Chemometrics in Food Technology

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1. Introduction

The food sector is one of the most important voices in the economic field as it fulfills one of the main needs of man. The changes in the society in recent years have radically modified the food industry by combining the concept of globalization with the revaluation of local production. Besides the production needs to be global, in fact, there are always strong forces that tend to re-evaluate the expression of the deep local production like social history and centuries-old tradition.

The increase in productivity, in ever-expanding market, has prompted a reorganization of control systems to maximize product standardization, ensuring a high level of food security, promote greater compliance among all batches produced. The protection of large quantities of production, however, necessarily passes through systems to highlight possible fraud present throughout the production chain: from the raw materials (controlled by the producer) to the finished products (controlled by large sales organizations). The fraud also concern the protection of local productions: the products of guaranteed origin must be characterized in such a way to identify specific properties easily and detectable by objective means.

The laboratories employ analytical techniques that are often inadequate because they require many samples, a long time to get the response, staff with high analytical ability. In a context where the speed is an imperative, technology solutions must require fewer samples or, at least no one (non-destructive techniques); they have to provide quick answers, if not immediate, in order to allow the operator to decide quickly about further steps to control or release the product to market; they must be easy to use, to promote their use throughout the production chain where it is not always possible to have analytical laboratories. The technologies must therefore be adapted to this new approach to production: the sensors and the necessary related data modeling, which allows the "measure", are evolving to meet the needs of the agri-food sector. The trial involves, often, Research Institutions on the side of Companies, a sign of a great interest and a high level of expectations. The manufacturers of technologies, often, provide devices that require calibration phases not always easy to perform, but that are often the subject of actual researches. These are particularly complex when the modeling approach must be based on chemometrics.

This chapter is essentially divided into two parts: the first part analyzes the theoretical principles of the most important technologies, currently used in the food industry, that used

a chemometric approach for the analysis of data (spectrophotometry Vis/NIR (Visible and Near InfraRed) and NIR (Near InfraRed), Image Analysis with particular regard to Hyperspectral Image Analysis and Electronic Nose); the second part will present some case studies of particular interest related to the same technologies (fruit and vegetables, wine, meat, fish, dairy, olive, coffee, baked goods, etc.) (Frank & Todeschini, 1994; Massart et al., 1997 and 1998; Basilevsk, 1994; Jackson, 1991).

2. Technologies used in the food sector combined with chemometrics

2.1 NIR and Vis/NIR spectroscopy

Among the non-destructive techniques has met a significant development in the last 20 years the optical analysis in the region of near infrared (NIR) and visible-near infrared (Vis/NIR), based on the use of information arising from the interaction between the structure of food and light.

2.1.1 Electromagnetic radiation

Spectroscopic analysis is a group of techniques allowing to get information on the structure of matter through its interaction with electromagnetic radiation.

Radiation is characterized by (Fessenden & Fessenden, 1993):

- a wavelength (λ), which is the distance between two adjacent maxima and is measured in nm;
- a frequency (v), representing the number of oscillations described by the wave per unit of time and is measured in hertz (cycles/s);
- a wave number (n), which represents the number of cycles per centimeter and is measured in cm^{-1}.

The entire electromagnetic spectrum is divided into several regions, each characterized by a range of wavelengths (Fig.1)
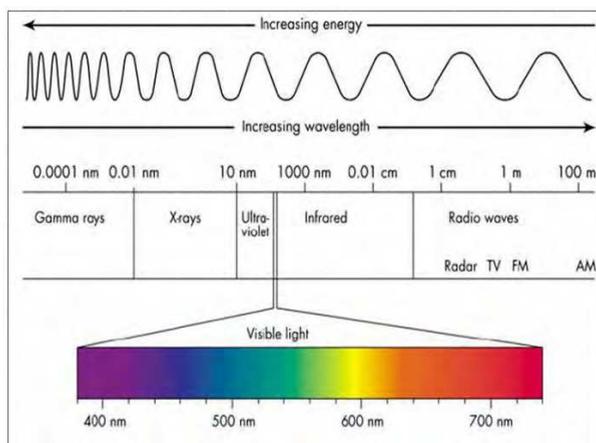

Fig. 1. The electromagnetic spectrum (Lunadei, 2008).

2.1.2 Transitions in the near infrared region (NIR)

The radiation from the infrared region is able to promote transitions at vibrational level. The infrared spectroscopy is used to acquire information about the nature of the functional groups present in a molecule. The infrared region is conventionally divided into three sub-regions: near (750-2500 nm), medium (2500-50000 nm) and far infrared (50-1000 µm).

Fundamental vibrational transitions, namely between the ground state and first excited state, take place in the mid-infrared, while in the region of near-infrared absorption bands are due to transitions between the ground state and the second or the third excited state. This type of transitions are called overtones and their absorption bands are generally very weak. The absorption bands associated with overtones can be identified and correlated to the corresponding absorption bands arising from the fundamental vibrational transitions because they fall at multiple wavelengths of these.

Following the process of absorption of photons by molecules the intensity of the radiation undergoes a decrease. The law that governs the absorption process is known as the Beer-Lambert Law:

$$A = \log (I_0/I) = \log (1/T) = \varepsilon \cdot l \cdot c \qquad (1)$$

where:

A = absorbance [log (incident light intensity/transmitted beam intensity)];
T = transmittance [beam intensity transmitted/incident light intensity];
I_0 = radiation intensity before interacting with the sample;
I = radiation intensity after interaction with the sample;
ε = molar extinction coefficient characteristic of each molecule ($l \bullet mol^{-1} \bullet cm^{-1}$);
l = optical path length crossed by radiation (cm);
c = sample concentration (mol/l).

The spectrum is a graph where in the abscissa is reported a magnitude related to the nature of radiation such as the wavelength (λ) or the wave number (n) and in the Y-axis a quantity related to the change in the intensity of radiation as absorbance (A) or transmittance (T).

2.1.3 Instruments

Since '70s producers developed analysis instruments specifically for NIR analysis trying to simplify them to fit also less skillful users, thanks to integrated statistical software and to partial automation of analysis.

Instruments built in this period can be divided in three groups: desk instruments, compact portable instruments and on-line compatible devices.

Devices evolved over the years also for the systems employed to select wavelength. First instruments used filter devices able to select only some wavelength (Fig. 2). These devices are efficient when specific wavelength are needed. Since the second half of '80s instruments capable to acquire simultaneously the sample spectrum in a specific interval of wavelength were introduced, recording the average spectrum of a single defined sample area (diode array systems and FT-NIR instruments) (Stark & Luchter, 2003). At the same time, chemometric data analysis growth helped to diffuse NIR analysis.
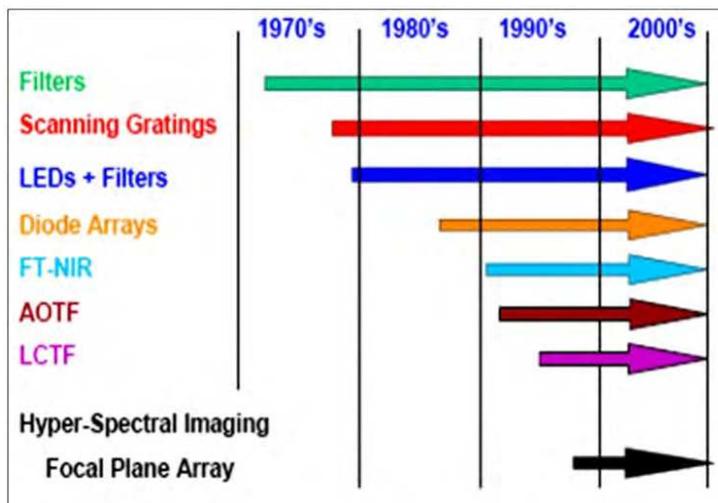
Fig. 2. Development of the different analysis technologies scheme (Stark & Luchter, 2003).

Particularly, food sector showed interest towards NIR and Vis/NIR instruments, both mobile and on-line. Devices based on diode array spectrophotometers and FT-NIR desk systems proved to be the best for this sector.

Both in the case of portable and stationary instruments, the fundamental components of these systems are common and are four:

- Light source;
- Light radiation transport system;
- Sample compartment and measurement zone;
- Spectrophotometer and Personal Computers.

Light source

Tungsten filament halogen lamps are chosen as the light source by most of the instruments. This is due to a good compromise between good performance and relatively low cost. This type of lamps are particularly suitable for use in low voltage. A little drawback may be represented by sensitivity to vibration of the filament.

Halogen bulbs are filled with halogen gas to extend their lives by using the return of evaporated tungsten to the filament. The life of the lamp depends on the design of the filament and the temperature of use, on average ranges from a minimum of 50 hours and a maximum of 10000 hours at rated voltage. The lamp should be chosen according to the use conditions and the spectral region of interest. An increase in the voltage of the lamp may cause a shift of the peaks of the emission spectrum towards the visible region but can also lead to a reduction of 30% of its useful life. On the contrary, use of lower voltages can increase the lamp life together, however, with an intensity reduction of light radiation, especially in the visible region. Emission spectrum of the tungsten filament changes as a function of temperature and emissivity of the tungsten filament. The spectrum shows high intensity in the VNIR region (NIR region close to the area of the visible).

Even if less common, alternative light sources are available. For example, LED light sources and ad laser sources could be used. LED sources (light emitting diodes) are certainly interesting sources thank to their efficiency and their small size. They meet, however, a limited distribution due to limited availability of LEDs emitting at wavelengths in the NIR region. Technology to produce LEDs to cover most of the NIR region already exists, but demand for this type of light sources is currently too low and the development of commercial product of this type is still in an early stage.

The use of laser sources guarantees very intense emission in a narrow band. But the reduced spectral range covered by each specific laser source can cause problems in some applications. In any case the complexity and high cost of these devices have limited very much their use so far, mostly restricted to the world of research.

Light radiation transport system

Light source must be very close to the sample to light it up with good intensity. This is not always possible, so systems able to convey light on the samples are needed. Thanks to optic fibers this problem was solved, allowing the development of different shapes devices.

The use of fiber optics allows to separate the area of placement of the instrument from the measuring proper area. There are indeed numerous circumstances on products sorting line in which environmental conditions do not fulfill direct installation of measure instruments. For example, high temperature, excessive vibrations or lack of space are restricting factors to the use of on-line NIR devices. In all these situations optic fibers are the solution to the problem of conveying light. They transmit light from lamp to sample and from sample to spectrophotometer. They allow to have an immediate measure on a localized sample area, thanks to their small dimensions, reaching areas difficult to access. Furthermore, they are made of a dielectric material that protects from electric and electromagnetic interferences. 'Optic fibers' means fibers optically transparent, purposely studied to transmit light thanks to total internal reflection phenomenon. Internal reflection is said to be total because it is highly efficient, in fact more than 99,999% radiation energy is transmitted in every reflection. This means that radiation can be reflected thousands of times during the way without suffer an appreciable attenuation of intensity (Osborne et al., 1993).

Optic fiber consists of an inner core, a covering zone and of an external protection cover. The core is usually made of pure silica, but can also be used plastics or special glasses. The cladding area consists of material with a lower refractive index, while the exterior is only to protect the fiber from mechanical, thermal and chemical stress.

In figure 3 are shown the inner core and the cladding of an optical fiber. Index of refraction of inner core have to be bigger than cladding one. Each ray of light that penetrates inside the fiber with an angle $\leq \theta_{max}$ (acceptance angle) is totally reflected with high efficiency within the fiber.

Sample compartment and measurement zone

Samples compartment and measurement zone are highly influenced by the technique of acquisition of spectra. Different techniques are employed, depending on type of samples, solid or liquid, small or large, to be measured in plan or in line, that influence the geometry of the measurement zone.
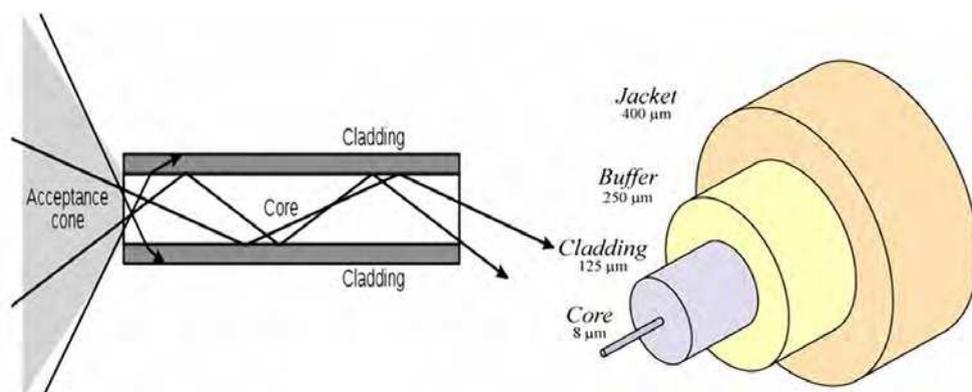
Fig. 3. Scheme of an optical fiber. The acceptance cone is determined by the critical angle for incoming light radiation. Buffer absorbs the radiation not reflected by the cladding. Jacket has a protective function.

The techniques to acquire spectra are four: transmittance, reflectance, transflectance and interactance. They are different mainly for the different positioning of the light source and of the measurement sensor around the sample (Fig. 4).

a. **Transmittance** - The transmittance measurements are based on the acquisition of spectral information by measuring the light that goes through the whole sample (Lu & Ariana, 2002). The use of analysis in transmittance can explore much of the internal structure of the product. This showed that is a technique particularly well suited to detect internal defects. To achieve significant results with this technique is required a high intensity light source and a high sensitivity measuring device. This because intensity of light able to cross the product is often very low. The transmittance measurements generally require a particular geometry of the measuring chamber, which can greatly influence the design of the instrument.

b. **Reflectance** - This technique measures the component of radiation reflected from the sample. The radiation is not reflected on the surface but penetrates into the sample a few millimeters, radiation is partly absorbed and partly reflected back again. Measuring this component of reflected radiation after interacting with the sample is possible to establish a relationship of proportionality between reflectance and analyte concentration in the sample. The reflectance measurement technique is well suited to the analysis of solid matrices because the levels of intensity of light radiation after the interaction with the sample are high.

This technique also allows to put in a limited space inside a tip the bundle of fibers that illuminate the sample and the fibers leading to the spectrophotometer the radiation after the interaction with the product. Therefore the use of this type of acquisition technique is particularly versatile and is suitable for compact, portable instruments, designed for use in field or on the process line. The major drawback using this technique is related to the possibility to investigate only the outer area of the sample without having the chance to go deep inside.

c. **Transflectance –** This technique is used in case it is preferable to have a single point of measurement, as in the case of acquisitions in reflectance. In this case, however, the incident light passes through the whole sample, is reflected by a special reflective surface, recross the sample and strikes the sensor located near the area of illumination. The incident light so makes a double passage through the sample. Obviously this type of technique can be used only in the case of samples very permeable to light radiation such as partially transparent fluid. It is therefore not applicable to solid samples.

d. **Interactance** - This technique is considered a hybrid between transmittance and reflectance, as it uses characteristics of both techniques previously seen. In this case the light source and sensor are located in areas near the sample but between them physically separated. So the radiation reaches the measurement sensor after interacting with part of internal structure of the sample. This technique is mainly used in the analysis of big solid samples, for example, a whole fruit. Interactance is thus a compromise between reflectance and transmittance and has good ability to detect internal defects of the product combined with a good intensity of light radiation. This analysis is widely used on static equipment where, through the use of special holders, is easily obtained the separation between the areas of incidence of light radiation and the area to which the sensor is placed. It is instead difficult to use this configuration on-line because is complicated to place a barrier between incident and returning light to the sensor directly on the process line.
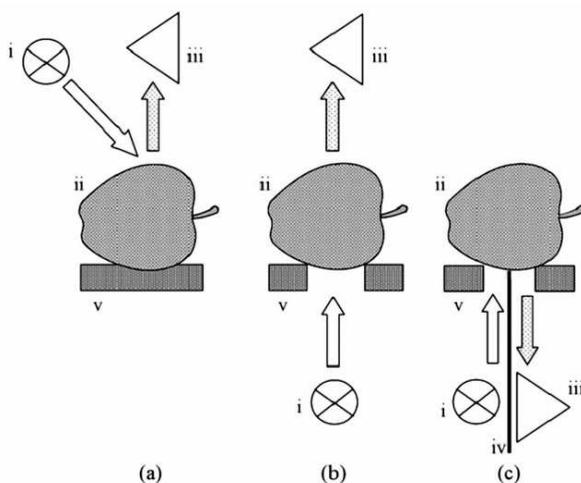

Fig. 4. Setup for the acquisition of (a) reflectance, (b) transmittance, and (c) interactance spectra, with (i) the light source, (ii) fruit, (iii) monochromator/detector, (iv) light barrier, and (v) support. In interactance mode, light due to specular reflection is physically prevented from entering the monochromator by means of a light barrier (Nicolai et al., 2007).

Spectrophotometer and Personal Computers

Spectrophotometer can be considered the heart of an instrument for NIR analysis. The employed technology for the wavelengths selection greatly influences the performance of

the instrument. For example, the use of filters allows instruments to record the signal of a single wavelength at a time. Modern instruments (diode array instruments and interferometers) allow to record the spectrum of the entire wavelengths range.

Instruments equipped with a diode array spectrophotometer are those who have met the increased use for portable and online applications in food sector. This is due to their compact size, versatility and robustness, thanks to the lack of moving parts during operation and also thanks to a relatively low cost.

As seen before, fiber optic sensor collects the portion of the electromagnetic radiation after interaction with the internal structure of the sample and transfers it to the spectrophotometer. The optical fiber is connected to the optical bench of the instrument. The optical bench allows to decompose the electromagnetic radiation and recording the intensity at different wavelengths.

Optical bench of this type of instrument generally consists of five components:

a.   Optical fiber connector: connects the fiber optic with the optical bench of the instrument.
b.   First spherical mirror (collimating mirror), has the function of collimating the light and send it to the diffraction grating.
c.   Diffraction grating: in this area of the instrument, the light is split into different wavelengths and sent to the second spherical mirror.
d.   Second spherical mirror (focussing mirror), collects diffracted radiation from the grating and sends them to the CCD sensor.
e.   Matrix CCD sensor (diode array): records the signal intensity at each wavelength.

High sensitivity of the CCD matrix sensor compensate the low intensity of light radiation input due to the reduced diameter of the optical fibers used. Sensors used are generally Si-diode array or InGaAs-diode array. The first ones are certainly the most common and cheap and allow the acquisition of the spectrum in the range between 400 and 1100 nm, so are used for Vis/NIR analysis. InGaAs sensors, more expensive, are used in applications requiring the acquisition of spectra at longer wavelengths, their use should range from 900 to 2300 nm.

Recorded signal by the CCD sensor is digitized and acquired by a PC using the software management tool of the instruments. Software records and allows to display graphically the spectrum of the analyzed sample. The management software also allows to interface with the spectrophotometer enabling to change some parameters during the acquisition of spectra.

2.2 Image analysis

In the food industry, since some time, there is a growing interest in image analysis techniques, since the appearance of a food contains a variety of information directly related to the quality of the product itself and this characteristics are difficult to measure through use of classical methods of analysis. In addition, image analysis techniques: provide information much more accurate than human vision, are objective and continuous over time and offer the great advantage of being non-destructive. These features, enable vision

systems to be used in real time on the process lines, allowing on-line control and automation of sorting and classification within the production cycle (Guanasekaran & Ding, 1994).

The objective of the application of image analysis techniques, in the food sector, is the quantification of geometric and densitometric characteristic of image, acquired in a form that represents meaningful information (at macro and microscopic level) of appearance of an object (Diezak, 1988). The evolution of these techniques and their implementation in the vision machine in form of hardware and specialized software, allows a wide flexibility of applications, a high capacity of calculation and a rigorous statistical approach.

The benefits of image analysis techniques (Brosnan & Sun, 2004) that rely on the use of machine vision systems can be summarized as follows:

a. are non-destructive techniques;
b. techniques are use-friendly, rapid, precise, accurate and efficient;
c. generate objective data that can be recorded for analysis deferred;
d. allow a complete analysis of the lots and not just a single sample of the lot;
e. reduce the involvement of human personnel in performing tedious tasks and allow the automation of various functions that would require intensive work shifts;
f. are reasonably affordable cost.

These suggest the reason that drives scientific research, of the agro-food sector, to devote to the study and analysis of machine vision systems to analyze the internal and external quality characteristics of food, valued according to the optical properties of the products. With a suitable light source, it is possible to extract information about color, shape, size and texture. From these features, it is possible to know many objective aspects of the sample, to be able to correlate, through statistical analysis, the characteristics defined by quality parameters (degree of maturation, the presence of external or internal mechanical defects, class, etc.) (Du & Sun, 2006, Zheng et al., 2006).

The image analysis may have several applications in the food industry: as a descriptor or as gastronomic and technologic parameter. Vision machine can also be used to know size, structure, color in order to quantify the macro and microscopic surface defects of a product or for the characterization and identification of foods or to monitor the shelf life (Riva, 1999). "Image analysis" is a wide designation that include, in addition to classical studies in grayscale and RGB images, the analysis of images collected by mean multiple spectral channels (multispectral) or, more recently, hyperspectral images, technique exploited for its full extension in the spectral direction.

The hyperspectral image (Chemical and Spectroscopic Imaging) is an emerging technology, non-destructive, which complements the conventional imaging with spectroscopy in order to obtain, from an object, information, both spectral and spatial. The hyperspectral images are digital images in which each element (pixel) is not a single number or a set of three numbers, like the color pictures (RGB), but a whole spectrum associated with that point. They are three-dimensional blocks of data. Their main advantage is that they provide spatial information necessary for the study of non-homogeneous samples. The advantage of this technique is the ability to detect in a foodstuff even minor constituents, isolated spatially.

To support image analysis, chemometric techniques are necessary to process and to model, data sets, in order to extract the highest possible information content. Methods of

classification, modeling, multivariate regression, similarity analysis, principal components analysis, methods of experimental design and optimization, must be applied on the basis of each different condition and needs.

2.2.1 The vision system

The machine vision systems, appeared in the early sixties and then spread over time, in many fields of application, are composed of a lighting system, a data acquisition system connected to a computer, via a capture card, which digitizes (converts the signal into numerical form) and stores the analogic electrical signal, at the output from the camera sensor (Russ et al., 1988). The scanned image is then "converted" into a numerical matrix. Captured images are elaborated by appropriate processing softwares in order to acquire the useful information. In figure 5 shows an example of vision machine.
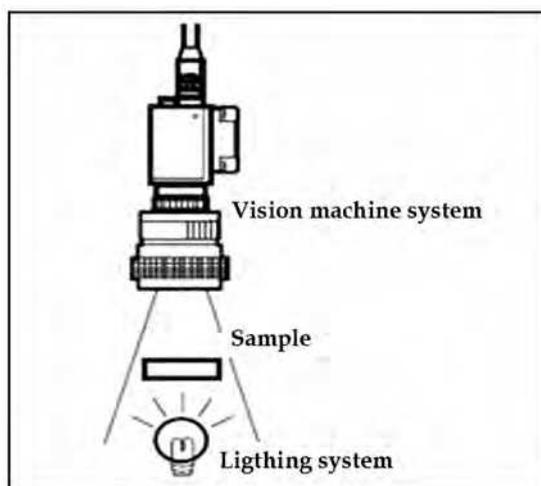

Fig. 5. Example of image acquisition of an inspected sample.

It is important to choose the localization of light source, but also the type of light source (incandescent, halogen, fluorescent, etc.) influences the performance of the analysis. In fact, although the light sources emitting electromagnetic radiation corresponding to the visible (VIS, 400-700 nm), ultraviolet (UV 10-400 nm) and near infrared (NIR, 700-1400 nm) are the most widely used, to create a digital image can also be used other types of light sources in order to emit different radiations, depending on the purpose of analysis. For example, to determine the internal structure of objects and/or identify any internal defects, it's possible to use an X-ray source, even if, although this type of source gives good results, its application is much more widespread in the medical field than in the agro-food, this is due to high costs of equipment and low speed of operating.

2.2.2 The digital image

A digital image is generated from the conversion of an analogic video signal produced by a digital camera into an electronic signal (scanning), then stored in the memory of a PC in the

form of binary information. Any digital image can be considered as an array of points, the pixels, that make up the smallest element of an image. Each pixel contains a double set of information: its position in space, identified by the values (x, y) and the value of its intensity. Digital images can be represented using only two colors, typically black and white (binary image), or shades of gray (monochrome image) or a range of colors (multichannel image). The value of light intensity will be different depending on the type of image.

The pixels, in the binary images, can have, as the intensity value, or 0 (equivalent to black) or 1 (white). The value of intensity in monochrome images, will be within a range, defined gray scale, from 0 to L, which usually corresponds to the interval from 0 (or 1) to 255 (or 256), where a value of 0 corresponds to black, a value of 255 corresponds to white, and intermediate values to the various shades of gray.

Finally, in multi-channel images, the color of each pixel will be identified by three or four values, depending on the reference color model. For example, in RGB color space, each pixel will be characterized by a three values, each between 0 and 255, respectively, corresponding to the intensity in the red, green and blue. When all three values are 0, the color of object is black, and when all three have maximum value, the object will be white, while, when there are equal levels of R, G and B, the gray color is generated. The images of this type, in fact, may be considered as a three-dimensional matrix, consisting of three overlapping matrices having the same number of rows and columns, where the elements of the first matrix represent the pixel intensity in the red channel, those in the second matrix, the green channel and those of third matrix, in the blue channel.

2.2.3 Multispectral and hyperspectral images

RGB images, represented by three overlapping monochrome images, are the simplest example of multichannel images. In medical applications, in geotechnical, in the analysis of materials and of remote sensing, instead, are often used sensors capable of acquiring multispectral and hyperspectral images, two particular types of multi-channel images. The multispectral images are typically acquired in three/ten spectral bands including in the range of Vis, but also in the field of IR, fairly spaced (Aleixos et al., 2002). In this way it's possible to extract a larger number of information from the images respect those normally obtained from the analysis of RGB images.

An example of bands normally used in this type of analysis, are the band of blue (430-490 nm), green (491-560 nm), red (620-700 nm), NIR (700-1400 nm), MIR (1400-1750 nm). The spectral combinations can be different depending on the purpose of analysis. The combination of NIR-RG (near infrared, red, green) is often used to identify green areas in satellite images, because the green color reflects a lot in the NIR wavelength. The combination of NIR-R-B (near infrared, red, blue) is very useful to verify the ripening stage of fruit, this is due to the chlorophyll that shows a peak of adsorption in the wavelength of the red. Finally, the combination of NIR-MIR-blue (NIR, MIR and blue) is useful to observe the sea depth, the green areas in remote sensing images.

Hyperspectral imaging (HSI) combines spectroscopy and the traditional imaging to form a three-dimensional structure of multivariate data (hypercube). The hyperspectral images are consist of many spectral bands acquired in a narrow and contiguous way, allowing to analyze each pixel in the multiple wavelengths simultaneously and, therefore, to obtain a

spectrum associated with a single pixels. The set of data constituting an hyperspectral image can be thought as a kind of data cube, with two spatial directions, ideally resting on the surface observed, and a spectral dimension. Extracting a horizontal plane from the cube it is possible to get a monochrome image, while the set of values, corresponding to a fixed position in the plane (x, y), is the spectrum of a pixel of the image (Fig. 6).
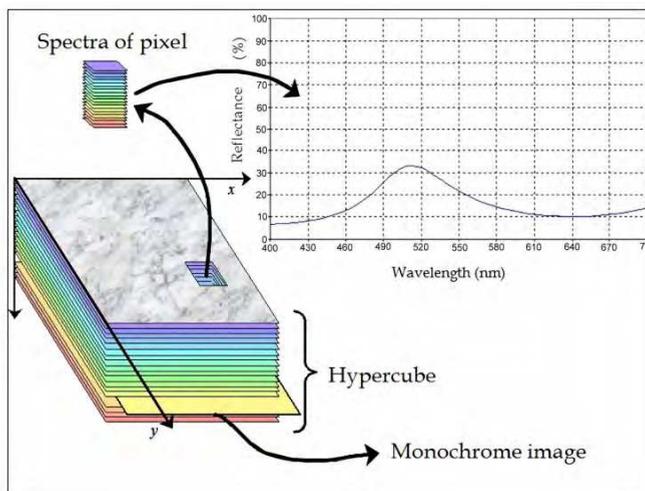

Fig. 6. Example of hyperspectral image.

With the hyperspectral imaging, you can acquire the spectra in reflectance, in transmission and fluorescence as a function of the different kind of sample to analysis, even if the most of the scientific works, present in the literature, using spectral images acquired in reflectance, transmission and emission.

The significant time savings that can be made to the industrial production processes, encourage the use of this instrumentation. The hyperspectral image analysis has many advantages, but still has some defects. The advantages of using hyperspectral analysis for what concerns the agro-food sector can be summarized as follows:

a. does not necessary to prepare the test sample;
b. it is a non-invasive, non-destructive methodology, it avoids the sample loss that can be used for other purposes or analysis;
c. can be regarded as an economic tool that it allows a saving of time, labor, reagents, and a strong cost-saving for the waste treatment;
d. for each pixel of the analyzed sample is possible to have the full spectrum and not a only absorbance value for few wavelength;
e. many constituents can be determined simultaneously within a sample, such as color and morphological characteristics;
f. due to its high spectral resolution, it is possible to estimate both qualitative than quantitative information;
g. it is also possible to select a single region of interest of the sample, and save it in a spectral library.

As mentioned previously, one of the advantages HSI is the large volume of data available in each hypercube, with which to create the calibration and validation set. But, the information derived from the analysis, contain also redundant information. This abundance of data has two drawback, one due to the high computational load of heavy data size and the second is due to the long acquisition times, given the size of the data being collected (Firtha et al. 2008). Therefore, it is desirable to reduce the load to manageable levels, especially if the goal is the application of HSI techniques in real time, on-line on production lines. In fact, in many cases, the large amount of data acquired from the spectral image, is appropriately reduced (with chemometric processing) so as to select only those wavelengths interesting for the intended purpose. Once the spectral bands of interest were identified, a multispectral system, with only selected wavelengths, can be engineered a system for industrial application. Another negative aspect is that the spectral image analysis is an indirect method to which it is necessary to apply appropriate chemometric techniques and a procedure of data transfer.

The spectral image is not suitable for liquid and homogeneous samples. In fact, the value of this type of image is evident when applied to heterogeneous samples, and many foods are an excellent heterogeneous matrix. Despite the novelty of applying HSI in the food sector, many jobs are already present in the literature.

The traditional image analysis, based on a computer system, has had a strong development in the food sector with the aim of replacing the human eye on saving costs and improving efficiency, speed and accuracy. But the computer vision technology is not able to select between objects of similar colors, to make complex classifications, to predict quality characteristics (e.g. chemical composition) or detect internal defects. Since the quality of a food is not an individual attribute but it contains a number of inherent characteristics of the food itself, to measure the optical properties of food products has been one of the most studied non-destructive techniques for the simultaneous detection of different quality parameters. In fact, the light reflected from the food contains information about constituents near and at the surface of the foodstuff. Near-infrared spectroscopy technology (NIRS) is rapid, non-destructive, easy to apply on-line and off-line. With this technology, it is possible to obtain spectroscopic information about the components of analyzed sample, but it is not possible to know the position of the component.

The only characteristic of appearance (color, shape, etc.) however, are easily detectable with conventional image analysis. The combination of image analysis technology and spectroscopy is the chemical imaging spectroscopy that allows to get spatial and spectral information for each pixel of the foodstuff. This technology allowing to know the location of each chemical component in the scanned image. Table 1 summarizes the main differences between the three analytical technologies: imaging, spectroscopy and hyperspectral imaging.

2.3 Electronic nose (e-nose)

"An instrument which comprises an array of electronic chemical sensors with partial specificity and appropriate pattern recognition system, capable of recognizing simple or complex odors" is the term of "electronic nose" coined in 1988 by Gardner and Bartlett (Gardner and Bartlett, 1994).

Features	Imaging	Spectroscopy	Hyperspectral Imaging
Spatial information	√	x	√
Spectral information	x	√	√
Multi-costituent information	x	√	√
Building chimica images	x	x	√
Flexibility of spectral information extraction	x	x	√

Table 1. Main differences among imaging, spectroscopy and hyperspectral imaging techniques (ElMarsy & Sun, 2010).

Scientific interest in the use of electronic noses was formalised, the first time, in a workshop on chemosensory information processing during a session of the North Atlantic Treaty Organization (NATO) that was entirely dedicated to the topic of artificial olfaction. Since 1991, interest in biological sensors technology has grown considerably as is evident by numerous scientific articles. Moreover, commercial efforts to improve sensor technologies and to develop tools of greater sophistication and improved capabilities, with diverse sensitivities, are with ever-expanding (Wilson & Baietto, 2009).

Electronic noses are emerging as an innovative analytical-sensorial tool to characterize the sensory comparison of food in terms of freshness, determination of geographical origin, seasoning. The first electronic nose goes back to the '80s, when Persaud and Dodd of the University of Warwick (UK) tried to model and simulate the operation of the olfactory system of mammals with solid state sensors. Since then, artificial olfactory systems are designed closer to the natural one.

The electronic nose is a technology that tends to replace/complement the human olfactory system. The tool does not analyze the chemical composition of the volatile fraction, but it identifies the olfactory fingerprint.

Currently, these electronic devices are characterized by complex architecture, where it is possible to try to reproduce the functioning of the olfactory system of mammals. The tool is a biomimetic system that is designed to mimic the functioning of the olfactory systems that we find in nature, specifically human olfactory system. Typically, an electronic nose collects information through an array of sensors, able to respond in a selective mode and reversible to the presence of chemicals, generating electrical signals as a function of their concentration. Currently, the sensors that have reached the highest level of development are made from metal oxides semiconductor (MOS). The sensors are usually characterized by fast response, low energy consumption, small size, high sensitivity, reliability, stability and reproducibility. In addition to semiconductor of metal, the sensor can be made of transistors, plated with metal semiconductor (MOSFETs), or conductive polymers. The MOS sensors are inorganic, typically made of tin oxide, zinc oxide, titanium oxide, tungsten oxide. The absorption of gas by them change their conductivity. These sensors operate at high temperatures, between 200 and 500 °C and are relatively cheap. In figure 7 is represented the main parts of a typical sensor.
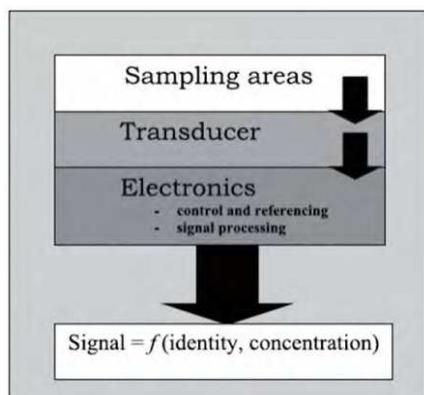
Fig. 7. The main parts of a typical sensor (Deisingh et al. 2004)

Below, ten possible MOS sensors for reading specific molecules (Table 2):

Sensor	Molecules detected
W1C	Aromatic compounds
W5S	Oxides of nitrogen, low specificity
W3C	Ammonium compounds, aromatic
W6S	Hydrogen
W5C	Alkanes, aromatic compounds, less polar compounds
W1S	Methane, low specificity
W1W	Sulfur compounds, terpenes, limonene, pyrazines
W2S	Alcohol, partially aromatic compounds, low specificity
W2W	Aromatic compounds, organic sulfur compounds
W3S	Methane

Table 2. Example of sensors in the electronic nose, with their categories of compounds that can to determine

The information is initially encoded as electrical unit, but are immediately captured and digitized in order to be numerically translated by a computer system. In practice, an odorant is described by the electronic nose, based on the responses of individual sensors, as a point or a region of a multidimensional space.

Thanks to special algorithms, derived from the discipline called pattern recognition, the system is able to build an olfactory map in order to allow a qualitative and quantitative analysis, discriminating a foodstuff simply by its olfactory fingerprint.

The architecture of an electronic nose (Fig. 8) is significantly dependent on the application for which it is designed. In general, the electronic nose, is characterized by the presence of a vacuum system, a large number of gas sensors, a subsystem of acquisition and digitization and by a processing subsystem able to implement appropriate algorithms for classification or regression.
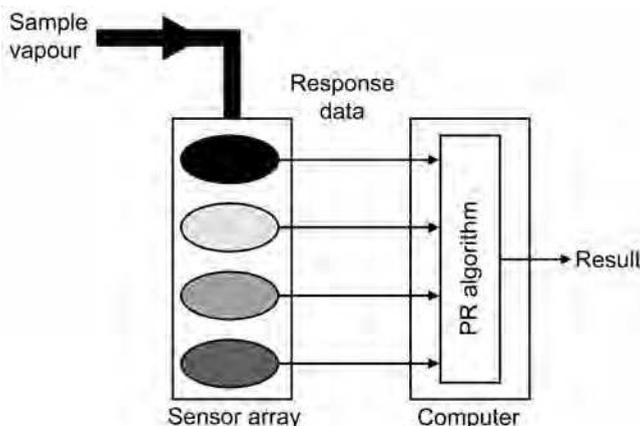
Fig. 8. A generalized structure of an electronic nose. (Deisingh et al. 2004)

The principle of working which operates the electronic nose is distinctly different from that of commonly used analytical instruments (e.g. gas chromatograph). The e-nose gives an overall assessment of the volatile fraction of the foodstuff that is, in large part responsible for the perception of the aroma of the investigated sample, without the need to separate and identify the various components. All the responses of the sensors resulted from the electronic nose creates a "map" of non-specific signals that constitute the profile of the food product, also called olfactory fingerprints.

The goal is to find a relationship between the set of independent variables, resulted from the sensor, and the set of dependent variables, characteristics of the sample. Chemometrics software required for data set processing, in environmental and food sectors, allows to process the data by methods of multivariate analysis such as PCA (Principal Component Analysis), LDA (Linear Discriminant Analysis), PLS (Partial Least Square Analysis), DFA (Discriminant Function Analysis). As example the Principal Component Analysis (PCA) is a method for detecting patterns in data sets and express them in order to highlight their similarities and/or differences. Example of electronic nose applications, in the food sector, could be: to monitor of foodstuff shelf life, to check certified quality or the trademark DOP, to make microbiological tests, to check controlled atmosphere in the packaging, to control fermentation stage or to identify the presence of components of the packaging transferred in the product, or to verify the state of cleaning of kegs (on-line measures).

2.4 Chemometrics in food sector

Chemometrics is an essential part of NIR and Vis/NIR spectroscopy in food sector. NIR and Vis/NIR instrumentation in fact must always be complemented with chemometric analysis to enable to extract useful information present in the spectra separating it both from not useful information to solve the problem and from spectral noise. Chemometric techniques most used are the principal component analysis (PCA) as a technique of qualitative analysis of the data and PLS regression analysis as a technique to obtain quantitative prediction of the parameters of interest (Naes et al., 2002; Wold et al., 2001; Nicolai et al., 2007; Cen & He, 2007).

The developed models should be tested using independent samples as validation sets to verify model accuracy and robustness. To evaluate model accuracy, the statistics used were the coefficient of correlation in calibration (r_{cal}), coefficient of correlation in prediction (r_{pred}), root mean square error of calibration (RMSEC), and root mean square error of prediction (RMSEP).

Correlation coefficients (r_{cal} and r_{pred}):

$$r_{cal} \quad or \quad r_{pred} = \sqrt{1 - \frac{\sum_{i=1}^{n}\left(y_i - \hat{y}_i\right)^2}{\sum_{i=1}^{n}\left(y_i - \bar{y}\right)^2}} \tag{2}$$

where y_i are the reference values, $\hat{y}_i$ are the values predicted by the PLS model, and $\bar{y}$ is the averaged reference value.

Standard errors of calibration and prediction (RMSEC and RMSEP):

$$RMSEC \; or \; RMSEP = \sqrt{\frac{\sum_{i=1}^{n}\left(y_i - \hat{y}_i\right)^2}{n}} \tag{3}$$

where n is the number of validated objects, and $\hat{y}_i$ and y_i are the predicted and measured values of the ith observation in the calibration or validation set, respectively. This value gives the average uncertainty that can be expected for predictions of future samples. The optimum calibrations should be selected based on minimizing the RMSEP. Percent errors (RMSEC% and RMSEP%) could be also calculated as: RMSEC (%) = RMSEC/averaged reference values of each parameter.

Prediction capacity of a model can be evaluated with the ratio performance deviation (RPD) (Williams & Sobering, 1996). The RPD is defined as the ratio of the standard deviation of the response variable to the RMSEP. RPD value > 2.5 means that the model has good prediction accuracy.

3. Applications

3.1 NIR and Vis/NIR spectroscopy

During the last 50 years, there has been a lot of emphasis on the quality and safety of the food products, of the production processes, and the relationship between the two (Burns and Ciurczak, 2001).

Near infrared (NIR) spectroscopy has proved to be one of the most efficient and advanced tools for monitoring and controlling of process and product quality in food industry. A lot of work has been done in this area. This review focuses on the use of NIR spectroscopy for the analysis of foods such as meat, fruit, grain, dairy products, oil, honey, wine and other areas, and looks at the literature published in the last 10 years.

3.1.1 Fruit and vegetables

Water is the most important chemical constituent of fruits and vegetables and water highly absorbs NIR radiation, so the NIR spectrum of such materials is dominated by water. Further, the NIR spectrum is essentially composed of a large set of overtones and combination bands. This, in combination with the complex chemical composition of a typical fruit or vegetable causes the NIR spectrum to be highly convoluted. Multivariate statistical techniques are required to extract the information about quality attributes which is buried in the NIR spectrum. Developments in multivariate statistical techniques such as partial least squares (PLS) regression and principal component analysis (PCA) are then applied to extract the required information from such convoluted spectra (Cozzolino et al., 2006b; McClure, 2003; Naes et al., 2004; Nicolai et al., 2007;).

The availability of low cost miniaturised spectrophotometers has opened up the possibility of portable devices which can be used directly on field for monitoring the maturity of fruit.

Guidetti et al. (2008) tested a portable Vis/NIR device (450-980 nm) for the prediction of ripening indexes (soluble solids content and firmness) and presence of compounds with functional properties (total anthocyanins, total flavonoids, total polyphenols and ascorbic acid) of of blueberries ('Brigitta' and 'Duke' varieties). Good predictive statistics were obtained with correlation coefficients (r) between 0.80 and 0.92 for the regression models built for fresh berries (Table 3). Similar results were obtained for the regression models for homogenized samples with r > 0.8 for all the indexes. Results showed that Vis/NIR spectroscopy is an interesting and rapid tool for assessing blueberry ripeness.

Dependent variable	LV	Calibration		Cross validation	
		r_{cal}	RMSEC	r_{cv}	RMSECV
TSS (°Brix)	4	0.86	0.78	0.85	0.79
Young's Module (MPa)	3	0.87	0.65	0.87	0.66
Total anthocyanins (mg/g f. w.)	4	0.87	0.31	0.87	0.31
Total flavonoids (mg cat/g)	4	0.87	0.37	0.86	0.37
Total polyphenols (mg cat/g f. w.)	11	0.82	0.20	0.81	0.20
Ascorbic acid (mg/100 g f. w.)	4	0.84	1.01	0.83	1.02

Table 3. Results of PLS models for fresh 'Duke' berry samples (r = coefficient of correlation; RMSEC = root mean square of the standard error in calibration; RMSECV = root mean square of the standard error in cross-validation; LV = latent variables). All data were preprocessed by second derivative of reduced and smoothed data.

3.1.2 Meat

In literature there are numerous applications of NIR spectroscopy for the analysis of meat quality. One of the most important aim is to monitor the freshness of meat products. Sinelli et al. in 2010 investigated the ability of Near Infrared spectroscopy to follow meat freshness decay. PCA was applied by authors to the data and was able to discriminate samples on the basis of storage time and temperature. The modelling of PC scores versus time allowed the setting of the time of initial freshness decay for the samples (6–7 days at 4.3 °C, 2–3 days at 8.1 °C and less than 1 day at 15.5 °C). Authors reported that results showed the feasibility of NIR for estimating quality decay of fresh minced beef during marketing.

Sierra et al. in 2007 conducted a study for the rapid prediction of the fatty acid (FA) profile of ground using near infrared transmittance spectroscopy (NIT). The samples were scanned in transmittance mode from 850 to 1050 nm. NIT spectra were able to accurately predict saturated R^2=0,837, branched R^2=0,701 and monounsaturated R^2=0,852 FAs. Results were considered interesting because intramuscular fat content and composition influence consumer selection of meat products.

Andrés et al. in 2007 implemented a study to evaluate the potential of visible and near infrared reflectance (NIR) spectroscopy to predict sensory characteristics related to the eating quality of lamb meat samples. A total of 232 muscle samples from Texel and Scottish Blackface lambs was analyzed by chemical procedures and scored by assessors in a taste panel and these parameters were predicted from Vis/NIR spectra. The results obtained by authors suggested that the more important regions of the spectra to estimate the sensory characteristics are related to the absorbance of intramuscular fat and water content in meat samples.

Even in the meat industry have been tried online applications of NIR spectroscopy. A study was conducted by Prieto et al. in 2009a to assess the on-line implementation of visible and near infrared reflectance (Vis/NIR) spectroscopy as an early predictor of beef quality traits, by direct application of a fibre-optic probe to the muscle immediately after exposing the meat surface in the abattoir. Authors reported good correlation results only for prediction of colour parameters while less good results were achieved for sensory parameters.

NIR spectroscopy could be used for the detection of beef contamination from harmful pathogens and the protection of consumer safety. Amamcharla et al. in 2010 investigated the potential of Fourier transform infrared spectroscopy (FTIR) to discriminate the Salmonella contaminated packed beef. Principal component analysis was performed on the entire spectrum (4000–500 cm^{-1}). Authors obtained encouraging classification results with different techniques and confirmed that NIR could be used for non-destructive discrimination of Salmonella contaminated packed beef samples from uncontaminated ones.

A review published by Prieto et al. in 2009b indicates that NIR showed high potential to predict chemical meat properties and to categorize meat into quality classes. But authors underlined also that NIR showed in different cases limited ability for estimating technological and sensory attributes, which may be mainly due to the heterogeneity of the meat samples and their preparation, the low precision of the reference methods and the subjectivity of assessors in taste panels.

3.1.3 Grains, bread and pasta

Grains including wheat, rice, and corn are main agricultural products in most countries. Grain quality is an important parameter not only for harvesting, but also for shipping (Burns and Ciurczak, 2001). In many countries, the price of grain is determined by its protein content, starch content, and/or hardness, often with substantial price increments between grades.

Measurement of carotenoid content of maize by Vis/NIR spectroscopy was investigated by Brenna and Berardo (2004). They generated calibrations for several individual carotenoids and the total carotenoid content with good results (R^2 about 0,9).

Several applications can be found in literature regarding the use of NIR for the prediction of the main physical and rheological parameters of pasta and bread. De Temmerman et al. in 2007 proposed near-infrared (NIR) reflectance spectroscopy for in-line determination of moisture concentrations in semolina pasta immediately after the extrusion process. Several pasta samples with different moisture concentrations were extruded while the reflectance spectra between 308 and 1704 nm were measured. An adequate prediction model was developed based on the Partial Least Squares (PLS) method using leave-one-out cross-validation. Good results were obtained with $R^2 = 0,956$ and very low level of RMSECV. This creates opportunities for measuring the moisture content with a low-cost sensor.

Zardetto & Dalla Rosa in 2006 studied the evaluation of the chemical and physical characteristics of fresh egg pasta samples obtained by using two different production methodologies: extrusion and lamination. Authors evaluated that it is possible to discriminate the two kinds of products by using FT-NIR spectroscopy. FT-NIR analysis results suggest the presence of a different matrix–water association, a diverse level of starch gelatinization and a distinct starch–gluten interaction in the two kinds of pasteurised samples.

The feasibility of using near infrared spectroscopy for prediction of nutrients in a wide range of bread varieties mainly produced from wheat and rye was investigated by Sørensen in 2009. Very good results were reported for the prediction of total contents of carbohydrates and energy from NIR data with R^2 values of 0.98 and 0.99 respectively.

Finally, a quick, non-destructive method, based on Fourier transform near-infrared (FT-NIR) spectroscopy for egg content determination of dry pasta was presented by Fodor et al. (2011) with good results.

3.1.4 Wine

Quantification of phenolic compounds in wine and during key stages in wine production is therefore an important quality control goal for the industry and several reports describing the application of NIR spectroscopy to this problem have been published.

Grape composition at harvest is one of the most important factors determining the future quality of wine. Measurement of grape characteristics that impact product quality is a requirement for vineyard improvement and for optimum production of wines (Carrara et al., 2008). Inspection of grapes upon arrival at the winery is a critical point in the wine production chain (Elbatawi & Ebaid, 2006).

An optical, portable, experimental system (Vis/NIR spectrophotometer) for nondestructive and quick prediction of ripening parameters of fresh berries and homogenized samples of grapes in the wavelength range 450-980 nm was built and tested by Guidetti et al. (2010) (Fig. 9). Calibrations for technological ripening and for anthocyanins had good correlation coefficients ($r_{cv} > 0.90$). These models were extensively validated using independent sample sets. Good statistical parameters were obtained for soluble solids content (r > 0.8, SEP < 1.24 °Brix) and for titratable acidity (r > 0.8, SEP < 2.00 g tartaric acid L^{-1}), showing the validity of the Vis/NIR spectrometer. Similarly, anthocyanins could be predicted accurately compared with the reference determination (Table 4). Finally, for qualitative analysis, spectral data on grapes were divided into two groups on the basis of grapes' soluble content and acidity in order to apply a classification analysis (PLS-DA). Good results were obtained with the Vis/NIR device, with 89% of samples correctly classified for soluble content and 83% of samples correctly classified for acidity. Results indicate that the Vis/NIR portable device could be an interesting and rapid tool for assessing grape ripeness directly in the field or upon receiving grapes in the wine industry.

Fig. 9. Images of spectral acquisition phases on fresh berries and on homogenized samples.

Parameter	Pretreat-ment[a]	LV	Calibration		Validation	
			r	RMSEC	r	RMSEP
TSS (°Brix)	MSC+d2	5	0.93	0.95	0.75	0.95
Titratable acidity (g tart. acid dm^{-3})	MSC+d2	6	0.95	1.16	0.85	1.12
pH	MSC+d2	5	0.85	0.08	0.80	0.13
PA (mg dm^{-3})	MSC+d2	5	0.95	80.90	0.78	129.00
EA (mg dm^{-3})	MSC+d2	3	0.93	57.70	0.84	77.70
TP (OD 280 nm)	MSC+d2	4	0.80	3.74	0.70	5.81

[a] MSC = multiplicative scatter correction, and d2 = second derivative.

Table 4. Results of PLS models for homogenized samples.

The application of some chemometric techniques directly to NIR spectral data with the aim of following the progress of conventional fermentation and maturation was investigated by Cozzolino et al. (2006b). The application of principal components analysis (PCA) allowed similar spectral changes in all samples to be followed over time. The PCA loading structure could be explained on the basis of absorptions from anthocyanins, tannins, phenolics, sugar and ethanol, the content of which changed according to different fermentation time points. This study demonstrated the possibility of applying NIR spectroscopy as a process analytical tool for the wine industry.

Urbano-Cuadrado et al. (2004) analysed by Vis/NIR spectroscopy different parameters commonly monitored in wineries. Coefficients of determination obtained for the fifteen parameters were higher than 0.80 and in most cases higher than 0.90 while SECV values were close to those of the reference method. Authors said that these prediction accuracies were sufficient for screening purposes.

Römisch et al. in 2009 presented a study on the characterization and determination of the geographical origin of wines. In this paper, three methods of discrimination and classification of multivariate data were considered and tested: the classification and regression trees (CART), the regularized discriminant analysis (RDA) and the partial least squares discriminant analysis (PLS-DA). PLS-DA analysis showed better classification results with percentage of correct classified samples from 88 to 100%.

Finally, PLS and artificial neural networks (ANN) techniques were compared by Janik et al. in 2007 for the prediction of total anthocyanin content in redgrape homogenates.

3.1.5 Other applications

The applications of Vis/NIR and NIR spectroscopy and their chemometric techniques are present in many other sectors of the food industry. In literature are reported works relating to the dairy, oil, coffee, honey and chocolate industry. In particular, interesting studies have been conducted by some authors for the application of NIR spectroscopy in detecting the geographical origin of raw materials and finished products, defending the protected designation of origin (PDO).

Olivieri et al. (2011) worked out the exploration of three different class-modelling techniques to evaluate classification abilities based on geographical origin of two PDO food products: olive oil from Liguria and honey from Corsica. Authors developed the best models for both Ligurian olive oil and Corsican honey by a potential function technique (POTFUN) with values of correctly classified around 83%.

González-Martín et al. in 2011 presented a work on the evaluation by near infrared reflectance (NIR) spectroscopy of different sensorial attributes of different type of cheeses, taking as reference data the evaluation of the sensorial properties obtained by a panel of eight trained experts. NIR spectra were collected with a remote reflectance fibre optic probe applying the probe directly to the cheese samples and the calibration equations were developed by using modified partial least-squares (MPLS) regression for 50 samples of cheese. Authors stated that obtained results can be considered good and acceptable for all the parameters analyzed (presence of holes, hardness, chewiness, creamy, salty, buttery flavour, rancid flavour, pungency and retronasal sensation).

The quality of coffee is related to the chemical constituents of the roasted beans, whose composition depends on the composition of green beans (i.e., un-roasted). Unroasted coffee beans contain different chemical compounds, which react amongst themselves during coffee roasting influencing the final product. For this reason, monitoring the row materials and the roasting process is very important. Ribeiro et al. in 2011 elaborated PLS models correlating coffee beverage sensory data and NIR spectra of 51 Arabica roasted coffee samples. Acidity, bitterness, flavour, cleanliness, body and overall quality of coffee beverage were considered. Results were good and authors confirmed that it is possible to estimate the quality of coffee using PLS regression models obtained by using NIR spectra of roasted Arabica coffees.

Da Costa Filho in 2009 elaborated a rapid method to determine sucrose in chocolate mass using near infrared spectroscopy. Data were modelled using partial least squares (PLS) and multiple linear regression (MLR), achieving good results (correlation coefficient of 0.998 and 0.997 respectively for the two chemometric techniques). Results showed that NIR can be used as rapid method to determine sucrose in chocolate mass in chocolate factories.

3.2 Image analysis

The chemical imaging spectroscopy is applied to various fields, from astronomy to agriculture (Baranowski et al., 2008, Monteiro et al., 2007, V. Smail, 2006), from the pharmaceutical industry (Lyon et al. 2002, Roggo et al., 2005) to medicine (Ferris et al. 2001, Zheng et al., 2004). But in recent years, has also found use for quality control and safety in food (Gowen et al., 2007b).

In general, classify or quantify the presence of compounds in a sample is the main purpose of the application in the food hyperspectral analysis. There already exist algorithms for classification and regression but, improved algorithms efficiency, could be a target, as well as create datasets, identify anomalies or objects with different spectral characteristics, compared hyperspectral image with those of data library. These goals can be achieved only if the experimental data are processed with chemometric methods. K-nearest neighbors and hierarchical clustering are examples of multivariate analysis that allow to get information from spectral and spatial data (Burger & Gowen, 2011). With the use of spectral image, which allows to obtain in a single determination, spectral and spatial information characterizing the sample, it is possible to identify which chemical species are present and how they are distributed in a matrix. Several chemometric techniques are available for the development of regression models (for example partial least squares regression, principal components regression, and linear regression) capable of estimating the concentrations of constituents in a sample, at the pixel level, allowing the spatial distribution or the mapping of a particular component in the sample analyzed. Moreover the hyperspectral image, combined with chemometric technique, is a powerful method to identify key wavelengths in order to develop of multispectral system, for on-line applications.

Karoui & De Baerdemaeker (2006) wrote a review about the analytical methods coupled with chemometric tools for the determination of the quality and identity of dairy products. Spectroscopic techniques (NIR, MIR, FFFS front face fluorescence spectroscopy, etc.), coupled with chemometric tools have many potential advantages for the evaluation of the identity dairy products (milk, ice cream, yogurt, butter, cheese, etc).

In another review Sankaran et al. (2010), compared the benefits and limitations of advanced techniques and multivariate methods to detect plant diseases in order to assist in monitoring health in plants under field conditions. These technologies include evaluation of volatile profiling (Electronic Nose), spectroscopy (fluorescence, visible and infrared) and imaging (fluorescence and hyperspectral) techniques for disease detection.

In literature it's possible find several examples of applications of spectroscopic image analysis. Hyperspectral imaging could be used as critical control points of food processing to inspect for potential contaminants, defects or lesions. Their absence is essential for ensuring food quality and safety. In some case the application on-line was achieved.

Ariana & Lu (2010), evaluated the internal defect and surface color of whole pickles, in a commercial pickle processing. They used a prototype of on-line hyperspectral imaging system, operating in the wavelength range of 400–1000 nm. Color of the pickles was modeled using tristimulus values: there were no differences in chroma and hue angle of good and defective pickles. PCA was applied to the hyperspectral images: transmittance images at 675–1000 nm were much more effective for internal defect detection compared to reflectance images for the visible region of 500–675 nm. A defect classification accuracy was of 86% compared with 70% by the human inspectors.

Mehl et al. (2002), used hyperspectral image analysis and PCA, like chemometrics technique, to reduce the information resulting from HIS and to identify three spectral bands capable of separating normal from contaminated apples. These spectral bands were implemented in a multispectral imaging system. On 153 samples, it's possible to get a good separation between normal and contaminated (scabs, fungal, soil contaminations, and bruises) apples was obtained for Gala (95%) and Golden Delicious (85%), separations were limited for Red Delicious (76%).

HSI application for damage detection on the caps of white mushrooms (Agaricus bisporus) was investigated from Gowen et al. (2007a). They employed a pushbroom line-scanning HSI instrument (wavelength range: 400–1000 nm). They investigated two data reduction methods. In the first method, PCA was applied to the hypercube of each sample, and the second PC (PC 2) scores image was used for identification of bruise-damaged regions on the mushroom surface. In the second method PCA was applied to a dataset comprising of average spectra from regions normal and bruise-damaged tissue. The second method performed better than the first when applied to a set of independent mushroom samples. Further, they (Gowen et al., 2009) identified mushrooms subjected to freeze damage using hyperspectral imaging. In this case they used Standard Normal Variate (SNV) transformation to pretreat the data, then they applied a procedure based on PCA and LDA to classify spectra of mushrooms into undamaged and freeze-damaged groups. The undamaged mushrooms and freeze-damaged mushrooms could be classified with high accuracy (>95% correct classification) after only 45 min thawing (at 23 ± 2 °C) at that time freeze–thaw damage was not visibly evident.

A study on fruits and vegetables (Cubero et al., 2010) used ultraviolet or near-infrared spectra to explore defects or features that the human eye is unable to see, with the aim of applying them for automatic inspection. This work present a summary of inspection systems for fruit and vegetables and the latest developments in the application of this technology to the inspection of internal and external quality of fruits and vegetables.

Li et al. (2011) detected common defects on oranges using hyperspectral (wavelength range: 400-1000) reflectance imaging. The disadvantage of studied algorithm is that it could not discriminate between different types of defects.

Bhuvaneswari et al. (2011) compared three methods (electronic speck counter, acid hydrolysis and flotation and near-infrared hyperspectral imaging) to investigate the presence of insect fragments (Tribolium castaneum_ Coleoptera: Tenebrionidae) in the semolina (ingredient for pasta and couscous). NIR hyperspectral imaging is a rapid, non-destructive method, as electronic speck counter, but they showed different correlation between insect fragments in the semolina and detection of specks in the samples: $R^2 = 0.99$ and 0.639-0.767 respectively. For NIR hyperspectral image technique, the prediction model were developed by PLS regression.

The most important features in meat are tenderness, juiciness and flavour. Jackmana et al., (2011) wrote a review about recent advances in the use of computer vision technology in the quality assessment of fresh meats. The researcher support that the best opportunities for improving computer vision solutions is the application of hyperspectral imaging in combination with statistical modelling. This synergy can provide some additional information on meat composition and structure. However, in parallel, new image processing algorithms, developed in other scientific disciplines, should be carefully considered for potential application to meat images.

Other applications concern the possibility of estimating a correlation between characteristics (physical or chemical) of the food and the spectra acquired with spectroscopic image. Moreover these techniques were able to locate and quantify the characteristic of interest within the image.

In most cases the range of wavelength used in applications of hyperspectral images is 400-1000 nm but Maftoonazad et al. (2010) used artificial neural network (ANN) modeling of hyperspectral radiometric (350-2500 nm) data for quality changes associated with avocados during storage. Respiration rate, total color difference, texture and weight loss of samples were measured as conventional quality parameters during storage. Hyperspectral imaging was used to evaluate spectral properties of avocados. Results indicated ANN models can predict the quality changes in avocado fruits better than the conventional regression models.

While Mahesh et al. (2011) used near-infrared hyperspectral images (wavelength range: 960–1700 nm), applied to a bulk samples, to classify the moisture levels (12, 14, 16, 18, and 20%) on the wheat. Principal components analysis (PCA) was used to identify the region (1260–1360 nm) with more information. The linear and quadratic discriminant analyses (LDA) and quadratic discriminant analysis (QDA) could classify the sample based on moisture contents than also identifying specific moisture levels with a god levels of accuracy (61- 100% in several case). Spectral features at key wavelengths of 1060, 1090, 1340, and 1450 nm were ranked at top in classifying wheat classes with different moisture contents.

Manley et al. (2011) used near infrared hyperspectral imaging combined with chemometrics techniques for tracking diffusion of conditioning water in single wheat kernels of different hardnesses. NIR analysers is a commonly, non-destructive, non-contact and fast solution for quality control, and a used tool to detect the moisture-content of carrot samples during storage but Firtha (2009) used hyperspectral system that is able to detect the spatial

distribution of reflectance spectrum as well. Statistical analysis of the data has shown the optimal intensity function to describe moisture-content.

The intent of Junkwon et al. (2009), was to develop a technique for weight and ripeness estimation of palm oil (Elaeis guieensis Jacq. var. tenera) bunches by hyperspectral and RGB color images. In the hyperspectral images, the total number of pixels in the bunch was also counted from an image composed of three wavelengths (560 nm, 680 nm, and 740 nm), while the total number of pixels of space between fruits was obtained at a wavelength of 910 nm. Weight-estimation equations were determined by linear regression (LR) or multiple linear regression (MLR). As a result, the coefficient of determination (R^2) of actual weight and estimated weight were at a level of 0.989 and 0.992 for color and hyperspectral images, respectively. About the estimation of palm oil bunch ripeness the bunches was classified in 4 classes of ripeness (overripe, ripe, underripe, and unripe) (Fig. 10). Euclidean distances between the test sample and the standard 4 classes of ripeness were calculated, and the test sample was classified into the ripeness class. In the classification based on color image, (average RGB values of concealed and not-concealed areas), and by hyperspectral images (average intensity values of fruits pixels from the concealed area), the results of validation experiments with the developed estimation methods indicated acceptable estimation accuracy.

Fig. 10. Bunches of palm oil: a) unripe, b) underripe, c) ripe, and d) overripe (Junkwon et al., 2009)

Nguyen et al. (2011) illustrated the potential of combination of hyperspectral imaging chemometrics and image processing as a process monitoring tool for the potato processing industry. They predicted the optimal cooking time by hyperspectral imaging (wavelength range 400–1000 nm). By partial least squares discriminant analysis (PLS-DA), cooked and raw parts of boiled potatoes, were discriminated successfully. By modeling the evolution of the cooking front over time the optimal cooking time could be predicted with less than 10% relative error.

Yu H. & MacGregor J.F. (2003) applied multivariate image analysis and regression for prediction of coating content and distribution in the production of snack foods. Elaboration tools based on PCA and PLS was used for the extraction of features from RGB color images and for their use in predicting the average coating concentration and the coating distribution. On-line and off-line imaging were collected from several different snack food product lines and were used to develop and evaluate the methods. The better methods are now being used in the snack food industry for the on-line monitoring and control of product quality.

Siripatrawan et al. (2011) have developed a rapid method for the detection of *Escherichia coli* contamination in packaged fresh spinach using hyperspectral imaging (400–1000 nm) and chemometrics techniques. The PCA was implemented to remove redundant information of the hyperspectral data and artificial neural network (ANN) to correlate spectra with number of E. coli and to construct a prediction map of all pixel spectra of an image to display the number of E. coli in the sample.

In this study (Barbin et al. 2011) a hyperspectral imaging technique (range from 900 to 1700 nm) was developed to achieve fast, accurate, and objective determination of pork quality grades. The sample investigated were 75 pork cuts of *longissimus dorsi* muscle from three quality grades. Six significant wavelengths (960, 1074, 1124, 1147, 1207 and 1341 nm) that explain most of the variation among pork classes were identified from 2nd derivative spectra. PCA was carried out and the results indicated that pork classes could be precisely discriminated with overall accuracy of 96%. Algorithm was developed to produce classification maps of the investigated sample.

Valous et al. (2010) communicated perspectives and aspects, relating to imaging, spectroscopic and colorimetric techniques on the quality evaluation and control of hams. These no-contact and no-destructive techniques, can provide useful information regarding ham quality. Hams are considered a heterogenic solid system: varying colour, irregular shape and spatial distribution of pores. Fat-connective tissue, water, protein contribute to the microstructural complexity. This review paying attention on applications of imaging and spectroscopy techniques, for measuring properties and extracting features that correlate with ham quality.

In literature is present a review (Mathiassena et al., 2011) that focused the attention on application of imaging technologies (VIS/NIR imaging, VIS/NIR imaging spectroscopy, planar and computed tomography (CT) X-ray imaging, and magnetic resonance imaging) to inspection of fish and fish products.

Nicolai et al. (2007) wrote a review about the applications of non-destructive measurement of fruit and vegetable quality. Measurement principles are compared, and novel techniques (hyperspectral imaging) are reviewed. Special attention is paid to recent developments in portable systems. The problem of calibration transfer from one spectrophotometer to another is introduced, as well as techniques for calibration transfer. Chemometrics is an essential part of spectroscopy and the choice, of corrected techniques, is primary (linear or nonlinear regression, such as kernel-based methods are discussed). The principal objective of spectroscopy system applications in fruit and vegetables sector have focused on the nondestructive measurement of soluble solids content, texture, dry matter, acidity or disorders of fruit and vegetables. (root mean square error of prediction want to be achieved).

3.3 Electronic nose

The preservation of quality in post-harvest is the prerequisite for agri-food products in the final stages of commercialization. The fruit quality is related to the appearance (skin color, size, shape, integrity of the fruit), to the sensorial properties (hardness and crispness of the flesh, juicy, acid/sugars) and to safety (residues in fruit).

The agri-food products contain a variety of information, directly related to their quality, traditionally measured by means of tedious, time consuming and destructive analysis. For this reason, there is a growing interest in easy to use, rapid and non-destructive techniques useful for quality assessment.

Currently, electronic noses are mainly applied in the food industry to recognize the freshness of the products, the detection of fraud (source control, adulteration), the detection of contaminants.

An essential step in the analysis with an electronic nose, is the high performance of statistical elaboration. The electronic nose provides multivariated results that need to be processed using chemometric techniques. Even if the best performing programs are sophisticated and, consequently, require the operation of skilled personnel, most companies have implemented user-friendly software for data treatment in commercially available electronic noses (Ampuero & Bosset, 2003).

A commercial electronic nose, as a non-destructive tool, was used to characterise peach cultivars and to monitor their ripening stage during shelf-life (Benedetti et al. 2008). Principal component analysis (PCA) and linear discriminant analysis (LDA) were used to investigate whether the electronic nose was able to distinguish among four diverse cultivars. Classification and regression tree (CART) analysis was applied to characterise peach samples into the three classes of different ripening stages (unripe, ripe, over-ripe). Results classified samples in each respective group with a cross validation error rate of 4.87%.

Regarding the fruit and vegetable sector Torri et al. (2010) investigated the applicability of a commercial electronic nose in monitoring freshness of packaged pineapple slices during storage. The obtained results showed that the electronic nose was able to discriminate between several samples and to monitor the changes in volatile compounds correlated with quality decay. The second derivative of the transition function, used to interpolate the PC1 score trend versus the storage time at each temperature, was calculated to estimate the stability time.

Ampuero and Bosset (2003), presented a review about the application of electronic nose applied to dairy products. The present review deal with as examples the evaluation of the cheese ripening, the detection of mould in cheese, the classification of milk by trademark, by fat level and by preservation process, the classification and the quantification of off-flavours in milk, the evaluation of Maillard reactions during heating processes in block-milk, as well as the identification of single strains of disinfectant–resistant bacteria in mixed cultures in milk. For each application correspond the chemometric method to extrapolate the maximum information. PCA analysis was carried out in order to associate descriptors (chocolate, caramel, burnt and nutty), typical of volatiles generated by Maillard reactions during milk heating. In another case PCA showed a correctly classification of sample in function of the origin of off-flavours. In figure 11 is showed an example of result carried out by DFA

(discriminant function analysis) statistical technique. In this case the aim of researcher was to classify samples of a given product by their place of production.
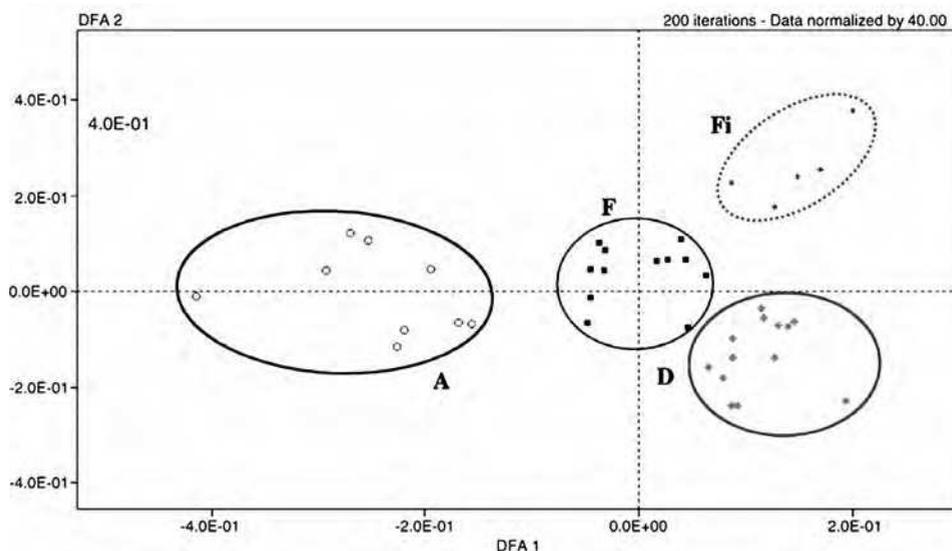

Fig. 11. Classification of Emmental cheese by the geographic origin performed with an electronic nose based on mass spectrometry. The graph shows DFA 1 vs. DFA 2 with 100% group classification based on five variables. No validation set was considered due to the limited number of samples. A: Austria, D: Germany, F: France, Fi: Finland (Pillonel et al, 2003)

The potential of electronic nose technique was investigated to monitoring storage time and the quality attribute of eggs by Yongwei et al. (2009). Using techniques of multivariate analysis was distinguished eggs under cool and room-temperature storage. Results showed that the E-nose could distinguish eggs of different storage time under cool and room-temperature storage by LDA, PCA, BPNN and GANN. Good distinction between eggs stored for different times were obtained by PCA and LDA (results by LDA were better than those obtained by PCA). By means BP neural network (BPNN) and the combination of a genetic algorithm and BP neural network (GANN) carried out good predictions for egg storage time (GANN demonstrated better correct classification rates than BPNN). The quadratic polynomial step regression (QPSR) algorithm established models that described the relationship between sensor signals and egg quality indices (Haugh unit and yolk factor). The QPST models showed an high predictive ability (R^2 = 0.91-0.93).

Guidetti et al. (2011) used electronic nose and infrared thermography to detect physiological disorders on apples (Golden Delicious and Stark Delicious). In particular the aim was to differentiate typical external apple diseases (in particular, physiological, pathological and entomological disorders). The applicability of the e-nose is based on the hypothesis that apples affected by physiopathology produce different volatile compounds from those produced by healthy fruits. The electronic nose data were elaborated by LDA

in order to classify the apples into the four classes. Figure 12 shows how the first two LDA functions discriminate among classes. Considering Stark variety, function 1 seems to discriminate among the physiopathologies while function 2 discriminate the healthy apples from those with physiological disorders. The error rate and the cross validation error rate were of 2.6% and 26.3% respectively. In the case of Golden variety, along the first function there is the separation of Control samples from the apples affected by diseases, while in the vertical direction (function 2) there is an evident discrimination among the three physiopathologies. The error rate and the cross validation error rate were of 0.8% and 18% respectively.

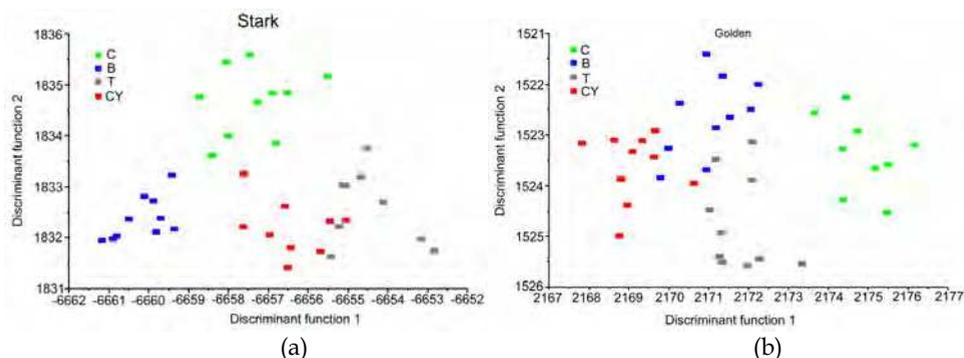(a)   (b)

Fig. 12. a) Canonical discriminant functions of LDA for Stark variety; b) Canonical discriminant functions of LDA for Golden variety. C=control, B=bitter pit, T=scab and CY=Cydia Pomonella.

Cerrato Oliveros et al. (2002) selected array of 12 metal oxide sensors to detected adulteration in virgin olive oils samples and to quantify the percentage of adulteration by electronic nose. Multivariate chemometric techniques such as PCA were applied to choose a set of optimally discriminant variables. Excellent results were obtained in the differentiation of adulterated and non-adulterated olive oils, by application of LDA, QDA. The models provide very satisfactory results, with prediction percentages >95%, and in some cases almost 100%. The results with ANN are slightly worse, although the classification criterion used here was very strict. To determine the percentage of adulteration in olive oil samples multivariate calibration techniques based on partial least squares and ANN were employed. Not so good results were carried out, even if there are exceptions. Finally, classification techniques can be used to determine the amount of adulterant oil added with excellent results.

4. Conclusion

This work shows the principal non-destructive applications for analysis in food sector. They are rapid techniques used in combination with chemometrics analysis for qualitative and quantitative analysis.

NIR spectroscopy is the technique that has been developed further in recent years. This success is because spectral measurement for one sample could be done in a few seconds. Numerous samples could be analyzed and multiindexes analysis can be carried out.

Compared with traditional methods, NIR and Vis/NIR are less expensive because of no demand of other materials such as chemical reagents except the electrical consumption. Many works are focused on the study of chemometrics. This is because an important challenge is to build robust calibration models, in fact it is important to apply chemometric methods able to select useful information from a great deal of spectral data. Moreover food researchers and analysts are looking for the sensitive wavelength in Vis/NIR region representing the characteristics of food products, with the aim of develop some simple and low-cost instruments (Cen & He, 2007).

HSI is the new frontier for optical analysis of foods. The performance of HSI instrumentation has developed such that a full hypercube can now be acquired in just a few seconds. In tandem with these developments, advances in component design have led to reductions in the size and cost of HSI systems. This has led to increased interest in their online implementation for quality monitoring in major industries such as food and pharmaceutical (Burger & Gowen, 2011). In future, with further improvement, the HSI system could meet the need of a commercial plant setting.

The equipment that the food industry has at its disposal is certainly complex and not easy to use. The chemometric approach has allowed, through different applicative researches, to arrive at algorithms that can support the analysis in the entire food chain from raw material producers to large retail organizations. Despite this, we are still faced with instrumentation with not easy usability and relatively high cost: the studies must move towards a more simplified instrumental approach through greater integration of hardware with software. The challenges are many: optimizing the information that you are able to extract from raw data and aimed at specific problems, simplify electronic components, increase the level of interaction tool/operator.

In conclusion the only way of an interdisciplinary approach can lead to the solution of a system that can provide at different level more immediate response and more food safety and quality.

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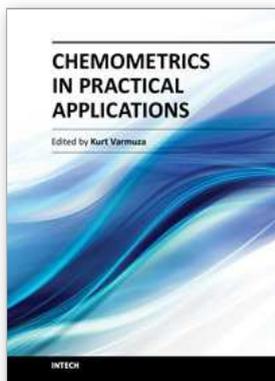
Chemometrics in Practical Applications

Edited by Dr. Kurt Varmuza

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