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The Use of Non-destructive Methods to Analyse Fruit Quality

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ABSTRACT

This article is divided into three parts. The first part, the most important one, deals with spectroscopic methods. Different regions of the electromagnetic spectrum are useful for fruit quality characterisation, in particular the visible and near-infrared regions. Concerning the visible one, studies have been carried out on apple, apricot, cherry, mango, peach, red table grape and tomato, when the near-infrared one has been used on apple, apricot, bayberry, citrus, kiwi, lemon, mango, peach, pear, red bell pepper and tomato. Results of other spectroscopic methods such as time-domain reflectance spectroscopy, multi- and hyperspectral imaging, fluorescence, nuclear magnetic resonance and magnetic resonance imaging were obtained on apple, grape berry, kiwifruit, mandarin, olive, papaya, peach, pear, plum and tomato. The second part concerns the studies of mechanical properties based on impact, acoustic and ultrasonic responses, which were developed and tested on apple, avocado, peach, pear, plum, tomato and watermelon. The third part presents the analysis of volatile compounds using the principle of electronic nose applied on apple, mandarin, peach, pear and tomato. According to the researched fruit quality traits, the adequate methods will be different for the assessment of colour, firmness, soluble solids or volatiles or for the detection of internal defects like brown heart. However, methods are developed to improve the fruit management and thus the general fruit quality for consumers.

Keywords: acoustic, electronic nose, intact samples, spectroscopy, ultrasonic

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INTRODUCTION

Quality of fruits is a complex multicriteria concept defined not only by sensory attributes such as appearance, texture and taste but also by compositional characteristics, nutritional properties, ability to undergo storage and absence of defects. The quality is evaluated by many participants of the fruit production chain, each having different quality criteria and requirements. Whereas production yield, orchard management and disease resistance interest growers, the fruit freshness and durability are the main needs for distributors. Consumers use their five senses to evaluate fruit quality. Sight and touch are important for purchase decision, and the internal characteristics perceived by smell, taste and mouth-feel will determine the decision to repurchase (Butz *et al*. 2005). According to a preference mapping recently performed on several apple cultivars from US consumer hedonic responses, the first preference dimension and firmness evaluated by a penetrometer were significantly correlated (Harker *et al.* 2008). Firmness is thus reaffirmed to be an important driver of consumer preference for apples in the USA. The sugar content and acidity play a significant role but depending on the cultivars and fruit firmness.

The fruit quality within plant species presents important variations depending on 1) the genetic effect with the variability of quality traits such as biochemical composition (sugars, pigments, phenolic and aroma compounds...) and physiological behaviour (ethylene production, respiration rate) observed between genotypes or cultivars and 2) the physiological effect with the change of these quality traits during fruit growth, ripening and post-harvest period. Hobson and Grierson (1993) described the ripening-related changes in tomato including the changes in colour, texture, flavour, taste and aroma. Recent reviews (Cara and Giovannoni 2008; Pech *et al.* 2008) present the co-existence of ethylene-dependent and independent processes in ripening of climacteric fruits. Climacteric fruits such as melon and tomato are characterized by a ripening-related increase in respiration and elevated ethylene synthesis to rapidly coordinate and synchronize ripening. It has been observed in melon that pulp coloration, accumulation of sugars and loss of acidity were ethylene independent, whereas yellowing of

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the rind, softening of the flesh, development of peduncular abscission zone, aroma formation and climacteric respiration were totally or partially ethylene-dependent. In tomato, the best characterized ethylene regulated fruit genes have been involved in ethylene synthesis, softening, carotenoid biosynthesis responsible for the fruit coloration. Moreover, with lesser importance, the fruit quality is dependent on environment in which plant is grown, cultural practices and post-harvest fruit management (Hobson and Grierson 1993). In relation with these causes of fruit variability, the development of prediction methods for fruit characterization can be considered according to two approaches. Firstly, methods can be developed on a homogeneous sample (single genetic background, same environment and agricultural practices), and the prediction of some quality traits such as a maturity index will be possible from the other measured traits using internal correlations. Secondly, methods can be developed on a heterogeneous sample (several varieties, different maturity stages, different environment conditions), and as the large variability will decrease or eliminate internal correlations, prediction methods will be really based on measured criteria. Whereas models based on a single cultivar and fairly homogeneous growth conditions may be useful for the growers to define the optimal date of harvesting, they lack robustness and portability and are restricted to this single variety. Models developed on a wide range of fruit varieties usually give less predictive precision but gain robustness and portability.

Instrumental measurements are preferred over sensory evaluation for many applications. Objective measurements allow reduction of the variability encountered with human inspection. A very large number of quality traits can be evaluated to characterise the fruit quality including external criteria like weight, diameter, firmness, colour, and internal criteria like soluble solids, titratable and total acidity, individual sugars and organic acids, starch, pigments (chlorophylls, carotenoids, anthocyanins), vitamins, volatile and glycoconjugated aroma molecules, phenolic compounds, ethylene production and respiratory activity, detection of defects... In apple, a combination of several traits is commonly used for determining the optimal harvesting date or the optimal storage conditions. It corresponds to the Streif-Index coefficient, the ratio between firmness versus soluble solids content per starch content. The fruit quality traits and particularly the internal criteria are usually characterised using destructive instrumental methods.

A large variability exists among fruits of the same tree and orchard partly due to different environmental conditions and physiological fruit states. Therefore a number of fruits sufficient to obtain representative data must be analysed for a good evaluation of the studied quality traits. Sorting is necessary to segregate fruits in homogeneous classes and to ensure a uniform quality. Sorting requires high-speed, non-destructive methodology and the possibility to measure several attributes for each fruit. According to Butz *et al.* (2005), among the 66,000 items found by an internet search for the keywords "non-destructive" or "non-invasive" in food context, 50% correspond to vision-based methods and the other 50% are equally separated between acoustic and spectroscopic methods. This present article is limited to fruit quality analysis using non-destructive methods and will focused on work published over the past five years approximately between the review of Butz *et al.* (2005) and the beginning of the year 2009. It is divided in three parts with the first concerning the spectroscopic methods including visible and near-infrared spectroscopy, fluorescence, nuclear magnetic resonance and magnetic resonance imaging, the second concerning the measurements of mechanical properties and the third concerning the electronic nose technology.

SPECTROSCOPIC METHODS

Spectroscopic methods are based on the interactions between electromagnetic radiations and tissues. The electromagnetic spectrum spans the wide range from γ-rays (emitted by radioactive materials) having wavelengths on the order of 10^{-12} m, through X-rays, ultraviolet, visible, infrared, microwave and finally radio waves with wavelengths as long as 10^3 m. The wavelength ranges commonly used for fruit quality analysis are the visible light covering the wavelength range of approximately 400 to 800 nm, the ultraviolet between 4 and 400 nm and near infrared between 750 to 2500 nm.

When a light beam reaches the fruit, several phenomena happen such as reflection, absorption, transmission and scattering of light by the fruit. According to Birth (1976), only about 4% of the incident radiation is reflected at the outer surface as specular reflectance or gloss. The rest of radiation (96%) penetrates the tissue in different directions where it is absorbed by constituents or scattered by small interfaces within the tissue. The depth of penetration in fruits varies according to the wavelength and the light energy. The light penetration depth defined as the depth at which the incident light was reduced by 99%, was estimated with a minimum (less than 1.38 cm) generally identified at wavelength of absorption peaks of the major pigments (535 nm for anthocyanins and 675 for chlorophyll) and a maximum (between 1.83 and 6.52 cm) occurring at different spectral regions according to the plant materials (Qin and Lu 2008). Light absorption is related to chemical structures of constituents in the fruit. The major absorbers in the visible wavelength range are the pigments such as chlorophylls, carotenoids, anthocyanins whereas water is the major absorber in the near-infrared region. Light that penetrates deeper in tissues is modified by the selected absorptions of constituents and thus contains useful compositional information.

Visible spectrum

1. Visible spectroscopy

Within the visible light, the major absorbers are pigments: chlorophylls, carotenoids and anthocyanins in relation with their structural characteristics and in particular their conjugated double bond system, alternating single and double bonds. Chlorophylls are a porphyrin pigment with a phytol chain. Carotenoids are characterised by a 40-carbon polyene chain, oxygenated (xanthophylls) or not (carotenes). Anthocyanins are derivatives of the flavylium cation.

The development of a non-destructive technique for pigment assessment was based on the light reflectance measurement at different wavelengths in the visible region (Merzlyak *et al.* 2003). Five apple cultivars with a wide range of peel pigments (chlorophylls *a* and *b*, carotenoids, anthocyanins) were used. Non-destructive assessment of pigments in apple peel is complicated by two difficulties including the overlapping light absorption by individual pigments and the non-linear relationship of reflectance versus pigment content in the bands of strong absorption. Two indices R_{800}/R_{700} and R_{800}/R_{640} have been shown to have a high correlation with chlorophyll content (r^2=0.93) in a wide range of pigment variation for all cultivars. The index in the form $R_{800}(1/R_{520}-1/R_{700})$ has a linear correlation (r^2=0.80) with carotenoid content providing reliable assessment of carotenoid ranging from 0.6 to 4.5 nmol/cm^2. And, the index in the form $R_{800}(1/R_{550}-1/R_{700})$, is suggested for anthocyanin estimation. This index is closely correlated (r^2=0.93) with anthocyanin ranging from 2.5 to 50 nmol/cm^2. This non-destructive method was used to study the changes in total chlorophyll and carotenoid contents in apple peel during on- and off-tree ripening (Solovchenko *et al.* 2005). A model taking on-tree chlorophyll contents as the only input was thus developed for the prediction of the ripening-associated changes in carotenoid content (r^2≈0.81) and carotenoid-to-chlorophyll molar ratio (r^2≈0.96). Another index, flavonol reflectance index (FRI) was suggested for the evaluation of apple flavonol content in the form $R_{800}/R_{410}-R_{800}/R_{460}$ (Merzlyak *et al.* 2005). FRI was linearly correlated (r^2=0.92) with the flavonol content between 8 and 220 nmol/cm^2. Expressions have been developed for evaluating the chlorophyll and anthocyanin concentrations in apple as normalised differential vegetation index (NDVI= $(I_{780}-I_{660})/(I_{780}-I_{660})$) for chlorphyll and as normalised anthocyanin index (NAI=$(I_{780}-I_{570})/(I_{780}-I_{570})$) for anthocyanin (Solomakhin and Blank 2007). The NDVI index displayed very good correlation with chlorophyll content in 'Golden delicious' and 'Jonagold' apples (r between 0.89 and 0.92) (Kuckenberg *et al.* 2008). Moreover, in order to monitor the peach ripening, Ziosi *et al.* (2008) have developed a non-destructive index using two wavelengths, 670 nm near the chlorophyll-a absorption peak and 720 nm the background of the spectrum, as $I_{AD}=A_{670}-A_{720}$. This index might be a marker of peach ripening because, in different years, the three stages defined according to ethylene emission level, class 0 for pre-climacteric, class 1 for onset of climacteric, and class 2 for full climacteric occurred in the same I_{AD} ranges. This study shows the potential of a non-destructive method for monitoring the fruit maturity only in the two well-characterized cultivars, 'Stark Red Gold' and 'Laura'. The partial light transmittance between 500 to 1000 nm was tested on 'Elstar' apples using a portable apparatus equipped with a glass-fibre probe (Herold *et al.* 2005). This technique presents a relative independence of environmental conditions and fruit properties in comparison with the total light reflectance. Three indices were calculated from spectral data to study the decreasing chlorophyll content and increasing anthocyanin content during pre-harvest and harvest periods.

2. Colour

Among sensory attributes traditionally used for fruit quality evaluation, colour plays an important role. It notably gives visual information to consumers of fruit appearance. Fruit colour varies during ripening from greens to yellows, oranges, reds or dark violets depending on the pigments such as chlorophylls (green), carotenoids (orange, red) or anthocyanins (red, violet). Colour is measured objectively using colorimeters, which are spectrophotometers taking into account the sensitivity of the human eyes. Colorimeters thus measure light in terms of a tristimulus colour space, restricted to visible light (400-800 nm). The human eye has three sets of sensors with peak sensitivities at 580 nm for red, 540 nm for green and 450 nm for blue. Any light wavelengths in the visual spectrum range from 400 to 700 nm will excite one or more of these three types of sensors. Colour can be described in several colour coordinate systems and among the most popular, there are RGB (red, green and blue), HunterLab and L*a*b* (Abbott 1999; Butz *et al.* 2005). The CIELAB or L*a*b* colour space (Commission Internationale de l'Eclairage 1986) is extensively used to evaluate fruit colours. The L*, a* and b* values describe a uniform three-dimensional colour space, where L* is the lightness or luminance component that goes from 0 (black) to 100 (white). The parameters a* (green to red) and b* (blue to yellow) are the two chromatic components varying between –60 and +60. In this system, the hue angle (H°) and the chroma (C) are defined as H°=arctg(b*/a*) (in degrees) and $C^*=[a^{*2}+b^{*2}]^{0.5}$. Some authors have used directly these colour coordinates to predict pigment contents. In a wide collection of apricot fruits, hue angle has been shown to be well-correlated with total carotenoid content in the flesh (r=0.92) and in the skin (r=0.84) (Ruiz *et al.* 2005). Moreover, with a logarithm transformation of carotenoid data and partial least squares (PLS) regression, the prediction of β-carotene and total carotenoid content was possible in apricot peel and flesh using the L*, H°, C* parameters (r ranged from 0.82 to 0.95 with low prediction errors) (Ruiz *et al.* 2008). Concerning anthocyanins, a negative correlation was observed between the anthocyanin concentration which increases in cherries of four cultivars during storage period at 1.5 ± 0.5°C and 15 ± 5°C and the colour parameters (L*, a*, b*, chroma and hue angle) (Gonçalves *et al.* 2007). The phenomenon whereby the anthocyanin content increases and the L*, a* and b* values decrease is presumed to occur when the increase of pigment content darkens the fruit and increases the chroma. The best fit was found between the anthocyanin content and colour parameters in cherries having less than 100 mg/100g of total anthocyanins. In 'Gala' apples, during pre- and post-harvest periods, the hue angle appears to be negatively well-correlated with anthocyanin content (r^2=0.74) (Iglesias *et al.* 2008). Chromatic parameters can be a good tool for a rapid, cheap and non-destructive prediction of pigments such as anthocyanins and carotenoids.

These coordinates can also be combined in various combinations and equations. For example, Carreno *et al.* (1995) have developed the CIRG index = (180-H)/(L*+C). It allows the significant discrimination between five groups of red table grapes during ripening with variation from 1.55 (yellow), 2.49 (pink), 3.66 (red), 4.75 (violet) to 5.57 (dark violet). The a*/b* ratio has been used for predicting the lycopene content in tomatoes (Arias *et al.* 2000) and the anthocyanins in apples (Iglesias *et al.* 2008). In mango, a model using HunterLab colour values, a, b and the product ab, was developed for predicting the maturity index (I_m= total soluble solids/8x100) (Jha *et al.* 2007).

3. Computer vision system

The Minolta or HunterLab colorimeters evaluate the fruit colour on a small viewing area (few cm^2), which may be sufficient for homogeneously coloured fruits. For the other fruits, such as peach or apple, which have a secondary colour (blush), a computer vision system has been developed to evaluate several quality traits such as secondary colour spots or blemishes over the whole surface fruits of oranges, peaches and apples (Blasco *et al.* 2003). The computer vision system (CVS) consists of a standard illuminant, a camera for image acquisition and software for image processing. It appears suitable to use L*a*b* colour system to study curved surface such as fruits (Mendoza *et al.* 2006). Indeed, the *L*a*b** parameters were less affected by the degree of curvature, shadows and glossiness of the surfaces than the other colour systems. The system has been applied to discriminate ripening stages of bananas and has been showed to assess the colour change during ripening close to human perception (Mendoza and Aguilera 2004). Using five parameters (L*, a*, b*, brown spots as a percentage of the total area and contrast), discriminant analysis permitted the correct classification of 49 samples in seven ripening stages with an accuracy of 98%. Moreover, the system allows the study of hue angle change during storage of mango (Kang *et al.* 2008). After eight days, there was a difference between fruits stored at 13°C and 22°C, but the fruits stored at 22°C for 14 days were very similar to those stored at 13°C for 46 days. Colour-based systems may predict pigment concentration across a broad range of fruit varieties. However they fail to predict maturity traits in relation with biochemical changes in sugars and acids for example, except when restricted to a single well-characterized cultivar.

Near-Infrared Spectroscopy

1. Applications

Near-infrared (NIR) radiations cover the range of the electromagnetic spectrum between 750 and 2500 nm and provide structural information related to the vibration behaviour of combinations of bonds. These radiations are suitable for the analysis of chemical compounds containing OH-, CH-, C-O and NH- groups for which overtone bands are observed in the near infrared. The typical NIR reflectance spectra are dominated by the water spectrum with overtone bands of the OH-bonds at 760, 970 and 1450 nm, and a combination band at 1940 nm. The NIR range is often enlarged for fruit quality analysis since a large number of researches has been carried out with the combination of Visible and NIR spectroscopy. This is the case for example for the assessment of fruit mango maturation (Subedi *et al.* 2007) and the internal fruit quality measurements of pear (Liu *et al.* 2008). Three recent reviews deal with the NIR spectroscopy. The first concerns the non-destructive measurement of fruits and vegetables (Nicolaï *et al.* 2007) and presents principles and instrumentation, chemometrics, applications and future researches. The second one concerns the use of NIR spectroscopy for the on/in-line analysis of food and beverage quality with a part on fruits and vegetables (Huang *et al.* 2008). The on-line application demands a simple and rapid analysis without any sample preparation. This is the case for NIR technique that allows in addition the simultaneous measurement of several compounds. The third review concerns the application of NIR spectroscopy in both raw and prepared foods (Woodcock *et al.* 2008). On fruits and vegetables, the recent applications concern three areas of interest; 1) authenticity with the determination of origin, 2) detection of defects such as diseases and 3) quality analysis with the evaluation of several quality traits.

Nicolaï *et al.* (2007) and Woodcock *et al.* (2008) summarized in tables applications of NIR spectroscopy with an overview of evaluated quality attributes and studied fruit species. Soluble solids content (SSC) is the main quality trait studied in a very large number of horticultural products such as apple, apricot, cherry, citrus, grape, guava, kiwifruit, mandarin, mango, melon, nectarine, papaya, peach, pear, pineapple or plum. In general, RMSEP is around 0.5% but in external validation (other orchards and/or years), RMSEP is higher (1-1.5%). Other quality traits have been considered like dry matter, pH, acidity, firmness, optimal harvest date, internal browning disorders. Some recent works using NIR spectroscopy were carried out on a single cultivar for estimating soluble solids content in melon and watermelon (Flores *et al.* 2008), SSC and firmness in pear (Liu *et al.* 2008; Nicolaï *et al.* 2008) and for detecting brown heart in pears (Fu *et al.* 2007). In some works, fruits were put in environmental conditions involving fruit disorders and thus variability in the studied quality traits. Other works, carried out on several cultivars including from two to nine cultivars, concerned the study of dry matter, total soluble solids and colour Hunter *b* value in mango fruits (Subedi *et al.* 2007), the study of SSC in nectarine (Reita *et al.* 2008), the study of SSC and firmness in plums (Paz *et al.* 2008), and the study of SSC, titratable acidity, firmness and individual sugars and organic acids in apricot (Bureau *et al.* 2009). The fruit variability, at the genetic, physiological, or agro-environmental levels, used in these studies, will have a positive effect on the robustness and the portability of the obtained results. Moreover, combining two methods such as Visible-NIR spectra and acoustic data allowed the improvement of the prediction performance for 'Golden delicious' and 'Idared' apple firmness on tree and during storage (Zude *et al.* 2006). The Visible-Near spectroscopy was compared to the non-destructive density measurement using the total fruit immersion in water using Archimedes' principle to predict dry matter, SSC and flesh colour of a yellow-fleshed kiwifruit cultivar harvested in four different orchards (McGlone *et al.* 2007). The three quality traits were well-predicted with Visible-NIR spectroscopy (r^2 between 0.83 to 0.97) whereas density method presented poor performances (r^2 between 0.46 to 0.78).

2. Chemometrics

The typical spectra are often similar between different fruit species. So, to extract the useful information from spectra, the use of sophisticated multivariate statistical or chemometrics is needed (Nicolaï *et al.* 2007). The first step is the application of preprocessing techniques to remove the irrelevant information such as standardisation, normalisation, first or second derivative calculation. The second step is the application of regression techniques of which the objective is to establish a numerical relationship between the reference data (measurements of quality traits with classical techniques such as soluble solids and titratable acidity) and the spectral data. Linear regression techniques such as multiple linear regression (MLR), principal component regression (PCR) and partial least squares regression (PLS) are commonly used. Non-linear regression techniques such as artificial neural network (ANN) or kernel-based techniques (Nicolaï *et al.* 2007) have also been used. Recently, for establishing prediction models of SSC and firmness in a single pear variety, PLS was shown to give better results than MLR and PCR (Liu *et al.* 2008). Liu, He, Wang (2008) compared the partial least squares discriminant analysis (PLS-DA) and the least squares-support vector machine (LS-SVM) coupled with different methods of selection of effective wavelengths to discriminate fruit vinegars including aloe, apple, lemon and peach. The best results were achieved by LS-SVM with regression coefficients allowing the selection of seven effective wavelengths. To discriminate Chinese bayberry varieties, Li *et al.* (2007), used PCA-ANN, with PCA for the reduction of the matrix dimension in new variables (first 20 principal components used) and ANN for the establishment of classification model. Among forty unknown bayberries, only two samples were inaccurately classified showing the good performance of these non-destructive techniques to discriminate varieties. In order to carry out a validation test of the established models, several procedures can be used such as the leave-one out cross-validation (the model is established using all data except one and a prediction is made for that data, the operation is repeated for each data and results are computed to evaluate the model), the internal cross-validation (data are divided into two subsets with two thirds of samples used for calibration and one third for validation) and the external validation (the evaluation of the established model is made with samples from other cultivars, orchards or years). The model performance was then evaluated by errors of calibration (SEC, RMSEC) and of prediction (SEP, RMSEP) and by the correlation coefficient r between the predicted and the measured parameters.

3. Equipments

In NIR spectroscopy, different measurement modes can be used. In practice, the common modes are transmittance, interactance, transflectance, diffuse transmittance and diffuse reflectance. The transmission appeared to be more efficient than the diffuse reflectance for detecting brown heart in pears (Fu *et al.* 2007). This was probably in relation with the penetration depth in fruit, less than 10 mm in diffuse reflectance mode in the use of a low power light source in the cited work. The penetration of NIR radiation into the fruit tissues depends indeed on the wavelength range and decreases exponentially with the depth. Moreover, the skin constitutes a major barrier notably for citrus fruits. The spectrometers used in laboratories are generally expensive in relation with a high resolution and thus not feasible for an on-line implementation. Some low-cost and robust NIR apparatus have been developed for an application in automated fruit grading systems; and those equipped with a photodiode array (PDA) spectrometers with a high acquisition speed are well-adapted (Nicolaï *et al.* 2007). Recently, a PDA instrument has been shown to be sufficiently accurate for the prediction of SSC and TA in 'Raf' tomatoes using the range between 400 and 1700 nm (Flores *et al.* 2009). Different manufacturers propose NIR sensors, but often, their accuracy is not compared to those used in laboratories in static conditions. However, two prototype on-line transmission systems were compared for the non-destructive measurement of the percentage on internal tissue browning in apples at typical grading speed of five fruits per second (500 $mm.s^{-1}$) (McGlone *et al.* 2005). It appeared that despite its poorer spatial resolution, the LAS (large aperture spectrometer) system was superior to the TDIS (time-delayed integration spectroscopy) system. Three fruit moving speeds (0.3, 0.5 and 0.7 $m.s^{-1}$) were compared for the evaluation of SSC in pears and few differences were observed in the data of the cross-validation with determination coefficients of 0.873, 0.857 and 0.824 respectively (Sun *et al.* 2009). Some low cost portable spectrophotometers are commercially available and can be used in orchards to monitor fruit ripening. Zude *et al.* (2008) have used a handheld photodiode array spectrophotometer instrument (MMS1, Zeiss, Germany) in the wavelength range between 450 and 1100 nm to study the SSC of citrus fruit on trees during ripening. For mango, Subedi *et al.* (2007) used a prototype handheld spectrophotometer ('iQ', Integrated Spectronics, Australia) in the wavelength range between 300 and 1150 nm.

A machine vision system using the reflective NIR (between 750 and 1200 nm) imaging was developed for the date grading (Lee *et al.* 2008). The images are processed and converted into values quantifying both fruit size and skin delamination. In fact, the NIR images provided the required contrast for the detection of skin delamination. The system is able to work in commercial production (20 pieces of fruit per second) and improved the grading accuracy by about 10% compared to the human grading. An experimental tomography system was built with relatively low-cost components using the Visible-NIR technique with the objective of reconstructing images and thus detecting internal defects in entire fruits (Kemsley *et al.* 2008). The example was given for sectioned tomatoes. A work reports the use of NIR-FT-Raman spectroscopy to analyse carotenoids in living plant materials (Baranski *et al.* 2005). Usually the sensitivity of this technique is lower than that of other analytical methods. However, in Raman, carotenoids give two intense bands (near 1525 and 1155 cm^{-1}) attributed to stretching modes of conjugated C=C and C-C bonds in the central chain and their detection is dramatically increased. For example, in pepper, the change of carotenoids was studied during ripening with the disappearance of lutein and the appearance of capsanthin. In tomato, the non-affected red tissue was characterized by lycopene and the necrotic tissue of sunscald injury was characterized by β-carotene. The NIR-FT-Raman technique can be a powerful tool to identify, quantify and study the distribution of different carotenoids in intact tissues.

Time-domain reflectance spectroscopy (TRS)

In opposition with the continuous wave spectroscopy, another non-destructive technique exists, the time-resolved or time-domain reflectance spectroscopy (TRS). It allows the complete optical characterization of highly diffuse media, such as fruit, because absorption and scattering are obtained simultaneously (Cubeddu *et al.* 2001). Absorbance depends on light attenuation in the fruit, and is affected by both light absorption and light scattering. In TRS, a very short (typically tens to hundred of picoseconds) light pulse is injected into the sample and the temporal distribution of re-emitted photons is detected and fitted with a theoretical model of light propagation. The detector measures photon time of flight distribution expressed with an absorption coefficient μ_a and a reduced scattering coefficient μ_s' as a function of wavelength. According to the tissue properties, the photons may take more or less time to reach the detector positioned at some distance from the light entry point. The absorption coefficient at a given wavelength μ_a can be interpreted as the linear combination of the extinction coefficients of main fruit components such as water, chlorophyll, carotenoids, sugars…. weighted by their average concentration. The reduced scattering μ_s' is related to the cellular structure and to air and water distribution. TRS measurement is probing a depth of about 2 cm in the pulp (Zerbini *et al.* 2002). The technique can be useful for the detection of brown heart and for the assessment of fruit ripening. In 'Conference' pears, brown heart-affected tissues had a higher μ_a value than sound tissues at 720 nm (Zerbini *et al.* 2002). Moreover according to Cubeddu *et al.* (2001), the main contributor to μ_a at 670 nm is chlorophyll, μ_a increasing with chlorophyll content. This particularity was used to classify fruits of two nectarine cultivars at harvest and evaluate their softening rate during a shelf-life period at 20°C (Zerbini *et al.* 2006). A model established using μ_a and time at 20°C as independent variables explain more than 75% of the variation of fruit firmness. Softening occurred earlier in fruit having lower μ_a at harvest and later in fruit having higher μ_a at harvest. So, measuring μ_a at harvest and using the established model independent of climatic conditions but dependent of cultivars, make possible the prediction of nectarine fruit softening at 20°C. This technique may be used for the online fruit analysis for sorting fruits according to their shelf-life potential and for elimination of fruits presenting internal disorders such as brown heart localised at a depth lower than 2 cm. According to Nicolaï *et al.* (2008), the range between 875 and 1030 nm, dominated by the overtone of the hydroxyl group at 975 nm, did not allow the construction of accurate PLS models for soluble solids content and firmness predictions in 'Conference' pears. A non-linear relationship was found between firmness and μ_s' at 900 nm.

Multi and hyperspectral imaging - light backscattering imaging

Recent studies used a computer-assisted image processing system equipped with a high performance CCD camera for capturing scattering images on intact fruits using laser diodes as light source. Lu (2004) developed a new technique to estimate fruit firmness and SSC based on the multispectral imaging. The radial light scattering profiles were extracted from 'red delicious' apples at selected spectral bands in the visible and near-infrared regions between 680 and 1060 nm. Spectral scattering images were reduced to one-dimensional scattering profile. The best prediction of fruit firmness (r=0.87 and SEP=5.8 N) was obtained with three ratio combinations with four wavelengths (680, 880, 905, 940 nm) and for predicting SSC (r=0.77, SEP=0.78%), two ratio with three wavelengths (880, 905, 940 nm) were needed. As corrections of the images are important when using scattering images captured by a video camera, Qing *et al.* (2007) used for the first time a calibration method based on the corrected intensity frequency of the raw data set. The frequencies of grey scale intensities obtained for the five selected wavelengths (680, 780, 880, 940, 980 nm) were used to calibrate on the fruit firmness and SSC using PLS regression. The prediction of SSC and flesh firmness of 'Elstar' apples presented a good performance (r=0.90), %SECV=4.14 and r=0.90, %SECV=5.49 respectively). On 'Elstar' and 'Pinosa' apples, the models established during their ripening for predicting SSC and firmness were tested on fruits grown in different growing conditions (Qing *et al.* 2008). The errors of validation (%SEP) were about 10% for SSC and 9% for firmness. Peng and Lu (2007) proposed an approach of correcting scattering image profiles to minimize the effect of light source variation by using a reference standard. Scattering images were acquired from a white Teflon disk for every 10 apples and were used as reference images. Spectral scattering images were obtained from 'Golden delicious' apples at four wavelengths (680, 800, 900 and 950 nm). The scattering intensity and distance were corrected by incorporating the effect of individual apples' size. Better predictions were obtained with r=0.896 and SEP=6.50N for firmness and r=0.816 and SEP=0.92% for SSC. It is technically feasible to develop an on-line system that is designed and built based on the proposed methods to achieve good prediction results for apple fruit firmness and SSC.

While multispectral imaging allows the acquisition of spectral images at a few wavelengths (less than ten), hyperspectral imaging is a powerful tool for acquiring information from a sample using a continuous wavelength range. This technique allows the analysis of spatial variations of food and agricultural products. For example, for assessing peach fruit firmness, 153 spectral scattering profiles in the range between 500 and 1000 nm have been simultaneously acquired (Lu and Peng 2006). A combination of 10 or 11 wavelengths, depending on the cultivars and including the chlorophyll and water absorption bands, are needed to obtain the best correlation with the peach firmness. The technique has been used with a configuration appropriate to measure spectral absorption and scattering properties (μ_a and μ_s') using spatially resolved reflectance imaging on several fruits such as apple, peach, pear, kiwi and plum (Qin and Lu 2008). Contrary to time-resolved reflectance spectroscopy discussed above, needing a good contact between the fruit and the sensor, the hyperspectral imaging using the spatially resolved reflectance technique is a non-contact instrument, more suitable to scan fruits. For example the technique allows the discrimination of three ripening stages for tomatoes based on anthocyanin and chlorophyll content changes (ratio μ_a at 675 nm to that at 535 nm) (Qin and Lu 2008). The reduced scattering coefficient μ_s' was positively correlated with the firmness values of the same tomatoes, the best correlation coefficient (r=0.66) being obtained at 790 nm. Spectral images between 400 and 700 nm were recorded on tomatoes at different stages of ripening with the aim of predicting carotene and chlorophyll concentrations and studying their surface distribution (Polder *et al.* 2004). The images have a spatial dimension of 318 × 256 square pixels and a spectral dimension of 257 bands. For each tomato, 200 spectra were extracted (25 spectra for each of the eight circular patches defined on all tomato surface, except on the center part ignored because of circular reflection). The prediction performance was evaluated at pixel and tomato levels. For lycopene, the main compound, the prediction was the best with a predicted percentage error (Q^2) of 0.95 on the individual pixel and 0.96 for the whole tomatoes. For the other compounds, Q^2 ranged between 0.72 and 0.82 for the pixel and tomato classification. It appeared possible to construct concentration images by applying models to the spectra of all pixels.

Fluorescence

Fluorescence is based on the relaxation of a molecule with the emission of electromagnetic energy within the visible range after its excitation by short wavelength light such as UV. Many biological materials fluoresce; however, the main application concerns chlorophyll fluorescence. It is a measure of the efficiency in energy transfer process and chloroplast activity, and thus, an indirect measurement of the physiological status of chlorophyll-containing biological materials such as fruits. Before chlorophyll fluorescence measurements, fruit must be dark-adapted for 30 min to avoid disturbing influences of the photosynthesis apparatus (Abbott 1999; Butz *et al.* 2005). The chlorophyll fluorescence yield decreased with the ripening of papaya fruits and allowed the discrimination of ripening stages (Bron *et al.* 2004). The decrease of chlorophyll fluorescence parameters suggests the decrease in chlorophyll content and loss in photosynthetic membrane activity with ripeness of papaya. As the flavonoids are highly concentrated in the epidermis above the chloroplasts, the technique using chlorophyll fluorescence has been developed to assess the UV-absorbing phenolic compounds in the leaf epidermis. According to the study of chlorophyll and anthocyanin distribution in grape berries, it was shown that chlorophyll molecules are located 10-20 µm deeper than anthocyanin layers with thickness of about 70 µm in the hypodermis cells (Agati *et al.* 2007). The technique was used, for example, for a non-destructive evaluation of anthocyanins in olive fruits and grape berries (Agati *et al.* 2005, 2007). The method is based on the comparison of chlorophyll fluorescence signal excited with light particularly well-absorbed and attenuated by anthocyanin and the signal induced by light reaching chlorophyll without attenuation. The logarithm of the chlorophyll fluorescence excitation ratio is then calculated as logFER between two wavelengths, absorbed and not absorbed by anthocyanins for their evaluation. In olive, a good correlation (r^2=0.96) was found between the logFER method using two excitation wavelengths, 625 and 550 nm, and emission at 740 nm and the analysis of anthocyanin extracts (Agati *et al.* 2005). During the ripening of grape berries, from green to purple skin change, a good correlation was observed between logFER, at two excitation wavelengths 540 and 635 nm, and anthocyanin concentration (r^2=0.92, standard error Se=0.087) (Agati *et al.* 2007). Moreover, the use of three excitation wavelengths, 375, 470 and 655 nm, with two fluorometers (UV-A-PAM and PAM-2000) has made possible the evaluation of both flavonoid and anthocyanin contents separately in apples (Hagen *et al.* 2006). The relative UV-A absorbance (375 nm) was correlated with the total flavonoid content (r^2=0.899, P<0.001), and that of blue light (470 nm) was correlated with anthocyanin content (r^2=0.889, P<0.001). The red light, used as reference measurement, was not absorbed before being capture by chlorophyll. Compared to other non-destructive methods based on reflectance measurements, according to Agati *et al.* (2007), the logFER appears to be superior to the index developed by Merzlyak *et al.* (2003) but as good as the CIRG index developed by Carreno *et al.* (1995). Two portable devices, Dualex FLAV™ and Dualex ANTH™, and a prototype Multiplex have been tested for assessing the phenolic maturity based on berry fluorescence (Goulas *et al.* 2004; Cerovic *et al.* 2008). These instruments (FORCE-A, Orsay, France) are based on chlorophyll fluorescence having different excitation wavelengths: a UV-A source (375 nm) for Dualex FLAV™, a green light source (530 nm) for Dualex ANTH™, and three light sources for Multiplex at 375 and 530 nm as above and a red light at 630 nm. Dualex ANTH gave a good estimation of the skin anthocyanin content (r^2=0.98) and Dualex FLAV gave a good estimation of flavonols (r^2=0.91). But, in grape berries in relation with their high flavonoid contents, the Dualex response is not linear above 100 nmol/cm^2 for anthocyanins and 200 nmol/cm^2 for flavonols. Concerning the Multiplex, it was capable of estimating anthocyanin content throughout the ripening in relation with the signal obtained on the far-red detector with the red and UV light excitation.

Pulse amplitude modulated (PAM) fluorescence is commonly used to obtained the minimal and maximum chlorophyll fluorescence related to the photochemical function (Bron *et al.* 2004; Hagen *et al.* 2006). The measurements are usually performed on dark-adapted samples in a room with dim light. Laser-induced chlorophyll fluorescence (LIF), allows measurement under ambient light conditions (Kuckenberg *et al.* 2008). In tomato fruits, the laser excitation wavelength at 266 nm involved different fluorescence spectra along the fruit ripening (Lai *et al.* 2007). Indeed, the unripe fruits presented a maximum fluorescence emission between 330 and 450 nm, corresponding to the anthocyanins and flavonoids, whereas in the overripe fruits, the maximum was between 450 and 550 nm, in relation with the carotenoids. In apple peel, a good correlation was found between chlorophyll content and LIF, induced with a red light (662 nm) and a signal detection at 730 nm, with r=0.87 and 0.93 according to the sunlit or shaded fruit sides and cultivars (Kuckenberg *et al.* 2008). Slaughter *et al.* (2008) have compared two detection methods, visual and vision machine using UV fluorescence for the detection of freeze-damaged oranges. The fluorescence pattern, in this case, is due to the fluorescence of tangeritin, a polymethoxylated flavone causing yellow spots on the peel surface when viewed under UV light (365 nm). Results indicated the feasibility of using an on-line machine vision based on fluorescence technique for sorting fruits with moderate to severe damage but not fruits with low levels of damage.

As for the scattering imaging, multi and hyperspectral fluorescence imaging has been developed to provide both spectral and spatial information about fluorescence emission of fruits. The system consisted of a hyperspectral imaging unit, a blue diode laser unit, a fruit holder and an imaging chamber (Noh and Lu 2007). At the beginning of excitation illumination, fluorescence rises quickly and then drops slowly until it reaches a steady state after a few minutes with a continuous illumination. The system captured the first fluorescence scattering image immediately at the beginning of laser illumination and continued the capturing after 1, 2, 3, 4 and 5 minutes at which time fluorescence was stabilized. The models established for predicting firmness, SSC, TA, skin and flesh colour in 'Golden delicious' apples had generally the lowest coefficient of correlations and the highest standard errors of prediction (SEP) using fluorescence emission at 0 min. The best results were generally obtained using fluorescence at 1 min and at other longer time periods until 5 min (Noh and Lu 2007).

Nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI)

Some nuclei of atoms, including ^{1}H, ^{13}C and ^{31}P, have a magnetic moment and are able to absorb resonance energy when placed in a strong magnetic field and irradiated with a proper radio frequency. The ^{1}H magnetic resonance is the most interesting for horticultural applications in relation with its high abundance, its high sensitivity, its narrow chemical shift with sharp signals. A weak pulse of the proper radiofrequency (RF, based on magnetic field strength) will cause the net magnetic moment to rotate 90°. When the RF signal is removed, the moment loses energy and relaxes back to its previous position. Energy released by relaxation induces an RF signal in a receiver. Energy loss is dependent on the environment surrounding each nucleus. By applying magnetic field gradients in 3 directions, MRI images can be created (Abbott 1999; Hills and Clark 2003; Butz *et al.* 2005).

MRI has been used to study the distribution of core breakdown disorder symptoms in pears (Lammertyn *et al.* 2003a, 2003b). Three images (256 × 256 pixels) can be obtained taking into account the proton density and the T_1 and T_2 relaxation times. The proton density equals the numbers of mobile protons in water, fat and in the hydration layers of biological macromolecules such as proteins. Brown tissues have a low signal intensity corresponding to a low free water content compared to healthy tissues. The cavities were clearly visible with a null intensity because absent or non-mobile protons have no intensity signal. Concerning the T_1 relaxation time, free protons have high T_1 values (high intensities) and protons bound to macromolecules have short T_1 values (low intensities). It appeared that the T_1 values (average of 1199 ms) of brown tissue were significantly lower than the T_1 values (average of 1521 ms) of unaffected tissue. Concerning the T_2 relaxation time, the dark regions (area with restricted proton mobility and short T_2 values) and regions with free water content (high intensities and long T_2 values) were distinguished. The radial tissues around the core had higher free water content than the brown and healthy tissue near the skin. So, the MRI images were able to estimate the location and the proportion of healthy and brown tissues, and cavities in fruits. Moreover, based on the same principle of water mobility, MRI has been recently used to evaluate the effect of storage conditions on minimal structural changes of kiwifruit (Taglienti *et al.* 2009).

However, for an on-line implementation, the technique requires three characteristics: the use of ultrafast sequences (below 1 s), the efficient image acquisition in dynamic conditions and the use of appropriate technology with low magnetic field strengths (Hills and Clark 2003). In order to minimize the motion artefacts, fast low-angle shot sequence (FLASH) was used as a fast imaging sequence for the detection of seeds in mandarins (Hernandez-Sanchez *et al.* 2006). The correct classification under on-line conditions (fruit speed at 54 mm/s) were 92.5 and 79.5% for the seedless and seed-containing fruits respectively and were similar to those under static conditions. The system was tested for the on-line detection of internal browning in pears (Hernandez-Sanchez *et al.* 2007). The FLASH sequence has been compared to another fast sequence, the spiral and radial image acquisition (COMSPIRA) for the seed detection in mandarins (Barreiro *et al.* 2008). Very good results of classification were obtained, 98.7 and 100% for FLASH and COMSPIRA, respectively, using particular image segmentation and features. The major objective now identified is the development of technology using low magnetic field strength, because the MRI spectrometer commonly used is the spectrometer BIOSPEC 47/40 (Bruker, Ettlingen, Germany) equipped with superconducting magnets (4.7 T or 200 MHz). In the review dealing with the NMR and horticultural products, Hills and Clark (2003) noted the use of sophisticated equipment with superconducting magnets and the need to repeat experiments with simple sensors and low field magnets, which are more suitable for fruit analysis. The effectiveness of a MR sensor with a low field magnet (0.13 T or 5.55 MHz) has been tested for a rapid detection of internal browning in apples using the relaxation signals from Carr-Purcell-Meiboom-Gill (CPMG) decay curves (Chayaprasert and Stroshine 2005). With a dynamic system at a conveyor speed of 50 mm/s, the error of classification between healthy and affected apples was 12.5% for 'Rome' and 0% for 'Red delicious'. But this error increased with the conveyor speed and the incorrect positioning of fruit. The equipment need improvements to be used in on-line conditions for sorting affected fruits.

MRI and X-ray technique were compared for studying time spatial distribution and course of core breakdown in pears which is characterized by brown coloration of the tissue and development of cavities (Lammertyn *et al.* 2003a, 2003b). On the X-ray computed tomography (CT) images, the intensities and contrasts are mainly based on differences in mass density and absorption of the sample, and water dominates X-ray absorption (Abbott 1999). But, according to Lammertyn *et al.* (2003a, 2003b), MRI appeared to offer a higher sensitivity for detecting disorders and a higher contrast between affected and sound tissues than the X-ray computed tomography (CT) technique. No recent study has been performed for the non-destructive fruit analysis using the X-ray technique.

MECHANICAL PROPERTIES

For most fruits, firmness is a very important quality property. It varies during ripening and storage period. Firmness of horticultural products has been generally evaluated using force/deformation tests. Many devices and techniques have been developed. Most of them are based on puncture, compression or response to shear, stress, creep or impact. Due to their low speed and often destructive nature, compression or penetration techniques are not very suitable for on-line sorting of fruits. Other non-destructive techniques have been described such as the measurement, using a laser displacement sensor, of the deformation produced by a small puff of air on the fruit surface or the measurement of fruit density used as a quality index. These techniques were reviewed by Abbott (1999) and Butz *et al.* (2005). Recently, De Ketelaere *et al.* (2006) have tested the commercially firmness tester (Sinclair^{TM}) that evaluates the firmness as a 'SIQ-FT' value based on the impact signal produced by air pressure. The technique appears suitable for apples and tomatoes studied during storage and particularly for soft samples. Moreover, an impact tester, LPF-Lateral Impact Sensor 2.0' has been used for evaluating peach firmness during storage (Diezma-Iglesias *et al.* 2006). It consisted of a spherical low mass (10 g) which impacts samples, and characteristic parameters of impact were registered such as acceleration versus time, velocity, deformation, energy, force versus deformation or maximum acceleration registered during the impact. The last one showed a high correlation (r=0.87) with the reference measurement being the maximum force in ball compression (Diezma-Iglesias *et al.* 2006). A failing impact apparatus has been used for assessing different maturity stages of tomatoes (Lien *et al.* 2009). It consists of a pneumatic holding mechanism to hold the fruit and release it to fall from 15 mm onto a load cell. The failing height has been defined to avoid bruise damages. The best classification was 82.3% in three maturity classes, unripe, half-ripe and ripe. This system could be used for an on-line quality sorter.

Acoustic impulse response was largely presented by Butz *et al.* (2005). The fruit is placed with its equatorial region close to a microphone. It is tapped at a point diametrically opposite to the microphone, using a small hand-held rod. The impact must be short and sharp to avoid dulling the resonance of the fruit through contact with the rod. Acoustic (or sonic) waves can be transmitted, reflected, refracted or diffracted as they interact with the material. Wave propagation velocity, attenuation and reflection are the important parameters used to evaluate the tissue properties of horticultural commodities. The acoustic signal captured by the microphone is amplified by a sound meter and stored in a digital form using a digital oscilloscope. The frequency with the greatest amplitude is determined using a Fast Fourier Transform (FFT). An elasticity coefficient proportional to the Young's modulus is calculated from this frequency, the volumetric mass and the mass or the grade of the fruit. The technique was used for detecting defects such as voids in the flesh. When tapped, the defective fruit responds with a different resonant sound. A device was developed to measure acoustic response of watermelons equipped with a metal ball fixed on a pendulum to hit the fruit surface and a microphone in the opposite face to detect the output sound (Diezma-Iglesias *et al.* 2004). The band magnitude (BM) parameters obtained by summing the normalised spectrum magnitude between 85 and 160 Hz were the best indicators for distinguishing good and hollow watermelon. Compared to the inspection by human experts (82.5%), the acoustic test allowed a better classification (94.5%) of watermelons. The same technique was used to study the fruit ripening. On spherical fruits such as apples, a stiffness factor *S* is calculated using the natural dominant frequency where the magnitude is the greatest and the mass of the intact fruit ($S= f^2m^{2/3}$). On 'Idared' and 'Golden delicious' cultivars, the acoustic resonance frequency decreased during storage duration and was correlated with the flesh firmness (r^2=0.65 and 0.73 for 'Golden delicious' and 'Idared' respectively) (Zude *et al.* 2006). However, to improve the robustness of models for the prediction of flesh firmness on tree and during shelf-life, it was necessary to use both the acoustic impulse resonance frequency and Visible data. De Ketelaere *et al.* (2006) have tested the commercial acoustic firmness sensors (AFS, Aweta) that appear to be adapted for firm samples among apples and tomatoes during storage. An experimental setup was developed using a piezoelectric film-type sensor for firmness detection (Wang *et al.* 2004). Pears were thus excited by a pendulum and the response signals were detected by flexible piezoelectric film sensors. Because these sensors cling to the surface of the fruit, it was possible to detect the signal immediately from excitation and thus the dynamic characteristics. The dominant resonance frequency (the response magnitude is the greatest) was shown to increase with increasing the reference Magness-Taylor firmness (destructive penetration corresponding to a measurement of the crushing and shearing strength of the tissue) (r^2=0.833). For peach, similar results were obtained with a good correlation (r^2=0.827) between the Magness-Taylor firmness and the dominant frequency (Wang *et al.* 2006). This technique has been used in an experimental fruit packing line (Garcia-Ramos *et al.* 2003) and was tested on three types of spherical balls (cork, tennis and rubber) with 100% of well-classified balls. In another work, pears were impacted by free drop onto a plate and signals were detected by a piezoelectric film sensor (Wang *et al.* 2007). A good correlation was shown between the dominant frequency and the Magness-Taylor firmness (r^2=0.716) and, a good linear relationship was shown between the stiffness coefficient calculated as $S=f^2m^{2/3}$ and the Magness-Taylor firmness (r^2=0.819). Moreover, according to Diezma-Iglesias *et al.* (2006), the combination of impact and acoustic tests allowed an improvement of the prediction of peach firmness.

Ultrasonic vibrations are above the audible frequencies (> 20 kHz). The ultrasonic system is based on the emission of known energy into a fruit and the measurement of the ultrasonic energy after its propagation through the fruit tissues. The ultrasound signal emerging from the test specimen is sensed by a piezoelectric element that acts as a receiver, converting any ultrasound impinging on it back to electrical energy. When the system operates in 'pulse-echo' mode, the same piezoelectric element acts as a transmittance and a receiver alternatively; when a 'through-transmission' mode is used, a second piezoelectric element acts as a receiver. The mechanical properties of the tissue and its quality attribute changes affect the energy of the received signal. The most important trait that correlates with ultrasonic vibration is firmness (Abbott 1999; Butz *et al.* 2005). An ultrasonic method measuring the changes of ultrasonic waves passing through the peel and flesh has been shown to non-destructively evaluate the firmness of mangoes, plums and tomatoes during their shelf-life (Mizrach *et al.* 1997; Mizrach 2004, 2007) and, the firmness, dry matter or oil content in avocado during growth and ripening (Mizrach *et al.* 1999, 2000; Gaete-Garreton *et al.* 2005). It was shown that contrary to the wave velocity, the attenuation of ultrasonic signal changes dramatically during storage and shelf-life. The ultrasonic technique has been tested to determine the mealiness of apples in comparison with destructive measurements of maximum force and hardness in confined compression (Bechar *et al.* 2005). A good correlation was obtained for 'Cox' and not for 'Jonagold' apples. And for 'Cox' apples, a linear discriminant analysis allows the separation between the fresh and the overripe apples and revealed a misclassification error rate of 5.8%. Moreover the chilling injury involving the increase of the amount of air space thus increased the attenuation of ultrasonic waves in tomatoes harvested at a mature stage (Verlinden *et al.* 2004). Because of the very high attenuation of the ultrasonic wave propagation in the fruits, the studied area is limited to the peel and the internal tissue next to the peel. So the area must be considered to be representative of the entire fruit. A recent review presents the concepts, technologies and applications of ultrasonic techniques for assessment of quality traits in fruits and vegetables (Mizrach 2008). Most of techniques are not yet applicable in fruit quality evaluation, but remain only as an efficient research tool.

ELECTRONIC NOSE

During ripening, fruits release volatiles in their surrounding atmosphere. Among volatiles, compounds are responsible for the fruit odour but some others are markers of ripening or shelf-life processes such as ethylene, ethanol and acetaldehyde. One of the used commercially electronic nose is the portable electronic nose device (PEN 2) provided by WMA (Airsense Analysentechnik GmbH, Schwerin, Germany). The sensor arrays are composed of ten different metal oxide semiconductors (MOS) type chemical sensors. When the sensors are exposed to volatiles, the absorption and the subsequent surface reactions involve changes in conductivity that is recorded by computer. In presence of volatiles, the conductivity increases and then stabilizes after 30 s and the signal at 42 s is generally used. The data are the ratio of conductivity G and G_0 (conductivity of the sensors when the sample gas or zero gas blows over). Another principle is an electronic nose (Libra Nose, Technobiochip, Elba Island, Italy) based on quartz microbalance sensors and in this case the data correspond to the difference between the frequency of measurement and the frequency of cleaning (Saevels *et al.* 2004). The technique has been used for fruit quality analysis. Each fruit was placed into an airtight glass jar and after one hour of equilibrium the headspace gas was pumped over the sensors. The electronic nose has been used for the classification of peach cultivars and their shelf-life (Di Natale *et al.* 2002; Benedetti *et al.* 2008), the determination of the optimal date of harvest of apple and their classification into three maturity groups (Saevels *et al.* 2003; Pathange *et al.* 2006), the discrimination of mandarin according to their ripening stages (Gomez *et al.* 2006), the discrimination of tomatoes stored in box or in plastic bag (Gomez *et al.* 2008), the detection of freeze damage of orange (Tan *et al.* 2005). The technique has been used for the prediction of quality traits of a Chinese pear such as soluble solids content (r^2 of prediction = 0.87) and the compression force (r^2 of prediction = 0.92) using multiple linear regression (Zhang *et al.* 2008). Moreover the changes of volatile components, particularly α-farnesene and straight-chained esters, involved in apple aroma during different storage conditions were studied using an electronic nose in comparison with a traditional technique using solid-phase microextraction and gas chromatography combined with mass spectrometry (SPME-GC/MS) (Saevels *et al.* 2004). The electronic nose measurement was not capable of discriminating the effect of two trends of storage and shelf-life conditions contrary to the traditional technique, probably because no sensor was specific of involved compounds. Moreover, a correlation was observed between one of sensors (W5S) and ethylene production during ripening that allowed the classification of peaches in three maturity classes (Benedetti *et al.* 2008). The electronic nose technique is simple, rapid and appears to be useful for discriminating fruits on condition to use sensors specific of studied volatiles. Most of quoted works were carried out on a single cultivar, except for studies of Benedetti *et al.* (2008), Di Natale *et al.* (2002) and Saevels *et al.* (2003), carried out on two or four cultivars. Attention should be given for the determination of quality traits in a single cultivar. Among volatiles detected by electronic nose, the major phenomena in fruit ripening concern aroma, ethylene and respiration rate. Prediction of other criteria such as texture or biochemical composition could result from possible internal correlations occurring in a well-known cultivar. In this case, results can not be generalized to any other fruit set.

CONCLUSIONS

Fruit quality is defined by many attributes such as appearance, texture, taste, absence of defects; its analysis is therefore complex. None of the different approaches can provide all the information to completely characterise fruit quality and its evolution during ripening and post-harvest periods. The non-destructive methods appear to be very important for sorting fruits in classes with homogeneous quality levels, but these methods are often suitable for a single criterium. To evaluate the appearance and particularly the pigment composition, some portable equipments, colorimeters and spectrophotometers, have been developed to easily monitor the fruit ripening based on visible light reflectance using colour spaces such as L*a*b* or using different indexes calculated with the absorption at particular wavelengths. According to Ziozi *et al.* (2008), concerning one of the described index, it can be regarded as a marker of fruit ripening more sensitive and confident than the physico-chemical parameters commonly used. In the near-infrared region, it is possible to predict different composition traits and good results were obtained for the prediction of composition (SSC, acidity) and for the detection of defects. This technique requires a statistical processing of data using samples to calibrate the model and other samples to validate it, and can be adapted for on-line applications. Fluorescence is restricted to the non-destructive evaluation of chlorophyll, anthocyanin and total flavonoid content. Two portable devices and one prototypes have been developed based on chlorophyll fluorescence for assessing the phenolic maturity in grape berries. Multispectral and hyperspectral imaging provide both spectral and spatial information with the acquisition of images at less than ten wavelengths for multispectral and with a continuous wavelength range for hyperspectral in the visible and near-infrared ranges. The technique appears suitable for the prediction of SSC and firmness and feasible

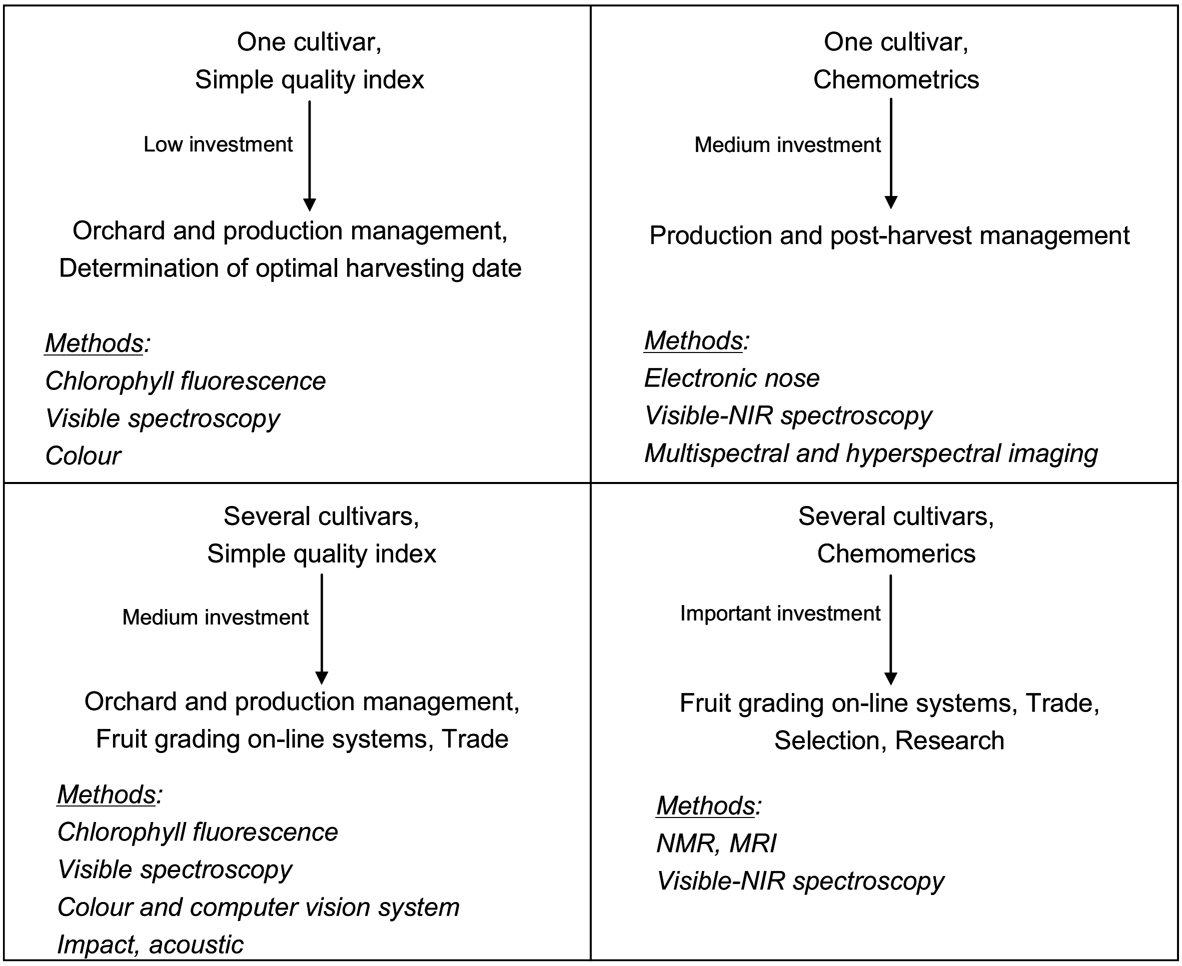

Fig. 1 Schematic diagram of classification of non-destructive methods.

in on-line conditions. Based on chlorophyll fluorescence, multi and hyperspectral imaging has been developed for the prediction of firmness, SSC, skin and flesh colour. The magnetic resonance imaging (MRI) is able to localise and quantify healthy and brown tissues and cavities in fruits. Under on-line conditions, it provides a good detection of seeds in citrus fruit. The major objective now identified is to develop the technology using low magnetic field strength more suitable for fruit analysis. Concerning the measurement of mechanical properties, some testers are commercially available based on the impact signal produced by air pressure or produced by a spherical low mass. The technique using acoustic and ultrasonic waves are used for fruit firmness prediction. However, for instance, the ultrasonic techniques remain only as an efficient research tool. The volatile compounds studied using a commercially portable electronic nose device can be useful quality traits for the fruit discrimination or for the damage detection.

A classification of the non-destructive methods can be tentatively proposed depending on the used sample variability, data treatment, and possible applications in fruit field (**Fig. 1**).

According to Butz *et al.* (2005), the ideal method allowing the global fruit quality characterisation in a wide range of applications has not yet emerged and probably will not be found in the foreseeable future. However a combination of several techniques can be useful for a better determination of fruit quality. For example the combination of acoustic technique and visible spectroscopy provides a better prediction of flesh firmness.

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