C H A P T E R

3

*c*0003

Near-Infrared, Mid-Infrared, and Raman Spectroscopy

Ouissam Abbas, Pierre Dardenne, Vincent Baeten

O U T L I N E

10003-PICO-9780123848628

List of Abbreviation

NIR Near Infrared
MIR Mid-Infrared
ATR Attenuated Total Reflectance
FT Fourier Transform
PCA Principal-Component Analysis
PLS Partial Least Squares
MPLS Modified Partial Least Squares
PLS-DA Partial Least Squares − Discriminant
    Analysis
PLSR Partial Least Squares Regression
SVM Support Vector Machine
LS-SVM Least Squares Support Vector Machine
LDA Linear Discriminant Analysis
SEP Standard Errors of Prediction
RMSEP Root Mean Standard Errors of Prediction
SECV Standard Errors of Cross-Validation

---

advances and their applications (Wilson & Tapp, 1999; Cen & He, 2007). The spectroscopic approach can be applied both in laboratory basic research and in the factory as an on-line tool for monitoring food products, production processes, and quality (Baeten et al., 2010). In this case, reference methods would be applied if deviation from standard values was observed.

p0110   In this review, we highlight the new advances in infrared (NIR and MIR) and Raman spectroscopic methods which, combined with multivariate analyses, have broad food applications, mainly in relation to composition analysis, quality control authentication, and adulteration detection (Trends in analytical chemistry, 1998; Da-Wen Sun; Vermeulen et al., 2010; Karoui & De Baerdemaeker, 2007).

3.1. INTRODUCTION

p0100   Consumers are increasingly aware of food safety and quality issues. One response to this has been the gradual substitution of tedious and time-consuming reference chemical and classical methods by rapid and environment-friendly analytical techniques. Among the panoply of analytical tools used are vibrational spectroscopic techniques (near-infrared [NIR], mid-infrared [MIR], and Raman), now attracting growing interest and based on the fact that food products have a specific composition of characteristics that gives them an individual "fingerprint". Vibrational spectroscopy techniques also offer rapid, nondestructive, and inexpensive analysis.

p0105   For many years, spectroscopic methods have been considered as tools for molecular structure and organic matter studies. The rapid development of spectroscopic instrumentation has expanded the application of these techniques to many areas of food research and the food industry. There is a growing output of scientific papers describing the new technological

3.2. THEORY

p0115   Spectroscopy can be defined as the study of the interaction between electromagnetic radiation and matter. Electromagnetic radiation is characterized by its wavelength λ (the length of one wave, cm), its frequency ν (the number of vibrations per unit time, Hz), and its wave number ν (the number of waves per unit length, cm^{-1}).

p0120   When photons of electromagnetic radiation interact with a molecule, radiation can be absorbed, transmitted, or scattered (Baranska, 1987). Radiation is absorbed in the case of IR spectroscopy where the absorption of incident radiation at a particular frequency in the IR region is related to this specific vibrational excitation energy. Radiation is scattered in the case of Raman spectroscopy. The incident radiation is at a frequency that might be in the visible, UV, or NIR region; it is scattered without any change in the energy of the incident photon (Rayleigh scattering) or when there is a change in that energy (Raman scattering). Both IR absorption and Raman scattering are mainly

based on vibrational transitions that occur in the ground electronic state of the molecule (Li-Chan, 1996). The energy possessed by a molecule at any given moment is defined as the combination of the contributing energy components: electronic, vibrational, rotational, and translational (Adapa et al., February, 2009). Translational energy relates to the displacement of molecules in a space as a function of the normal thermal motions of matter. Rotational energy is observed as the tumbling motion of a molecule, resulting from the absorption of energy in the microwave region. Vibrational energy corresponds to the absorption of energy by a molecule as the component atoms vibrate around the mean center of their chemical bonds. Electronic energy is linked to the transitions of electrons while they are distributed throughout the molecule, either localized within specific bonds or delocalized over structures.

p0125   In essence, the interaction of electromagnetic radiation with a molecule might lead to an absorption that then induces an electronic, vibrational, or rotational transition, depending on the energy of this radiation. Energy E in eV for a single photon is calculated using the following equation:

$$E = hv = \frac{hc}{\lambda}$$

where h is the Planck constant (6.6256×10^{-34} Js) and c the velocity of light in vacuum (2.998×10^{10} cm/s).

p0130   Vibrational energy, like other molecular energies, is quantized. Molecules can occupy discrete energy levels defined by whole numbers (0, 1, 2, etc.). Normally, molecules occupy the lowest energy level 0. A transition from level 0 to 1 leads to a fundamental transition in the molecule, whereas transitions from energy level 0 to 2 or 3 are defined as first and second overtones. Overtone frequencies are in the NIR spectral region, whereas fundamentals are in the MIR spectral region. This section outlines the theory behind each technique, in order to better understand the basic principles of the information provided by each of the studied methods: NIR, MIR, and Raman spectroscopy.

Infrared spectroscopy is the absorption p0135 measurement of different IR frequencies by a sample positioned in the path of an IR beam (i.e. NIR and MIR beams); when the frequency of a specific vibration is equal to the frequency of the IR radiation directed at the molecule, this molecule absorbs the radiation.

Absorption spectroscopy is based on the p0140 Beer–Lambert law that says that, for a homogeneous and nonscattering liquid sample, the concentration of an absorber is proportional to the sample absorbance.

This absorption information is presented in p0145 the form of a spectrum with wave numbers in MIR spectroscopy or wavelengths in NIR spectroscopy on the x-axis and absorbance intensity or percentage transmittance on the y-axis (see, as an example, MIR and NIR spectra of linseed oil in Fig. 3.1).

Mid-infrared spectroscopy allows structural p0150 elucidation and compound identification; functional groups absorb photons at characteristic frequencies of MIR radiation. The MIR region is between 4000 and 400 cm^{-1}. Absorption positions are presented according to wave numbers (v) (in cm^{-1}). MIR spectra include mainly bands that come from stretching and bending fundamental vibrations. Stretching vibrations are those where the distance between atoms decreases or increases while atoms remain in the same bond axis. In bending vibrations, the positions of the atoms change with respect to their original bond axis (Introduction to Infrared and Raman Spectroscopy, 1990; Yadav, 2005). They need less energy than stretching vibrations do, hence the lower frequencies for bending vibrations. Absorption bands resulting from these vibrations provide information on the structure of the sample analyzed. The spectra are divided in three regions rich in structural information: the region above 3000 cm^{-1}, including bands of hydroxyl or amino groups;

I. CHEMICAL ANALYSIS OF FOOD

the region between 3000 and 1500 cm^{-1}, including stretching vibrations of the acyl chain and carbonyl and alkene groups; and the region below 1500 cm^{-1}, characterized mainly by bending vibrations and some stretching vibrations of the acyl chain and functionalized groups, respectively. The region below 1500 cm^{-1} is considered as a fingerprint of one compound because of its specificity and the high number of bands occurring in this region, making it difficult to have two samples with an identical spectral signature (Coates, 2000). Compounds with similar structures might exhibit similar spectra profiles in the region above 1500 cm^{-1}. It is important to note that multiple functional groups might absorb photons at one frequency range, but that a functional group often has multiple characteristic absorptions (Handbook of Instrumental Techniques for Analytical Chemistry). In order to evaluate the composition of a complex food sample, spectral interpretations should not be limited to one or two bands — the whole spectrum needs to be taken into consideration. For MIR and NIR techniques, the overlapping of many different overtone and combination vibrations results in broad bands with low structural selectivity in NIR spectra compared with MIR spectra where fundamentals are more resolved, allowing the structure of a sample to be better elucidated (Karoui et al., 2003). On the other hand, the higher energy of NIR radiation and the implication of combination vibrations enable NIR spectroscopy to provide more complex structural information than MIR (Luykx & van Ruth, 2008).

Near-infrared spectroscopy is widely used to determine organic matter constituents. It is based on the absorption of electromagnetic radiation by a sample at wavelengths in the 800–2500 nm range. NIR absorption frequencies are presented as wavelengths (λ) expressed in nm. NIR spectra are composed of broad bands arising from overlapping absorption corresponding mainly to overtones and combinations of vibrational mode C–H, N–H, and O–H

f0010 **FIGURE 3.1** MIR and NIR spectra of linseed oil.

I. CHEMICAL ANALYSIS OF FOOD
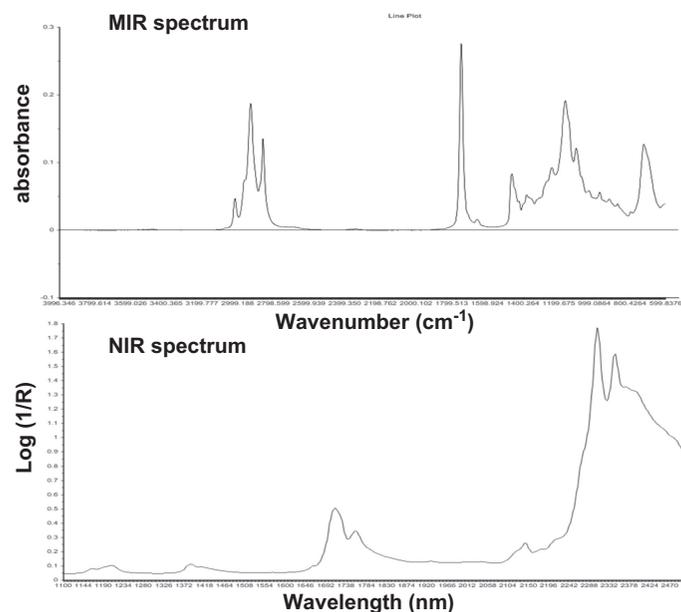
[AU1] chemical bonds (Osborne, 2000a,b). Overtones correspond to energy transitions that are higher than those for fundamentals. The frequencies of first and second overtones correspond to about two or three times that of the fundamentals. Combination bands result from transitions involving two or more different vibrational modes of one functional group occurring simultaneously; the frequency of a combination band is the sum or the multiples of the relevant frequencies. The absorption intensity decreases when the overtone level increases.

p0160 *Raman spectroscopy* provides chemical and structural information. A sample is radiated with monochromatic UV, visible, or NIR beam generated by a laser. Raman scattering occurs as a result of the interactions of the incident photons with the polarizability or shape of the electron distribution in a molecule as it vibrates. The vibrational energy levels in the molecules rise from the ground state to a short-lived, high-energy collision state, which returns to a lower energy state through the scattering of a photon with a lower frequency than the laser beam (Stokes Raman scattering). The difference between the frequency of the laser and that of the scattered photon is known as the Raman shift. This shift corresponds to the frequency of the fundamental MIR absorbance band of the bond. The spectra are presented as the intensity of the scattered light *vs.* the shift in the frequency between the incident and the scattered light defined by wave numbers. The interpretation of Raman spectra bands is carried out in the same way as for MIR signals.

p0165 Spectroscopic methods give complementary information about a molecule vibration. In the MIR and Raman techniques, vibration that results in changes in the dipole moment leads to be MIR active, whereas vibration that results in a change in polarizability leads to be Raman active (Pistorius, 1995). Some vibrations can be both MIR and Raman active. For example, the $C=C$ bond is generally more intense in Raman than in IR spectra because the double bond connects two identical parts of the molecule that lead to high polarizability changes, whereas a $C=O$ bond exhibits a high electric dipole moment leading to a more intense band in MIR than in Raman spectra. Water bands are very weak in Raman spectra, but they present a high broad band in MIR spectra because of the weakness of $O-H$ bond polarizability. Bonds such as $C-H$ are visible in both MIR and Raman spectra. Major food compounds (fat, protein, and carbohydrates) present $C-H$ bands in both Raman and MIR, but with variable intensities.

3.3. INSTRUMENTATION

s0020

p0170 Raman and IR spectroscopic techniques are suitable for both at-line (e.g. in the lab) analyses and on-/in-line process control. Infrared instruments allow spectra to be collected by detecting changes in the absorption or transmittance intensity at different frequencies, whereas Raman instruments allow spectra to be recorded by detecting changes in the scattering intensity at different frequencies (Raman shift).

3.3.1. Near-Infrared Spectrometers

s0025

p0175 Near-infrared spectrometers can be classified on the basis of such features as radiation source, wavelength selectors, sampling accessories, and detectors. There are two types of radiation sources: thermal and nonthermal. Thermal sources (Nernst filament, quartz—halogen, or tungsten—halogen lamps) consist of a radiant filament that produces thermal radiation covering a narrow or a wide range of frequencies in the NIR spectral range (Osborne et al., 1993). Nonthermal sources (discharge lamps, light-emitting diodes, laser diodes, or lasers) emit narrower bands of radiation than those emitted by thermal sources. They are considered to be more efficient because most of the energy consumed is emitted and can be electronically adjusted (McClure, 2001).

I. CHEMICAL ANALYSIS OF FOOD

p0180   Wavelength selectors allow NIR instruments to be classified into two groups; those based on a discrete wavelength selection and those based on a continuous spectrum. Discrete wavelength instruments using filters or light-emitting diodes irradiate at only few wavelengths selected for specific molecules for special applications. Continuous-spectrum instruments are more flexible and can be used for a wide range of applications (McClure, 2001). They occur in several configurations, such as grating monochromator, acousto-optical tunable filter, photodiode array, and Fourier transform (FT) interferometer technologies (Blanco & Villarroya, 2002):

u0010 • grating monochromators allow radiation to be spread out according to wavelengths (McClure, 2001); corresponding instruments allow measurements to be made in both transmittance and reflectance mode, and are suitable for a large number of applications and to solve analytical issues that need a wide range of wavelengths (Osborne, 2000a,b),

u0015 • acousto-optical tunable filters produce discrete wavelengths over a wide spectral range (McClure, 2001); they are characterized by their great stability and scan reproducibility, making the instruments containing them suitable for use under difficult measurement conditions, such as production plants,

u0020 • photodiode array systems allow all wavelengths to be measured simultaneously (McClure, 2001; Blanco & Villarroya, 2002; Osborne, 2000a,b); instruments equipped with this system are suitable for analyzing moving samples such as on-line applications or rotating sample holders,

u0025 • FT interferometer-based instruments are systems in which the detector collects information at several frequencies simultaneously; it offers high wavelength precision, accurate scan speed, and a high signal-to-noise ratio (SNR). More details

about this technology are given later (in the paragraph on FT-MIR spectroscopy).

p0205   After this, light is directed to the sample. NIR spectrometers can be equipped with a large variety of sampling accessories that make it possible to measure solid or liquid samples. There is more detail on this later (in the paragraph on the sample presentation of the different spectroscopic techniques discussed in this chapter). Finally, light from the sample is oriented to single- or multichannel photon detectors (Osborne et al., 1993). The way single-channel detectors function depends on the type of semiconductor that they include; lead sulfide covers the 1100−2500 nm spectral range, silicon the 400−1100 nm range, and epitaxially grown indium gallium arsenide (InGaAs) the 800−1700 nm range (Osborne et al., 1993; Blanco & Villarroya, 2002). Multichannel detectors consist of diode arrays where the detection elements are arranged in rows or charge-coupled devices (CCDs) in which the detection elements are arranged in planes (Stchur et al., 2002).

3.3.2. Mid-Infrared Spectrometer   s0030

p0210   Infrared instruments can be classified into two groups: dispersive and FT spectrometers (Handbook of Instrumental Techniques for Analytical Chemistry).

3.3.2.1. Dispersive Spectrometers   s0035

p0215   Dispersive spectrometers were the first IR instruments. They were invented in the 1940s. They are composed of three basic parts: a radiation source, a monochromator, and a detector. The common radiation source is an inert solid heated electrically to 1000−1800 °C, providing different radiation energy profiles. The monochromator is a device that allows a broad spectrum of radiation to be dispersed and provides a continuous calibrated series of electromagnetic energy bands with a defined wavelength range. Prisms or

gratings are the dispersive components used in conjunction with variable-slit mechanisms, mirrors, and filters. There are two types of detectors: thermal detectors for measuring the heating effect produced by IR radiation and photon detectors based on the interaction between the IR radiation and the semiconductor material. Thermal detectors provide a linear response over a wide range of frequencies, whereas photon detectors have shorter response times and higher sensitivity. In dispersive IR spectrometers, radiation from a broad-band source passes through the sample and is dispersed by a monochromator into component frequencies; each component frequency is viewed sequentially. The beam is directed onto the detector, producing an electrical signal that is converted into a recorded spectral response.

s0040 **3.3.2.2. Fourier Transform Spectrometers**

p0220   Fourier transform MIR spectrometers have replaced dispersive spectrometers because of their higher speed and sensitivity; all frequencies are examined simultaneously. FT-MIR spectrometers have significantly increased the capabilities and applications of MIR spectroscopy.

p0225   FT-MIR instruments have three components: a radiation source, an interferometer, and a detector. The source radiation is the same as that used for dispersive instruments, but with the advantage being water-cooled in order to obtain more power and stability. Light is then directed onto an interferometer. The most common one is a Michelson interferometer. It consists of a beam splitter and two mirrors — a moving mirror and a fixed mirror — that are perpendicular to each other. Radiation from a broad-band source is collimated and directed into the interferometer, and then goes through the beam splitter, where the half of it is transmitted to the fixed mirror and the remaining half is reflected to the moving mirror. The divided beams are then reflected from the two mirrors and are recombined at the beam splitter.

With the changes in the position of the moving mirror in relation to the fixed one, an interference pattern is generated. The generated beam passes through the sample and focuses on the detector. The record of the interference signal is known as an interferogram, which is a time domain spectrum and records the detector response changes in relation to the time of the mirror scan. The interferogram is then converted by applying FT (a mathematical operation) to the final MIR spectrum, which is the usual frequency domain spectrum (intensity versus frequency). Two types of detectors are generally used: a deuterated-triglycine sulfate (DTGS) detector and a nitrogen-cooled mercury cadmium telluride (MCT) photon detector. Both detectors provide very fast responses and high sensitivity, with a better performance obtained with the MCT detector.

p0230   FT-MIR spectrometers have several advantages over dispersive spectrometers, including faster speed and higher sensitivity, as well as making it possible to observe all frequencies simultaneously and to obtain a complete spectrum in a single scan. Other advantages include increased optical throughput, an internal laser reference that allows automatic calibration (without the need for an external one), greater reliability because of the simpler mechanical design, elimination of stray light and emission contributions, and a powerful computerized data system.

3.3.3. Raman Spectrometers   s0045

p0235   Two kinds of Raman instruments are usually used: dispersive spectrometer and an FT spectrometer. In addition, Raman spectrometers can be classified according to the frequency of the exciting laser.

p0240   In *dispersive spectrometers*, the scattered light is collected through a filter and focused onto a monochromator that allows the different energies of the Raman scattering to be separated. The radiation is then directed to a CCD; frequencies

I. CHEMICAL ANALYSIS OF FOOD

of the scattered light are separated and the Raman spectrum is collected. It should be noted that with the use of CCDs, all scattering is accumulated during the exposure of the sample to the exciting light, thus improving the intensity of recorded signals. The main disadvantage of visible dispersive spectrometers is the problem of fluorescence. The likelihood of this happening is much higher in the VIS region than it is in NIR region; large signals could interfere with the weak Raman scattering peaks.

p0245 *Fourier transform spectrometers* use an NIR laser source, for instance, a neodymium-doped yttrium aluminum garnet (Nd^{3+}:YAG) laser emitting at 1064 nm. At this wavelength, radiation energy is weak, completely or partly overcoming the fluorescence problem. But because absorption in this region is not as efficient as it in the VIS one, high laser powers are used. In addition, the FT system provides more sensitivity, and detectors functioning at room temperature or cooled with nitrogen for more sensitivity are used. FT spectrometers have an advantage over dispersive spectrometers in terms of analyzing a sample in its bottle, because dispersion from nonideal surfaces is less important in FT systems and there is less fluorescence from the bottles.

s0050 ## 3.4. SAMPLE PRESENTATION

p0250 Sampling is a very important issue in achieving good qualitative and quantitative analyses. IR and Raman spectroscopy have the advantage of little or no need for sample preparation before conducting measurements. Depending on the case, grinding, slicing, or cutting might be necessary. For some products, such as milk, homogenization is performed before analyses. However, parameters such as temperature and moisture have to be controlled and kept constant before and during measurements.

p0255 Raman and IR spectroscopic methods provide a wide range of sample presentation devices for conducting measurements in optimum conditions. More details on each technique are presented here.

3.4.1. Near-Infrared Accessories s0055

p0260 NIR spectrometers make it possible to measure a great variety of food samples in various forms, including liquids, powders, and all kinds of solid products (Fig. 3.2). Transparent liquids can be measured in *transmittance* mode where the pathlength is constant; it means where the thickness of the sample, quartz cuvette, or flow cell is constant. In these conditions, the absorption depends only on the concentration of the absorbing component. If the sample is opaque, such as milk (because of the presence of fat globule), measurement will be conducted in a *diffuse transmittance* mode because in this case part of light is scattered (Coventory, 1988; Osborne, 2000a,b). Some solid products, such as meat and cheese, are also analyzed in this mode (Penner, 1994). However, solid and granular samples (Osborne, 2000a,b) are measured using the *diffuse reflectance* mode. The information collected is based on the absorbed light and the scattered light that lacks any information on the chemical composition of the sample. Another mode combines reflectance and transmittance, forming the *transflectance mode* that is suitable for analyzing turbid or clear liquids (Osborne, 2000a,b). The sample is placed between a quartz window and a diffusely
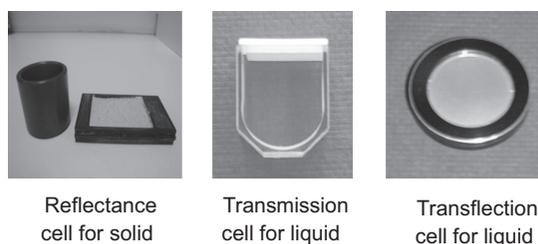

Reflectance cell for solid   Transmission cell for liquid   Transflection cell for liquid

FIGURE 3.2 Examples of sample presentation in near f0015 infrared spectroscopy.

reflecting metal plate. The incident radiation is transmitted through the sample, reflected from the diffusely reflecting plate and then transmitted back through the sample.

s0060 ### 3.4.2. Mid-Infrared Accessories

p0265   FT-MIR spectrometers are used also for food analyses. Several sample presentation techniques are proposed for liquid analyses such as transmission cells, thermostated flow cells, and polymer thin films such as IR-cards in polyethylene. For solids, halide pellets (KBr) are used. Recently, more flexible presentation techniques have been proposed as attenuated total reflectance (ATR) accessories (Fahrenfort, 1961; Harrick, 1967). With these accessories, the sample is put in a close contact with a crystal with a high refraction index, made mainly of ZnSe, Ge, ZnS, Si, or diamond. ATR is suitable for both solid and liquid analyses. It is particularly useful for sampling the surface of flat materials that are too thick or too opaque for IR transmission (Fig. 3.3).

s0065 ### 3.4.3. Raman Accessories

p0270   Raman spectra can be obtained at room temperature. There is a great variety of ways to analyze a given sample. Most applications relate to liquid and solid samples that can be analyzed by Raman spectroscopy in their glass container,

Flow cell for liquid	ATR cell for liquid & solid	transmission accessory for liquid

f0020 **FIGURE 3.3** Examples of sample presentation in mid-infrared spectroscopy.

whatever the volume (capillary tubes, vials, and brown bottles). Plastic and brown holders can also be used. Small solid holders for small quantities, as well as rotating accessories for samples suffering from thermal degradation, are also available. In addition, working across a range of temperatures (from −170 to 950 °C) is possible using specific cells designed for this purpose (Modern Raman spectroscopy).

3.5. NEW GENERATION OF SPECTROMETERS   s0070

### 3.5.1. On-line Systems   s0075

p0275   In the food-processing industry, the production of food is preceded by analyses of the raw materials and followed by analyses of the final products. Monitoring during the process is also desirable. For this, at-line or on-line analytical tools can be used. At-line (laboratory) analyses require removing the sample from the production line, to pre-process it and send it to a laboratory, which might be expensive (price of the laboratory instruments) and time consuming, whereas on- and in-line methods are time-saving and relatively inexpensive. Raman and IR, including NIR and MIR, are the most suitable techniques for providing real-time measurements that can be integrated into an industrial process. In addition, recent developments in in- and on-line spectrometers make it possible to analyze a sample in a vessel, during a production process or in the field because of the use of fiber optics that connect the spectrometer to the [AU2] sensing device (Fig. 3.4).

p0280   *On-line NIR spectroscopy* has several advantages, such as high precision, speed of measurement, low-cost, well-developed equipment and devices, no need for sample preparation, and simultaneous multi-analytes' detection. The main disadvantage is the need for robust calibration models and calibration transfer between instruments (Kondepati & Heise, 2008). Its applications in food systems have significantly

f0025

FIGURE 3.4 Examples of sample presentation used in Raman spectroscopy (from Bruker).
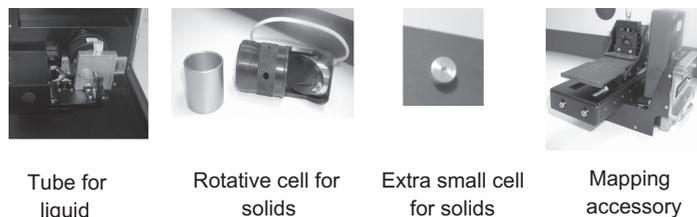
Tube for liquid

Rotative cell for solids

Extra small cell for solids

Mapping accessory

increased recently. Huang et al. (2008) published a review on NIR on-/in-line analysis of foods such as meat, fruit, grain, dairy products, and beverages. It covered the preceding 10 years of research in this field (Huang et al., 2008).

p0285   *On-line MIR spectroscopy* has several advantages over NIR spectroscopy, such as high sensitivity, quantification at low analytes levels, ability to distinguish between very similar structures, and good calibration transfer between instruments. It is less frequently used than NIR spectroscopy for on-line applications. It suffers from the strong absorption of water, limiting its use for aqueous solutions, and it needs further development in terms of fiber optics. Only few studies on the use of MIR for online applications, such as monitoring a fermentation reaction, have been reported (Bellon-Maurel et al., 1994; Ph. et al., 2000).

p0290   Unlike IR on-line spectroscopy, *on-line Raman spectroscopy* has little application in the food industry. It is used mainly in the pharmaceutical processing industry.

s0080 ## 3.5.2. Mapping and Imaging Systems

p0295   Spectroscopy is usually used for analyzing most of a sample at the same time, but it can be linked to microscopic technology for the analysis of localized regions of the sample. This can be achieved using one of two techniques: mapping and imaging.

p0300   *Mapping* enables the spectra of single points on a sample to be measured sequentially; the sample holder is moved so that the position of the sample is changed after each measurement. The spectrometer is connected to a microscope in order to clearly identify the chemical content of the sample components and their spatial distribution. The instrument allows spectra to be collected from a small surface (scale of 10 microns).

p0305   One drawback is that measurements are very time consuming, and the spectra, when measured with a high spatial resolution, tend to have a lower SNR. To accelerate the process, a *hybrid linear array mapping* approach has been proposed. It consists of linear array detectors that allow spectra over a line of points on a sample to be measured simultaneously, so that a line image is produced. As in the case of mapping measurements, in this approach the sample is moved after each measurement with a single-element detector, so that the spectra of the next linear region can be measured. The spectra are then linked to form the complete image (Salzer & Siesler, 2009). Although this approach allows for much faster measurements than single-point mapping, higher SNR, and better spatial resolution, it is considered to be less efficient than imaging systems.

p0310   *Imaging technology* allows samples to be analyzed more quickly. An imaging spectrometer gathers spectral and spatial data simultaneously by recording sequential images of the analyzed sample; each image plane is collected at a single wavelength band (The Spectral dimensions Website, 2004). Taking the example of NIR imaging, the compilation of the reflected energy images, taken sequentially at each wavelength, produces a *hyperspectral* cube. For each pixel, the compilation of the absorbances at each wavelength produces a spectrum. This technique is called *near-infrared hyperspectral imaging*.

p0315   The mapping, hybrid linear array mapping, and imaging technologies can be applied within IR (either NIR or MIR) and Raman spectroscopy. NIR imaging is the most commonly used technology in food analyses. NIR imaging technology can now be used in the laboratory or in on-line food and agricultural systems. Analyses conducted in the laboratory seek to obtain information on product composition or to perform routine quality control. In addition, by scanning small pixel size, imaging helps to improve the limits of detection; many applications are then possible for the detection of contaminants, such as animal proteins in feed (BaetenV. et al., 2005; Fernandez Pierna et al., 2005; Baeten et al., 2005; von Holst et al., 2008; Abbas et al., 2010; Fernandez Pierna et al., 2010; Fumière et al., 2009), ergot in food and feed (Vermeulen & de Jong, 2009), and apple surface defects and contamination (Mehl et al., 2004), and for the detection of small biochemical changes such as differentiating genetically modified soy or barley (Baeten et al., 2010). NIR imaging technology is also used in industry for the detection of foreign bodies; in the tobacco industry, for example, it is important to identify foreign bodies such as polypropylene strings or pieces of rubber using a rapid system such as multispectral imaging (Izumyia et al., 2004). Product defects can also be examined using this technique; an example is the use of imaging to detect fecal contamination in poultry carcasses (Lawrence et al., 2003; Park et al., 2006). Another application is the evaluation of fruit quality by NIR imaging where the scattering properties are related to firmness and therefore to the structure of the fruit tissues, particularly in peaches and apples (Lu, 2003; Lu & Peng, 2006).

s0085   3.6. ADVANTAGES AND LIMITATIONS OF SPECTROSCOPIC TECHNIQUES

p0320   In general, Raman, NIR, and MIR spectroscopic techniques provide a means of high-speed analysis with many advantages: little or no sample preparation, environmentally friendly (no use of solvents), cost effective, and nondestructive. They can be used on-line or in the laboratory, but some techniques are more suitable for on-line analysis than others. The major drawback in all these methods is the influence of temperature, which has to be kept constant during measurement. More details on the advantages and limitations (Baeten & Dardenne, 2002) of each technique are discussed here.

p0325   *Near-infrared spectroscopy* allows qualitative and quantitative analysis to be performed, spectra with high intensity and repeatability to provided, and a large variety of samples to be handled, irrespective of their shape or size, or whether they are liquid or solid, combined with the advantage of easy and simple sample presentation. NIR reflectance is influenced by particle-size properties. It can be considered to be very advantageous for on-line powder analysis; only one measurement is enough to monitor both chemical constituents and physical structure (Ilari et al., 1988; O'Neil et al., 1999; Chapelle et al., 1989). NIR spectroscopy provides proven reliability and speed in multiconstituent monitoring (Bickel, 1989; Robertson et al., 1989) in addition to its compatibility with fiber optics, making it very suitable for at-, on-, and in-line process control. It has some limitations, however, such as the need for large data sets to calibrate the spectrometer, which requires recording hundreds or thousands of spectra with reference values, which in turn requires many hours of work. Spectra with a lot of data are obtained, and it is then necessary to extract the significant information. For this, a wide range of chemometric tools can be used to characterize the spectral data set and select significant variables that can be correlated to the information of interest.

p0330   *Mid-infrared spectroscopy* allows information to be obtained rapidly on the structure of samples analyzed. Functional groups are characterized by several absorptions at particular

frequencies. Because every molecule has its spectral fingerprint, it is possible to identify unknown compounds on the basis of their spectra or to support results of other identification methods such as mass spectrometry (MS) or nuclear magnetic resonance (NMR) spectrometry. The use of large spectral databases also helps to identify unknown compounds by comparing their spectra with those on the database. The technique has some limitations, such as the need for the background solvent to be relatively transparent in the spectral region of interest. Sample molecules have to be active in the IR region in order to be observed. Infrared spectroscopy is more suitable for qualitative and semi-quantitative analysis. Its application in quantitative analyses was very limited when only dispersive spectrometers were used, but with the development of FT-MIR spectrometers and chemometric tools its use in this area has become more common. An example is the application of MIR spectroscopy for milk analyses (Soyeurt et al., 2009; Soyeurt et al., 2010).

p0335 *Raman spectroscopy* has good spatial resolution because of the low wavelength, allowing researchers to focus on a level below the sample surface and then to take measurements through its packaging without exposing the sample to the atmosphere. The technique has some limitations, however. The SNR is very low. If the sample contains a fluorescent compound, it becomes difficult to obtain Raman spectra, a problem that could be overcome if the Raman instrument is equipped with an NIR laser instead of a visible one. The disadvantage in this case is lower spatial resolution (Thygesen et al., 2003). In addition, a sample could be heated during measurement because of the laser (West, 1996), which might alter or destroy it. It is then important to find a good compromise between the laser power and the time of measurement in order to obtain a spectrum with a high SNR without heating the sample.

3.7. CHEMOMETRIC APPROACH   s0090

p0340 Raman and IR spectroscopy techniques are now largely used as routine analytical tools, both in monitoring processes and in research and development. The expansion in their application has been greatly helped and reinforced by the parallel development of chemometric methods. The chemometric field is very large; the mathematical and statistical tools involved are mainly biometrics and econometrics (Massart et al., 1988; Massart et al., 1998), but the use of this science in support of chemistry has made the use of multivariate data analyses essential for Raman and IR spectroscopy in order to obtain qualitative and quantitative information. Multivariate analyses allow researchers to extract significant information from data, to reach lower detection limits, to detect outliers when building a model, and to determine confidence and prediction intervals. Chemometrics help to improve the analytical method by making more use of the information available in spectra. For quantitative analyses, calibration models have been developed connecting spectra to the concentration of one component, such as protein, fat, sugar, or a physico-chemical property such as humidity, whereas qualitative analyses focus instead on continuous variables and discrete values, such as the origin of one compound or the quality properties. Chemometric tools can be classified into two main groups: unsupervised methods, such as principal-component analysis (PCA), used to visualize the natural distribution of a sample in a three-dimensional space, and supervised methods such as partial least-squares regression (PLSR), used to predict compound properties on the basis of a model. Several methods in each group have been proposed (Brown et al., 2009), but before using chemometric tools to develop a calibration it is often necessary to apply a pretreatment of the spectra. The purpose is to correct spectral

variations due to light scattering from a solid or a turbid liquid, a variation in the pathlength during measurement or spectral distortion induced by the spectrometer hardware, such as baseline drift, wavelength shift, and the effects of nonlinearity and noise from the detector or noise from an amplifier and analog–digital converter (Siesler, 2002). A spectroscopist has to choose a suitable pretreatment and its optimum parameters. Techniques could include, for example, local filters, smoothing, derivatives, baseline correction, and orthogonal signal correction. Chemometric methods were discussed in detail in the previous chapter.

s0095 3.8. APPLICATIONS IN FOOD ANALYSIS

p0345 Vibrational spectroscopy offers many possibilities for the study of food systems. In this section, its use and potential are discussed by giving examples where IR and Raman spectroscopy have been successfully applied to food for a variety of objectives: determining geographic origin, species discrimination, adulteration detection, physicochemical properties, process control and food quality, etc. We present examples of some applications of IR and Raman spectroscopic tools in the food domain, grouped according to these objectives. For each objective, for each technique, one or more examples are given (NIR, MIR, Raman, and a combination of two or more of them).

s0100 3.8.1. Geographic Origin

p0350 Food origin authentication involves establishing whether or not a sample belongs to a predefined origin. In recent years, combining spectroscopic techniques and chemometric methods has been used mainly for food origin authentication (Karoui & et al, 2008; Manley et al., 2008; Baeten et al., 2008; Downey, 1996); the applications relate to a wide range of foods,

such as cereals, milk, meat, fish, fruit, vegetable, edible oils, and alcoholic beverages. Authentication by spectroscopic methods is based essentially on discriminant analysis where the spectrum of a sample is compared with a reference library, or included in a chemometric model to check whether or not the sample belongs to a predefined class.

3.8.1.1. MIR Spectroscopy for the s0105 Geographic Authentication of Wines

p0355 Wine is routinely transported to bottling and packaging facilities, and it is very important to assess and monitor it easily and rapidly, particularly in terms of its geographic authenticity. Several studies have demonstrated the ability of NIR spectroscopy to classify wines in terms of geographic origin (Liu et al., 2006; Capron et al., 2007; Yu et al., 2007). FT-MIR spectroscopy has been used to discriminate red wines according to geographical origin. Within the framework of the TYPIC project (TYPIC project), researchers at the Walloon Agricultural Research Centre (CRA-W) in Belgium worked on the geographic authentication of red wines. A total of 120 red wines from Germany and France, each wine from two vintages, were studied using MIR spectroscopy. The application of PCA to the collected data led to a tendency to separate samples in terms of their origin. Using a similar approach, Picque et al., (2005) applied the technique to dry extracts of 338 wines of the same variety, collected in three areas in France (Gaillac, Beaujolais, and Touraine) over four years (Picque et al., 2005). The spectra were collected between 1800 and 800 cm^{-1}, and PCA was then applied, which showed a good distribution of wines according to their year of production, but no separation according to geographic origin. In order to achieve the latter goal, PLSR was applied. The results showed that 85% of the validation samples had been correctly classified. The authors succeeded in discriminating samples in terms of their geographic origin and concluded

that phenolic compounds are significant in enabling this discrimination.

s0110 ### 3.8.1.2. NIR Spectroscopy for the Geographic Authentication of Olive Oil

p0360   Increasing consumer interest in olive oil due to its nutritional and sensory properties, as well as its economic value, makes this product prone to a fraud or incorrect information about its source. The geographic origin of olive oil constitutes one of the important parameters that determines consumer choice and confidence in the product's quality. The authentication of virgin olive oil samples usually requires the use of sophisticated and time-consuming analytical techniques. There is a need for fast and simple analytical techniques to develop a quality control methodology (De Luca, 2011; Casale, 2010; Downey & Flynn, 2002). Galtier et al., (2007) used NIR spectroscopy to classify virgin olive oil in terms of geographic origin (Galtier et al., 2007). The NIR spectra of 125 samples were collected and treated by PLS1 discriminant analysis (DA). The samples corresponded to five geographically registered designations of origin (RDOs) for French virgin olive oils ("Aix-en-Provence", "Haute-Provence", "Nice", "Nyons," and "Vallée des Baux"). The interpretation of spectral profiles of regression vectors showed that each RDO was correlated to one or two specific components of virgin olive oil, depending on cultivar composition. Although there was some similarity in cultivar composition in two denominations of origin ("Aix-en-Provence" and Vallée des Baux"), the results can be considered satisfactory. The correlation of chemometrics to NIR spectra allowed similar results to be obtained as rapidly as those obtained using time-consuming analytical chromatographic techniques.

s0115 ### 3.8.1.3. FT-Raman Spectroscopy for the Geographic Authentication of Honey

p0365   Honey is a complex and challenging product to analyze, mainly because of the composition of its various botanical sources. The discrimination of the origin of honey is of prime importance in order to reinforce consumer trust in this product, but only a few studies have been undertaken to define geographical provenance. Davies & et al., (2002) noted that the distinction of honey samples in terms of geographic region is less appropriate than floral origin, but it might be possible with large sample sets (Davies & et al., 2002). A combination of IR spectroscopy and chemometric treatments has been used to determine the geographical origin of honey (Ruoff et al., 2006; Woodcock et al., 2007). Recently, FT-Raman spectroscopy combined with chemometric tools as a fingerprint technique was investigated as a rapid and reliable method for discriminating honey according to source (Fernández Pierna et al., accepted for publication). The objective was to discriminate Corsican honeys from honey coming from other regions in France, Italy, Austria, Germany, and Ireland, based on their FT-Raman spectra. The developed models include the use of exploratory techniques, such as the Fisher criterion, for the selection of significant wave numbers and supervised methods, such as PLS-DA (Fig. 3.5) or support vector machine (SVM) (Fig. 3.6). All these models showed that
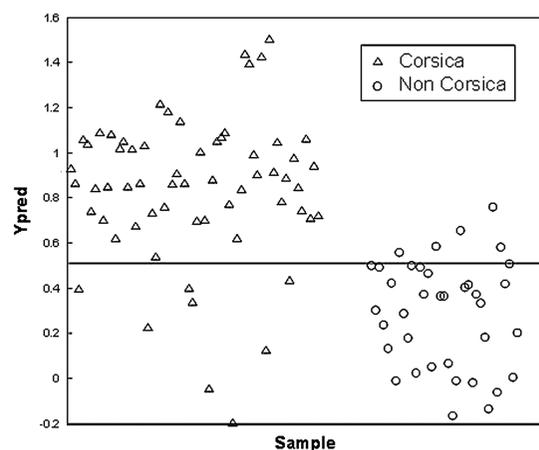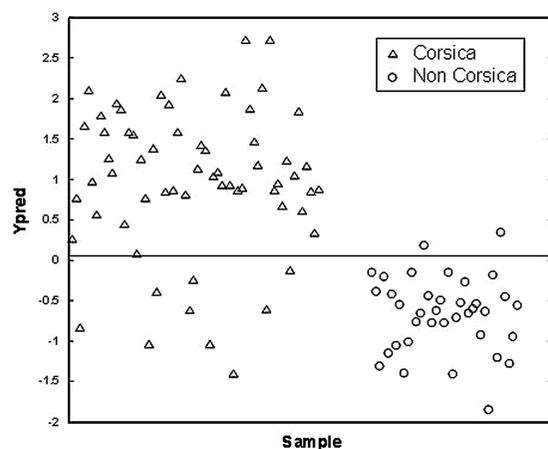

FIGURE 3.5 PLS-DA prediction results for the test f0030 data set.

f0035 **FIGURE 3.6** SVM prediction results for the test data set.

85−90% of the Corsican honey samples were correctly classified, indicating that Raman spectroscopy combined with chemometric treatments is a promising approach for the rapid and inexpensive discrimination of honey according to origin.

s0120 ### 3.8.1.4. Spectroscopic Methods for the Geographic Authentication of Cheese

p0370 Spectroscopic techniques have been used to assess the authenticity of cheeses expected to benefit from protected designation of origin (PDO). Cheeses produced in different regions might have typical features that are related, for example, to ripening time or the producing season. Pillonel et al., (2003) conducted a preliminary study to determine the geographic origin of Emmental cheese using MIR and NIR spectroscopic methods: NIR diffuse reflection, MIR attenuated total reflection using two different instruments, and MIR transmission spectroscopy in combination with multivariate chemometrics (Pillonel et al., 2003). The potential of each method was investigated for its potential to discriminate Emmental cheese of various geographic origins. A total of 20 Emmental cheese samples from Switzerland, Allgäu (Germany), Bretagne (France), Savoie (France), Vorarlberg (Austria), and Finland were analyzed. The normalized spectra or their 2nd derivatives were analyzed using PCA and linear discriminant analysis (LDA) of the PCA-scores. Although this study was based on a reduced number of samples, clear trends were observed. LDA applied to MIR transmission data produced a 100% correct classification of Swiss Emmental, and NIR diffuse reflection spectroscopy allowed a 100% correct classification of the Emmental cheeses produced in all six European regions.

3.8.2. Species Discrimination s0125

p0375 In addition to the geographic authentication of food products, establishing authenticity also requires checking the correspondence with defined criteria that characterize one species or a variety of ingredients. Spectroscopic techniques combined with chemometrics have been investigated to achieve these objectives. Some examples are cited here.

3.8.2.1. FT-MIR Spectroscopy for the Discrimination of Meat Products s0130

p0380 The authenticity of meat and meat products is important for the consumer, particularly because of the possibility of the total or partial substitution of high-value raw materials with less costly alternative animal species (Al-Jowder et al., 1999; Cordella et al., 2002). Analytical spectroscopic methods can be useful in the control of the authenticity of a meat product. Several studies have been conducted using NIR spectroscopy in order to identify and differentiate between meat categories, such as kangaroo, beef, pork, chicken, turkey, and lamb (Ding & Xu, 1999; Rannou & Downey, 1997; Cozzolino & Murray, 2004). The potential of FT-MIR to discriminate three meats − turkey, chicken, and pork − was shown by Al-Jowder et al., (1997) in a preliminary study. Spectra were collected using an FT-MIR spectrometer in an attenuated total reflectance mode. The application of PCA to the spectral data sets

produced good discrimination between fresh and frozen-then-thawed turkey, chicken, or pork samples (Al-Jowder et al., 1997). The results showed that it was possible to distinguish minced chicken, pork, and turkey meats from their infrared spectra, and for each meat species it was possible to differentiate between fresh and frozen—thawed samples. The authors concluded that the IR method could, with further development, be used for meat product authentication and quality control.

s0135 ### 3.8.2.2. NIR Spectroscopy for the Discrimination of Botanical Honey Origin

p0385   Many studies have been conducted on the use of vibrational spectroscopy for assessing the botanical origin of honey (Goodacre et al., 2002; Tewari & Irudayaraj, 2005; Davies et al., 2002; Ruoff et al., 2006B). Ruoff et al. (2006) used NIR spectroscopy for this purpose, with measurements taken on heated honey samples (Ding & Xu, 1999). The spectra were collected in the 1000—2500 nm range in transflection mode. The most important absorption bands observed were in the 1400—2380 nm region, with a water band at 1940 nm and several bands in the 1540—2380 nm region characteristic of C—O and C—C bond vibrations of saccharides. A total of 364 honey samples were produced over seven years, mainly from Switzerland. They corresponded to eight honey types that could be classified into two groups of 185 and 179 unifloral and multifloral samples, respectively. The application of LDA led to a correct classification of 29—100% of unifloral honey samples from the validation set, whereas only 19% of the multifloral samples were correctly classified. It appeared to be easier to classify unifloral honey samples than multifloral ones.

s0140 ### 3.8.2.3. Raman Spectroscopy for the Discrimination of Green Coffee Varieties

p0390   The two main varieties of commercial coffee are Arabica (*Coffea arabica* Linnaeus) and Robusta (*Coffea canephora* Pierre ex Froehner) (Downey et al., 1994). Arabica is considered to be higher quality than Robusta (Pizarro et al., 2007). The discrimination between them has been studied using FT-MIR spectroscopy (Briandet et al., 1996a; Briandet et al., 1996b; Kemsley et al., 1995) and NIR spectroscopy (Esteban-Díez et al., 2004; Esteban-Díez et al., 2007). Recently, El-Abassy et al. (in press) worked on the discrimination of green coffee varieties (El-Abassy et al., in press). Visible micro-Raman spectroscopy combined with PCA was applied for a rapid discrimination between Arabica and Robusta, based on their chlorogenic acid (CGA) and lipid contents. The comparison of the Raman spectra of Arabica and Robusta green coffee revealed different CGA and lipid compositions. The application of PCA to the whole Raman spectrum showed a clear separation between Arabica and Robusta. The region between 1000 and 1750 cm^{-1} corresponding to CGA Raman bands appeared to produce the most significant spectral range responsible for the discrimination obtained. The application of PCA to the 2700—3050 cm^{-1} range corresponding to lipid bands meant it was possible to obtain reliable discrimination between the two coffee species.

s0145 ### 3.8.2.4. Spectroscopic Methods for the Discrimination of Edible Oils

p0395   The discrimination of fats and edible oils using various spectroscopic methods (FT-NIR, FT-MIR, and FT-Raman) was studied in different papers (Baeten et al., 1996; Baeten et al., 1998; Hourant et al., 2000; Baeten et al., 2001). More recently, Yang et al. (2007) conducted a study on 110 samples (butter, cod-liver oil, lard, canola oil, coconut oil, corn oil, olive oil, peanut oil, safflower oil, and soybean oil). All the samples came from the same batch; the calibration and validation sets were not totally independent. The results of the correct classification of the validation set samples showed that the FT-NIR method gave a correct classification of

84.4–93.3%, the FT-MIR model 95.6–98.9%, and the FT-Raman method 85.6–94.4%. The authors drew conclusions on the ability of spectroscopic techniques to rapidly classify edible oils and fats according to their type.

s0150 ### 3.8.3. Detection of Adulteration

p0400 Authentication also involves differentiation between pure and adulterated samples. A product must match the description given by the producer or the manufacturer. Rapid methods such as spectroscopy for confirming the description and detecting adulteration are being developed in order to ensure the safety and the quality of a controlled product. Some examples of the use of spectroscopic methods are given here.

s0155 #### 3.8.3.1. FT-MIR Spectroscopy for the Detection of Adulteration of Vegetable Oils

p0405 Extra virgin olive oil (EVOO) is a product with high added-value for the consumer, increasing the likelihood of adulteration or a fraud. Several studies have focused on the use of NIR and FT-NIR spectroscopic methods to detect and/or quantify the adulteration of olive oil (Wesley et al., 1995; Wesley et al., 1996; Downey et al., 2002; Kasemsumran et al., 2005; Oliveira et al., 2007), in addition to the use of FT-Raman for this purpose (Baeten et al., 2005). In this review, there is more focus on the potential of FT-MIR spectroscopy for detecting the adulteration of vegetable oils. Marigheto et al. (1998) succeeded in discriminating oils from different botanical sources and detecting their adulteration (Marigheto et al., 1998). A total of 140 spectra of pure oils were divided into three sets for calibration ($n = 84$), validation ($n = 27$), and prediction ($n = 29$). Some samples were adulterated at different levels. Using LDA or artificial neural network (ANN), a 100% correct classification of oils was achieved. Later, several studies were done on the role of FT-MIR spectroscopy in detecting added adulterants, and they confirmed

the results obtained by Marigheto et al. (1998). The results showed that the technique could discriminate EVOO from oils adulterated with sunflower oil (Tay et al., 2002), show the difference in the content of free fatty acids in olive oil and determine the content of free fatty acids with an R^2 equal to 0.99 (Iňón et al., 2003b), and detect the presence of hazelnut oil in olive oil at low percentages (Baeten et al., 2005).

s0160 #### 3.8.3.2. FT-NIR Spectroscopy for the Detection of Adulteration of Milk Powder

p0410 In 2008, Chinese-manufactured milk infant formula was contaminated with melamine, leading to the hospitalization of thousands of children, some of whom died (http://wwwn.cdc.gov/travel/content/in-the-news/melamine-china.aspx, 2009); melamine had been added to give an artificial boost to the nitrogen content of food. Many studies were carried out to develop accurate and sensitive analytical techniques for assessing the quality and safety of food products. Among these techniques, NIR spectroscopy was used to detect melamine and/or to determine its content through the development of chemometric methods. The results showed that NIR spectroscopy could provide a rapid way of detecting melamine in infant milk formula (Dong et al., 2009; Yuan et al., 2009). In the first study, undertaken by Dong et al. (2009), 22 pure milk samples and 50 adulterated milk samples with added and varying amounts of melamine ($0.1–1500 \text{ mg} \times \text{kg}^{-1}$) were prepared, and the NIR spectra were then measured. PLSR was applied to build the calibration model between the NIR spectra and the melamine content. A combination of NIR spectra and PLS-DA was applied to differentiate the pure milk and the adulterated milk samples. The classification accuracy was 100%. This indicates that NIR spectra could be used initially to detect whether or not milk has been adulterated with melamine. The same conclusion was obtained in a subsequent study conducted by Yuan et al. (2009), who worked on 160 samples prepared by adding

different amounts of melamine to pure milk. The spectral data collected using a handheld spectrometer were smoothed, and then mathematical models were established. A total of 120 samples were selected randomly from 160 samples to build the model, and the remaining 40 samples were left for the validation step. Two discriminant analysis models were developed using the PLS method and the least-squares SVM method. The coefficients of correlation (r) between the real values and those predicted by the discriminant analysis models were equal to 0.9174 (PLS) and 0.9109 (LS-SVM). The root mean standard errors of prediction (RMSEP) were 0.0304 (PLS) and 0.0467 (LS-SVM). The results of this study indicated that the NIRS method could provide a rapid determination of melamine in milk.

s0165 3.8.3.3. FT-Raman Spectroscopy for the Detection of Adulteration of Honey

p0415 One of the main concerns about honey quality is to ensure that no food ingredients have been added to it; adulteration with sweeteners such as cane or corn sugar is the most common. Many studies have been conducted to detect and quantify honey adulteration with different kinds of syrups and cheap invert sugars using IR spectroscopic methods (Downey et al., 2003; Kelly et al., 2006; Toher et al., 2007). FT-Raman spectroscopy was used by Paradkar and Irudayaraj (2002) to detect

adulterants such as cane and beet invert in honey (Paradkar & Irudayaraj, 2002). The FT-Raman spectrum of honey (Fig. 3.7) has a large band in the vicinity of 3234 cm^{-1} characteristic of the O–H group of stretching vibrations, with intense peaks centered around 2941 and 2904 cm^{-1}, corresponding to C–H stretching vibrations, and several sharp peaks in the 200–1500 cm^{-1} region (also called the fingerprinting region), characteristic of several chemical groups. The honey Raman spectrum is considered to be a combination of absorption due to different compounds (Batsoulis et al., 2005; De Luca, 2011); the major compounds are carbohydrates. Honey contains small amounts of proteins, amino acids and organic acids, as well as vitamins and minerals at very low level (Arvanitoyannis et al., 2005).

p0420 Some authors have considered only the 200–1600 cm^{-1} region of adulterated sample spectra in order to study the adulteration of honey samples by beet and cane invert; three floral types of honey have been studied. PLDS and PCRA were used for quantitative analysis, and LDA and canonical variate analysis (CVA) were used for discriminant analysis. The results show that FT-Raman spectroscopy was efficient in predicting beet and cane invert adulterants ($R^2 > 0.91$) in all honey samples. The classification of adulterants in honey using CVA gave a minimum classification accuracy of about 96%.
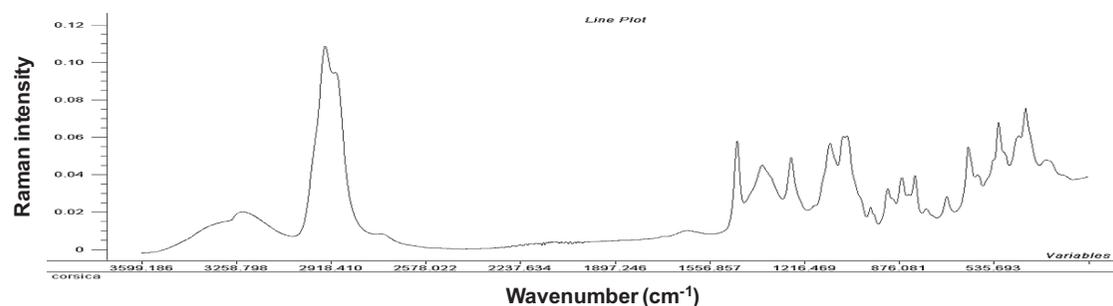
f0040 FIGURE 3.7 Example of the FT-Raman spectrum of honey.

s0170 ### 3.8.3.4. Spectroscopic Methods for the Detection of Adulteration of Camellia Oils

p0425   A feasibility study for the quantification and discrimination of soybean oil adulteration in camellia oils by attenuated total reflectance FT-MIR and fiber-optic diffuse reflectance NIR was undertaken by Wang et al. (2006) on 50 adulterated samples (Wang et al., 2006). The amount of soybean oil added to camellia oil ranged from 5% to 25%. The $1132-885 \, cm^{-1}$ spectral region proved to be useful in showing differences between adulterated and pure camellia oil samples, including C$-$H bending and C$-$H deformation of fatty acid. A PLS regression on FT-MIR spectra showed the potential of the technique for determining camellia oil adulteration; the R-value of the model was about 0.99, and the RMSEP and RMSECV values were 0.67 and 0.85, respectively. The authors concluded that FT-MIR spectroscopy could be considered as a powerful tool for authenticating pure camellia oil.

s0175 ## 3.8.4. Process Control

p0430   On-line analyses need to be automatic, rapid, accurate, and precise, and to require little or no sample preparation. The objective is to ensure rapid control of the input raw materials, the production process, and the final product. In the food industry, NIR spectroscopy is used more often than MIR or Raman spectroscopic methods. NIR spectrometers make it possible to measure a great variety of food samples such as liquids, powders, and all types of solid samples in a simple way, without sample preparation except for grinding some types of samples. Fiber optics, cameras, and a large variety of accessories can be used. Huang et al. (2008) wrote a review on the main applications of NIR spectroscopy in on-line monitoring of quality in food and beverages such as meat, fruits, vegetables, grain, dairy products, oils, fish and fish products, and beverages (Huang et al., 2008).

p0435   Only a few applications of NIR spectroscopy are described here. Examples of the application of MIR and Raman spectroscopy are given in the sections headed 'Spectroscopic methods to control oil properties' and 'Spectroscopic methods to monitor wine fermentation'.

s0180 ### 3.8.4.1. FT-NIR Spectroscopy to Control Meat Composition

p0440   The meat-processing industry is one of the important food industries because of the high demand for this product throughout the world. Meat has a good nutritional value; it contains high essential amino acids and is a good source of vitamin B, dietary iron, and zinc. It is therefore important to apply spectroscopic methods to continuously monitor its quality and composition in a rapid and nondestructive way. Some studies have indicated the possibility of using MIR spectroscopy in industrial processes to verify the quality attributes of meat (Lizuka & Aishima, 1999; Adhikari et al., 2003). NIR spectroscopy has been more often used in the on-line control of meat composition, particularly for the simultaneous determination of fat, moisture, and protein content. It was first applied by Isaksson et al. (1996), who tried to determine these parameters for ground beef in a conveyor using a diffuse instrument set at the outlet of the meat grinder (Isaksson et al., 1996). Later, the concept was adapted by TØgersen et al. (1999), who used five filters with an on-line NIR instrument in industrial-scale batches of beef and pork (TØgersen et al., 1999). Filters at 1441 and 1510 nm were used for moisture measurement, the filter at 1728 nm for fat measurement, and two other low-absorbing filters at 1655 and 1810 nm for reference. Fat and water were measured using the multiple linear regression method, and protein content was calculated from the total, fat, and moisture values. The prediction errors were similar to those obtained previously by Isaksson et al.; they were 0.82$-$1.49%, 0.94$-$1.33%, and 0.35$-$0.70% for fat, water, and protein, respectively. TØgersen

et al., (2003) continued to work with the same equipment using the reflectance mode to determine fat, water, and protein in frozen raw meat (TØgersen et al., 2003). Later, successive studies were conducted on using NIR spectroscopy in reflectance, transmission mode, or remote reflectance fiber-optic probes for the on-line monitoring of the proximal composition of ground beef during meat processing (Hildrum et al., 2004; Anderson and Walker, 2003a; Anderson and Walker, 2003b; González-Martín et al., 2003; González-Martín et al., 2005).

3.8.4.2. Spectroscopic Methods to Control Oil Properties

Vegetable oils are widely used in the food sector and are subjected to a series of analyses to verify their oxidation, unsaturation degree, and adulteration. Because conventional chemical techniques are tedious and time consuming, it became necessary to replace these methods by spectroscopic methods. NIR spectroscopy has been widely used for monitoring oxidation levels and peroxide value in soybean oils (Yildiz et al., 2001; Yildiz et al., 2002); by applying forward stepwise multiple linear regression, the 1100—2200 nm region was revealed as the most informative. PLS models based on derived spectra for the prediction of peroxide value and conjugated diene values were successfully developed. VIS/NIR spectroscopy was used for detecting and quantifying sunflower adulteration in extra virgin oil (Downey et al., 2002); the measurements were made in transflectance mode. The SIMCA model has made it possible to discriminate authentic extra virgin oils before and after adulteration by sunflower oil at a level of 1% (w/w), and PLS has made it possible to determine the adulteration percentage, the level of accuracy being acceptable for industrial use. Another study showed that NIR transmittance used for the on-line determination of acid value and fatty acid in virgin olive oils was feasible with the development of PLS models on spectra collected between 750 and 2500 nm (Márquez &

Díaz Reguera, 2005); the measurements were made in flow cells. MIR spectroscopy was also investigated in order to assess its use for product monitoring (Küpper et al., 2001). Extra virgin olive oils from various Mediterranean sites, adulterated or not with sunflower oils, have been analyzed by attenuated total reflectance IR spectroscopy using silver halide fiber probes. PLS models have been developed and leave-one-out cross-validation applied. The optimum standard error for prediction was 1.2% by weight when using a special variable selection strategy based on a pairwise consideration of significant respective minima and maxima of the optimum PLS regression vector, calculated for large spectral intervals. The results of the prediction showed that adulteration greater than 2% by weight could be quantified with this fiber probe. The device could be used in production processes. Olive oils are rich in unsaturated structures, and because Raman spectroscopy makes it possible to obtain detailed information on those structures, the method has also been investigated for on-line purposes. Barthus & Poppi, (2001) combined FT-Raman spectroscopy with the PLS chemometric method to determine iodine value (Barthus & Poppi, 2001). The spectra of various vegetables and mixtures of them were collected between 3000 and 1000 cm^{-1}. The spectra were normalized and related to reference values of iodine measured using an official titrimetric methodology to build the calibration model. The results of the prediction showed good agreement among data obtained from the conventional methodology and those predicted by the PLS model; the correlation coefficient was 0.996. The authors concluded that the spectroscopic method could be implemented in industrial processes as an on-line system.

3.8.4.3. Spectroscopic Methods to Monitor Wine Fermentation

During wine fermentation, it is important to measure some parameters, such as sugar and ethanol concentration, in addition to evaluating

the quality characteristics of the final product, such as the phenolic composition. For rapid and instantaneous analyses suited to an industrial process, IR spectroscopic methods were tested. Di Egidio et al. (2010) proposed FT-NIR and FT-MIR spectroscopic methods to monitor red wine fermentation (Di Egidio et al., 2010). Fifteen micro-fermentation essays were conducted during the 2008 vintage harvest in the Valtellina (northern Italy) viticultural area. NIR and MIR spectra were collected during fermentation in on-line mode. Reference measurements were carried out at the same time, in order to evaluate the sugar, alcohol, and phenol compounds. Pretreated spectral data were processed using PCA. The algorithm SELECT was applied for feature selection, and LDA was then used to classify the samples and to predict the fermentation stage, from the initial to the final phase. A correct classification of 87% and 100% of the samples, based on fermentation stage, was reached using NIR and MIR spectroscopy, respectively. Compositional changes during alcoholic fermentation were well predicted with either FT-NIR or FT-MIR, showing the advantage of both methods for the on-line monitoring of red wine fermentation.

s0195 3.8.5. Physico-Chemical Properties

p0455   The increase in food manufacture and trade means that there are a high number of products on the market that require constant control of product composition and properties. The objective is to ensure the safety, conformity, and quality of food products.

s0200 3.8.5.1. FT-MIR Spectroscopy for the Determination of Peroxide Value of Vegetable Oils

p0460   Lipid oxidation has an adverse effect on edible oil quality; it leads to the production of products that have a high impact on sensory attributes, reducing the economic value of the oil. The measurement of peroxide value (PV) and anisidine value (AV), representing the primary and secondary oxidation products of edible oils, is necessary to ensure the quality and safety of the oil. Several studies have been conducted to show the use of FT-NIR (Dong et al., 1997; Li et al., 200b) and FT-MIR techniques (Guillén & Cabo, 1997; Van de Voort et al., 1994; María Guillén Nerea Cabo, 2002) for determining the peroxide value in vegetable oils. Yu *et al.* (2007) developed a technique to determine the PV of edible oils by FT-IR spectroscopy, using the spectral reconstitution technique to simplify and automate the FT-IR method for this purpose (Yu et al., 2007). The basis of PV determination is the rapid reaction of triphenylphosphine (TPP) with the hydroperoxides present in an oil to produce triphenylphosphine oxide (TPPO), which exhibits a readily measurable absorption band at 542 cm^{-1}. In the SR procedure, the viscosity of oil samples is reduced by mixing them with a diluent, allowing them to be readily placed in a flow-through transmission cell. The spectra of the neat oil samples are then reconstituted from those of the diluted samples, using the absorption of a spectral marker present in the diluent to determine the dilution ratio. For the SR-based PV method, the TPP reagent was added to the diluent, which consisted of odorless mineral spirits (OMSs) containing methylcyclopentadienyl manganese tricarbonyl (MMT) as the spectral marker. Sample preparation for PV analysis involved mixing 10 ml of oil with 25 ml of the TPP-containing diluents. Calibration standards, prepared by the gravimetric addition of TPPO to a peroxide-free oil, were handled in the same manner, and a linear calibration equation relating the concentration of TPPO (expressed as the equivalent PV) to the absorbance of TPPO at 542 cm^{-1} relative to a baseline at 530 cm^{-1} in the reconstituted spectra was obtained, with a regression standard deviation of ± 0.15 meq/kg oil. PV determinations on two sets of validation samples with PV ranges of 0–20 and 0–2 meq/kg oil

were conducted at the same time using the AOCS titrimetric and SR-based FT-IR methods. The results indicate that the FT-IR procedure was more reproducible and slightly more sensitive. The authors reported that the SR-based FT-IR method allowed an automated analysis of 90 samples per hour.

s0205 ### 3.8.5.2. NIR Spectroscopy to Estimate the Anti-Oxidant Capacity

p0465 Some foods are rich in bioactive compounds such as polyphenols associated with the reduced risk of developing chronic diseases such as cardiovascular disease, diabetes, or some cancers. Chemical analyses of polyphenolic content or anti-oxidant activity are expensive, time consuming and need a plenty of solvent. Spectroscopic techniques have been investigated in order to overcome these disadvantages. Chen et al. (2006) investigated the possibility of using NIR spectroscopy to predict the content of caffeine and total polyphenols in green tea (Chen Zhao et al., 2006). The spectra collected in reflectance mode in the $11,000-3800$ cm^{-1} range were composed of bands corresponding to 2nd overtone vibrations of the carbonyl group (5352 cm^{-1}), C$-$H stretch and C$-$H deformation vibration (7212 cm^{-1}), $-$CH2 (5742 cm^{-1}) and $-$CH3 overtone (5808 cm^{-1}). The carbonyl group, and $-$CH and $-$CH$_2$ vibrations are due to polyphenols, alkaloids, proteins, volatile and nonvolatile acids, and some aroma compounds. The investigation of spectra led to the selection of the $4500-9000$ cm^{-1} spectral region to build the PLS model, excluding bands associated with water at about 5155 cm^{-1} and 7000 cm^{-1}; these bands corresponded to the OH stretching and OH deformation vibrations. The results showed that the correlation coefficients of the prediction models R were 0.9688 and 0.9299 for caffeine and total polyphenols, respectively. The method can be used successfully to determine the valid ingredients of tea in order to control industrial processes. A study undertaken by Zhang et al. (2008) focused on the use of NIR

reflectance spectroscopy for predicting total phenolic and flavonoid content, and the antioxidant capacity of rice grain (Zhang et al., 2008). Rice is a staple food containing several phytochemicals characterizing its nutritional quality that could be improved through breeding efforts. A total of 475 rice accessions were analyzed; reflectance spectra of dehulled rice grains were collected using a visible$-$NIR spectrometer in the $1100-2498$ nm range. At the same time, reference analyses using wet chemistry were conducted. PLS and MPLS models were developed with the spectra of dehulled grain. On the basis of PCA results, 10 outliers were determined, and therefore 310 samples were used for calibration and 155 others were used to evaluate the calibration equations. The results showed their efficiency in predicting total phenolic content and antioxidant capacity. The standard errors of prediction (SEP) were 47.1 and 45.9 mg gallic acid equivalent (GAE) for phenolic content, and the coefficients of determination (R^2) were 0.849 and 0.864 for the PLS and MPLS models, respectively. Both methods gave a similarly accurate performance for predicting antioxidant capacity with an SEP of 0.28 mM Trolox equivalent antioxidant capacity (TEAC) and an R^2 of 0.82. However, the flavonoid content was not well predicted; the models showed a coefficient R^2 of less than 0.4. The NIR method can be considered as a good tool for the routine screening of large number of samples in breeding programs.

s0210 ### 3.8.5.3. FT-Raman for the Determination of Honey Composition

p0470 Honey is an important agricultural compound used as food and for medicinal purposes. It is composed mainly of sugars such as fructose, glucose, sucrose, maltose, and mono- and oligosaccharides. The content on each of these sugars depends largely on the floral origin of the honey. Spectroscopic methods have been used to rapidly quantify these components through routine control analysis (Justino et al., 1997;

Lichtenberg-Krag et al., 2002; Goodacre 2002). De Oliveira et al. (2002) conducted a qualitative study on the characterization of major components of honey using FT-Raman spectroscopy (De Oliveira et al., 2002). Fluid and crystallized samples were studied. Vibrational bands of honey samples were interpreted; several vibrational bands were identified as specific fingerprints of fructose and glucose. At least one Raman signal could be associated with the presence of sucrose. It should be noted that some vibrational bands of the saccharides were influenced and exhibited subtle relative intensity changes by the water content. Minor compounds such as flavonoids, and some saccharides and carboxylic acids were masked by the major saccharides present in high concentration in honey samples. Batsoulis et al. (2005) proposed a new method for determining the mass percentage of fructose and glucose in honey based on FT-Raman spectroscopy (Batsoulis et al., 2005). A total of 21 unifloral honey samples were analyzed using FT-Raman spectroscopy. The PLS models for predicting sugar content were based on two groups of 11 and 10 samples as calibration and validation sets, respectively. The simultaneous quantitative determination of sugars used an input range between 1700 and 700 cm^{-1} without correction of the baseline. Values were also measured using the reference method based on high-performance liquid chromatography (HPLC). The honey content of fructose and glucose determined by HPLC was 24.1–42.9% and 16.2–33.1%, respectively, and honey content determined by FT-Raman was 24.0–40.8% and 21.1–32.2%, respectively. The reproducibility and accuracy of the two methods were checked by the application of F-test and t-test. The results showed that the score from the two methods was statistically below the theoretical value of 19 for the F-test, and in four out of 20 cases it was above the theoretical value of 2.776 for the t-test. The two methods are statistically equivalent in terms of accuracy and reproducibility.

3.8.5.4. Spectroscopic Methods for the Determination of Alcohol Content in Alcohol Beverages

s0215

The determination of ethanol content in alcoholic beverages is usually defined by density measurements that are conducted off-line. Analyses made in the laboratory lead to a delay in the reporting of the value, as well as being destructive and time consuming in some cases, such as in determining the density of an alcoholic beverage with a high dissolved solid content (e.g., sugars). In order to perform faster analyses that can be conducted on-line, MIR, NIR, and Raman spectroscopic methods have been investigated (Gallignani et al., 1994; Perez-Ponce et al., 1996; Gallignani et al., 1993; Gallignani et al., 1994; Stanford & Mantooth, 2001). NIR and MIR spectroscopy techniques were used to determine a series of wine parameters such as level of alcohol (Urbano Cuadrado et al., 2005). PLS prediction results indicated that NIR spectroscopy gave a better validation performance ($R^2 = 0.978$, SEP $= 0.24$) than MIR ($R^2 = 0.961$, SEP $= 0.29$) or than when NIR and MIR (sum of spectra) were combined ($R^2 = 0.953$, SEP $= 0.35$). Lachenmeier (2007) combined FT-IR spectra and multivariate analysis to control the quality of spirit drink and beer by determining a series of parameters such as ethanol (Lachenmeier, 2007). The spectra were collected between 926 and 5012 cm^{-1}, water spectral regions were eliminated (1447–1887 cm^{-1}, 2971–3696 cm^{-1}) and PCA was then applied to detect sample outliers. Excellent quantitative information was obtained for alcohol levels in both spirits and beers. The PLS performance when applied to the validation test set showed low prediction errors (SEP of 0.21) and high correlation coefficients (R^2 of 0.94 and 0.973) for spirits and beers, respectively. In other studies, NIR and Raman techniques have been used and compared to determine ethanol in beverages (Mendes et al., 2003) and spirits (Nordon et al., 2005). Nordon et al. (2005) investigated the suitability of NIR and Raman spectroscopic

p0475

techniques for determining ethanol levels. Samples of whisky, vodka, and sugar alcoholic drinks were analyzed using NIR in transmission mode; the signal at 10,000 cm^{-1} associated with water and ethanol in the samples was investigated. Raman measurements were conducted using a 785 nm laser; the signal at 880 cm^{-1} related to ethanol was studied. For both techniques, measurements were done in clear glass bottles. A multivariate calibration model, based on a combined PCA-PLS algorithm, was developed for NIR data, but a univariate model was sufficient for Raman data. Depending on the shape of the bottle (round or flat), the bottle-to-bottle variability contributed more or less to the uncertainty of measurements.

s0220 ### 3.8.6. Food Quality

p0480   Food quality is an important parameter that is usually assessed in the food industry. Consumers look for high-quality food products, expecting the manufacturer and the retailer to provide a product meeting this requirement. This underlines the need for reliable and rapid analytical techniques to evaluate and control food quality, such as spectroscopic techniques. Here, some examples of the application of Raman, NIR, and MIR spectroscopy methods to achieve this objective are given.

s0225 #### 3.8.6.1. FT-MIR Spectroscopy for the Determination of Quality Parameters of Beers

p0485   The most important quality parameters for beers are related to water, carbohydrates, and ethanol, known in the industrial world as real extract, original extract, and ethanol content. They determine the sweetness of the beer and its fermentation grade, as well as its alcohol level. Apart from the official reference methods, the FT-IR/attenuated total reflection (ATR) method was proposed by Llario et al., (2006) for assessing these parameters using a rapid, environmentally friendly method such as MIR spectroscopy

(Llario et al., 2006). A total of 45 beer samples were analyzed using FT-IR/ATR and reference methods. The samples were divided into two sets, the first used for developing and validating the model, and the second measured seven months later and used for evaluating its robustness. A calibration set of 12 samples was selected using hierarchical cluster analysis in order to obtain a good representation of the whole population of samples analyzed, and a validation set of 11 samples was selected. The absolute mean difference and standard deviation of mean differences of the real extract, original extract, and alcohol content were 0.009 and 0.069% (w/w), −0.021 and 0.20% (w/w), and −0.003 and 0.130% (v/v), respectively. The PLS predictions based on FT-IR/ATR data made it possible to determine the real extract, original extract, and ethanol with relative prediction errors of 2.8, 1.9, and 1.5%, respectively. The performance of the developed methodology compared favorably with that of the reference methodology.

3.8.6.2. NIR Spectroscopy for the Analysis of Functional Foods   s0230

p0490   The quality of food is related to several parameters, such as the presence of specific molecules known as bioactive compounds. These compounds are reported to have antioxidant effects and to induce a beneficial pharmacological effect when consumed in sufficient quantities. Functional foods containing these molecules are known to help prevent the development of degenerative diseases (Sloan, 2008) and there is a growing market for them. Accurate and efficient analytical methods are needed to ensure the rapid quantitative screening of the raw materials of functional foods, as well as to ensure the quality of finished products. NIR spectroscopy, known for its speed and nondestructivity, has been used for the analysis of bioactive compounds. McGoverin et al., (2010) published a review on the application of NIR spectroscopy for measuring bioactive

compounds such as carotenoides, fatty acids, glucosinolates, and polyphenols in food commodities such as wine, dairy products, tea, fruit, vegetables, herbs, spices, and cereals (McGoverin et al., 2010). The spectra generally measured in the 1100–2500 nm range in reflectance or transflectance mode were used to establish PLS, mPLS, LS-SVM, or ANN models for predicting the bioactive compound content. An example of these investigations is one that focused on the quality control of tomatoes. Lycopene content and other quality parameters were measured using NIR spectroscopy (Clement et al., 2008). The spectra of whole tomatoes and tomatoes at all maturity stages were collected in the visible and NIR range (400–1500 nm). The models developed gave an R^2 of 0.98, an RMSECV of 3.15 mg kg^{-1}, and an SD/SECV of 6.35 for lycopene. Other models based on the subdivided spectral regions, 400–1000 nm and 900–1500 nm, showed that the visible region was necessary for accurate lycopene prediction.

s0235 3.8.6.3. *Raman Spectroscopy for Analysis of Fish*

p0495   Fish quality is defined in terms of freshness, texture, color, and chemical composition. These attributes are based on the carotenoid, collagen, and fat composition in fish muscle. Marquardt et al. (2004) investigated the use of Raman spectroscopy for collecting information on carotenoid, collagen, and fat content simultaneously (Marquardt & Wold, 2004). A 785 nm excitation laser and a CCD detector were used. Fluorescence signals were removed through a pretreatment routine, and the spectra were then analyzed. Fat had relatively strong bands at about 1657, 1440, 1301 cm^{-1} (CH$_2$ in phase twist), 1267 cm^{-1} (=C–H symmetric rock), 1076, 1064 cm^{-1} (CCC stretch), peaks of carotenoids were present at 1159 and 1518 cm^{-1}, and those of collagen were detected at 857 (proline) and 940 cm^{-1} (C–C stretch of peptide backbone). PCA was applied on the spectra of white

fish and salmon separately. A study of the variance percentage of principal components and their associated loadings showed that Raman spectra contained spectral information and relative concentration information about all the studied constituents.

3.9. CONCLUSION   s0240

The versatility of Raman and IR spectroscopy p0500 in food science has been demonstrated in this chapter. Methods can be applied in order to obtain basic knowledge about a food product or to evaluate its quality or properties for industrial purposes. Spectroscopic methods – rapid, easy-to-use, and nondestructive, combined or not with chemometric tools – allow qualitative and quantitative analyses to be conducted. Efforts are being made to develop reliable and stable calibration models.

Spectroscopic analyses are cost effective, but p0505 the instruments remain quite expensive. In order to facilitate and better integrate this technology in industrial processes, ongoing research is oriented toward building more compact, more robust, and less expensive Raman and IR instruments, as well as developing a wide range of new devices in order to extend the area of application.

References

Abbas, O., Fernández Pierna, J.A., Boix, A., von Holst, C., Dardenne, P., Baeten, V., 2010. Key parameters for the development of a NIR microscopic method for the quantification of by-products of animal origin in compound feedingstuffs. Analytical and Bioanalytical Chemistry 397, 1965–1973.

Adapa, P., Karunakaran, C., Tabil, L., Schoenau, G., February, 2009. Potential applications of infrared and Raman spectromicroscopy for agricultural biomass. Manuscript 1081. Agricultural Engineering International: the CIGR Ejournal XI.

Adhikari, C., Balasubramaniam, V.M., Abbott, U.R., 2003. A rapid FTIR method for screening methyl sulphide and hexanal in modified atmosphere meal, ready-to-eat entrees. Lebensmittel-Wissenschaft und -Technologie 36, 21–27.

Al-Jowder, O., Kemsley, E.K., Wilson, R.H., 1997. Mid-infrared spectroscopy and authenticity problems in selected meats: a feasibility study. Food Chemistry 59 (2), 195–201.

Al-Jowder, O., Defernez, M., Kemsley, E.K., Wilson, R.H., 1999. Mid-infrared spectroscopy and chemometrics for the authentication of meat products. Journal of Agricultural and Food Chemistry 47, 3210–3218.

Anderson, N.M., Walker, P.N., 2003a. Measuring fat content of ground beef stream using on-line visible/NIR spectroscopy. Transactions of the ASAE 46, 117–124.

Anderson, N.M., Walker, P.N., 2003b. Blending ground beef to control fat content using simulated on-line spectroscopic measurements. Transactions of the ASAE 46, 1135–1141.

Arvanitoyannis, I.S., Chalhoub, C., Gotsiou, P., Lydakis-Simantiris, N., Kefalas, P., 2005. Novel quality control methods in conjunction with chemometrics (multivariate analysis) for detecting honey authenticity. Critical Reviews in Food Science and Nutrition 45, 193–203.

Baeten, V., Dardenne, P., 2002. Spectroscopy: developments in instrumentation and analysis. Grasas y Aceites 53 (1), 45–63.

Baeten, V., Meurens, M., Morales, M.T., Aparicio, R., 1996. Detection of virgin olive oil adulteration by Fourier transform Raman spectroscopy. Agricultural and Food Chemistry 44 (8), 2225–2230.

Baeten, V., Hourant, P., Morales, M.T., Aparicio, R., 1998. Oils and fats classification by Fourier transform Raman spectroscopy. Agricultural and Food Chemistry 46 (7), 2638–2646.

Baeten, V., Dardenne, P., Aparicio, R., 2001. Interpretation of Fourier transform Raman spectra of the unsaponifiable matter in a selection of edible oils. Journal of Agricultural Food Chemistry 49, 5098–5107.

Baeten, V., Fernández Pierna, J.A., Dardenne, P., Meurens, M., García-González, D.L., Aparicio-Ruiz, R., 2005. Detection of the presence of hazelnut oil in olive oil by FT-raman and FT-MIR spectroscopy. Journal of Agricultural Food Chemistry 53 (16), 6201–6206.

Baeten, V., von Holst, C., Garrido, A., VanCutsem, J., Michotte Renier, A., Dardenne, P., 2005. Detection of banned meat and bone meal in feeding stuffs by near-infrared microscopy analysis of the sediment fraction. Analytical and Bioanalytical Chemistry 382, 149–157.

Baeten, V., Fernández Pierna, J.A., Dardenne, P., et al., 2005. Detection of the presence of hazelnut oil in olive oil by FT-Raman and FT-MIR spectroscopy. Journal of Agricultural and Food Chemistry 53, 6201–6206.

Baeten, V., Manley, M., Fernández Pierna, J.A., Downey, G., Dardenne, P., 2008. Technique: Fourier Transform Near Infrared (FT-NIR) Spectroscopy. In: Sun, Da-Wen (Ed.), Modern Techniques for food authentication. Academic Press, pp. 117–148. Chapter 4.

Baeten, V., Fernández Pierna, J.A., Vermeulen, Ph., Dardenne, P., 2010. NIR hyperspectral imaging methods for quality and safety control of food and feed products: contributions to 4 European projects. Nirsnews 21 (6), 10–13.

Baeten, V., Fernandez Pierna, J., Dehareng, F., Sinnaeve, G., Dardenne, P., 2010. Regulatory considerations in applying vibrational spectroscopic methods for quality control. In: Applications of Vibrational Spectroscopy in Food Science, vol. 2. John Wiley & Sons, Ltd, pp. 595–607.

Baeten, V., Fernandez Pierna, J., Michotte Renier, A., Dardenne, P., 2005. Imagerie infrarouge: analyse des aliments à destination animale. Techniques de l'ingénieur, RE 34, 1–8.

Baranska, H., 1987. An introduction to Raman scattering. In: Baranska, H., Labudzinska, A., Terpinski, J. (Eds.), Laser Raman Spectrometry: Analytical Applications. Ellis Horwood, Chichester, UK, pp. 9–31 (Chapter 1).

Barthus, R.C., Poppi, R.J., 2001. determination of the total unsaturation in vegetable oils by Fourier transform Raman spectroscopy and multivariate calibration. Vibrational Spectroscopy 26, 99–105.

Batsoulis, A.N., Siatis, N.G., Kimbaris, A.C., Alissandrakis, A.K., Pappas, C.S., Tarantilis, P.A., Harizanis, P.C., Polissiou, M.G., 2005. FT-Raman spectroscopic simultaneous determination of fructose and glucose in honey. Journal of Agricultural and Food Chemistry 53, 207–210.

Bellon-Maurel, V., Vigneau, J.L., Sévila, F., 1994. Infrared and near-infrared technology for the food industry and agricultural uses: on-line applications. Food Control 5 (1), 21–27.

Bickel, A., 1989. I & CS 62, 45.

Blanco, M., Villarroya, I., 2002. NIR spectroscopy: a rapid-response analytical tool. Trends in Analytical Chemistry 21 (4), 240–250.

Briandet, R., Kemsley, E.K., Wilson, R.H., 1996a. Approaches to adulteration detection in instant coffees using infrared spectroscopy and chemometrics. Journal of the Science of Food and Agriculture 71, 359–366.

Briandet, R., Kemsley, E.K., Wilson, R.H., 1996b. Discrimination of Arabica and Robusta in instant coffee by Fourier transform infrared spectroscopy and chemometrics. Journal of Agricultural and Food Chemistry 44, 170–174.

Brown, S., Tauler, R., Walczak, B., 2009. In: Comprehensive Chemometrics. Elsevier, Oxford Steve Brown, Romà Tauler and Beata Walczak.

[AU3]

Capron, X., Verbeke, J., Massart, D.L., 2007. Multivariate determination of the geographical origin of wines from four different countries. Food Chemistry 101, 1585–3597.

Casale, Monica, Chiara, Casolino, Paolo, Oliveri, Forina, Michele, 2010. The potential of coupling infor- mation using three analytical techniques for identifying the geographical origin of Liguria extra virgin olive oil. Food Chemistry 118 (1), 163–170.

Cen, H., He, Y., 2007. Theory and application of near infrared reflectance spectroscopy in determination of food quality. Trends in food science & technology 18, 72–83.

Chapelle, V., Melcion, J.P., Robert, P., Bertrand, D., 1989. Science des Aliments 9, 387.

Chen, Q., Zhao, J., Huang, X., Zhang, H., Liu, M., 2006. Simultaneous determination of total polyphenols and caffeine contents of green tea by near-infrared reflectance spectroscopy. Microchemical Journal 83, 42–47.

Clement, A., Dorais, M., Vernon, M., 2008. Non-destructive measurement of fresh tomato lycopene content and other physicochemical characteristics using visible-NIR spectroscopy. Journal of Agricultural and Food Chem- istry 56, 9813.

Coates, J., 2000. Interpretation of infrared spectra, a practical approach. In: Meyers, R.A. (Ed.), Encyclopaedia of Analytical Chemistry. John Wiley & Sons Ltd., Chi- chester, pp. 10815–10837.

Cordella, C., Moussa, I., Martel, A., et al., 2002. Recent developments in food characterization and adulteration detection: technique-oriented perspectives. Journal of Agricultural and Food Chemistry 50, 1751–1764.

Coventory, 1988.

Cozzolino, D., Murray, I., 2004. Identification of animal meat muscles by visible and near-infrared reflectance spec- troscopy. Lebensmittel-Wissenschaft und -Technologie 37, 447–452.

Davies, et al., 2002.

Davies, A.M.C., Radovic, B., Fearn, T., Anklam, E., 2002. A Preliminary study on the characterisation of honey by near infrared spectroscopy. Journal of Near Infrared Spectroscopy 10, 121.

Da-Wen Sun. Modern Techniques for Food Authentication (Ed. Da-Wen Sun) Academic Press.

De Luca, Michele, Terouzi, Wafa, Ioele, Giuseppina, Kzaiber, Fouzia, Oussama, Abdelkhalek, Oliverio, Filomena, Tauler, Romà, Ragno, Gaetano, 2011. Derivative FTIR spectroscopy for cluster analysis and classification of morocco olive oils. Food Chemistry 124 (3), 1113–1118.

De Oliveira, L.F., Colombara, R., Edwards, H.G.M., 2002. Fourier transform Raman spectroscopy of honey. Applied Spectroscopy 56 (3), 306–311.

Di Egidio, V., Sinelli, N., Giovanelli, G., Moles, A., Casiraghi, E., 2010. NIR and MIR spectroscopy as rapid methods to monitor red wine fermentation. European Food Research and Technology 230, 947–955.

Ding, H.B., Xu, R.-J., 1999. Differentiation of beef and kangaroo meat by visible/ near-infrared reflectance spectroscopy. Journal of Food Science 64 (5), 814–817.

Fernández Pierna, J.A., Abbas, O., Dardenne, P., Baeten, V., Discrimination of Corsican honey by FT-Raman spec- troscopy and chemometrics. Biotechnol. Agron. Soc. Environ., accepted for publication.

Dong, J., Van de Voort, F.R., Ismail, A.A., 1997. Stochio- metric determination of hydroperoxides in oils by Fourier transform near-infrared spectroscopy. Journal of American Official Analytical Chemists 80 (2), 345–352.

Dong, Y.W., Tu, Z.H., Zhu, D.Z., Liu, Y.W., Wang, Y.N., Huang, J.L., Sun, B.L., Fan, Z.N., 2009. Feasibility of NIR spectroscopy to detect melamine in melamine. PubMed 29 (11), 2934–2938.

Downey, G., Flynn, S.J., 2002. Discrimination between virgin olive oils from Crete, the Peloponese and other Greek Islands using near-infrared transfl ectance spectroscopy. In: Davies, A.M.C., Cho, R.K. (Eds.), Near-infrared Spectroscopy: Proceedings of the 10th International Conference. NIR Publications, Chichester, pp. 239–241.

Downey, G., Boussion, J., Beauchêne, D., 1994. Authentica- tion of whole and ground coffee beans by near-infrared refl ectance spectroscopy. Journal of Near Infrared Spectroscopy 2, 85–92.

Downey, G., Mcintyre, P., Davies, A.N., 2002. , detecting and quantifying sunflower oil adulteration in extra virgin olive oils from the eastern Mediterranean by visible and near infrared spectroscopy. Journal of Agricultural and Food Chemistry 50, 5520–5525.

Downey, G., McIntyre, P., Davies, A.N., 2002. Journal of Agricultural and Food Chemistry 50, 5520–5525.

Downey, G., Fouratier, V., Kelly, J.D., 2003. Detection of honey adulteration by addition of fructose and glucose using near infrared transflectance spectroscopy. Journal of Near Infrared Spectroscopy 11, 447.

Downey, G., 1996. Authentication of food and food ingre- dients by near infrared spectroscopy. Journal of Near Infrared Spectroscopy 4, 47–61.

El-Abassy R.M., Donfack P., Materny A. Discrimination between Arabica and Robusta green coffee using visible micro Raman spectroscopy and chemometric analysis, Food Chem., in press.

Esteban-Díez, I., Gonzáles-Sáiz, J.M., Pizarro, C., 2004b. An evaluation of orthogonal signal correction methods for the characterisation of Arabica and Robusta coffee varieties by NIRS. Analytica Chimica Acta 514, 57–67.

I. CHEMICAL ANALYSIS OF FOOD

Esteban-Díez, I., Gonzáles-Sáiz, J.M., Sáenz-González, C., Pizarro, C., 2007. Coffee varietal differentiation based on near-infrared spectroscopy. Talanta 71, 221–229.

Fahrenfort, J., 1961. Attenuated total refl ection: a new principle for the production of useful infra-red reflection spectra of organic compounds. Spectrochimica Acta 17, 698–709.

Fernandez Pierna, J.A., Baeten, V., Michotte Renier, A., Cogdill, R.P., Dardenne, P., 2005. Combination of SVM and NIR imaging spectroscopy for the detection of MBM in compound feeds. Journal of Chemometrics 18 (7-8), 341–349.

Fernandez Pierna, J.A., Dardenne, P., Baeten, V., 2010. In-house validation of a near infrared hyperspectral imaging method for detecting processed animal proteins (PAP) in compound feed. Journal of Near Infrared Spectroscopy 18, 121–133.

Fumière, O., Veys, P., Boix, A., von holst, C., Baeten, V., Berben, G., 2009. Methods of detection, species identification and quantification of processed animal proteins in feedingstuffs. Biotechnologie, Agronomie, Société et Environnement (BASE) 13, 59–70 (numéro spécial).

Gallignani, M., Garrigues, S., de la Guardia, M. 1993. 118, 1167.

Gallignani, M., Garrigues, S., de la Guardia, M., 1994. Analytica Chimica Acta 287, 275.

Gallignani, M., Garrigues, S., de la Guardia, M., 1994. Analytica Chimica Acta 296, 155.

Galtier, O., Dupuy, N., Le Dréau, Y., Ollivier, D., Pinatel, C., Kister, J., Artaud, J., 2007. Geographic origins and compositions of virgin olive oils determinated by chemometric analysis of NIR spectra. Analytica Chimica Acta 595 (1–2), 136–144.

González-Martín, I., González-Pérez, C., Hernández-Méndez, J., Alvarez-García, N., 2003. Determination of fatty-acids in the subcutaneous fat of Iberian breed swine by near infrared spectroscopy (NIRS) with a fibre-optic probe. Meat Science 65, 713–719.

González-Martín, I., González-Pérez, C., Alvarez-García, N., González-Cabrera, J.M., 2005. on line determination of fatty acid composition in intramuscular fat of Iberian pork loin by NIRs with a remotre reflectance fibre optic probe. Meat Science 69, 243–248.

[AU4] Goodacre, 2002. cité + haut.

Goodacre, R., Radovic, B.S., Anklam, E., 2002. Progress toward the rapid nondestructive assessment of the floral origin of European honey using dispersive Raman spectroscopy. Applied Spectroscopy 56 (4), 521–527.

Guillén, M.D., Cabo, N., 1997. Infrared spectroscopy in the study of edible oils and fats. Journal of the Science of Food and Agriculture 75, 1–11.

Handbook of instrumental techniques for analytical chemistry.

Harrick, N.J., 1967. Internal Reflectance Spectroscopy. Interscience, New York, NY.

Hildrum, K.I., Nilsen, B.N., Westad, F., Wahlgren, N.M., 2004. In-line analysis of ground beef using a diode array near infrared instrument on a conveyor belt. Journal of Near Infrared Spectroscopy 12, 367–376.

Hourant, P., Baeten, V., Morales, M.T., Meurens, M., Aparicio, R., 2000. Oils and fats classification by selected bands of near-infrared spectroscopy. Applied Spectroscopy 54 (8), 1168–1174.

http://wwwn.cdc.gov/travel/content/in-the-news/melamine-china.aspx, 21.05.2009.

Huang, H., Yu, H., Xu, H., Ying, Y., 2008. Near infrared spectroscopy for on/in-line monitoring of quality in foods and beverages: A review. Journal of Food Engineering 87 (3), 303–313.

Ilari, J.L., Martens, H., Isaksson, T., 1988. Applied Spectroscopy 42, 722.

Iňón, F.A., Garrigues, J.M., Garrigues, S., et al., 2003. Selection of calibration set samples in determination of olive oil acidity by partial least squares-attenuated total reflectance Fourier transform infrared spectroscopy. Analytica Chimica Acta 489, 59–75.

Colthup, N.B., Daly , Wiberley S.E, L.H., 1990. Introduction to Infrared and Raman Spectroscopy, 3rd ed. Academic Press, Boston, MA. [AU5]

Isaksson, T., Nilsen, B.N., TØgersen, G., Hammond, R.P., Hildrum, K.I., 1996. On-line, proximate analysis of ground beef directly at a meat grinder outlet. Meat Science 43, 245–253.

Izumyia, T., Futamura, T., Fukuchi, J., 2004. CORESTA Congress Kyoto, Japan, October, 3–7.

Justino, L.G., Caldeira, M., Gil, V.M.S., Baptista, M.T., Cunha, A.P., Gil, M.A., 1997. , Determination of changes in sugar composition during the ageing of honey by HPLC, FTIR, and NMR spectroscopy. Carbohydrate Polymers 34, 435.

Karoui, R., De Baerdemaeker, J., 2007. A review of the analytical methods coupled with chemometric tools for the determination of the quality and identity of dairy products. Food Chemistry 102, 621–640.

Karoui, et al., 2008. In: Sun, Da-Wen (Ed.), Modern Techniques for Food Authentication. Academic Press (Chapter, pp).

Karoui, R., Mazerolles, G., Dufour, E., 2003. Spectroscopic techniques coupled with chemometric tools for structure and texture determinations in dairy products. International Dairy Journal 13 (8), 607–620.

Kasemsumran, S., Kang, N., Christy, A., Ozaki, Y., 2005. Spectroscopy Letters 38, 839–851.

Kelly, J.D., Petisco, C., Downey, G., 2006. Potential of near infrared transflectance spectroscopy to detect adulteration of Irish honey by beet invert syrup and high

I. CHEMICAL ANALYSIS OF FOOD

fructose corn syrup. Journal of Near Infrared Spectroscopy 14, 139—146.

Kemsley, E.K., Ruault, S., Wilson, R.H., 1995. Discrimination between *Coffea arabica* and *Coffea canephora* variant robusta beans using infrared spectroscopy. Food Chemistry 54, 321—326.

Kondepati, V.R., Heise, H.M., 2008. the potential of mid- and near infrared spectroscopy for reliable monitoring of bioprocesses. In: Current Trends in Biotechnology and Pharmacy, 2(1), pp. 117—132.

Küpper, L., Heise, H.M., Lampen, P., Davies, A.N., McIntyre, P., 2001. Authentication and quantification of extra virgin olive oils by attenuated total reflectance infrared spectroscopy using silver halide fiber probes and partial least-squares calibration. Applied Spectroscopy 55 (5), 563—570.

Lachenmeier, D.W., 2007. Rapid quality control of spirit drinks and beer using multivariate data analysis of Fourier transform infrared spectra. Food Chemistry 101, 825—832.

Lawrence, K.W., Windham, W.R., Prk, B., Buhr, R.J., 2003. Journal of Near Infrared Spectroscopy 11, 269—281.

Li, H., Van De Voort, F.R., Ismail, A.A., Cox, R. (200b), Determination of peroxide value by Fourier transform near-infrared spectroscopy. J. Am. Oil Chem. Soc., 77 (2), 137—142.

[AU6]

Li-Chan, E., 1996. The application of Raman spectroscopy in food science. Trends in Food Science and Technology 7, 361—370.

Lichtenberg-Krag, B., Hedtke, C., Bienefeld, K., 2002. Infrared spectroscopy in routine quality analysis of honey. Apidologie 33, 327—337.

Liu, L., Cozzolino, D., Cynkar, W.U., Gishen, M., Colby, C.B., 2006. Geographic classification of Spanish and Australian Tempranillo red wines by visible and near-infrared spectroscopy combined with multivariate analysis. Journal of Agricultural and Food Chemistry 54, 6754—6759.

Lizuka, K., Aishima, T., 1999. Tenderization of beef with pineapple juice monitored by Fourier transformed infrared spectroscopy and chemometric analysis. Journal of Food Science 64, 973—977.

Llario, R., Iñon, F.A., Garrigues, S., de la Guardia, M., 2006. Determination of quality parameters of beers by the use of attenuated total reflectance — Fourier transform infrared spectroscopy. Talanta 69, 469—480.

Lu, R., Peng, Y., 2006. Biosystems Engineering 93 (2), 161—171.

Lu, R. ASAE International Meeting, st Joseph, Minichigan, 2003, Paper no. 036012.

Luykx, D.M.A.M., van Ruth, S.M., 2008. An overview of analytical methods for determining the geographical origin of food products. Food Chemistry 107, 897—911.

Manley, M., Downey, G., Baeten, V., 2008. Spectroscopic technique: near infrared (NIR) spectroscopy. In: Sun, Da-Wen (Ed.), Modern Techniques for Food Authentication. Academic Press, pp. 65—116 (Chapter 3).

María GuillénNerea Cabo, D., 2002. Fourier transform infrared spectra data versus peroxide and anisidine values to determine oxidative stability of edible oils. Food Chemistry 77 (4), 503—510.

Marigheto, N.A., Kemsley, E.K., Defernez, M., Wilson, R.H., 1998. A comparison of mid-infrared and Raman spectroscopies for the authentication of edible oils. Journal of the American Oil Chemists Society 75, 987—992.

Marquardt, B.J., Wold, J.P., 2004. Raman analysis of fish: a potential method for rapid quality screening. Lebensmittel-Wissenschaft und -Technologie 37, 1—8.

Márquez, A.J., Díaz, A.M., Reguera, M.I.P., 2005. Using optical NIR sensor for on-line virgin olive oils characterization. Sensors and Actuators B 107, 64—68.

Massart, D.L., Vandeginste, B.G.M., Deming, S.N., Michottz, Y., Kaifmann, L., 1988. Chemometrics: A Textbook. Elsevier, Amsterdam.

Massart. D.L., Vandeginste, B.G.M., Buydens, L.M.C., De Jong, S., Lewi, P.J., Smeyers-Verbeke, J. Handbook of Chemometrics and Qualimetrics, Elsevier, Amsterdam, Parts A, 1997 and B, 1998.

McClure, W.F., 2001. Near-infrared instrumentation. In: Williams, P., Norris, K. (Eds.), Near-infrared technology in the agricultural and food industries. American Association of Cereal Chemists, St Paul, MN, pp. 109—127.

McGoverin, C.M., Weeranantanaphan, J., Downey, G., Manley, M., 2010. The application of near infrared spectroscopy to the measurement of bioactive compounds in food commodities. Journal of Near Infrared Spectroscopy 18, 87—111.

Mehl, P.M., Chen, Y.-R., Kim, M.S., Chan, D.E., 2004. Development of hyperspectral imaging technique for the detection of apple surface defects and contaminations. Journal of Food Engineering 61 (n°1), 67—81.

Mendes, L.S., Oliveira, F.C.C., Suarez, A.A.Z., Rubim, J.C., 2003. Determination of ethanol in fuel ethanol and beverages by Fourier transform (FT)-near infrared and FT-Raman spectrometries. Analytica Chimica Acta 493, 219—231.

Modern Raman spectroscopy.

Nordon, A., Mills, A., Burn, R.T., Cusick, F.M., Littlejohn, D., 2005. Comparison on non-invasive NIR and Raman spectrometries for determination of alcohol content of spirits. Analytica Chimica Acta 548, 148—158.

O'Neil, A.J., Jee, R.D., Moffatt, A.C., 1999. Analyst 124, 33.

I. CHEMICAL ANALYSIS OF FOOD

Oliveira, F.C., Brandao, C.R., Ramalho, H.F., da Costa, L.A.F., Suarez, P.A.Z., Rubim, J.C., 2007. Analytica Chimica Acta 587 (2), 194–199.

Osborne, B.G., Fearn, T., Hindle, P.H., 1993. Spectroscopy with Application in Food and Beverage Analysis, 1–77. Longman Scientific and Technical, Singapore. 120–141.

Osborne, B.G., 2000a. Near-infrared spectroscopy in food analysis. In: Meyers, R.A. (Ed.), Encyclopedia of Analytical chemistry. John Wiley & Sons, Chichester, pp. 1–13.

Osborne, B.G., 2000b. Near infrared spectroscopy in food analysis. BRI Australia Ltd, North Ryde, Australia, Copyright © 2000 Wiley, New York, pp. 1–14 (Chapter 1).

Paradkar, M., Irudayaraj, J.M.K., 2002. Discrimination and classification of beet and cane inverts in honey by FT-Raman spectroscopy. Food Chemistry 76, 231.

Park, B., Lawrence, K.C., Windham, W.R., Smith, D.P., 2006. Journal of Food Engineering 75, 340–348.

Penner, 1994.

Perez-Ponce, A., Garrigues, S., de la Guardia, M., 1996. Analyst 121, 923.

Ph., Fayolle, Picque, D., Corrieu, G., 2000. On-line monitoring of fermentation processes by a new remote dispersive middle-infrared spectrometer. Food Control 11 (4), 291–296.

Picque, D., Cattenoz, T., Corrieu, G., Berger, J.L., 2005. Discrimination of red wines according to their geographical origin and vintage year by the use of mid-infrared spectroscopy. Sciences des Aliments 25, 207–220.

Pillonel, L., Luginbühl, W., Picque, D., Schaller, E., Tabacchi, R., Bosset, J.O., 2003. Analytical methods for the determination of the geographic origin of Emmental cheese: mid- and near-infrared spectroscopy. European Food Research & Technology 216 (2), 174–178.

Pistorius, A.M.A., 1995. Biochemical Applications of FT-IR Spectroscopy, 7. Spectroscopy Europe. 8–15.

Pizarro, C., Esteban-Díez, I., Conzález-Sáiz, J.M., 2007. Mixture resolution according to the percentage of robusta variety in order to detect adulteration in roasted coffee by near-infrared spectroscopy. Analytical Chimica Acta 585, 266–276.

Rannou, H., Downey, G., 1997. Discrimination of raw pork, chicken and turkey meat by spectroscopy in the visible, near- and mid-infrared ranges. Analytical Communications 34, 401–404.

Robertson, A., Hall, M., Scotter, C., 1989. Food Science and Technology Today 3, 102.

Ruoff, K., Luginbühl, W., Künzli, R., Iglesias, M., Bogdanov, S., Bosset, J.O., von der Ohe, K., von der Ohe, W., Amadò, R., 2006. authentication of the botanical and geographical origin of honey by mid-infrared spectroscopy. Journal of Agricultural and Food Chemistry 54, 6873.

Ruoff, K., Luginbühl, W., Bogdanov, S., Bosset, J.O., Estermann, B., Ziolko, T., Amadò, R., 2006B. Authentication of the botanical origin of honey by near-infrared spectroscopy. Journal of Agricultural and Food Chemistry 54, 6867.

Salzer, R., Siesler, H.W., 2009. Infrared and Raman Spectroscopic Imaging. Wiley-VCH, Verlag GmbH & Co. KGaA, Weinheim.

Siesler, H.W., Ozaki, Y., Kawata, S., Heise, H.M., 2002. Near-infrared Spectroscopy Principles, Instruments, Applications. Wiley-VCH Verlag GmbH D-69469, Weinheim (Germany).

Sloan, A.E., 2008. , the top 10 functional food trends. Food Technology – Chicago 62, 25.

Soyeurt, H., Bruwier, D., Romnee, J.M., Gengler, N., Bertozzi, C., Veselko, D., Dardenne, P., 2009. Potential estimation of major mineral contents in cow milk using mid-infrared spectrometry. Journal of Dairy Sciences 92, 2444–2544.

Soyeurt, H., McParland, S., Berry, D., Wall, E., Gengler, N., Dehareng, F., Dardenne, P. (2010). Improvement and validation of mid-infrared predictions of milk fatty acid. Annual Meetings of the American Dairy Science Association (ADSA), Denver, Colorado.

Stanford, C.L., Mantooth, B.A., 2001. J. Chem.. Ed 78, 1221.

Stchur, P., Cleveland, D., Zhou, J., Michel, R.G., 2002. A review of recent applications of near-infrared spectroscopy, and of the characteristics of a novel PbS CCD array-based near-infrared spectrometer. Applied Spectroscopy Reviews 37 (4), 383–428.

Tay, A., Singh, R.K., Krishnan, S.S., Gore, J.P., 2002. Authentication of olive oil adulterated with vegetable oils using Fourier transform infrared spectroscopy. Lebensmittel-Wissenschaft und -Technologie 35, 99–103.

Tewari, J.C., Irudayaraj, J.M.K., 2005. Floral classification of honey using mid-infrared spectroscopy. Journal of Agricultural and Food Chemistry 53, 6955.

The Spectral dimensions Website. http://www.spectraldimensions.com (accessed 30.07.04.).

Thygesen, L.G., LØkke, M.M., Micklander, E., Engelsen, S.B., 2003. Vibrational Microspectrometry of Food Raman vs FT-IR.

TØgersen, G., Isaksson, T., Nilsen, B.N., Bakker, E.A., Hildrum, K.I., 1999. On-line NIR analysis of fat, water and protein in industrial scale ground meat batches. Meat Science 43, 245–253.

TØgersen, G., Arnesen, G., Nilsen, B.N., Hildrum, K.I., 2003. On-line prediction of chemical composition of semi-frozen ground beef by non-invasive NIR spectroscopy. Meat Science 63, 515–523.

Toher, D., Downey, G., Murphy, T.B., 2007. A comparison of model-based and regression classification techniques applied to near infrared spectroscopic data in food

authentication studies. Chemometrics and Intelligent Lab Systems 89 (2), 102.

Trends in Analytical Chemistry 17 (7), 1998.

TYPIC project (QLK1-CT-2002-02225; http://www.typic.org/).

Urbano Cuadrado, M., Luque de Castro, M.D., Pérez Juan, P.M., Gómez-Nieto, M.A., 2005. Comparison and joint use of near infrared spectroscopy and Fourier transform mid infrared spectroscopy for the determination of wine parameters. Talanta 66, 218–224.

Van de Voort, F.R., Ismail, A.A., Sedman, J., 1994. The determination of peroxide value by Fourier transform infrared spectroscopy. Journal of the American Oil Chemists Society 71, 921–926.

Vermeulen, P., de Jong, J., 2009. Safer food through rapid tests for chemical contaminants. Food Science & Technology 23 (3), 26–28.

Vermeulen, Ph., Fernández Pierna, J.A., Abbas, O., Dardenne, P., Baeten, V., 2010. Aunthentication and traceability of agricultural and food products using vibrational spectroscopy. In: Li-Chan, Eunice, Griffiths, Peter R., Chalmers, John M. (Eds.), Applications of vibrational spectroscopy in food science. © 2010 John Wiley & Sons, Ltd ISBN978-0-470-74299-0.

von Holst, C., Baeten, V., Boix, A., Slowikowski, B., Fernández Pierna, J.A., Tirendi, S., Dardenne, P., 2008. Transferability study of a near-infrared microscopic method for the detection of banned meat and bone meal in feedingstuffs. Analytical and Bioanalytical Chemistry 392, 313–317.

Wang, L., Lee, F.S.C., Wang, X., He, Y., 2006. Feasibility study of quantifying and discriminating soybean oil adulteration in camellia oils by attenuated total reflectance MIR and fiber optic diffuse reflectance NIR. Food Chemistry 95, 529–536.

Wesley, I.J., Barnes, R.J., McGill, A.E.J., 1995. Journal of the American Oil Chemists Society 72 (3), 289–292.

Wesley, I.J., Pacheco, F., McGill, A.E.J., 1996. Journal of the American Oil Chemists Society 73 (4), 515–518.

West, Y.D., 1996. Study of sample heating effects arising duringlaser raman spectroscopy. The Internet Journal of Vibrational Spectroscopy 1, 5.

Wilson, R.H., Tapp, H.S., 1999. Mid-infrared spectroscopy for food analysis: recent new applications and relevant developments in sample presentation methods. Trends in Analytical Chemistry 18 (2), 85–93.

Woodcock, T., Downey, G., Kelly, J.D., O'Donnell, C., 2007. Geographical classification of honey samples by near-infrared spectroscopy: a feasibility study. Journal of Agricultural and Food Chemistry 55 (22), 9128.

Yadav, L.D.S., 2005. Organic Spectroscopy. Kluwer Academic Publishers, Norwell, MA, USA.

Yang, et al., 2007.

Yildiz, G., Wehling, R.L., Cuppett, S.L., 2001. Method for determining oxidation of vegetable oils by near infrared spectroscopy. Journal of the American Oil Chemist's Society 78 (5), 495–502.

Yildiz, G., Wehling, R.L., Cuppett, S.L., 2002. Monitoring PV in corn and soybean oils by NIR spectroscopy. Journal of the American Oil Chemist's Society 79 (11), 1085–1089.

Yu, Xiuzhu, van de Voort, F.R., Sedman, J., 2007. Determination of peroxide value of edible oils by FTIR spectroscopy with the use of the spectral reconstitution technique. Talanta 74 (2), 241–246.

Yu, H., Zhou, Y., Fu, X., et al., 2007. Discrimination between Chinese rice wines of different geographical origins by NIRS and AAS. European Food Research and Technology 225, 313–320.

Yuan, S.L., He, Y., Ma, T.Y., Wu, D., Nie, P.C., 2009. Fast determination of melamine content in milk base on Vis/NIR spectroscopy method. Guang Pu Xue Yu Guang Pu Fen Xi 29 (11), 2939–2942.

Zhang, C., Shen, Y., Chen, J., Xiao, P., Bao, J., 2008. Nondestructive prediction of total phenolics, flavonoid contents, and antioxidant capacity of rice grain using near-infrared spectroscopy. Journal of Agricultural and Food Chemistry 56, 8268–8272.

I. CHEMICAL ANALYSIS OF FOOD
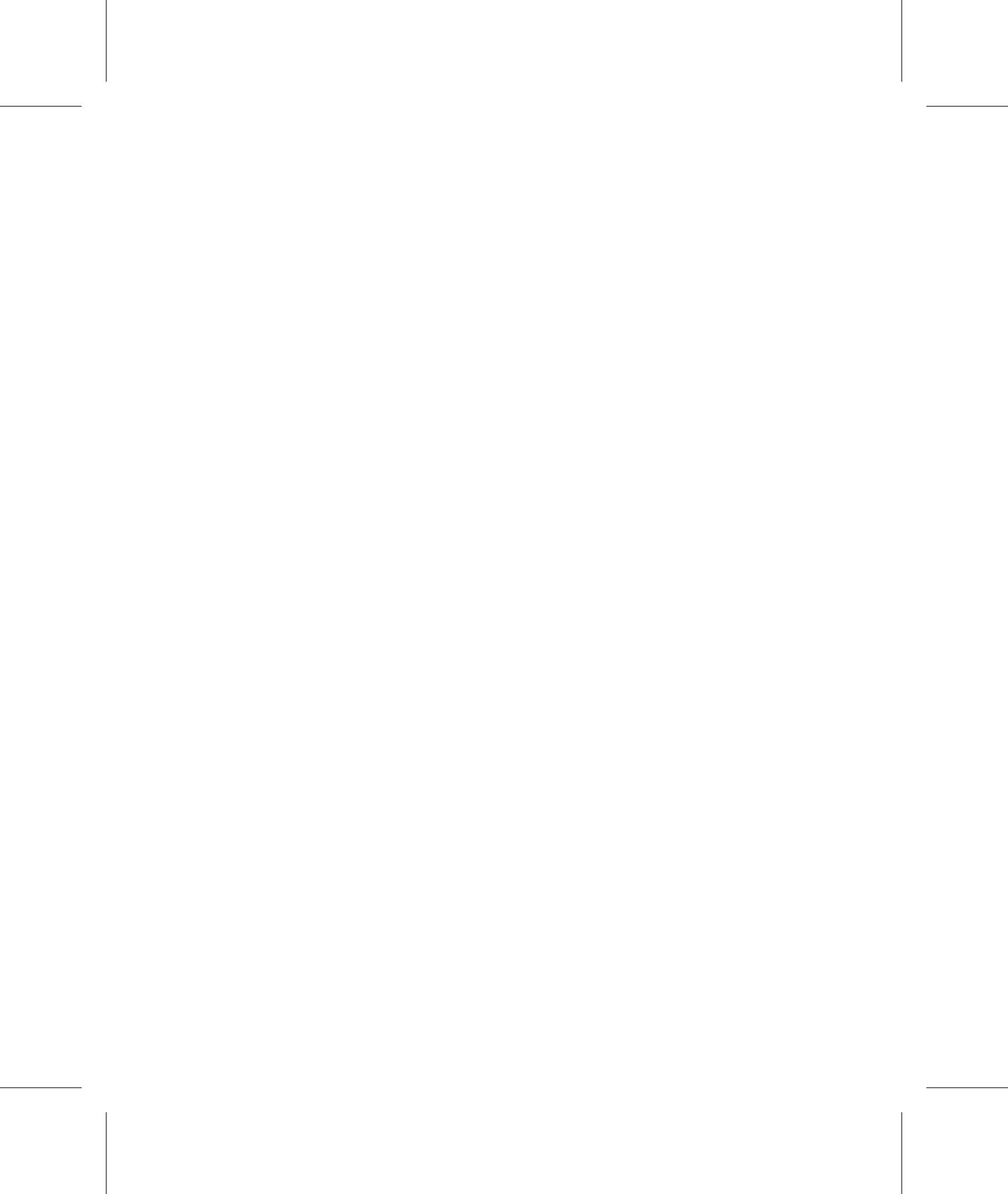
AUTHOR QUERY FORM

ELSEVIER	**Book:** PICO-9780123848628 **Chapter:** 03	**Please e-mail your responses and any corrections to:** **E-mail: S.Vadivelan@elsevier.com**

Dear Author,

Any queries or remarks that have arisen during the processing of your manuscript are listed below and are highlighted by flags in the proof. (AU indicates author queries; ED indicates editor queries; and TS/TY indicates typesetter queries.) Please check your proof carefully and answer all AU queries. Mark all corrections and query answers at the appropriate place in the proof (e.g., by using on-screen annotation in the PDF file http://www.elsevier.com/framework_authors/ tutorials/ePDF_voice_skin.swf) or compile them in a separate list, and tick off below to indicate that you have answered the query.

Please return your input as instructed by the project manager.

Uncited reference: References that occur in the reference list but are not cited in the text. Please position each reference in the text or delete it from the reference list. NIL	
Missing reference: References listed below were noted in the text but are missing from the reference list. Please make the reference list complete or remove the references from the text. NIL	

Location in Chapter	Query / Remark	
AU:1, page 65	In the reference list "Osborne, 2000a and 2000b" are mentioned as separate references. Therefore we have changed all citations of 'Osborne, 2000' to Osborne, 2000a,b. Please amend the citations in the text if necessary.	☐
AU:2, page 69	Please note that 'Figure 3.4' was not cited in the text. Kindly check whether the citation has been inserted at appropriate place and correct if necessary.	☐
AU:3, page 86	Citations "Batsoulis et al., 2005; Blanco and Villarroya, 2002; Osborne 2000" were given twice in the reference list. Hence we have removed the second occurrence. Kindly check.	☐
AU:4, page 88	Please check and update "Refs. Goodacre, 2002; Handbook of instrumental…; Modern Raman spectroscopy; TYPIC project; Fernández Pierna et al., accepted for publication; El-Abassy et al., in press; Da-Wen Sun".	☐
AU:5, page 88	Reference "Colthup and Daly, 1990" has not been cited in text. Please provide citation for this reference or delete it from the reference list.	☐
AU:6, page 89	Please check and correct the year of publication for "Ref. Li et al., 200b".	☐

PICO: 03

Non-Print Items

Abstract:
Consumers are more and more interested in food safety and quality. Various analytical techniques are proposed. Among them we can find vibrational spectroscopic techniques (e.g. NIR, MIR, and Raman). Food products have their specific composition which allows characteristic spectra considered as "fingerprint". Spectroscopic techniques can be applied as a first approach to obtain basic knowledge about a food product as well as a way to undergo qualitative and quantitative analyses. These techniques have the advantage to be rapid, easy-to-use, and nondestructive in comparison to tedious reference chemical and classical techniques which require solvents and are time consuming. Moreover, combination with multivariate analyses makes it easier to extract the significant information from the huge collected data. Spectroscopy techniques allow both at-line and on-line analyses. They can be used at laboratory or in a production line; recent developments in on-line spectrometers make it possible to analyze a sample in a vessel, during a production process or in the field.

In this chapter, we highlight the new advances in near- and mid-infrared (NIR and MIR) and Raman spectroscopic techniques which, combined with chemometric treatments, have large food applications. Some developments of theory and instrumentation used for those spectroscopic analyses are discussed in addition to on-line, mapping, and imaging systems that can be considered as new generation of instruments. After that, some applications mainly in relation to geographic origin authentication, species discrimination, detection of adulteration, process control, physico-chemical properties, as well as food quality are presented.