, a norma dell'art. 50 della L.146/94 (as cited by Cocchi et al., 2006).
- Armenta, S., Moros, J., Garrigues, S., De La Guardia, M., 2010. The use of near-infrared spectrometry in the olive oil industry. *Crit. Rev. Food Sci. Nutr.* 50, 567–582.
- Arvanitoyannis, I.S., Tzouros, N.E., 2005. Implementation of quality control methods in conjunction with chemometrics toward authentication of dairy products. *Crit. Rev. Food Sci. Nutr.* 45, 231–249.
- Arvanitoyannis, I.S., Katsota, M.N., Psarra, E.P., Soufleros, E.H., Kallithraka, S., 1999. Application of quality control methods for assessing wine authenticity: use of multivariate analysis (chemometrics). *Trends Food Sci. Technol.* 10, 321–336.
- Baeten, V., Dardenne, P., 2005. Applications of near-infrared imaging for monitoring agricultural food and feed products. In: Bhargava, R., Levin, I.W. (Eds.), *Spectrochemical Analysis Using Infrared Multichannel Detectors*. Blackwell Publishing, Oxford, pp. 283–301.
- Baeten, V., Rogez, H., Fernández Pierna, J.A., Vermeulen, P., Dardenne, P., 2015. Vibrational spectroscopy methods for the rapid control of agro-food products. In: Toldra, J., Nollet, H. (Eds.), *Handbook of Food Analysis*. third ed. In: vol. II. pp. 591–614. (Chapter 32).
- Balabin, R.M., Smirnov, S.V., 2011. Melamine detection by mid- and near-infrared (MIR/NIR) spectroscopy: a quick and sensitive method for dairy products analysis including liquid milk, infant formula, and milk powder. *Talanta* 85 (2011), 562–568.
- Bao, J.S., Cai, Y.Z., Corke, H., 2001. Prediction of rice starch quality parameters by near-infrared reflectance spectroscopy. *J. Food Sci.* 66 (7), 936–939.
- Barnes, R.J., Dhanoa, M.S., Lister, S.J., 1989. Standard normal variate transformation and de-trending of near-infrared diffuse reflectance spectra. *Appl. Spectrosc.* 43 (5), 772–777.
- Barton, F.E., 2002. Theory and principles of near infrared spectroscopy. *Spectrosc. Eur.* 14 (1), 12–18.

- Basri, K.N., Hussain, M.N., Bakar, J., Sharif, Z., Khir, M.F.A., Zoolfakar, A.S., 2017. Classification and quantification of palm oil adulteration via portable NIR spectroscopy. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 173, 335–342.
- Baumgarten, G., 1987. The determination of alcohol in wines by means of near infrared technology. *South Afr. J. Enol. Viticult.* 8 (2), 75–77.
- Bazar, G., Romvari, R., Szabo, A., Somogyi, T., Éles, V., Tsenkova, R., 2016. NIR detection of honey adulteration reveals differences in water spectral pattern. *Food Chem.* 194, 873–880.
- Beebe, K.R., Pell, R.J., Seasholtz, M.B., 1998. *Chemometrics: A Practical Guide*. John Wiley & Sons, Inc., New York, p. 348
- Ben-Gera, I., Norris, K.H., 1968a. Determination of moisture content in soybeans by direct spectrophotometry. *Israel J. Agric. Res.* 18, 125–132.
- Ben-Gera, I., Norris, K.H., 1968b. Direct spectrophotometric determination of fat and moisture in meat products. *J. Food Sci.* 33, 64–67.
- Bereton, R.G., 2011. One-class classifiers. *J. Chemometr.* 25, 225–246.
- Bertrand, D., Robert, P., Loisel, W., 1985. Identification of some wheat varieties by near infrared reflectance spectroscopy. *J. Sci. Food Agric.* 36, 1120–1124.
- Bewig, K.M., Clarke, A.D., Roberts, C., Unklesbay, N., 1994. Discriminant analysis of vegetable oils by near-infrared reflectance spectroscopy. *J. Am. Oil Chem. Soc.* 71 (2), 195–200.
- Blanco, M., Villarroya, I., 2002. NIR spectroscopy: a rapid-response analytical tool. *Trends Anal. Chem.* 21 (4), 240–250.
- Blazquez, C., Downey, G., O'Donnell, C., O'Callaghan, D., Howard, V., 2004. Prediction of moisture, fat and inorganic salts in processed cheese by near infrared reflectance spectroscopy and multivariate data analysis. *J. Near Infrared Spectrosc.* 12, 149–157.
- Blazquez, C., Downey, G., O'Callaghan, D., Howard, V., Delahunty, C., Sheehan, E., 2006. Modeling of sensory and instrumental texture parameters in processed cheese by near infrared reflectance spectroscopy. *J. Dairy Res.* 73, 58–69.
- Bosset, J.O., Berger, T., Bühler-Moor, U., Bütikofer, U., Collomb, M., Dafflon, O., 1997. Comparison of some highland and lowland Gruyère type cheese of Switzerland: a study of their potential PDO/AOC/AOP characteristics. Authenticity and adulteration of food—the analytical approach. *Proc. Eur. Food Chem.* 220, 395–400.
- Budínová, G., Vlácil, D., Mestek, O., Volka, K., 1998. Application of infrared spectroscopy to the assessment of authenticity of tea. *Talanta* 47, 255–260.
- Burges, C.J.C., 1998. A tutorial on support vector machines for pattern recognition. *Data Min. Knowl. Disc.* 2, 121–167.
- Burns, G.H., 1994. Introduction: overview of wine analysis. In: Zoecklein, B.W., Fugelsang, K.C., Gump, B.H., Nury, F.S. (Eds.), *Wine Analysis and Production*. Chapman & Hall, New York, p. 5.
- Butler, L.A., 1983. The history and background. *Cereal Foods World.* 28, 238–240.
- Cattaneo, T.M.P., Holroyd, S.E., 2013. The use of near infrared spectroscopy for determination of adulteration and contamination in milk and milk powder: updating knowledge. *J. Near Infrared Spectrosc.* 21, 341–349.
- Cattaneo, T.M.P., Giardina, C., Sinelli, N., Riva, M., Giangiacomo, R., 2005. Application of FT-NIR and FT-IR spectroscopy to study the shelf-life of Crescenza cheese. *Int. Dairy J.* 15, 693–700.
- Centner, V., Verdu-Andres, J., Walczak, B., Jouan-Rimbaud, D., Depagne, F., Pasti, L., Poppi, R., Massart, D.L., De Noord, O.E., 2000. Comparison of multivariate calibration techniques applied to experimental NIR data sets. *Appl. Spectrosc.* 54, 608–623.



- Chauchard, F., Cogdill, R., Roussel, S., Roger, J.M., Bellon-Maurel, V., 2004. Application of LS-SVM to non-linear phenomena in NIR spectroscopy: development of a robust and portable sensor for acidity prediction in grapes. *Chemom. Intel. Lab. Syst.* 71, 141–150.
- Chen, Q., Zhao, J., Zhang, G., Wang, X., 2006. Feasibility study on qualitative and quantitative analysis in tea by near infrared spectroscopy with multivariate calibration. *Anal. Chim. Acta* 572, 77–84.
- Chen, Q., Zhao, J., Fang, C.H., Wang, D., 2007. Feasibility study on identification of green, black and oolong teas using near-infrared spectroscopy based on support vector machine (SVM). *Spectrochim. Acta A* 66, 568–574.
- Chen, L., Xue, X., Ye, Z., Zhou, J., Chen, F., Zhao, J., 2011. Determination of Chinese honey adulterated with high fructose corn syrup by near infrared spectroscopy. *Food Chem.* 128, 1110–1114.
- Cho, H.J., Hong, S.H., 1998. Acacia honey quality measurement by near-infrared spectroscopy. *J. Near Infrared Spectrosc.* 6, A329–A331.
- Christopoulou, E., Lazaraki, M., Komaitis, M., Kaselimis, K., 2004. Effectiveness of determinations of fatty acids and triglycerides for the detection of adulteration of olive oils with vegetable oils. *Food Chem.* 84, 463–474.
- Christy, A.A., Kasemsumran, S., Du, Y., Ozaki, Y., 2004. The detection and quantification of adulteration in olive oil by near infrared spectroscopy and chemometrics. *Anal. Sci.* 20, 935–940.
- Cilliers, J., 2001. Nuus: bedrog met tafelolie oopgevelek (vervalste olyfolie). *Landbou Weekblad.* (19 Oktober).
- Ciurczak, E.W., 1992. Principles of near-infrared spectroscopy. In: Burns, D.A., Ciurczak, E.M. (Eds.), *Handbook of Near-Infrared Analysis*. Marcel Dekker, Inc., New York, pp. 7–11.
- Ciurczak, E.W., 2005. Revisiting the polarization interferometer. *Spectroscopy* 20 (2), 68–73.
- Cocchi, M., Seeber, R., Ulrici, A., 2003. Multivariate calibration of analytical signals by WILMA (wavelet interface to linear modelling analysis). *J. Chemometr.* 17, 512–527.
- Cocchi, M., Corbellini, M., Foca, G., Lucisano, M., Pagani, M.A., Tassi, L., Ulrici, A., 2005. Classification of bread wheat flours in different quality categories by a wavelet-based feature selection/classification algorithm on NIR spectra. *Anal. Chim. Acta* 544, 100–107.
- Cocchi, M., Durante, C., Foca, G., Marchetti, A., Tassi, L., Ulrici, A., 2006. Durum wheat adulteration detection by NIR spectroscopy multivariate calibration. *Talanta* 68, 1505–1511.
- Codex Alimentarius Commissions Standards, 1987. Codex Standards for Sugars: Standard 12-1981. Review 1.
- Contal, L., León, V., Downey, G., 2002. Detection and quantification of apple adulteration in strawberry and raspberry purees using visible and near infrared spectroscopy. *J. Near Infrared Spectrosc.* 10, 289–299.
- Cope, A., 2000. Industry moves closer to rapid colour testing. *Aust. N. Z. Wine Ind. J.* 15, 78–79.
- Cordella, C., Moussa, I., Martel, A., Sbirrazzuoli, N., Lizzani-Couvelier, L., 2002. Recent developments in food characterization and adulteration detection: technique-oriented perspectives. *J. Agric. Food Chem.* 50, 1751–1764.
- Correia, R.M., Tosato, F., Domingos, E., Rodrigues, R.R.T., Aquino, L.F.M., Filgueiras, P.R., Lacerda Jr., V., Romão, W., 2018. Portable near infrared spectroscopy applied to quality control of Brazilian coffee. *Talanta* 176, 59–68.
- Coventry, G., 1988. The development and application of NIR with particular reference to the food industry. *Food Sci. Technol. Today* 2, 130–139.
- Cowe, I.A., McNicol, J.W., 1985. The use of principal components in the analysis of near-infrared spectra. *Appl. Spectrosc.* 39, 257–266.



- Cowe, I.A., McNicol, J.W., Cuthbertson, D.C., 1990. Principal component analysis: a chemometric approach to the analysis of near infrared spectra. *Anal. Proc.* 27, 61–63.
- Cozzolino, D., 2014. An overview of the use of infrared spectroscopy and chemometrics in authenticity and traceability of cereals. *Food Res. Int.* 60, 262–265.
- Cozzolino, D., Murray, I., 2004. Identification of animal meat muscles by visible and near infrared reflectance spectroscopy. *Lebensm. Wiss. Technol.* 37, 447–452.
- Cozzolino, D., Fassio, A., Gimenez, A., 2000. The use of near-infrared reflectance spectroscopy (NIRS) to predict the composition of whole maize plants. *J. Sci. Food Agric.* 81, 142–146.
- Cozzolino, D., Smyth, H.E., Gishen, M., 2003. Feasibility study on the use of visible and near-infrared spectroscopy together with chemometrics to discriminate between commercial white wines of different varietal origins. *J. Agric. Food Chem.* 51, 7703–7708.
- Cozzolino, D., Kwiatkowski, M.J., Parker, M., Cynkar, W.U., Dambergs, R.G., Gishen, M., Herderich, M.J., 2004. Prediction of phenolic compounds in red wine fermentations by visible and near infrared spectroscopy. *Anal. Chim. Acta* 513, 73–80.
- Cozzolino, D., Smyth, H.E., Lattey, K.A., Cynkar, W., Janik, L., Damberg, R.G., Francis, I.L., Gishen, M., 2005. Relationship between sensory analysis and near infrared spectroscopy in Australian Riesling and chardonnay wines. *Anal. Chim. Acta* 539, 341–348.
- Cozzolino, D., Parker, M., Damsberg, R.G., Herderich, M., Gishen, M., 2006. Chemometrics and visible-near infrared spectroscopic monitoring of red wine fermentation in a pilot scale. *Bio-technol. Bioeng.* 95 (6), 1101–1107.
- Crocombe, R.A., 2004. MEMS technology moves process spectroscopy into a new dimension. *Spectrosc. Eur.* 16 (3), 16–19.
- Dambergs, R.G., Kambouris, A., Schumacher, N., Francis, I.L., Esler, M.B., Gishen, M., 2001. Wine Quality Grading by near Infrared Spectroscopy. **Technical Publication**, The Australian Wine Research Institute, Glen Osmond.
- Davies, A.M.C., 1991. The history of near infrared spectroscopy. 1. The first NIR spectrum. *NIR news* 2, 12.
- Davies, T., 1998. The history of near infrared spectroscopic analysis: Past, present and future—“from sleeping technique to the morning star of spectroscopy” *Anal. Magazine* 26, 17–19.
- Davies, A.M.C., McClure, F., 1985. Near infrared analysis in the Fourier domain with special reference to process control. *Anal. Proc.* 22, 321–322.
- Day, M.S., Fearn, F.R.B., 1982. Near infra-red reflectance as an analytical technique, part 1. History and development. *Lab. Pract.* 31, 328–330.
- Devaux, M.F., Bertrand, D., Martin, 1986. Discrimination of bread-baking quality of wheats according to their variety by near infrared reflectance spectroscopy. *Cereal Chem.* 63 (2), 151–154.
- Devaux, M.F., Bertrand, D., Robert, P., Morat, J.L., 1987. Extraction of near infrared spectral information by fast Fourier transform and principal component analysis. Application to the discrimination of baking quality of wheat flours. *J. Chemometr.* 1, 103–110.
- Devaux, M.F., Bertrand, D., Robert, P., Qannari, M., 1988. Application of multidimensional analysis to the extraction of discriminant spectral patterns from NIR spectra. *Appl. Spectrosc.* 42, 1015–1019.
- Ding, H.B., Xu, R.-J., 1999. Differentiation of beef and kangaroo meat by visible/near-infrared reflectance spectroscopy. *J. Food Sci.* 64 (5), 814–817.
- Ding, H.B., Xu, R.-J., Chan, D.K.O., 1999. Identification of broiler chicken meat using a visible/near-infrared spectroscopic technique. *J. Sci. Food Agric.* 79, 1382–1388.
- Domingo, E., Tirelli, A.A., Nunes, C.A., Guerreiro, M.C., Pinto, S.M., 2014. Melamine detection in milk using vibrational spectroscopy and chemometrics analysis: a review. *Food Res. Int.* 60, 131–139.

- Dong, Y.W., Tu, Z.H., Zhu, D.Z., Liu, Y.W., Wang, Y.N., Huang, J.L., Sun, B.L., Fan, Z.N., 2009. Feasibility of using NIR spectroscopy to detect melamine in milk. *Spectrosc. Spectr. Anal.* 29, 2934–2938.
- Dos Santos Neto, J.P., Dantas de Assis, M.W., Parkutz Casagrande, I., Cunha Júnior, L.C., De Almeida Teixeira, G.H., 2017. Determination of 'palmer' mango maturity indices using portable near infrared (VIS-NIR) spectrometer. *Postharvest Biol. Technol.* 130, 75–80.
- Dourtoglou, V.G., Dourtoglou, T., Antonopoulos, A., Stefanou, E., Lalas, S., Poulos, C., 2003. Detection of olive oil adulteration using principal component analysis applied on total and regio FA content. *J. Am. Oil Chem. Soc.* 80, 203–208.
- Downey, G., 1995. Food quality and authenticity measurement. *Farm Food* 21–24. (July/September).
- Downey, G., 1996a. Authentication of food and food ingredients by near infrared spectroscopy. *J. Near Infrared Spectrosc.* 4, 47–61.
- Downey, G., 1996b. Non-invasive and non-destructive percutaneous analysis of farmed salmon flesh by near infra-red spectroscopy. *Food Chem.* 55 (3), 305–311.
- Downey, G., 1998a. Direct measurement of food quality and authenticity. *Anal. Contr.* 1, 27–30.
- Downey, G., 1998b. Food and food ingredient authentication by mid-infrared spectroscopy and chemometrics. *Trends Anal. Chem.* 17 (7), 418–424.
- Downey, G., Beauchêne, D., 1997a. Discrimination between fresh and frozen-then-thawed beef *M. longissimus dorsi* by combined visible-near infrared reflectance spectroscopy: a feasibility study. *Meat Sci.* 45, 353–363.
- Downey, G., Beauchêne, D., 1997b. Authentication of fresh vs. frozen-then-thawed beef by near infrared reflectance spectroscopy of dried drip juice. *Lebensm. Wiss. Technol.* 30, 721–726.
- Downey, G., Boussion, J., 1996. Authentication of coffee bean variety by near-infrared reflectance spectroscopy of dried extract. *J. Sci. Food Agric.* 71, 41–49.
- Downey, G., Flynn, S.J., 2002. Davies, A.M.C., Cho, R.K. (Eds.), Discrimination between virgin olive oils from Crete, the Peloponese and other Greek Islands using near infrared transreflectance spectroscopy. *Near Infrared Spectroscopy: Proceedings of the 10th International Conference*. NIR Publications, Chichester, pp. 239–241.
- Downey, G., Spengler, B., 1996. Compositional analysis of coffee blends by near infrared spectroscopy. *Irish J. Agric. Food Res.* 35, 179–188.
- Downey, G., Byrne, S., Dwyer, E., 1986. Wheat trading in the Republic of Ireland: the utility of a hardness index derived by near infrared reflectance spectroscopy. *J. Sci. Food Agric.* 37, 762–766.
- Downey, G., Boussion, J., Beauchêne, D., 1994. Authentication of whole and ground coffee beans by near infrared reflectance spectroscopy. *J. Near Infrared Spectrosc.* 2, 85–92.
- Downey, G., Briandet, R., Wilson, R.H., Kemsley, E.K., 1997. Near- and mid-infrared spectroscopies in food authentication: coffee varietal identification. *J. Agric. Food Chem.* 45, 4357–4361.
- Downey, G., McElhinney, J., Fearn, T., 2000. Species identification in selected raw homogenized meats by reflectance spectroscopy in the mid-infrared, near-infrared, and visible ranges. *Appl. Spectrosc.* 54 (6), 894–899.
- Downey, G., McIntyre, P., Davies, A.N., 2002. Detection and quantifying sunflower oil adulteration in extra virgin olive oils from the eastern Mediterranean by visible and near-infrared spectroscopy. *J. Agric. Food Chem.* 50, 5520–5525.
- Downey, G., Fouratier, V., Kelly, J.D., 2003. Detection of honey adulteration by addition of fructose and glucose using near infrared transreflectance spectroscopy. *J. Near Infrared Spectrosc.* 11, 447–456.

- Downey, G., Howard, V., Delahunty, C., O'Callaghan, D., Sheehan, E., Guinee, T., 2005. Prediction of maturity and sensory attributes of cheddar cheese using near-infrared spectroscopy. *Int. Dairy J.* 15 (6/9), 701–709.
- Downey, G., Kelly, J.D., Petisco, C., 2006. Food authenticity—has near infrared spectroscopy a role? *Spectrosc. Eur.* 18 (3), 1012–14.
- Ellis, J.W., Bath, J., 1938. Alterations in the infrared absorption spectrum of water in gelatin. *J. Chem. Phys.* 6, 723–729.
- Esbensen, K.H., 2000. *Multivariate Data Analysis in Practice: An Introduction to Multivariate Data Analysis and Experimental Design*, fourth ed. Camo ASA, Oslo, pp. 1–352.
- Escribano, S., Biasi, W.V., Lerud, R., Slaughter, D.C., Mitcham, E.J., 2017. Non-destructive prediction of soluble solids and dry matter content using NIR spectroscopy and its relationship with sensory quality in sweet cherries. *Postharvest Biol. Technol.* 128, 112–120.
- Esler, M.B., Gishen, M., Francis, I.L., Damberg, R.G., Kambouris, A., Cyncar, W.U., Boehm, D.R., 2002. Davies, A.M.C., Cho, R.K. (Eds.), Effects of variety and region on near infrared reflectance spectroscopic analysis of quality parameters in red wine grapes. *Near Infrared Spectroscopy: Proceedings of the 10th International Conference*. NIR Publications, Chichester, pp. 249–253.
- Esteban-Díez, I., Gonzáles-Sáiz, J.M., Pizarro, C., 2004a. OWAVEC: a combination of wavelet analysis and an orthogonalization algorithm as a pre-processing step in multivariate calibration. *Anal. Chim. Acta* 515, 31–41.
- Esteban-Díez, I., Gonzáles-Sáiz, J.M., Pizarro, C., 2004b. An evaluation of orthogonal signal correction methods for the characterisation of arabica and robusta coffee varieties by NIRS. *Anal. Chim. Acta* 514, 57–67.
- Esteban-Díez, I., Gonzáles-Sáiz, J.M., Pizarro, C., 2005. Generalization of OWAVEC method for simultaneous noise suppression, data compression and orthogonal signal correction. *Anal. Chim. Acta* 544, 89–99.
- Esteban-Díez, I., Gonzáles-Sáiz, J.M., Sáenz-González, C., Pizarro, C., 2007. Coffee varietal differentiation based on near infrared spectroscopy. *Talanta* 71, 221–229.
- Evans, D.G., Scotter, C.N.G., Day, L.Z., Hall, M.N., 1993. Determination of the authenticity of orange juice by discriminant analysis of near infrared spectra. *J. Near Infrared Spectrosc.* 1, 33–44.
- Fearn, T., 2002. Assessing calibrations: SEP, RPD, RER and  $R^2$ . *NIR News* 13, 12–14.
- Fernández Pierna, J.A., Vermeulen, P., Lecler, B., Baeten, V., Dardenne, P., 2010. Calibration transfer from dispersive instruments to handheld spectrometers (MEMS). *Appl. Spectrosc.* 64 (6), 644–648.
- Ferrari, E., Foca, G., Vignali, M., Tassia, L., Ulrici, A., 2011. Adulteration of the anthocyanin content of red wines: perspectives for authentication by Fourier transform-near infrared and  $^1\text{H}$  NMR spectroscopies. *Anal. Chim. Acta* 701, 139–151.
- Filho, P.A.D.A., Volery, P., 2005. Broad-based versus specific NIRS calibration: determination of total solids in fresh cheeses. *Anal. Chim. Acta* 544, 82–88.
- Friedrich, D.M., Hulse, C.A., Von Gunten, M., Williamson, E.P., Pederson, C.G., O'Brien, N.A., 2014. Miniature near-infrared spectrometer for point-of-use chemical analysis. *Proc. SPIE* 8992(2014).
- Fu, X., Kim, M.S., Chao, K., Qin, J., Lim, J., Lee, H., Garrido-Varo, A., Pérez-Marín, D., Ying, Y., 2014. Detection of melamine in milk powders based on NIR hyperspectral imaging and spectral similarity analyses. *J. Food Eng.* 124, 97–104.
- Fumière, O., Sinnaeve, G., Dardenne, P., 2000. Attempted authentication of cut pieces of chicken meat from certified production using near infrared spectroscopy. *J. Near Infrared Spectrosc.* 8, 27–34.

- García-Alvarez, M., Huidobro, J.F., Hermida, M., Rodríguez-Otero, J.L., 2000. Major components of honey analysis by near-infrared transreflectance spectroscopy. *J. Agric. Food Chem.* 48, 5154–5158.
- García-Jares, C.M., Médina, B., 1997. Application of multivariate calibration to the simultaneous routine determination of ethanol, glycerol, fructose, glucose and total residual sugars in botrytized-grape sweet wines by means of near-infrared reflectance spectroscopy. *Fresenius J. Anal. Chem.* 357, 86–92.
- Geladi, P., 2002. Some recent trends in the calibration literature. *Chemom. Intel. Lab. Syst.* 60, 211–224.
- Geladi, P., MacDougall, D., Martens, H., 1985. Linearization and scatter-correction for near-infrared reflectance spectra of meat. *Appl. Spectrosc.* 39 (3), 491–500.
- Giardina, C., Cattaneo, T.M.P., Barzaghi, S., 2003. Study of modifications in delactosated milk during shelf-life by NIR and FT-IR spectroscopy. *Milchwissenschaft* 58, 363–366.
- Giardina, C., Sinelli, N., Cattaneo, T.M.P., Giangiacomo, R., 2004. Davies, A.M.C., Garrido-Varo, A. (Eds.), 2D-IR-COSS as a tool in understanding milk rennet coagulation processes. *Near Infrared Spectroscopy: Proceedings of the 11th International Conference. NIR Publications, Chichester*, pp. 187–190.
- Gishen, M., Damberg, B., 1998. Some Preliminary Trails in the Application of Scanning near Infrared Spectroscopy (NIRS) for Determining the Compositional Quality of Grape, Wine and Spirits. *The Australian Grapegrower and Winemaker*, pp. 43–47. **The Annual Technical Issue.**
- Gómez-Cordovés, C., Bartolome, B., 1993. Application of principal component analysis to simple determinations of brandies as a means of verifying quality. *Zeitschrift für Lebensmittel Untersuchung und Forschung* 197, 260–263.
- Goula, A.M., Adamopoulos, K.G., 2003. Estimating the composition of tomato juice products by near infrared spectroscopy. *J. Near Infrared Spectrosc.* 11, 123–136.
- Grant, A., Franklin, J.G., Davies, A.M.C., 1988. Near infra-red analysis: the use of multivariate statistics for investigation of variables in sample preparation and presentation of tea leaf. *J. Sci. Food Agric.* 42, 129–139.
- Grassi, S., Casiraghi, E., Alamprese, C., 2018. Handheld NIR device: a non-targeted approach to assess authenticity of fish fillets and patties. *Food Chem.* 243, 382–388.
- Guelpa, A., Marini, F., Du Plessis, A., Slabbert, R., Manley, M., 2017. Verification of authenticity of South African honey and fraud detection using NIR spectroscopy. *Food Control* 74, 1388–1396.
- Gunasekaran, S., Irudayaraj, J., 2001. Optical methods: visible, NIR, and FTIR spectroscopy. In: Gunasekaran, S. (Ed.), *Nondestructive Food Evaluation Techniques to Analyze Properties and Quality*. Marcel Dekker, Inc., New York, NY, pp. 1–37.
- Ha, J., Koo, M., OK, H., 1998. Determination of the constituents of honey by near-infrared spectroscopy. *J. Near Infrared Spectrosc.* 6, A367–A369.
- Hall, M.N., Robertson, A., Scotter, C.N.G., 1988. Near-infrared reflectance prediction of quality, theaflavin content and moisture content in black tea. *Food Chem.* 27, 61–75.
- Hargin, K.D., 1996. Authenticity issues in meat and meat products. *Meat Sci.* 43, S277–S289.
- Hermida, M., Gonzalez, J.M., Sanchez, M., Rodriguez-Otero, J.L., 2001. Moisture, solids-non-fat and fat analysis in butter by near infrared spectroscopy. *Int. Dairy J.* 11, 93–98.
- Herschel, W., 1800. Investigation of the power to the prismatic colours to heat and illuminate objects; with remarks, that prove the different refrangibility of radiant heat. To which is added, an inquiry into the method of viewing the sun advantageously with telescopes of large apertures and high magnifying powers. *Philos. Trans. Royal Soc.* 90, 255–283. (as cited by Davies, 1991).
- Holman, R.T., Edmondson, P.R., 1956. Near infrared spectra of fatty acids and some related substances. *Anal. Chem.* 28 (10), 1533–1538.

- Holroyd, S.E., 2013. The use of near infrared spectroscopy on milk and milk products. *J. Near Infrared Spectrosc.* 21, 311–322.
- Hopkins, D.W., 2001. Derivatives in spectroscopy. *Near Infrared Anal.* 2 (1), 1–13.
- Hourant, P., Baeten, V., Morales, M.T., Meurens, M., Aparicio, R., 2000. Oils and fats classification by selected bands of near-infrared spectroscopy. *Appl. Spectrosc.* 54 (8), 1168–1174.
- Hoyer, H., 1997. NIR on-line analysis in the food industry. *Process. Control. Qual.* 9, 143–152.
- IDF, 1983. International Dairy Federation. IDF Standard 1B, Brussels, Belgium.
- Iizuka, K., Aishima, T., 1999. Differentiation of soy sauce by pattern recognition analysis of mid- and near-IR spectra. *J. Food Compos. Anal.* 12, 197–209.
- IOC (2016). Trade standard applying to olive oils and olive-pomace oils. COI/T.15/NC no.3/Rev. 11, July 2016.
- ISO (2017). Norm ISO 12099:2017. Animal feeding stuffs, cereals and milled cereal products. Guidelines for the application of near Infrared spectrometry.
- Joubert, E., Manley, M., Gray, B.G., Schulz, H., 2005. Rapid measurement and evaluation of the effect of drying conditions on harpagoside content in *Harpagophytum procumbens* (Devil's Claw) root. *J. Agric. Food Chem.* 53 (9), 3493–3502.
- Joubert, E., Manley, M., Botha, M., 2006. The use of NIRS for quantification of mangiferin and hesperidin contents of dried, green honeybush (*Cyclopia genistoides*) plant material. *J. Agric. Food Chem.* 54, 5279–5283.
- Kaffka, K.J., Norris, K.H., 1976. Rapid instrumental analysis of composition of wine. *Acta Aliment.* 5, 199–217.
- Karoui, R., De Baerdemaeker, J., 2007. A review of the analytical methods coupled with chemometric tools for the determination of the quality and identity of dairy products. *Food Chem.* 102, 621–640.
- Karoui, R., Mazerolles, G., Dufour, E., 2003. Spectroscopic techniques coupled with chemometric tools for structure and texture determinations in dairy products: a review. *Int. Dairy J.* 13, 607–620.
- Karoui, R., Bosset, J.O., Mazerolles, G., Kulmyrzaev, Dufour, E., 2005a. Monitoring the geographic origin of both experimental French Jura hard cheeses and Swiss Gruyère and L'Évêque PDO cheese using mid-infrared and fluorescence spectroscopies: a preliminary investigation. *Int. Dairy J.* 15, 275–286.
- Karoui, R., Dufour, E., Pillonel, L., Schaller, E., Picque, D., Cattenoz, T., Bosset, J., 2005b. The potential of combined infrared and fluorescence spectroscopies as a method of determination of the geographic origin of Emmentaler cheeses. *Int. Dairy J.* 15, 287–298.
- Kasemsumran, S., Kang, N., Christy, A., Ozaki, Y., 2005. Partial least square processing of near-infrared spectra for discrimination and quantification of adulterated olive oils. *Spectrosc. Lett.* 38, 839–851.
- Katsumoto, Y., Jiang, J.-H., Berry, R.J., Ozaki, Y., 2001. Modern pretreatment methods in NIR spectroscopy. *Near Infrared Anal.* 2, 29–36.
- Kawano, S., Watanabe, H., Iwamoto, M., 1992. Determination of sugar content in intact peaches by near infrared spectroscopy with fiber optics in interreflectance mode. *J. Jpn. Soc. Hortic. Sci.* 61, 445–451.
- Kelly, J.D., Petisco, C., Downey, G., 2006. Potential of near infrared transreflectance spectroscopy to detect adulteration of Irish honey by beet invert sugar and high fructose corn syrup. *J. Near Infrared Spectrosc.* 14, 139–146.
- Kumaravelu, C., Gopal, A., 2015. Detection and quantification of adulteration in honey through near infrared spectroscopy. *Int. J. Food Prop.* 18, 1930–1935.
- Laasonen, M., Harmia-Pulkkinen, T., Simard, C.L., Michiels, E., Rasanen, M., Vuorela, H., 2002. Fast identification of *Echinacea purpurea* dried roots using near-infrared spectroscopy. *Anal. Chem.* 74, 2493–2499.

- Laporte, M.-F., Martel, R., Paquin, P., 1998. The near-infrared optic probe for monitoring rennet coagulation in cow's milk. *Int. Dairy J.* 8, 659–666.
- Léon, L., Kelly, J.D., Downey, 2005. Detection of apple juice adulteration using near-infrared transreflectance spectroscopy. *Appl. Spectrosc.* 59 (5), 593–599.
- Li-Chan, E., 1994. Developments in the detection of adulteration of olive oil. *Trends Food Sci. Technol.* 5, 3–11.
- Lohumi, S., Lee, S., Lee, H., Cho, B.K., 2015. A review of vibrational spectroscopic techniques for the detection of food authenticity and adulteration. *Trends Food Sci. Technol.* 46, 85–98.
- Lu, C., Xiang, B., Hao, G., Xu, J., Wang, Z., Chen, C., 2009. Rapid detection of melamine in milk powder by near infrared spectroscopy. *J. Near Infrared Spectrosc.* 17, 59–67.
- Luyckaert, J., Heuerding, S., De Jong, S., Massart, D.L., 2002. An evaluation of direct orthogonal signal correction and other preprocessing methods for the classification of clinical study lots of a dermatological cream. *J. Pharm. Biomed. Anal.* 30 (3), 453–466.
- Luyckaert, J., Zhang, M.H., Massart, D.L., 2003. Feasibility study for the use of near infrared spectroscopy in the qualitative and quantitative analysis of green tea, *Camellia sinensis* (L.). *Anal. Chim. Acta* 478, 303–312.
- Manley, M., 2014. Near-infrared spectroscopy and hyperspectral imaging: non-destructive analysis of biological materials. *Chem. Soc. Rev.* 43, 8200–8214.
- Manley, M., Van Zyl, A., Wolf, E.E.H., 2001. The evaluation of the applicability of Fourier transform near-infrared (FT-NIR) spectroscopy in the measurement of analytical parameters in must and wine. *South Afr. J. Enol. Viticult.* 2, 93–100.
- Manley, M., Bruyn, D., Downey, G., 2003. Classification of three-year old, unblended South African brandy with near infrared spectroscopy. *NIR news* 14 (5), 8–911.
- Manley, M., Gray, B.G., Joubert, E., Schulz, H., 2004. Garrido-Varo, A., Davies, A.M.C. (Eds.), *NIRS: an invaluable tool for the quality control of Devil's Claw (Harpagophytum procumbens)*. *Near Infrared Spectroscopy: Proceedings of the 11th International Conference*. NIR Publications, Chichester, pp. 879–882.
- Manley, M., Joubert, E., Botha, M., 2006. Quantification of the major phenolic compounds, soluble solid content and total antioxidant activity of green rooibos (*Aspalathus linearis*) by means of near infrared spectroscopy. *J. Near Infrared Spectrosc.* 14, 213–222.
- Manley, M., Joubert, E., Myburgh, L., Lotz, E., Kidd, M., 2007. Prediction of soluble solids content and post-storage internal quality of Bulida apricots using near infrared spectroscopy (NIRS) with PLS, MARS and SIMCA as chemometric regression and classification techniques. *J. Near Infrared Spectrosc.* 15 (3), 179–188.
- Mao, J., Xu, J., 2006. Discrimination of herbal medicines by molecular spectroscopy and chemical pattern recognition. *Spectrochim. Acta A* 65, 497–500.
- Maraboli, A., Cattaneo, T.M.P., Giangiacomo, R., 2002. Detection of vegetable proteins from soy, pea and wheat isolates in milk powder by near infrared spectroscopy. *J. Near Infrared Spectrosc.* 10, 63–69.
- Mark, H., 1992. Qualitative discriminant analysis. In: Burns, D.A., Ciurczak, E.M. (Eds.), *Handbook of Near-Infrared Analysis*. Marcel Dekker Inc., New York, pp. 360–361.
- Martens, H., Næs, T., 1989. *Multivariate Calibration*. John Wiley & Sons, Chichester, pp. 86–100. 241–254.
- Martinez, I., Aursand, M., Erikson, U., Singstad, T.E., Veliyulin, T.E., Van der Zwaag, C., 2003. Destructive and non-destructive analytical techniques for authentication and composition analyses of foodstuffs. *Trends Food Sci. Technol.* 14, 489–498.
- Massart, D.L., Vandeginste, B.G.M., Buydens, L.M.C., De Jong, S., Lewi, J.P., Smeyers-Verbeke, J., 1988. *Chemometrics: A Textbook*. vol. 2. Elsevier, Amsterdam.

- Mauer, L.J., Chernyshova, A.A., Hiatt, A., Deering, A., Davis, R., 2009. Melamine detection in infant formula powder using near- and mid-infrared spectroscopy. *J. Agric. Food Chem.* 57, 3974–3980.
- McClure, W.F., 2001. Near-infrared instrumentation. In: Williams, P., Norris, K. (Eds.), *Near-Infrared Technology in the Agricultural and Food Industries*. American Association of Cereal Chemists, St. Paul, pp. 109–127.
- McElhinney, J., Downey, G., O'Donnell, C., 1999. Quantification of lamp content in mixtures with raw minced beef using visible near and mid-infrared spectroscopy. *J. Food Sci.* 64 (4), 587–591.
- McGoverin, C.M., September, D.J.F., Geladi, P., Manley, M., 2012. Near infrared and mid-infrared spectroscopy for the quantification of adulterants in ground black pepper. *J. Near Infrared Spectrosc.* 20, 521–528.
- McKenzie, J.M., Koch, K.R., 2004. Rapid analysis of major components and potential authentication of South African extra virgin olive oils by quantitative  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy. *S. Afr. J. Sci.* 100, 349–354.
- Moh, M.H., Che Man, Y.B., Badlishah, B.S., Jinap, S., Saad, M.S., Abdullah, W.J.W., 1999. Quantitative analysis of palm carotene using Fourier transform infrared and near infrared spectroscopy. *J. Am. Oil Chem. Soc.* 76 (2), 249–254.
- Moscetti, R., Haff, R.P., Aernouts, B., Saeys, W., Monarca, D., Cecchini, M., Massantini, R., 2013. Feasibility of Vis/NIR spectroscopy for detection of flaws in hazelnut kernels. *J. Food Eng.* 118, 1–7.
- Næs, T., Isaksson, T., 1991. Fitting, prediction testing, cross-validation or leverage correction? *NIR News* 2, 10–13.
- Næs, T., Isaksson, T., Fearn, T., Davies, T., 2002. *A User-Friendly Guide to Multivariate Calibration and Classification*. NIR Publications, Chichester, p. 344.
- Nascimento Marques, E.J., De Freitas, S.T., Fernanda Pimentel, M., Celio, P., 2016. Rapid and non-destructive determination of quality parameters in the 'Tommy Atkins' mango using a novel handheld near infrared spectrometer. *Food Chem.* 197, 1207–1214.
- Nicolaï, B.M., Beullens K Bobelyn, E., Peirs, A., Saeys W Theron, K.I., Lammertyn, J., 2007. Non-destructive measurement of fruit and vegetable quality by means of NIR spectroscopy: a review. *Postharvest Biol. Technol.* 46, 99–118.
- Norris, K.H., 1989. NIRS instrumentation. In: Marten, G.C., Shenk, J.S., Barton II, F.E. (Eds.), *Near Infrared Reflectance Spectroscopy (NIRS): Analysis of Forage Quality*. United States Department of Agriculture, Washington, pp. 12–15.
- Norris, K.H., 1996. History of NIR. *J. Near Infrared Spectrosc.* 4, 31–37.
- Nunes, C.A., 2014. Vibrational spectroscopy and chemometrics to assess authenticity, adulteration and intrinsic quality parameters of edible oils and fats. *Food Res. Int.* 60, 255–261.
- O'Brien, N., Hulse, C.A., Friedrich, D.M., Van Milligen, F.J., Von Gunten, M.K., Pfeifer, F., Siesler, H.W., 2012. Miniature near-infrared (NIR) spectrometer engine for handheld applications. *Proceedings of SPIE 8374, Next-Generation Spectroscopic Technologies V*, 837404.
- O'Brien, N., Hulse, C.A., Pfeifer, F., Siesler, H.W., 2013. Near infrared spectroscopic authentication of seafood. *J. Near Infrared Spectrosc.* 21, 299–305.
- O'Callaghan, D.J., O'Donnel, C.P., Payne, F.A., 1999. A comparison of on-line techniques for determination of curd setting time using cheesemilks under different rates of coagulation. *J. Food Eng.* 41, 43–54.
- Osborne, B.G., 1991. Measurement of the hardness of wheat endosperm by near infrared spectroscopy. *Postharvest News Inf.* 2, 331–334.
- Osborne, B.G., 2000. Near-infrared spectroscopy in food analysis. In: Meyers, R.A. (Ed.), *Encyclopedia of Analytical Chemistry*. John Wiley & Sons Ltd, pp. 1–13.



- Osborne, B.G., Fearn, T., 1988. Discriminant analysis of black tea by near infrared reflectance spectroscopy. *Food Chem.* 29, 233–238.
- Osborne, B.G., Fearn, T., Hindle, P.H., 1993. *Spectroscopy With Application in Food and Beverage Analysis*. Longman Scientific & Technical, Singapore, pp. 1–77. 120–141.
- Osborne, B.G., Mertens, B., Thompson, M., Fearn, T., 1997. The authentication of basmati rice using near infrared spectroscopy. *J. Near Infrared Spectrosc.* 1, 77–83.
- Paradkar, M.M., Sakhamuri, S., Irudayaraj, J., 2002. Comparison of FTIR, FT-Raman and NIR spectroscopy in a maple syrup adulteration study. *J. Food Sci.* 67, 2009–2015.
- Pasquini, C., 2003. Near infrared spectroscopy: fundamentals, practical aspects and analytical applications. *J. Braz. Chem. Soc.* 14 (2), 198–219.
- Pedretti, N., Bertrand, D., Semenou, M., Robert, P., Giangiacomo, R., 1993. Application of an experimental design to detection of foreign substances in milk. *J. Near Infrared Spectrosc.* 1, 174–184.
- Penner, M.H., 1994. Basic principles of spectroscopy. In: Nielsen, S.S. (Ed.), *Introduction to the Chemical Analysis of Foods*. Jones and Bartlett Publishers, Boston, MA, pp. 317–324.
- Pillonel, L., Luginbühl, W., Picque, D., Scaller, E., Tabacchi, R., Bosset, J.O., 2003. Analytical methods for the determination of the geographic origin of Emmental cheese: mid- and near-infrared spectroscopy. *Eur. Food Res. Technol.* 216 (2), 174–178.
- Pink, J., Naczek, M., Pink, D., 1999. Evaluation of the quality of frozen minced red hake: use of Fourier transform near-infrared spectroscopy. *J. Agric. Food Chem.* 47, 4280–4284.
- Pizarro, C., Esteban-Díez, I., Nistal, A.-J., Conzález-Sáiz, J.-M., 2004. Influence of data pre-processing on the quantitative determination of the ash content and lipids in roasted coffee by near infrared spectroscopy. *Anal. Chim. Acta* 509, 217–227.
- Pizarro, C., Esteban-Díez, I., Conzález-Sáiz, J.M., 2007. Mixture resolution according to the percentage of robusta variety in order to detect adulteration in roasted coffee by near infrared spectroscopy. *Anal. Chim. Acta* 585, 266–276.
- Pontes, M.J.C., SRB, S., MCU, A., Almeida, L.F., Lima, R.A.C., Gaião, UTCP, S., 2006. Classification of distilled alcoholic beverages and verification of adulteration by near infrared spectrometry. *Food Res. Int.* 39, 182–189.
- Prieto, N., Roehe, R., Lavín, P., Batten, G., Andrés, S., 2009. Application of near infrared reflectance spectroscopy to predict meat and meat products quality: a review. *Meat Sci.* 83, 175–186.
- Prieto, N., Pawluczyk, O., Dugan, M.E.R., Aalhus, J.L., 2017. A review of the principles and applications of near-infrared spectroscopy to characterize meat, fat, and meat products. *Appl. Spectrosc.* 71, 1403–1426.
- Purnomoadi, A., Batajoo, K.K., Ueda, K., Terada, F., 1999. Influence of feed source on determination of fat and protein in milk by near-infrared spectroscopy. *Int. Dairy J.* 9, 447–452.
- Qui, P.Y., Ding, H.B., Tang, Y.K., Xu, R.J., 1999. Determination of chemical composition of commercial honey by near-infrared spectroscopy. *J. Agric. Food Chem.* 47, 2760–2765.
- Rannou, H., Downey, G., 1997. Discrimination of raw pork, chicken and Turkey meat by spectroscopy in the visible, near- and mid-infrared ranges. *Anal. Commun.* 34, 401–404.
- Realini, C.E., Duckett, S.K., Windham, W.R., 2004. Effect of vitamin C addition to ground beef from grass-fed or grain-fed sources on color and lipid stability, and prediction of fatty acid composition by near-infrared reflectance analysis. *Meat Sci.* 68, 35–43.
- Reid, L.M., Woodcock, A., O'Donnell, C.P., Kelly, J.D., Downey, G., 2005. Differentiation of apple juice samples on the basis of heat-treatment and variety using chemometric analysis of MIR and NIR data. *Food Res. Int.* 38, 1109–1115.
- Ren, G., Chen, F., 1997. Determination of moisture content of ginseng by near infra-red reflectance spectroscopy. *Food Chem.* 60, 433–436.



- Ren, G., Chen, F., 1999. Simultaneous quantification of ginsenosides in American ginseng (*Panax quinquefolium*) root powder by visible/near-infrared reflectance spectroscopy. *J. Agric. Food Chem.* 47, 2771–2775.
- Ren, G., Wang, S., Ning, J., Xu, R., Wang, Y., Xing, Z., Wan, X., Zhang, Z., 2013. Quantitative analysis and geographical traceability of black tea using Fourier transform near-infrared spectroscopy (FT-NIRS). *Food Res. Int.* 53, 822–826.
- Rinnan, A., 2014. Pre-processing in vibrational spectroscopy—when, why and how. *Anal. Methods* 6, 7124–7129.
- Rinnan, A., Van den Berg, F., Engelsen, S.B., 2009. Review of the most common pre-processing techniques for near-infrared spectra. *Trends Anal. Chem.* 28, 1201–1222.
- Rodriguez-Otero, J.L., Hermida, M., Centeno, J., 1997. Analysis of dairy products by near-infrared spectroscopy. *J. Agric. Food Chem.* 45 (8), 2815–2819.
- Saiz-Abajo, M.J., Gonzalez Saiz, J.M., Pizarro, C., 2004. Classification of wine and alcohol vinegar samples based on near-infrared spectroscopy. Feasibility study on the detection of adulterated vinegar samples. *J. Agric. Food Chem.* 52 (25), 7711–7719.
- Sato, T., 1994. Application of principal component analysis on near infrared spectroscopic data of vegetable oils for their classification. *J. Am. Oil Chem. Soc.* 71 (3), 293–298.
- Sato, T., Kawano, S., Iwamoto, M., 1990. Detection of foreign fat adulteration of milk fat by near infrared spectroscopic method. *J. Dairy Sci.* 73, 3408–3413.
- Sato, T., Kawano, S., Iwamoto, M., 1991. Near infrared spectral patterns of fatty acid analysis from fats and oils. *J. Am. Oil Chem. Soc.* 68 (11), 827–833.
- Sato, T., Uezono, I., Morishita, T., Tetsuka, T., 1998. Nondestructive estimation of fatty acid composition in seeds of *Brassica napus* L. by near-infrared spectroscopy. *J. Am. Oil Chem. Soc.* 75 (12), 1877–1881.
- Savitzky, A., Golay, M.J.E., 1964. Smoothing and differentiation of data by simplified least squares procedures. *Anal. Chem.* 36 (8), 1627–1639.
- Schoder, D., 2012. Food adulteration with melamine on an international scale: field work and troubleshooting in Africa. In: Hoorfar, J. (Ed.), *Case Studies in Food Safety and Authenticity: Lessons from Real-Life Situations*. Woodhead Publishing Ltd., Cambridge, pp. 309–318.
- Schulz, H., 2004. Analysis of coffee, tea, cocoa, tobacco, spices, medicinal and aromatic plants and related products. In: *Near-Infrared Spectroscopy in Agriculture*, Agronomy Monograph No. 44. American Society of Agronomy, Crop Science Society of America, Soil science Society of America, Madison, pp. 345–376.
- Schulz, H., Drews, H.-H., Quilitzsch, R., Krüger, H., 1998. Application of near infrared spectroscopy for the quantification of quality parameters in selected vegetable and essential oil plants. *J. Near Infrared Spectrosc.* 6, 125–130.
- Schulz, H., Engelhardt, U.H., Wegent, A., Drews, H., Lapczynski, S., 1999. Application of near-infrared reflectance spectroscopy to the simultaneous prediction of alkaloids and phenolic substances in green tea leaves. *J. Agric. Food Chem.* 47, 5064–5067.
- Schulz, H., Pfeffer, S., Quilitzsch, R., Steuer, B., Reif, K., 2002. Rapid and non-destructive determination of the echinacoside content in Echinacea root by ATR-IR and NIR spectroscopy. *Planta Med.* 68, 921–925.
- Schulz, H., Joubert, E., Schütze, W., 2003a. Quantification of quality parameters for reliable evaluation of green rooibos (*Aspalathus linearis*). *Eur. Food Res. Technol.* 216, 539–543.
- Schulz, H., Quilitzsch, R., Krüger, H., 2003b. Rapid evaluation and quantitative analysis of thyme, origano and chamomile essential oils by ATR-IR and NIR spectroscopy. *J. Mol. Struct.* 661–662, 299–306.

- Scotter, C.N.G., Legrand, A., 1994. NIR qualitative analysis—a new philosophy with special reference to rapid NIR screening for fruit juice authenticity. *Food Sci. Technol. Today* 8, 167–171.
- Scotter, C.N.G., Legrand, A., 1995. Near infrared (NIR) spectroscopy as a screening technique for fruit juice verification. *Fruit Proc.* 5, 255–260.
- Scotter, C.N.G., Hall, M.N., Day, L., Evans, D.G., 1992. The authentication of orange juice and other fruit juices. In: Hildrum, K.I., Isaksson, T., Næs, T., Tandberg, A. (Eds.), *Near Infrared Spectroscopy. Bridging the Gap between Data Analysis and NIR Applications*. Ellis Horwood, Chichester, pp. 309–314.
- Shilton, N., Downey, G., McNulty, P.B., 1998. Detection of orange juice adulteration by near-infrared spectroscopy. *Semin. Food Anal.* 3, 155–161.
- Singh Sahni, N., Isaksson, T., Næs, T., 2004. In-line near infrared spectroscopy for use in product and process monitoring in the food industry. *J. Near Infrared Spectrosc.* 12, 77–83.
- Sirieux, A., Downey, G., 1993. Commercial wheat flour authentication by discriminant analysis of near infrared reflectance spectra. *J. Near Infrared Spectrosc.* 1, 187–197.
- Sivakesava, S., Irudayaraj, J., 2001. Prediction of inverted cane sugar adulteration of honey by Fourier transform infrared spectroscopy. *J. Food Sci.* 66 (7), 972–978.
- Sjöblom, J., Svensson, O., Josefson, M., Kullberg, H., Wold, S., 1998. An evaluation of orthogonal signal correction applied to the calibration transfer of near-infrared spectra. *Chemom. Intel. Lab. Syst.* 44, 229–244.
- Sneyd, T.N., Bruer, N.G.C., Lee, T.H., 1989. A survey of five methods for analyzing the alcoholic strength of wine. *Proceedings of the Seventh Australian Wine Industry Technical Conference*. August 1989. Adelaide, Australia, p. 237.
- Sørensen, K.M., Khakimov, B., Engelsens, S.B., 2016. The use of rapid spectroscopic screening methods to detect adulteration of food raw materials and ingredients. *Curr. Opin. Food Sci.* 10, 45–51.
- Stark, E., Luchter, K., Margoshes, M., 1986. Near-infrared analysis (NIRA): a technology for quantitative and qualitative analysis. *Appl. Spectrosc. Rev.* 22, 335–399.
- Stchur, P., Cleveland, D., Zhou, J., Michel, R.G., 2002. A review of recent applications of near infrared spectroscopy, and of the characteristics of a novel PbS CCD array-based near infrared spectrometer. *Appl. Spectrosc. Rev.* 37 (4), 383–428.
- Suykens, J.A.K., Vandewalle, J., 1999. Least squares support vector machine classifiers. *Neural. Proc. Lett.* 9, 293–300.
- Tarkosová, J., Čopíková, J., 2000. Fourier transform near infrared spectroscopy applied to analysis of chocolate. *J. Near Infrared Spectrosc.* 8, 251–257.
- Twoney, M., Downey, G., McNulty, P.B., 1995. The potential of NIR spectroscopy for the detection of the adulteration of orange juice. *J. Sci. Food Agric.* 67, 77–84.
- Ulbert, F., 1994. Detection of milk fat adulteration by linear discriminant analysis of fatty acid data. *J. AOAC Int.* 77 (5), 1326–1334.
- Ulbert, F., 2003. Milk and Dairy products. In: Lees, M. (Ed.), *Food Traceability and Authenticity*. Woodhead Publishing Ltd, Cambridge, pp. 357–377.
- Van den Berg, F.W.J., Van Osenbruggen, W.A., Smilde, A.K., 1997. Process analytical chemistry in the distillation industry using near-infrared spectroscopy. *Process. Control. Qual.* 9, 51–57.
- Van de Voort, F.R., 1992. Fourier transform infrared spectroscopy applied to food analysis. *Food Res. Int.* 25, 397–403.
- Vapnik, V.N., 1995. *The Nature of Statistical Learning Theory*. Springer-Verlag, New York.
- Velasco, L., Goffman, F.D., Becker, H.C., 1999. Development of calibration equations to predict oil content and fatty acid composition in *Brassicaceae* germplasm by near-infrared reflectance spectroscopy. *J. Am. Oil Chem. Soc.* 76 (1), 25–30.

- Vermeulen, P., Fernandez Pierna, J.A., Abbas, O., Dardenne, P., Baeten, V., 2010. Authentication and traceability of agricultural and food products using vibrational spectroscopy. In: ECY, L.-C., Griffiths, P.R., Chalmers, J.M. (Eds.), *Applications of Vibrational Spectroscopy in Food Science*. John Wiley & Sons Ltd, 630, p. 609.
- Vermeulen, P., Fernández Pierna, J.A., Abbas, O., Rogez, H., Davrieux, F., Baeten, V., 2017. Authentication and traceability of agricultural and food products using vibrational spectroscopy. In: Montet, D., Ray, R.C. (Eds.), *Food Traceability and Authenticity: Analytical Techniques*. In: Biology series CRC Press, Boca Raton, p. 450.
- Vitale, R., Bevilacqua, M., Bucci, R., Magrì, A.D., Magrì, A.L., Marini, F., 2013. A rapid and non-invasive method for authenticating the origin of pistachio samples by NIR spectroscopy and chemometrics. *Chemom. Intel. Lab. Syst.* 121, 90–99.
- Walsh, K.B., Golic, M., Greensill, C.V., 2004. Sorting of fruit using near infrared spectroscopy: application to a range of fruit and vegetables for soluble solids and dry matter content. *J. Near Infrared Spectrosc.* 12, 141–148.
- Wang, F., Zhang, Z., Cui, X., Harrington, P.B., 2006. Identification of rhubarbs by using NIR spectrometry and temperature-constrained cascade correlation networks. *Talanta* 70, 1170–1176.
- Wang, L., Lee, F.S.C., Wang, X., 2007. Near-infrared spectroscopy for classification of licorice (*Glycyrrhiza uralensis* Fisch) and prediction of the glycyrrhizic acid (GA) content. *Lebensm. Wiss. Technol.* 40, 83–88.
- Wesley, I.J., Barnes, R.J., McGill, A.E.J., 1995. Measurement of adulteration of olive oils by near infrared spectroscopy. *J. Am. Oil Chem. Soc.* 72 (3), 289–292.
- Wesley, I.J., Pacheco, F., McGill, A.E.J., 1996. Identification of adulterants in olive oils. *J. Am. Oil Chem. Soc.* 73 (4), 515–518.
- Wesley, I.J., Uthayakumaran, S., Anderssen, R.S., Cornish, G.B., Bekes, F., Osborne, B.G., Skerritt, J.H., 1999. Curve-fitting approach to the near infrared reflectance measurement of wheat flour proteins which influence dough quality. *J. Near Infrared Spectrosc.* 7, 1–12.
- Westerhaus, W.O., 1989. Calibration: Interpretation of regression statistics. In: Marten, G.C., Shenk, J.S., Barton II, J.E. (Eds.), *Near Infrared Reflectance Spectroscopy (NIRS): Analysis of Forage Quality*. United States Department of Agriculture, Washington, pp. 39–40.
- Wetzel, D.L., 1983. Near infrared reflectance analysis of major components in foods. In: Charalambous, G., Inglett, G. (Eds.), *Instrumental Analysis of Foods—Recent Progress*. In: vol. 1. Academic Press, London, pp. 183–202.
- Wetzel, D.L.B., 1998. Analytical near infrared spectroscopy. In: Wetzel, D.L.B., Charalambous, G. (Eds.), *Instrumental Methods in Food and Beverage Analysis*. Elsevier, Amsterdam, pp. 141–194.
- Wetzel, D.L., 2001. Contemporary near-infrared instrumentation. In: Williams, P., Norris, K. (Eds.), *Near-Infrared Technology in the Agricultural and Food Industries*. American Association of Cereal Chemists, St. Paul, pp. 129–144.
- Williams, P.C., 2001. Implementation of near-infrared technology. In: Williams, P., Norris, K. (Eds.), *Near-Infrared Technology in the Agricultural and Food Industries*. second ed. American Association of Cereal Chemists, St. Paul, pp. 145–169.
- Williams, P.C., Sobering, D.C., 1993. Comparison of commercial near-infrared transmittance and reflectance instruments for analysis of whole grains and seeds. *J. Near Infrared Spectrosc.* 1, 25–32.
- Williams, P.C., Stevenson, S.G., 1990. Near-infrared reflectance analysis: food industry applications. *Trends Food Sci. Technol.* 1, 44–48.
- Williams, P., Dardenne, P., Flinn, P., 2017. Tutorial: Items to be included in a report on a near infrared spectroscopy project. *J. Near Infrared Spectrosc.* 25 (2), 85–90.

- Wilson, R.H., Goodfellow, B.J., Belton, P.S., Osborne, B.G., Oliver, G., Russell, P.L., 1991. Comparison of Fourier transform mid infrared spectroscopy and near infrared reflectance spectroscopy with differential scanning calorimetry for the study of the staling of bread. *J. Sci. Food Agric.* 54, 471–483.
- Windham, W.R., Gaines, C.S., Leffler, R.G., 1993. Effect of wheat moisture content on hardness scores determined by near-infrared reflectance and on hardness score standardization. *Cereal Chem.* 70, 662–666.
- Wold, S., 1995. Chemometrics; what do we mean with it, and what do we want from it? *Chemom. Intel. Lab. Syst.* 30, 109–115.
- Wold, J.P., Isaksson, T., 1997. Non-destructive determination of fat and moisture in whole Atlantic salmon by near-infrared diffuse reflectance spectroscopy. *J. Food Sci.* 62, 734–736.
- Wold, S., Sjöström, M., 1977. SIMCA: a method for analyzing chemical data in terms of similarity and analogy. In: Kowalski, B.R. (Ed.), *Chemometrics Theory and Application*. In: American Chemical Society Symposium Series 52 American Chemical Society, Washington, DC, pp. 243–282.
- Wold, S., Antio, H., Lindgren, F., Ohman, J., 1998. Orthogonal signal correction of near-infrared spectra. *Chemom. Intel. Lab. Syst.* 44, 175–185.
- Woodcock, T., Downey, G., O'Donnell, C.P., 2008. Better quality food and beverages: the role of near infrared spectroscopy. *J. Near Infrared Spectrosc.* 16, 1–29.
- Wüst, E., Rudzik, L., 2003. The use of infrared spectroscopy in the dairy industry. *J. Mol. Struct.* 661–662, 291–298.
- Xing, J., Landahl, S., Lammertyn, J., Vrindts, E., Baerdemaeker, J.D., 2003. Effects of bruise type on discrimination of bruised and non-bruised 'golden delicious' apples by VIS/NIR spectroscopy. *Postharvest Biol. Technol.* 30, 249–258.
- Yu, H., Ying, Y., Fu, X., Lu, H., 2006. Classification of Chinese rice wine with different marked age based on near infrared spectroscopy. *J. Food Qual.* 29, 339–352.
- Yu, H., Zhou, Y., Fu, X., Xie, L., Ying, Y., 2007a. Discrimination between Chinese rice wines of different geographical origins by NIRS and AAS. *Eur. Food Res. Technol.* 225, 313–320.
- Yu, H., Ying, Y., Sun, T., Niu, X., Pan, X., 2007b. Vintage year determination of bottled Chinese rice wine by Vis-NIR spectroscopy. *J. Food Sci.* 72 (3), E125–E129.
- Zhang, M.H., Luypaert, J., Fernández Pierna, J.A., Xu, Q.S., Massart, D.L., 2004. Determination of total antioxidant capacity in green tea by near-infrared spectroscopy and multivariate calibration. *Talanta* 62, 25–35.
- Zhao, J., Chen, Q., Huang, X., Fang, C.H., 2006. Qualitative identification of tea categories by near infrared spectroscopy and support vector machine. *J. Pharm. Biomed. Anal.* 41, 1198–1204.

## FURTHER READING

- Alamprese, C., Casale, M., Sinelli, N., Lanteri, S., Casiraghia, E., 2013. Detection of minced beef adulteration with Turkey meat by UV–Vis, NIR and MIR spectroscopy. *LWT- Food Sci. Technol.* 53, 225–232.
- Cozzolino, D., 2015. The role of vibrational spectroscopy as a tool to assess economically motivated fraud and counterfeit issues in agricultural products and foods. *Anal. Methods* 7, 9390–9400.
- Downey, G., Bertrand, R., Kelly, P.M., 1990. Classification of commercial skim milk powders according to heat treatment using factorial discriminant analysis of near-infrared reflectance spectroscopy. *Appl. Spectrosc.* 44 (1), 150–154.