Spectroscopic Technique: Near-infrared (NIR) Spectroscopy

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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 non-visible region in the absorption spectrum (Stark *et al*., 1986). From 1800 to the 1950s was a dormant period for NIR spectroscopy, when it took a back seat 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 co-workers (Butler, 1983) later in the 1950s that its potential was recognized (Day and Fearn, 1982). Today, NIR spectroscopy has become the quality control method of choice in the food industry because of its advantages over other analytical techniques.

Near-infrared spectroscopy was originally limited to quantitative grain analysis, but today quantitative applications are widely used in many fields (Table 3.1).

Table 3.1 Fields of NIR spectroscopy quantitative applications

Application	References
Animal feeds	Murray and Hall, 1983, Murray *et al.*, 2001
Cereals and cereal products	Osborne, 1991; Wilson *et al.*, 1991; Windham *et al.*, 1993; Wesley *et al.*, 1999; Cozzolino *et al.*, 2000; Bao *et al.*, 2001
Coffee	Pizarro et al., 2004
Confectionary	Tarkošová and Čopíková, 2000
Cosmetics	Grunewald *et al.*, 1998
Dairy	Rodriguez-Otero *et al.*, 1997; Wüst and Rudzik, 2003; Blazquez *et al.*, 2004
Distillation industry	Gómez-Cordovés and Bartolome, 1993; Manley *et al.*, 2003
Environment	Iwamoto *et al.*, 1995; Lister *et al.*, 2000
Essential oils	Schulz *et al.*, 1998; Schulz *et al.*, 2003a
Fats and oils	Schulz *et al.*, 1998; Moh *et al.*, 1999
Fruit and vegetables	Kawano *et al.*, 1992; Schulz *et al.*, 1998; Goula and Adamopoulos, 2003; Xing *et al.*, 2003; Walsh *et al.*, 2004; Manley *et al.*, 2007
Forage	Park *et al.*, 1998; Stuth *et al.*, 2003
Grapes	Cope, 2000; Esler *et al.*, 2002
Herbal products	Schulz *et al.*, 2002; Laasonen, 2003; Schulz *et al.*, 2003b; Manley *et al.*, 2004, 2006; Joubert *et al.*, 2005, 2006
Honey	García-Alvarez *et al.*, 2000
Manures	Reeves, 2001
Meat and fish	Downey, 1996b; Wold and Isaksson, 1997; Pink *et al.*, 1999; Cozzolino and Murray, 2004; Realini *et al.*, 2004
Medicine	Hock *et al.*, 1997; Suto *et al.*, 2004
Pharmaceuticals	Blanco *et al.*, 1998
Plant species	Ren and Chen, 1997, 1999; Sato *et al.*, 1998; Velasco *et al.*, 1999
Spreads and condiments	Iizuka & 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
Textiles	Cleve *et al.*, 2000
Tobacco	Hana *et al.*, 1997
Wine and grapes	Baumgarten, 1987; Chauchard *et al.*, 2004; Cozzolino *et al.*, 2004

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 3.2).

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, however, food adulteration has become more sophisticated (Karoui and De Baerdemaeker, 2007). Foods or food ingredients that are of high value and undergo a number of processing steps are most likely to be targets for adulteration, owing 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)

Table 3.2 Fields of NIRS qualitative applications

Application	References
Adulteration of extra virgin olive oils with sunflower oil	Downey *et al.*, 2002
Adulteration of honey	Downey *et al.*, 2003
Adulteration of maple syrup	Paradkar *et al.*, 2002
Adulteration of milk fat with foreign fat	Sato *et al.*, 1990
Adulteration of milk with other fats	Sato *et al.*, 1990; Ulbert, 1994
Adulteration of milk with non-milk fat	Sato, 1994
Adulteration of milk with substances like water, sodium chloride and skim milk powder	Pedretti *et al.*, 1993
Adulteration of orange juice	Scotter *et al.*, 1992; Shilton *et al.*, 1998
Basmati and other long-grain rice samples	Osborne *et al.*, 1997
Black teas of differing qualities	Osborne and Fearn, 1988
Bread-baking quality of different wheat varieties	Downey *et al.*, 1986; Devaux *et al.*, 1987
Classification of plant species	Lister *et al.*, 2000; Laasonen *et al.*, 2002
Classification of cultivation area	Woo *et al.*, 1999a, 1999b, 2002
Classification of processing methods	Schulz *et al.*, 2003b
Classification of herbal plants	Wang *et al.*, 2006, 2007; Mao and Xu, 2006
Classification of commercial teas	Osborne and Fearn, 1988; Budínová *et al.*, 1998
Classification of milk powders	Downey *et al.*, 1990
Classification of wines	Cozzolino *et al.*, 2003
Classification between frozen and frozen-then-thawed beef	Downey and Beauchêne, 1997a, 1997b
Classification between Robusta and Arabica coffee	Downey *et al.*, 1994, 1997; Downey and Spengler, 1996; Pizarro *et al.*, 2007
Vegetable oils	Sato, 1994
Virgin olive oils from different geographical origins	Downey and Flynn, 2002
Volatile oils	Kiskó and Seregély, 2002

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. Additionally, foods are chiefly or exclusively comprised of naturally-occurring biological material, the composition of which varies depending on the 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). 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 near-infrared 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 library of representative spectra is needed to characterize any given food, and the spectrum of material under investigation may be compared to 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.

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 (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 sub-regions (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). Near-infrared 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). Mid-infrared 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 inter-atomic bonds; these typically are groups containing carbon (C), nitrogen (N) and oxygen (O) bonded to hydrogen (H), i.e. 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.

Instrumentation

During the last decade of the twentieth century, great advances in instrumentation and data acquisition gave NIR spectroscopy a definite place among the other established analytical methods (Wetzel, 1998, 2001). When considering NIR instrumentation, a variety of possible configurations exist. These include discrete filter, *grating monochromator* and *acousto-optical tunable filter* (AOTF) instruments, as well as *photodiode array* and *Fourier-transform interferometer* systems (Osborne *et al.*, 1993; Wetzel, 1998, 2001; Barton, 2002). All NIR instruments possess the same essential building blocks (Figure 3.1): radiation source, wavelength selectors, sample presentation facility and detector (Blanco and Villarroya, 2002).
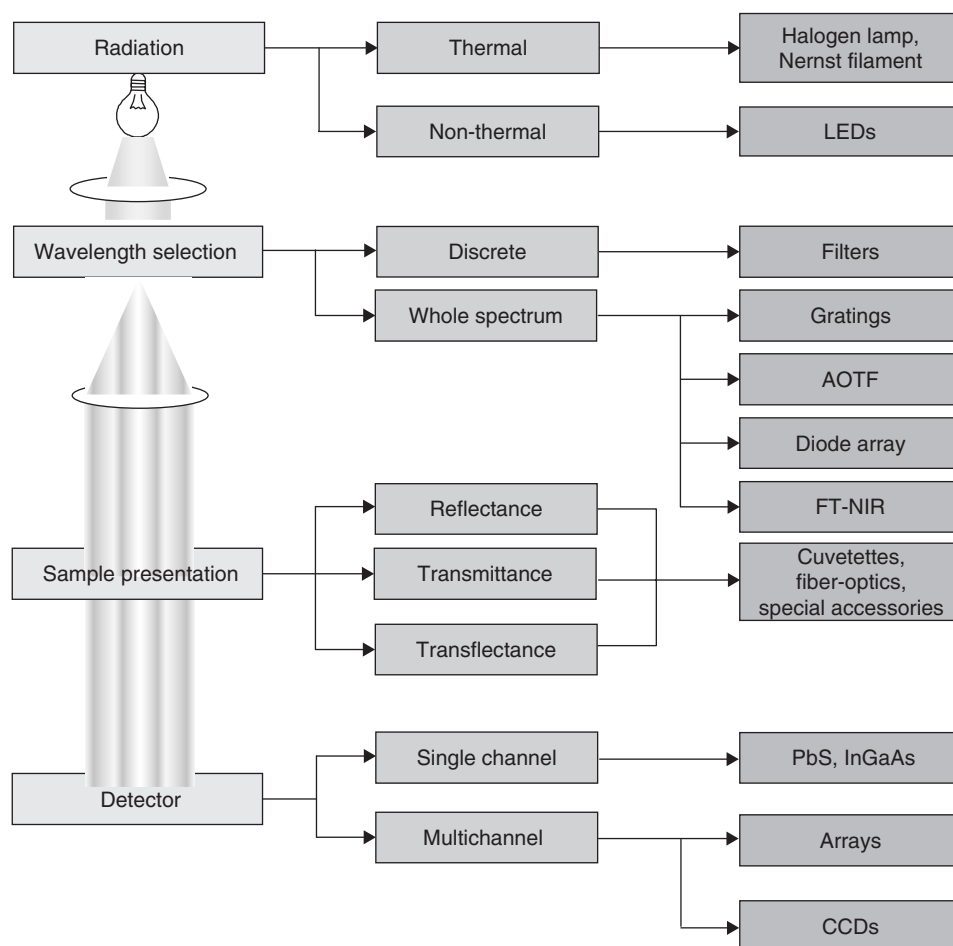
Figure 3.1 Principle features of NIRS instrumentation (LEDs, light-emitting diode; AOTF, acousto-optical tunable filter; FT-NIR, Fourier transform near-infrared; PbS, lead sulfide; InGaAs, indium gallium arsenide; CCD, charge-coupled devices). Reproduced with permission from Blanco and Villarroya, 2002; ©Elsevier Ltd 2002.

Radiation source

NIR radiation sources can be thermal or non-thermal. 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 non-thermal sources consist of discharge lamps, light-emitting diodes, laser diodes or lasers, and emit much narrower bands of radiation than the thermal sources (McClure, 2001). Non-thermal 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).

Wavelength selectors

Near-infrared spectrophotometers can be distinguished on the basis of wavelength selection, i.e. discrete wavelength or continuous spectrum. A *discrete-wavelength spectrophotometer* irradiates a sample with only a few wavelengths selected using filters or light-emitting diodes (LEDs) (McClure, 2001; Blanco and Villarroya, 2002). *Filter instruments* are designed for specific applications in specific spectral regions; usually between 6 and 20 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 much 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 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 on-line applications. Diode-array NIR instruments do not use any moving optical parts, which greatly improves instrument stability.

   Acousto-optical tunable filters generate discrete wavelengths across an extended range by using radio-frequency signals to change the refractive index of a crystal, usually tellurium dioxide (TeO_2) (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 – i.e., 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 measurement of all wavelengths allows 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.

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 (liquids, slurries, powdered or solid samples, gases, etc.). 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 – such as a petrol refinery or pharmaceutical production facility (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 path-length through which the light travels and the concentration of the constituent being measured (Wetzel, 1998). For *transmittance* measurements of liquids, the path-length is a constant determined by the thickness of the sample cuvette. This is, however, not the case for *diffuse reflectance*, with changes in both path-length 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 path-length 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).

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 path-length is described by the Lambert-Beer law. Since the path-length 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 path-length 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).

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 pre-treatment

methods such as *multiplicative scatter correction* (Geladi *et al*., 1985), derivatization (Osborne, 2000) and the *standard normal variate* transform (Barnes *et al*., 1989), among others, to address this problem.

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 (e.g. 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.

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.

Detectors

Infrared 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 either from 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 *multi-channel* 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 charge-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 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).

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 analysing 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, non-linearities 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, 2000; Geladi, 2002). A variety of multivariate analysis techniques can be used to (i) extract analytical information contained in NIR spectra to develop models, and (ii) predict relevant properties of unknown samples. There are two main groups of multivariate methods which may be distinguished by the type of analysis required; 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.

Due 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. The calculated principal components contain the spectral information in a reduced number of variables – for example, less than 20 – and these new variables can substitute the original data in subsequent calculations (Cowe and McNicol, 1985). 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). Principal component analysis is an *unsupervised method* (i.e. 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).

Pre-processing of spectral data

Maximizing the significance of any spectral differences is the main aim of using pre-processing algorithms (Osborne *et al.*, 1993; Hopkins, 2001). 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 much 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 – 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 pre-processing methods include normalization (Massart *et al.*, 1988; Næs *et al.*, 2002), derivatives (Massart *et al.*, 1988; Næs *et al.*, 2002), multiplicative scatter correction (MSC) (Geladi *et al.*, 1985) and standard normal variate (SNV) and de-trending (Barnes *et al.*, 1989). Pre-processing 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).

Smoothing

The *Savitzky-Golay moving average* (Savitzky and Golay, 1964) and other algorithms, i.e. 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.

Derivatives

One of the most common pre-processing 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 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).

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.

Multiplicative scatter correction

Another normalization procedure is *multiplicative scatter correction* (*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 divided by the curve-fit value. Multiplicative scatter correction is a very useful and powerful pre-processing 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). Multiplicative scatter correction separates the chemical light absorption from the physical light scatter (Geladi *et al.*, 1985).

Standard normal variate and de-trending

Standard normal variate (SNV) transforms spectral data by subtracting the mean of the spectra from the spectral values of each spectrum (Barnes *et al.*, 1989). These centerd spectra are then scaled by the standard deviation of the spectrum. Standard normal variate 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).

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 this statistically to a theoretically perfect line through the origin at 45° 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, and 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).

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 to 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.

Unsupervised methods
Unsupervised methods, e.g. PCA 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). Principal component analysis 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. Hierarchical cluster analysis (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.

Supervised methods

The more traditional supervised methods include *Bayes classification* or *Fisher's linear discriminant analysis* (Næs *et al*., 2002). Supervised methods commonly used to solve authenticity problems are soft independent modeling of class analogy (SIMCA), discriminant PLS (DPLS), linear discriminant analysis (LDA), multiple discriminant analysis (MDA), factorial discriminant analysis (FDA), 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 (Zhao *et al*., 2006; Chen *et al*., 2007), and wavelet interface to linear modeling analysis (WILMA) (Cocchi *et al*., 2003). Some of the most commonly used supervised methods are briefly described below; more exhaustive and detailed explanations of these methods can be found in Næs *et al*. (2002).

Soft independent modeling of class analogy (SIMCA)

Apart from problems relating to simple classification, *soft independent modeling of class analogy* (*SIMCA*) is applied to a more general class of discriminatory issues, i.e. identification. It is a procedure in which raw spectra are compressed by means of principal component analysis (Downey and Beauchêne, 1997a) – 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 to 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), but reported successful applications of SIMCA to food classification using NIR spectra are few in number (Downey, 1996a).

Discriminant PLS

With *discriminant PLS* (*DPLS*) 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 *DPLS1*, 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 non-members 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 greater than 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. *DPLS2* 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

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 minus one, 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 *factorial discriminant analysis* (*FDA*) is to predict membership of a single sample according to other defined groups; principal component analysis 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 is 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-Nearest neighbors (*k-NN*) is 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 are found; *k* typically has odd, integer values. The unknown is then classified to the group that has the most members amongst these neighbors (Næs *et al*., 2002).

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 best be 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 are *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). This 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 or slow, or is otherwise undesirable. It would be most economical to use all the 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 deleted from the calibration set. In partial cross-validation, samples are removed in groups; 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 is then replaced into the calibration data and the next sample 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 3.3, and include the *standard error of prediction* (*SEP*) or *standard error of cross-validation* (*SECV*); *bias*; the *coefficient of determination* (R^2)*; and the *ratio of standard error of performance to standard deviation* (*RPD*) (Osborne *et al.*, 1993; Williams, 2001). The SEP measures how well the calibration is going to perform in future

Table 3.3 Equations for statistical calculations		
Statistic	**Equation**	**Recommendations**
SD[a]	$\sqrt{\dfrac{\sum y^2 - \dfrac{\left[\left(\sum y\right)^2\right]}{n}}{n-1}}$	
SEL[b]	$\sqrt{\dfrac{\sum\left(y_1 - y_2\right)^2}{2n}}$	As small as possible
SEP[c]/SECV[d]	$\sqrt{\dfrac{\sum_{i=1}^{n}\left(y_i - \hat{y}_i - \text{BIAS}\right)^2}{n-1}}$	As small as possible or close as possible to SEL value
V-BIAS[e]	$\dfrac{1}{n}\sum_{i=1}^{n}\left(y_i - \hat{y}_i\right)$	As close to zero as possible
R^2[f]	$1 - \dfrac{\sum_i\left(y_i - \hat{y}_i\right)^2}{\sum_i\left(y_i - \bar{y}\right)^2}$	See Table 3.4
RPD[g]	$\dfrac{\text{SD}_{\hat{y}}}{\text{SEP}}$ or $\dfrac{\text{SD}_{\hat{y}}}{\text{SECV}}$	See Table 3.5

[a]Standard deviation; [b]standard error of laboratory; [c]standard error of prediction; [d]standard error of cross validation; [e]bias of the validation set; [f]coefficient of correlation; [g]ratio of standard error of performance to standard deviation.

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

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 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 more than 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 (≤ 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 non-membership 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 – i.e. 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 – i.e. 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.

Advantages and disadvantages

Advantages

Near-infrared spectroscopy has several advantages over other analytical techniques. It is a rapid, easily used technology that is non-destructive in nature (Day and Fearn, 1982; Osborne *et al.*, 1993; Wetzel, 1998) and does not require chemical consumables (Zoecklein *et al.*, 1994; Downey, 1998a, 1998b). The latter is important, as the disposal requirements for hazardous waste are becoming increasingly expensive for laboratories. Near-infrared spectroscopy requires minimal or no sample preparation or pre-treatment (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). Measurements can also be carried out on-line (Osborne *et al*., 1993; Hoyer, 1997) or in-line (Singh Sahni *et al*., 2004). Portable NIR spectrophotometers such as hand-held instruments (www.polychromix.com) using micro-electromechanical systems (MEMS) (Crocombe, 2004) 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 interesting advantages of NIR spectroscopy compared with other spectroscopic techniques are its ability to use longer path-lengths, 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 mid-infrared analyses. It is also possible to create a pseudo-homogenous spectrum from a non-homogenous 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 path-lengths compared with mid-infrared analyses (Osborne *et al*., 1993). This enables spectra to be measured by transmission through intact materials, which allows rapid and non-destructive 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 an ideal application for on-line analyses.

Disadvantages

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, though, 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 it is often difficult to obtain, is essential to build a robust calibration (Wetzel, 1998). Near-infrared 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 expense, 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 considering acquiring a NIR instrument for routine applications in a quality control laboratory. 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.

Applications in food and beverage authenticity

Increasing emphasis is being placed on non-destructive quality control methods for agricultural and biological materials necessary for composition analysis (Gunasekaran and Irudayaraj, 2001). Applications of NIR spectroscopy in the food industry were reported as early as 1938 in gelatin 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; Iwamoto *et al*., 1995; Wetzel, 1998); food adulteration and authenticity (Downey, 1995; Downey, 1996a); the detection of external and internal defects in foods and crops (Osborne *et al*., 1993); and qualitative and sensory determinations (Osborne *et al*., 1993; Downey, 1995, 1998b; Wetzel, 1998).

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.

Cereals and cereal products

Wheat used for food applications consist of mainly two species – 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; Downey *et al*., 1986a; Devaux *et al*., 1986, 1987). 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*., 1986a). Near-infrared spectroscopy and FDA was used to identify a range of commercial white flours, i.e. biscuit, self-raising, household, cake, bakers' and soda bread mix (Sirieix and Downey, 1993); using this approach, it was possible correctly to classify 97% of a set of 99 validation samples. Although the identification

was largely due to particle size difference between the flours, identification was also due to the presence of inorganic additives at different levels in some flours.

More recently, 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, i.e. hectoliter 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 (Figure 3.2). 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).

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. However, in northern
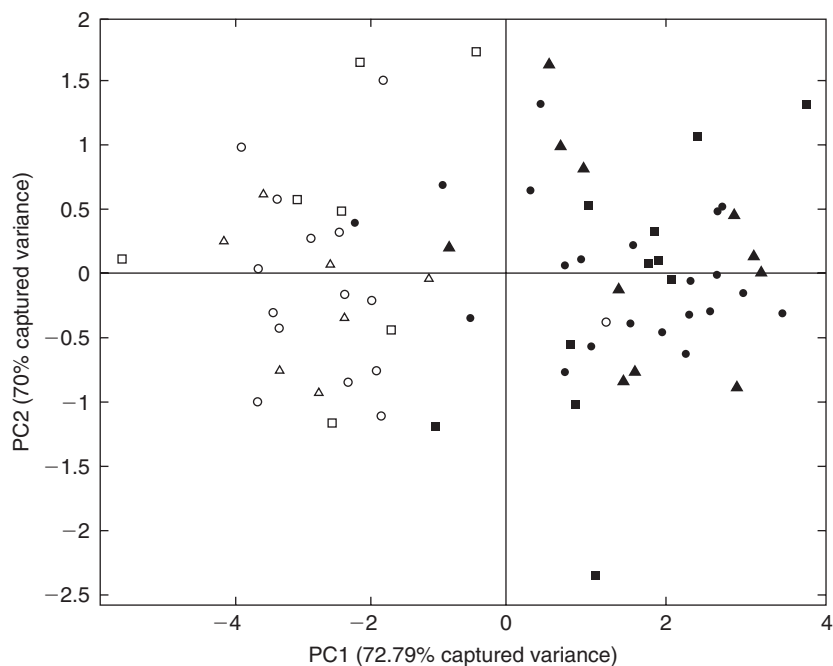
Figure 3.2 Scores plot of the first two PCs calculated by PCA on the wavelet coefficients from the WPTER selected model for the two FF (strongest) and FB (weakest) classes (circles, training set; triangles, monitoring set; squares, test set; FB, filled symbols; FF, empty symbols). Reproduced with permission from Cocchi *et al.* (2005); ©Elsevier Ltd 2005.

European and other countries, both bread and durum wheat are 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 (wavelet interface to linear modeling analysis) (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 set-up (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 non-Basmati (Osborne *et al*., 1997). Rice samples were analyzed using two presentation modes, i.e. bulk samples or single grains, using a Tecator Infratec 1225 grain analyzer over the wavelength range from 850 to 1050 nm. Fischer linear discriminant analysis was applied to the resulting datasets, and a perfect discrimination between Basmati and non-Basmati 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.

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 set-up 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% respectively were obtained on second derivative spectra of whole and ground beans (Figure 3.3); the application of FDA procedures was less 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.
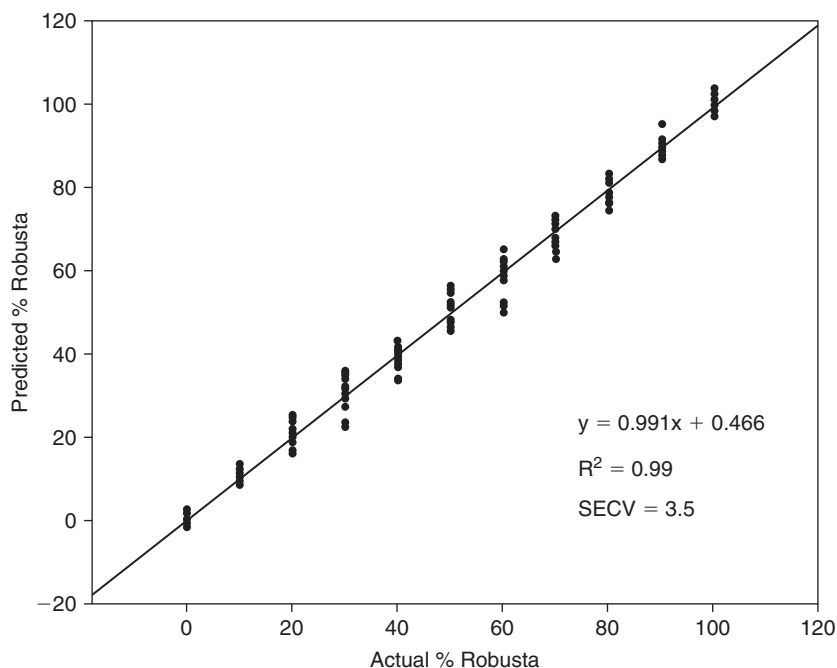
Figure 3.3 Prediction of percentage Robusta content in ground bean samples by modified partial least squares regression. Reproduced with permission from Downey and Spengler (1996); ©Irish Journal of Agricultural and Food Research 1996.

The use of combined NIR-MIR spectra for coffee varietal identification 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 a DOSC (direct orthogonal signal correction) method as a pre-processing 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 an 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 – pure Arabica, three Arabica/Robusta blends, and pure Robusta – and resulted in a 100% correct classification rate of prediction samples. Subsequently the pre-processing method OWAVEC (orthogonal wavelet correction) (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 pre-processing first derivative NIR spectra by OWAVEC were considerably better than the models obtained from raw data; results were also an improvement over other orthogonal signal correction methods tested (Table 3.4).

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

Table 3.4 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

Reprinted with permission from Pizarro *et al*. (2007); ©Elsevier Ltd 2007.

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.

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 an NIRSystems 6500 scanning monochromator equipped with a sample transport accessory and a short path-length transflectance 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 sub-samples of each purée were scanned in duplicate, with the sample cell being rotated through approximately 120° between duplicate scans; mean spectra were used for data analysis. It was consequently possible to quantify apple adulteration in strawberry purées rapidly and non-destructively at levels down to 20% (w/w) and in raspberry purées at a level between 10 and 20% (w/w).

Honey

Honey is a high-value, completely natural product, and is 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, and 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 DPLS can be used with a high degree of success to detect honey that has been adulterated by the addition of fructose and glucose, 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 transflectance mode using a 0.2-mm path length. The pure honeys were correctly identified 96% of the time. However, Downey *et al*. (2003) indicated that it might be necessary to apply temperature control during performance of the

NIR analysis. SIMCA and k-nearest neighbor models were reported not to be able to identify adulterated honey samples.

Kelly *et al*. (2006) used a similar instrument set-up, but collected spectra from 1100–2498 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, while 90.0% of the authentic honeys were correctly identified. When proof of authenticity is required, it is always important that no false positives occur in prediction tests (i.e. when selectivity is high) (Downey *et al*., 2006).

Meat and meat products

Regarding meat and meat products, major authenticity issues often concern the substitution or partial substitution of high-value raw materials with less costly alternatives. These 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); and 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). Typical spectra of the beef, sheep, pork and chicken muscle samples in the visible and NIR regions are shown in Figure 3.4. 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 more than 85% of samples using PLS (Table 3.5). 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 (such as muscle structure and type of muscle fibers) could add information to the model, and allowed discrimination between them. Cozzolino and Murray (2004) analyzed the ground meat in reflectance mode from 400–2500 nm with 2-nm intervals using an NIRSystems 6500 in a non-rotating circular cup.

Factorial discriminant analysis of combined visible-near-infrared 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 1100 nm on whole meat using a surface interactance fiber-optic accessory and an NIRSystems 6500. Applying FDA, a four-cluster model was found to classify all frozen samples
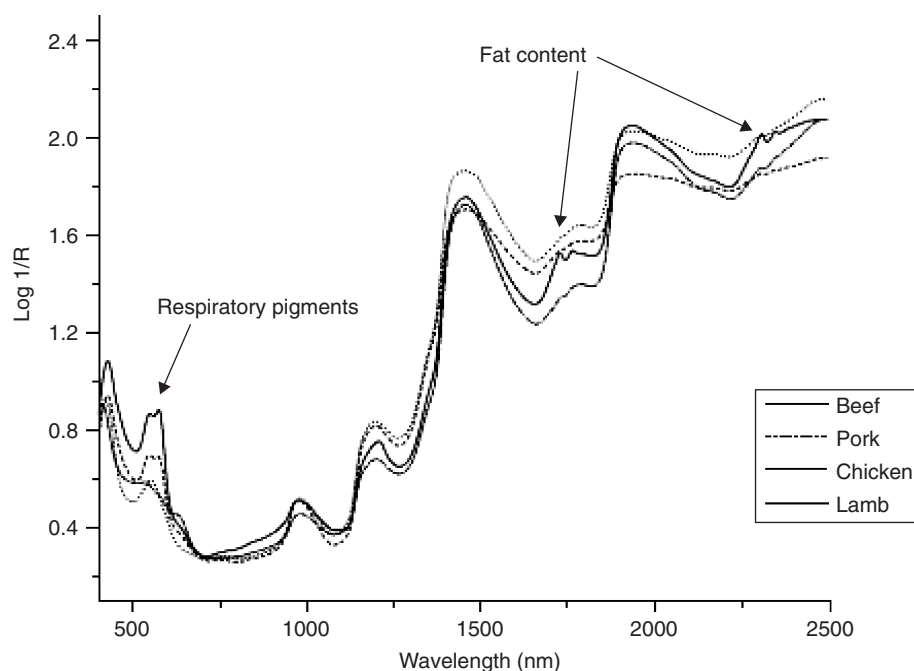
Figure 3.4   Visible and NIR mean spectra of pork, beef, lamb and chicken samples. Reproduced with permission from Cozzolino and Murray (2004); ©Elsevier Ltd 2004.

Table 3.5 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, non-classification.
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correctly. SIMCA did not perform as well as FDA; although it was possible to iden-
tify the fresh samples correctly, a large number of the frozen-then-thawed samples
were wrongly classified as being fresh. The latter study was followed up by an alterna-
tive 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 – 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 ground beef, it was reported that the accuracy of the prediction could be improved by concatenating the fingerprint region of the mid-infrared 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.

Milk and dairy products

Adulteration of milk products, either by substituting a more expensive ingredient with one of lower cost or by removing a valuable component in 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 either as not complying with legal requirements or erroneous addition of specific ingredients and material not of dairy origin, or non-compliance in terms of technological processes (Ulbert, 2003). The addition of water is one of the oldest and most obvious ways in which milk can be adulterated (Arvanitoyannis and Tzouros, 2005). Another common problem is the addition of sugar to milk.

NIR spectroscopy is widely used in the dairy industry. It was utilized for monitoring rennet coagulation in cows' milk (Laporte *et al*. 1998; O'Callaghan *et al*., 2000); 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 non-dairy 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 1100–2500 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 0.207% after analysis of 20 unknown milk powder samples.

Sato *et al*. (1990) showed that fat adulteration with as little as 3% foreign fat – for example, 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. However, if only the latter two wavelengths are 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 non-destructive techniques to determine quality and/or authenticity of dairy products including NIR spectroscopy, and the principles of spectroscopic techniques coupled with chemometrics has been reviewed by Karoui *et al*. (2003).

The potential of NIR spectroscopy to predict maturity and sensory attributes of 24 Cheddar cheeses produced using 5 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) (refer to Chapter 4 for more detailed discussion).

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 of the leaves produces 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 canonical variate analysis (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 the effects 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 (support vector machine) 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). These studies are discussed in more detail in Chapter 4.

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 transflectance 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 near-infrared studies applied discriminant (Bewig *et al*., 1994) and principal component (Sato, 1994) analysis to distinguish between different vegetable oils. Sato (1994) successfully classified nine varieties of vegetable oils 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, 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 1700–1800 and 2100–2400 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 to 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 is also 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; first, the blending of virgin olive oils with inferior quality olive oils such as refined olive oil or pomace oil, and secondly, 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. USA 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: 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 $\leqslant$0.05%, linolenic $\leqslant$1.0%, arachidic $\leqslant$0.6%, eicosenoic $\leqslant$0.4%, behenic $\leqslant$0.2% and lignoceric $\leqslant$0.2% (IOC, 2006). Any fatty acid present in amounts exceeding the abovementioned limits will be indicative of adulteration with seed oil. However, assessment of 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. Principal component analysis was used to detect and quantify adulterants in virgin olive oil (Wesley *et al*., 1995). Using principal components, 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 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) (refer to Chapter 4 for more detailed discussion).

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) by methods including 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 such as PCA, LDA CVA and cluster linear analysis (CLA) (Arvanitoyannis *et al*., 1999).

As is 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; Sneyd *et al*., 1989; Van de Voort, 1992; Van den Berg *et al*., 1997). Near-infrared 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 proposed the employment of NIR spectroscopy as a future analytical technique for determinations of total phenolics in wines (Burns, 1994). 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 was 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.

Near-infrared spectroscopy combined with multivariate analysis (PCA, DPLS 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. Fourier transform near-infrared 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 (refer to Chapter 4 for more detailed discussion).

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 – Riesling and Chardonnay (Cozzolino *et al.*, 2003). Figure 3.5 shows the visible and NIR spectra of the white wine samples analyzed. 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 to either C–H$_3$ stretch first overtone or compounds containing C–H aromatic groups, at 1790 nm related to C–H stretch first overtone, and at 1950 nm related to O–H stretch first overtone of water and ethanol. The models were constructed using PCA, PCR and DPLS on spectra collected from 400–2500 nm using a Foss NIRSystems 6500 and a 1-mm path-length cuvette. Figure 3.6 shows the PCA scores (PC1 vs PC2) derived from the second-derivative spectral data of the samples. Although there was separation of the samples by variety, some samples did overlap. The DPLS models were able accurately to classify 100% of the Riesling and 96% of the Chardonnay wines (Figure 3.7).

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 (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.
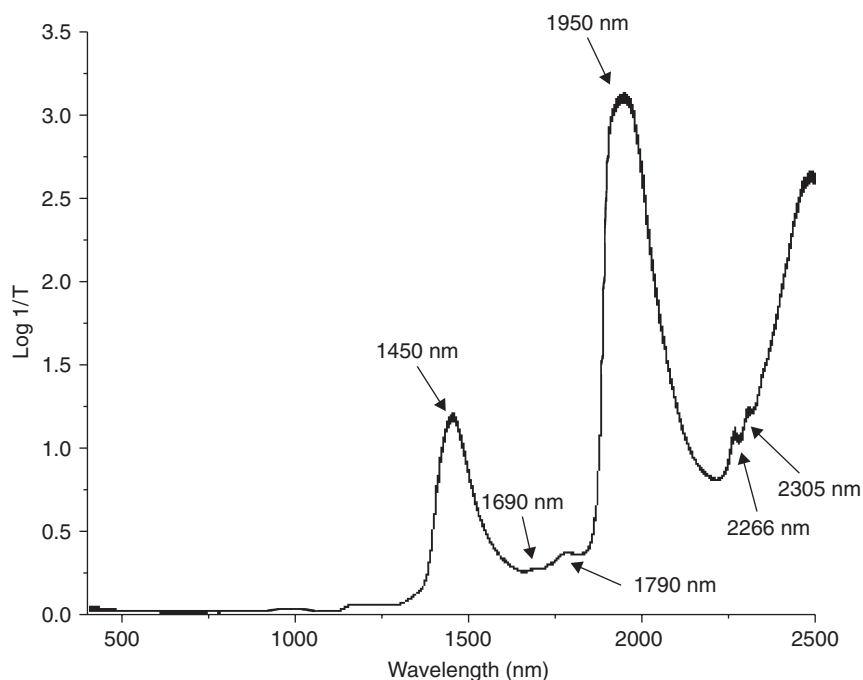
Figure 3.5 Visible and NIR spectra of white wine samples analyzed. Reproduced with permission from Cozzolino *et al.* (2003); ©American Chemical Society 2003.
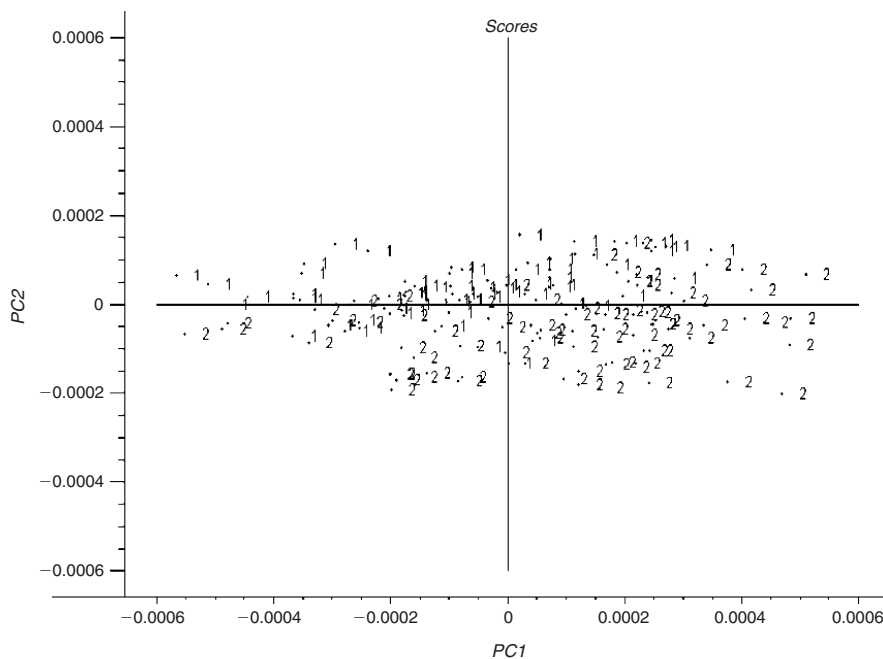
Figure 3.6 Sample score plot for PC1 and PC2 (second derivative, 400–2500 nm) for the white wines (1) = Riesling; 2 = Chardonnay). Reproduced with permission from Cozzolino *et al*. (2003); ©American Chemical Society 2003.
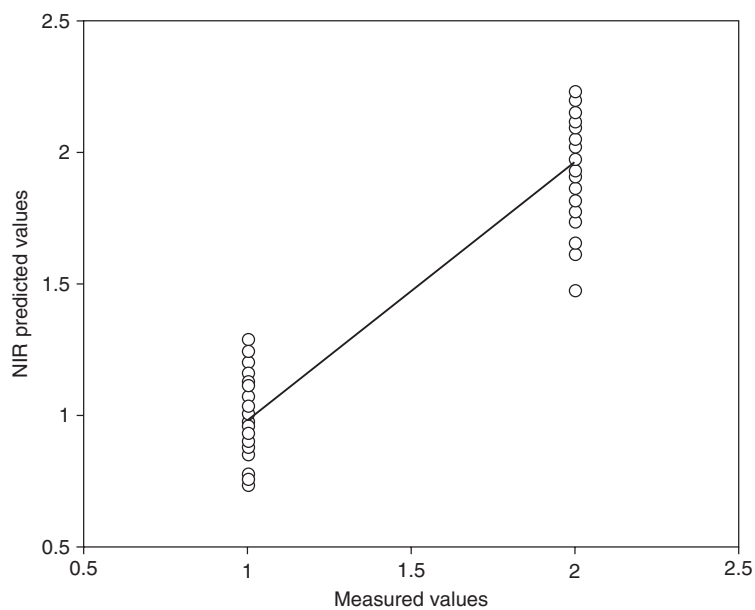
Figure 3.7 Prediction of commercial white wine varieties using DPLS regression (400–1100 nm) and second derivative (validation set). Reproduced with permission from Cozzolino *et al*. (2003); ©American Chemical Society 2003.

Yu *et al*. (2007b) evaluated the potential of visible and FT-NIR to predict the 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). Near-infrared spectra were collected from 1100–2500 nm 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.

Conclusions

Near-infrared 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 until now have, however, been only preliminary or only feasibility studies, 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 will play an important role in food authentication problems in the future is *NIR chemical imaging*. This non-destructive technique combines conventional NIR spectroscopy with digital imaging. As a NIR spectrum is collected for each pixel in the image, a three-dimensional cube consisting of both spatially resolved spectra and wavelength-dependent images is created. The ability not only to 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 in investigating issues of adulteration.

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