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Electronic nose and visible-near infrared spectroscopy in fruit and vegetable monitoring

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Abstract:
In recent decades, there has been a substantial increase in the consumption of fruits and vegetables due to their nutritional properties since they are known as sources of vitamins, minerals, fiber, and antioxidants. Moreover, a substantial growth in fresh-cut fruits and vegetables has been noticed because of their ease to use; in fact changes in human life styles have led consumers to move towards ready-to-eat products. In this context, product quality must be preserved at each step of product handling, processing, and storage, and therefore rapid methods should be available to provide useful information in process management. In this review an overview of the applications of widely used non-destructive techniques, namely, electronic nose and visible/near infrared spectroscopy, for measuring quality of fruits and vegetables is presented. A brief description of spectroscopic and electronic devices and a selection of applications are provided. Future perspectives about the simplification/application of these non-destructive techniques are finally explored.

Keywords: fruit and vegetable, non-destructive devices, postharvest, quality, shelf life

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Introduction

Flavor of fruits and vegetables is influenced by genetic, pre-harvest, harvesting, and postharvest factors. The longer the time between harvest and eating, the greater are the losses of flavor and the development of off-flavor in most fruits and vegetables. Much of the harvesting and handling procedures have been based only on reducing quantitative losses by maintenance of appearance and textural quality of fruits and vegetables (Bartz & Brecht, 2002; Kader, 2002a; Knee, 2002; Kays & Paull, 2004). It is not enough to harvest fruit with good flavor to provide high quality products, but flavor has to be maintained during storage and marketing (Forney, 2001) because postharvest life based on flavor and nutritional properties is often shorter than that based on appearance and textural characteristics (Kader, 2008). The stage of maturity at harvesting is one of the most important aspects to be considered, as it affects both the shelf life and the sensorial properties of a product. In recent decades, there has been a substantial increase in the consumption of fruits and vegetables, and in particular of fresh-cut or minimally processed products due to their high added value in comparison with the fresh one (5–6 times higher) (Lamikanra, 2002). This evident growth in the consumption of ready to use fruits and vegetables is related to their ease to use and nutritional properties since they are sources of vitamins, minerals, fiber, and antioxidants (Kader, 2002). Fresh-cut fruits are more difficult to preserve than other minimally processed products because some of them have to be completely ripe before processing (Gorny et al., 2000). Damages caused by mechanical operations on the tissues of fresh-cut fruit is influenced by the state of maturity of the processed fruit. The optimal stage of processing to minimize cutting damage also varies greatly, depending on the species, cultivar and multiple crop, harvest, and postharvest conditions (Corbo et al., 2010). By sorting harvested products according to their maturity, it is possible to split immature-green, partially mature, and fully mature products, in order to obtain the uniformity of lots at destination. Thus, the assessment of the maturity stage is of great importance for determining the optimal postharvest strategy for product handling and marketing (Slaughter, 2009). The maturity stage can be evaluated by biological (respiration rate), physical (color, texture), physico-chemical, microbiological, and nutritional parameters (Aguayo & Silveira, 2008; Kader, 2008; Rico et al., 2007; Soliva-Fortuny & Martin-Belloso, 2003). In addition, the same parameters are also studied to monitor and extend the shelf life of fruits and vegetables. However, these conventional analytical methods

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are generally expensive, time consuming, require sample pre-treatment, and are unsuitable for on-line monitoring or for automation. Thus, the application of visible/infrared spectroscopy and electronic nose as rapid and non-destructive analytical techniques could be useful for more efficient fruit and vegetable analysis to replace conventional methods. Moreover, electronic nose and visible/infrared spectroscopy could be considered complementary, and their combined application could provide rapid information about the appearance, the chemical composition, and the aromatic profile of the product.

Spectroscopy has been developed considerably over the years (Guidetti, Beghi & Giovenzana, 2012; Nicolaï et al., 2007) reaching a mature stage. Their applicability for the evaluation of agro-food products has widely been proven. Visible and near infrared (vis/NIR) spectroscopy fulfill all the requirements for continuous monitoring of compounds that can be related to the taste and nutritional value of the products. Nevertheless, these technologies are currently adopted mainly by research centers or big companies equipped with laboratories and trained personnel, due to their cost and complexity of use. A simplification of these technologies is necessary to make them accessible also to operative staff in small and medium enterprises. The sector is therefore interested in new simplified systems and low-cost compact tools in view of their application at different levels of the supply chain, with a real possibility of wide diffusion of these technologies from the manufacturing process up to the point of sale and to the consumer. For a simplification and a greater diffusion of these non-destructive techniques, in recent years, interest has shifted towards the development of portable systems usable in pre- and post-harvest (Temma, Hanamatsu & Shinoki, 2002; Walsh, Guthrie & Burney, 2000; Zude et al., 2006). Chemometrics can be applied for the selection of a small number of relevant variables representing the most useful information contained in the full spectra (Sun, 2010; Xiaobo et al., 2010).

Another of the most promising directions for the development of rapid, low-cost, and non-destructive methods is the application of sensor systems, whose speed and on-line capabilities meet the demand of automation. The electronic nose (e-nose) is a technological attempt to mimic the human sense of smell. This device consists of an array of weakly specific and broad-spectrum chemical sensors providing a digital fingerprint of the volatiles present in the sample headspace (Gardner & Bartlett, 1993). Furthermore, the e-nose is a portable device that can be applied directly in the orchard or in the packinghouse and retail store.

This review examines the advances on e-nose and vis/NIR and NIR (NIRs) spectroscopy and their applications for quality evaluation and shelf life assessment of fruits and vegetables. In the first part, the two devices are described in detail; in the second part, an overview of the recent applications on fruits and vegetables is reported, then the future perspectives in the implementation and application of these two devices are considered.

Instrumentation

Electronic nose

At the beginning of the 1990s the term “artificial” or “electronic” nose appeared. More extended research began, and applications, especially in food industry, developed. Gardner and Bartlett (1993) defined the electronic nose as “an instrument, which comprises an array of electronic chemical sensors with partial specificity and appropriate pattern-recognition system, capable of recognising simple or complex odours”.

Principle

The key principle involved in the e-nose system is the transfer of the sample headspace on an array of sensors able to provide signals that are dependent on sensors selectivity and sensitivity and on the volatile compounds present in the sample headspace (Gardner & Bartlett, 1993).

There are striking analogies between the human and electronic noses, and comparing the two is instructive (Pearce et al., 2003). The human nose uses the lungs to bring the odor to the epithelium layer; the e-nose has a pump. The human nose contains the olfactory epithelium, which has millions of sensing cells that interact with the odorous molecules; the e-nose has a sensor array that interacts with the sample headspace. The human receptors convert the chemical responses to electronic nerve impulses that are propagated by neurons through a complex network before reaching the higher brain for interpretation; similarly, the e-nose chemical sensors produce electrical signals that are acquired by a computer and elaborated by pattern recognition algorithms in order to identify and classify odors (Figure 1).

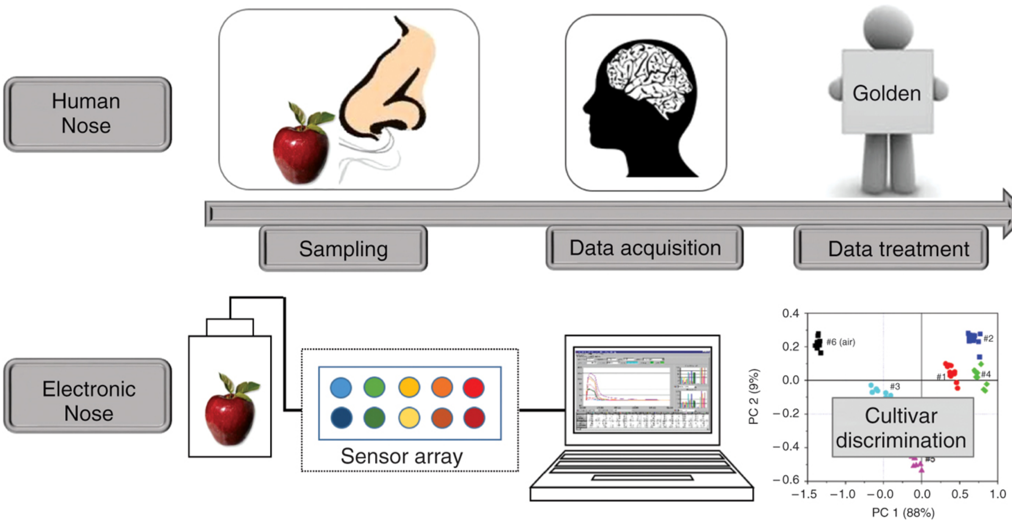

Figure 1: Schematic representation illustrating the principle of human nose and electronic nose.

The electronic nose is sensitive to a large number of aromatic compounds by using limited number of non-specific or semi-specific chemical sensors with different and partly overlapping selectivity, able to detect classes of volatile compound in sample headspace.

Compared to the human nose, the e-nose is faster, not influenced by environmental factors, provides reproducible response, and often is more sensitive.

E-nose technologies

The heart of the system is represented by the sensors that respond reversibly to volatile compounds, generating electrical signals that are immediately acquired by a computer and elaborated by multivariate statistical analysis. The combination of sensor signals defines the odor fingerprint typical of the analyzed product.

Different gas sensor technologies are available, but only four technologies are currently used in the commercial e-noses: metal oxide semiconductors (MOS), metal oxide semiconductor field effect transistors (MOSFET), conducting organic polymers (CP), and piezoelectric crystals (quartz crystal microbalance – QCM).

MOS were the first commercially used in the 1960s as household gas alarms in Japan under names of Taguchi (the inventor) or Figaro (the company's name). These sensors rely on changes of resistance induced by the adsorption of gases and subsequent surface reactions (Kohl, 1992). They consist of a ceramic substrate (round or flat) heated by wire and coated by a metal oxide semiconducting film. The metal oxide coating may be either of the n-type (mainly tin dioxide, zinc oxide, titanium dioxide, or iron oxide), which responds to oxidizing compounds, or of the p-type (mainly cobalt oxide or nickel oxide) which responds to reducing compounds (Mielle, 1996). Due to the high operating temperature (200–650°C), the organic volatiles transferred on the sensor surface are totally combusted to carbon dioxide and water, leading to the change in resistance.

MOSFET sensors rely on a change of electrostatic potential. A MOSFET sensor comprises three layers, a silicon semiconductor, a silicon oxide insulator, and a catalytic metal (usually palladium, platinum, iridium, or rhodium), also called the gate. When polar compounds interact with the metal gate, the electric field and the current flowing through the sensor are modified. The recorded response corresponds to the change of voltage necessary to keep a constant pre-set current (Lundstrom et al., 1990). The selectivity and sensitivity of MOSFET sensors may be influenced by the operating temperature (50–200°C), the composition of the metal gate, and the microstructure of the catalytic metal. MOSFET sensors have a relatively low sensitivity to moisture and are very robust.

CP sensors are based on changes of resistance by adsorption of gas. These sensors comprise a substrate (such as a fiber-glass or silicon), a pair of gold-plated electrodes, and a conducting organic polymer such as polypyrrol, polyaniline, or polythiophene as sensing element (Amrani, Persaud & Payne, 1995). The transfer of volatile compounds on the sensor surface alters the electron flow and therefore the resistance of the sensor. CP sensors show a good sensitivity especially for polar compounds; however, their low operating temperature (<50°C) makes them extremely sensitive to humidity.

Among the piezoelectric sensors, the QCM are widely used, and they are based on change of mass, which may be measured as a change in resonance frequency. These sensors are made of tiny discs, usually quartz, lithium niobate ($LiNbO_3$), or lithium tantalite ($LiTaO_3$), coated with materials such as chromatographic stationary phases, lipids, or non-volatile compounds that are chemically and thermally stable (Guilbault & Jordan, 1988). When an alternating electrical potential is applied at room temperature, the crystal vibrates at a very stable frequency, defined by its mechanical properties. Upon exposure to volatile compounds, the coating adsorbs molecules, increasing the mass of the sensing layer and hence decreasing the resonance frequency of the crystal. These devices are called QCM because, similar to a balance, their responses change in proportion to the amount of mass adsorbed. Since piezoelectric sensors may be coated with an unlimited number of materials, they have the best selectivity. However, the coating technology is not yet well controlled inducing poor batch-to-batch reproducibility.

Vis/NIR and NIR spectroscopy

Among the non-destructive techniques, the spectroscopic analyses in the region of NIRs have a significant role. Instruments for NIRs analysis were built since 1970s, and since the second half of 1980s 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 Fourier transform NIR spectroscopy (FT-NIR) instruments) (Stark & Luchter, 2003).

Principle

The NIRs spectroscopy is used to acquire information about the nature of the functional groups present in a molecule, by exploiting the interaction between the light and the structure of a sample. The radiation from the NIRs regions is in fact able to promote transitions at the vibrational level. Visible (400–780 nm) and NIR (780–2500 nm) spectra are composed of combination and overtone bands that are related to absorption frequencies in the mid-infrared region (2,500–50,000 nm). These combination and overtone bands correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the same vis/NIR spectra. With suitable algorithms and statistical analysis (chemometrics), NIRs spectroscopy is an excellent tool for quantitative analysis. In most case-studies, NIRs techniques do not require sample preparation, offering a practical alternative to time-consuming analytical methods (chemical and physical), and could be capable to analyze samples through glass and packaging materials. Thus, the agro-food sector has demonstrated interest towards NIRs technology for measuring quality parameters, also along the minimally processed fruit and vegetable chain. NIRs techniques have been applied to a wide range of agri-food applications, and the feasibility of NIRs spectroscopy to measure quality attributes of fruits and vegetables has been shown for many products (Nicolaï et al., 2007). Data complexity arising from NIRs requires specific statistical analyses and qualified operators.

During fruit ripening biochemical changes occur at skin level and also in the pulp, and these changes are rather homogeneous for the whole fruit. NIRs analyses allow to measure only in a limited area of the sample and are able to reach the inner layers of the sample when appropriate wavebands are used.

Several types of NIRs applications have been developed for non-destructive measurement of the internal composition of fruits and vegetables, with specific acquisition setups. Reflectance measurements are generally preferred for these products and are made using a fiber optic probe in contact with the sample. This setup allows light absorbance measurements to be made through a portion of the sample, typically at depths of a few millimeters, depending upon wavelengths range and skin thickness (Lammertyn et al., 2000).

The devices

Three main types of NIRs devices can be identified: (i) laboratory instruments for applications in research centers or in industry laboratories, (ii) sorting and grading devices designed specifically for the fruit and vegetable industries, e.g. in warehouses, and (iii) portable devices for the use also directly in the field. Table 1 shows the main differences between the three types of NIRs devices.

Table 1: Characteristics of the three main categories of NIRs devices.

Instrument type	Application area	Flexibility of use	Applicability	Measurement accuracy and reproducibility	Cost

Laboratory devices	Research/industry	Adaptable to different matrices	Fixed system	Optimal	Average/high
Sorting and grading	Industry	Specific categories of products	Fixed system	Fair	Average/high
Portable devices	Also in field	Dedicated for individual products	Portable/handheld	Fair	Average

There is an increasing demand of NIRs portable devices, so more research is required in this area. The availability of handheld spectrophotometers has opened up the possibility of using them in the orchard for monitoring the fruit ripeness and quality.

Both in the case of portable and stationary instruments, the fundamental components of these systems are common, and there are five: (i) light source, (ii) light radiation transport system, (iii) sample compartment and measurement zone, (iv) spectrophotometer sensor, and (v) electronic hardware.

NIRs devices have been recently developed with attention to their simplification, by integrating user-friendly software for statistical processing and partial automation of analysis, with the aim to fit less skilful users.

Data analysis

Chemometric is an essential tool for the elaboration of e-nose and NIRs spectroscopy data. Multivariate statistical analysis is necessary to extrapolate useful information present in the data matrices, splitting not useful information and data noise.

The statistical techniques applied to multivariate output data generated by the sensor array signals are based on commercial or specially designed software using multivariate calibration and classification methods like principal component analysis (PCA), linear discriminant analysis (LDA), cluster analysis (CA), artificial neural network (ANN), partial least squares (PLS) regression, and multilinear regression (MLR).

PCA is a procedure that permits to extract useful information from the data, to explore the data structure, the relationship between objects, the relationship between objects and variables, and the global correlation of variables. It identifies orthogonal directions of maximum variance in the original data and projects the data into a lower-dimensionality space formed of a subset of the highest-variance components. The orthogonal directions are linear combinations (principal components) of the original variables, and each component explains a part of the total variance of the data (Beebe, Pell & Seasholtz, 1998).

LDA is one of the mostly applied classification techniques. The method maximizes the variance between categories and minimizes the variance within categories. This method renders a number of orthogonal linear discriminant functions equal to the number of categories minus one (Meloun, Militky & Forina, 1992).

CA performs agglomerative hierarchical clustering of objects based on distance measures of dissimilarity or similarity. The hierarchy of clusters can be represented by a binary tree, called dendrogram. A final partition, i.e. the cluster assignment of each object, is obtained by cutting the tree at a specified level (Gardner & Bartlett, 1992).

The ANN are very sophisticated modeling techniques able to model extremely complex functions (Benedetti et al., 2004). The basic unit of an ANN is the neuron. A neural network consists of a set of interconnected network of neurons. The input layer has one neuron for each of the sensor signals, while the output layer has one neuron for each of different sample properties that should be predicted. Usually one hidden layer with a variable number of neurons is placed between the input and the output layers.

During the ANN training phase, the weights and transfer function parameters are adjusted such that the calculated output values for a set of input values are so close as possible to the unknown true values of the sample properties. The model estimation is more complex than for a linear regression model due to the non-linearity of the model (Principe, Euliano & Lefebvre, 2000).

The PLS regression analysis is widely employed to obtain quantitative prediction of the parameters of interest. In PLS regression, an orthogonal basis of latent variables is constructed one by one in such a way that they are oriented along directions of maximal covariance between spectral matrix X and response vector Y. This method ensures that the latent variables are ordered according to their relevance for predicting the Y variable. Interpretation of the relationship between the X data and the Y data (the regression model) is then simplified, as this relationship is concentrated on the smallest possible number of latent variables. The PLS method performs particularly well when the various X variables express common information, i.e. when there is a large amount of correlation, or even collinearity, which is the case for spectral data (Guidetti, Beghi & Bodria, 2010).

Based on PLS algorithm, a classification model could be also calculated (PLS discriminant analysis, PLS-DA). The objective of PLS-DA is to find models that allow the maximum separation among classes of objects (Wold, Sjöström & Eriksson, 2001). PLS-DA accomplishes a rotation of the projection to latent variables focusing on class separation. A matrix of artificial (dummy) variables, assuming a discrete numerical value (0 or 1), was used as Y data. The Y dummy matrix was constructed so that the value of the objects belonging to the class was 1, and the value of all other objects was 0 (Musumarra, Condorelli & Fortuna, 2011).

Moreover, starting from regression coefficients obtained by the PLS model, a variables selection procedure could be envisaged (regression coefficient analysis, RCA). High absolute values of the coefficients indicate the importance and the significance of the effect on the prediction of Y variable (Liu, Jiang & He, 2009).

This procedure could be used for the selection of a limited number of effective variables and can be coupled with the MLR method, which allows to develop models using only a few important variables, to test the effectiveness of the selected wavelengths (Fernández-Novales et al., 2009; Wu et al., 2010). In fact, MLR technique is well suited when the number of variables is less than the number of samples and is not affected by collinearity (Naes et al., 2002).

In order to assess the accuracy of the calibration model and to avoid overfitting, validation procedures have to be applied. Leverage correction is an equation-based procedure to estimate the prediction accuracy without performing any prediction and is to be avoided at all times because it always leads to overoptimistic estimates. In leave-one-out cross validation, one sample is removed from the data set, and a calibration model is constructed for the remaining subset. The removed samples are then used to calculate the prediction residual. The process is repeated with other subsets until every sample has been left out once, and in the end the variance of all prediction residuals is estimated. In multifold cross validation, a well-defined number of samples ("segment") are left out instead of one. In internal validation, the data set is split into a calibration set and a validation set. The calibration model is constructed using the calibration set, and the prediction residuals are then calculated by applying the calibration model to the validation set. In external validation, the validation data set is independent and is, for example, obtained from a different orchard or different season (Esbensen & Geladi, 2010). To evaluate model accuracy, the statistic parameters usually considered are as follows: the coefficient of determination in calibration (R^2_{cal}), the coefficient of determination in prediction (R^2_{pred}), the root mean square error of calibration (RMSEC), and the root mean square error of prediction (RMSEP) (Guidetti, Beghi & Bodria, 2010). Prediction capability of a model can be evaluated with the ratio performance deviation (RPD), which is defined as the ratio between the standard deviation of the response variable and the RMSEP. RPD showing values <1.5 mean that calibration is not usable; between 1.5 and 2.0 allow to distinguish high and low values; between 2.0 and 2.5 approximate quantitative predictions it is possible; and finally, RPD values >2.5 and >3.0 identify models with a good and excellent prediction accuracy, respectively (Williams & Sobering, 1996). Ratio error range (RER) value could be also calculated for the evaluation of model performance. The RER is the ratio of the range in reference values of the validation samples divided by the RMSEP. Williams and Sobering (1996) suggest that the RER value should be 10 or higher.

The large number of spectral variables in most data sets often results in an unreliable prediction of the dependent variable. Chemometrics can be used for the selection of a small number of relevant variables, which represent the most useful information contained in the full spectra. In order to extract this useful information from the NIRs spectra, different variable selection methods could be performed (Chong & Jun, 2005; Xiaobo et al., 2010; Mehmood et al., 2012). In this way the spectral noise and the variables containing redundant information can be eliminated, and the sampling time of each spectrum could be reduced. However, variables selection may not always lead to better predictive results. For instance, a variable that is completely useless by itself can provide a significant improvement in performance when taken in combination with others (Xiaobo et al., 2010).

Electronic nose applications

Aroma is the most important characteristic determining fruit and vegetable quality and consumer's choice. In this contest, e-nose is a useful device for identifying, characterizing, and grading fruits and vegetables of different cultivars and varieties, since this instrument is able to rapidly and consistently evaluate simple and complex volatile mixtures without identifying all of the chemical compounds present in the sample headspace but considering the total odor fingerprint of the product (Wilson, 2013).

In agriculture, e-nose is widely used for quality evaluation, process monitoring, and detection of crop diseases (Li et al., 2010). A review of e-nose applications on fruits and vegetables from 2000 up to 2016 is shown in Table 2. Works are grouped considering four general aims: (i) ripeness evaluation, (ii) shelf life assessment of fresh and ready to eat products, (iii) defect and disease detection, and (iv) process monitoring. Moreover, in

Table 2 are reported the sensors applied in commercial and in prototype e-noses and the specific aim of each referred work.

Table 2: Overview of applications of electronic nose on fruit and vegetables.

E-nose application	Common name	Species	Specific aim	Sensors	References
Ripeness evaluation	Apple	*Malus domestica* Borkh.	Cultivar discrimination and prediction of the optimal harvest date	QMB (Libra Nose)	Saevels et al. (2003)
	Apple	*M. domestica* Borkh.	Quality indices assessment and maturity evaluation	CPs (Cyranose 320)	Pathange et al. (2006)
	Apple, pear and peach		Fruit ripeness monitoring	MOS (Prototype)	Brezmes et al. (2000)
	Mandarin	*Citrus reticulata*	Maturity monitoring	MOS (PEN 2)	Gómez et al. (2006b)
	Mandarin and orange	*Citrus unshiu* and *Citrus sinensis*	Quality detection	MOS (PEN 2)	Qiu and Wang (2015)
	Peach and nectarine	*Prunus persica*	Sensorial properties investigation	QMB (Libra Nose)	Di Natale et al. (2001a)
	Peach	*P. persica*	Cultivar discrimination and quality assessment	QMB (Libra Nose)	Di Natale et al. (2002)
	Peach	*P. persica*	Quality indices evaluation	MOS (Prototype)	Zhang et al. (2008a)
	Nectarine and peach	*P. persica*	Cultivar discrimination and quality evaluation	MOS (EOS 835)	Infante et al. (2011)
	Peach	*P. persica*	Quality indices prediction	MOS (Prototype)	Zhang et al. (2012)
	Peach and nectarine	*P. persica*	Prediction of harvest time and quality assessment	MOS (FOX 4000)	Su et al. (2013)
	Mango	*Mangifera indica*	Maturity assessment	MOS (FOX 4000)	Lebrun et al. (2008)
	Mango	*M. indica*	Maturity assessment	CPs (Cyranose 320)	Zakaria et al. (2012)
	Apricot	*Prunus armeniaca*	Cultivar discrimination	MOS (FOX 4000)	Solis-Solis et al. (2007)
	Apricot	*P. armeniaca*	Cultivar discrimination	MOS (PEN 2)	Parpinello et al. (2007)
	Pear		Quality indices prediction	QMB (Prototype)	Zhang, Wang, and Ye (2008b)
	Cherry	*Prunus avium*	Cultivar discrimination and ripeness evaluation	MOS (PEN 2)	Benedetti et al. (2010)
	Tomato	*Lycopersicum esculentum*	Maturity assessment	MOS (PEN 2)	Gómez et al. (2006a)
	Spring onion	*Allium* spp.	Quality evaluation	CPs (AromaScan)	Abbey et al. (2005)
	Garlic	*Allium sativum* L.	Cultivar discrimination	MOS and QMB (Prototype)	Trirongjitmoah et al. (2015)
Shelf life assessment of fresh products	Apple	*M. domestica* Borkh.	Storage time prediction	MOS (Prototype)	Guohua et al. (2013)

	Apple	*Malus sylvestris*	Quality assessment during shelf life	QMB (Libra Nose)	Saevels et al. (2004)
	Apple	*M. domestica* Borkh.	Shelf life evaluation	MOS (Prototype)	Brezmes et al. (2001)
	Mandarin	*C. reticulata*	Shelf life evaluation	MOS (PEN 2)	Gómez et al. (2007)
	Peach	*P. persica*	Cultivar discrimination and shelf life evaluation	MOS (PEN 2)	Benedetti et al. (2008)
	Peach	*P. persica*	Sensorial quality and aroma monitoring during cold storage	MOS (EOS 835)	Infante, Farcuh, and Meneses (2008)
	Peach	*P. persica*	Shelf life evaluation	MOS (FOX 4000)	Zhang et al. (2011)
	Peach	*P. persica*	Freshness prediction	MOS and QMB (Prototype)	Guohua et al. (2012)
	Peach	*P. persica*	Quality changes during cold storage	MOS (PEN 3)	Rizzolo et al. (2013)
	Banana	*Musa acuminata*	Quality assessment	MOS (Prototype)	Sanaeifar et al. (2016)
	Apricot	*P. armeniaca*	Aroma evolution during storage	MOS (EOS 835)	Defilippi et al. (2009)
	Pear	*Pyrus communis*	Odor discrimination	CPs (AromaScan)	Oshita et al. (2000)
	Tomato	*L. esculentum*	Cultivar discrimination and shelf life evaluation	QMB (Libra Nose)	Berna et al. (2004)
	Tomato	*L. esculentum*	Cultivar discrimination and shelf life evaluation	QMB (Prototype)	Berna et al. (2005)
	Tomato	*L. esculentum*	Shelf life evaluation	MOS (PEN 2)	Gómez et al. (2008)
	Tomato	*L. esculentum*	Quality assessment	MOS (EN-MS Alpha Prometheus)	Messina et al. (2012)
Shelf life assessment of ready to eat products	Apple	*M. domestica* Borkh.	Quality and shelf life of fresh cut slices	MOS (Fox 4000)	Bai et al. (2004)
	Apple	*Malus communis*	Shelf life of fresh cut slices	MOS (PEN 2)	Siroli et al. (2014)
	Apple		Shelf life modeling of fresh cut slices	MOS (PEN 3)	Correa, Quicazan, and Hernandez (2015)
	Pineapple	*Ananas comosus*	Shelf life evaluation of fresh cut fruit	MOS (PEN 2)	Torri, Sinelli, and Limbo (2010)
	Cicorino and carrot	*Cichorium Intybus* and *Daucus carota* L.	Shelf life evaluation	MOS and MOSFET (NST 3220)	Riva, Benedetti, and Mannino (2001)
	Iceberg lettuce	*Lactuca sativa* L.	Shelf life evaluation	MOS (FOX 3000)	Odumeru et al. (2003)
	Valerianella	*V. locusta* L.	Shelf life evaluation	MOS (PEN 2)	Giovenzana et al. (2014a)
Defects and diseases detection	Apple	*M. domestica* Borkh.	Defect detection	CPs (Cyranose 320)	Li, Heinemann, and Sherry (2007)

	Apple and orange	*M. domestica* Borkh.	Defect detection and quality evaluation	QMB (Prototype of Libra Nose)	Di Natale et al. (2001b)
	Orange	*C. sinensis*	Fungal infection evaluation	QMB (Libra Nose)	Pallottino et al. (2012)
	Blueberry	*Vaccinus virgatum*	Disease detection and classification	CPs (Cyranose 320)	Li et al. (2010)
	Blueberry	*V. virgatum*	Mechanical injury effect	CPs (EN 4000)	Demir et al. (2011)
	Strawberry	*Fragaria x ananassa*	Fungal disease detection and classification	MOS (PEN 3)	Pan et al. (2014)
	Tomato	*L. esculentum*	Microbial contamination detection	MOS (EOS 835)	Concina et al. (2009)
	Cherry Tomato	*L. esculentum*	Treatment to prevent fungal infection	MOS (PEN 3)	Zhao et al. (2010)
	Onion	*Allium cepa* L.	Disease detection	CPs (Prototype)	Li, Schmidt, and Gitaitis (2011)
	Onion	*cepa* L.	Quality evaluation	MOS (Prototype)	Konduru, Rains, and Li (2015a)
	Onion	*cepa* L.	Disease evaluation	MOS (Prototype)	Konduru, Rains, and Li (2015b)
	Potato	*Solanum tuberosum* L.	Bacterial disease detection	MOS (Prototype)	de Lacy Costello et al. (2000)
	Potato	*S. tuberosum* L.	Bacterial disease detection	MOS (PEN 3)	Biondi et al. (2014)
	Potato	*S. tuberosum* L.	Bacterial disease detection	MOS (FOX 3000)	Rutolo et al. (2016)
Process monitoring	Grape	*V. vinifera* L.	Post-harvest dehydration study	QMB (Prototype)	Santonico et al. (2010)
	Grape	*V. vinifera* L.	Off-vine dehydration time	QMB (Prototype)	Lopez de Lerma et al. (2012)
	Grape	*V. vinifera* L.	Determination of sun-drying time	QMB (Prototype)	Lopez de Lerma, Moreno, and Peinado (2014)
	Strawberry	*Fragaria x ananassa*	Osmotic dehydration treatment	MOS (PEN 2)	Buratti et al. (2006)
	Tomato	*L. esculentum*	Osmotic dehydration treatment	MOS (PEN 2)	Pani et al. (2008)

Ripeness evaluation

The assessment of ripeness is an important part of quality evaluation since maturity at harvest can have an effect on sensory and storage properties of fruits and vegetables. Harvesting fruit at an optimal physiological condition assures good quality by enouncing a number of characteristics such as extended shelf life, slower rate of decline in firmness, acidity, and color. Many methods to monitor fruit ripeness have been proposed, but the majority of these are not practical and require the destruction of the sample (Christensen, 1983; Wang, Teng & Yu, 2004). This is why, nowadays, prediction of ripening stage is mainly based on practical experience or visual parameters such as color changes. An alternative strategy to determine the maturity level consists in the evaluation of volatiles emitted by fruit during ripening. In literature, there are several works concerning changes in volatile composition during ripening, investigated by gas chromatography (GC) with headspace sampling, and GC combined with mass spectrometry (GC-MS) (Boudhrioua, Giampaoli & Bonazzi, 2003; Lavilla et al., 2002; Plutowska & Wardencki, 2007). These methods are not normally used to assess maturity since they are difficult to undertake and require expensive devices. Furthermore, the high number of volatiles prevents a simple interpretation of results, and, even considering only the major volatile compounds, a skilled analyst is still required. Thus, there is a need to develop analytical methods for the evaluation of optimal harvest date of fruits eventually even on trees, and the e-nose could be a useful tool since it is easy to use, portable, non-destructive, and rapid.

The e-nose has been successfully used in monitoring aroma changes during ripening of climacteric fruits such as apple (Brezmes et al., 2000; Pathange et al., 2006; Saevels et al., 2003), peach (Brezmes et al., 2000; Di Natale et al. 2001a; 2002; Infante et al., 2011; Su et al., 2013; Zhang et al. 2008a; 2012), mango (Lebrun et al., 2008; Zakaria et al., 2012), pear (Brezmes et al., 2000), apricot (Parpinello et al., 2007), and tomato (Gómez et al., 2006a), while there is less information about the e-nose application on non-climacteric fruits such as cherry (Benedetti et al., 2010), mandarin (Gómez et al., 2006b; Qiu & Wang, 2015), and orange (Qiu & Wang, 2015). Moreover, in some of these papers e-nose was also applied to cultivar discrimination and classification. In the work of Saevels et al. (2003) e-nose has been evaluated to predict the optimal harvest data of apples by considering also the cultivar effects; Di Natale et al. (2002) illustrated a study aimed to evaluate the improvement derived by the fusion of visible spectra and e-nose data. The experiments were performed on yellow peaches belonging to two cultivars, and data collected were analyzed individually and then fused together in order to classify the two cultivars and estimate reference parameters (texture measurement, soluble solid content (SSC), and pigment evaluation). In the work of Infante et al. (2011) e-nose was applied to predict the quality of four nectarines and one peach cultivar. On each cultivar, quality indices (flesh firmness, fruit weight, titratable acidity (TA), and ground color) were measured, and sensory analysis was performed; the results of MLR indicated that three sensory attributes (acidity, acceptability, and sweetness) and one e-nose sensor (S6–SnO_2, RGTO Mo, 45 Å) were the main variables that best related to the aroma of the evaluated cultivars. Solis-Solis et al. (2007) applied the e-nose to discriminate eight apricot varieties, then in a second step, eight aromatic compounds (hexanol, limonene, 2-hexenal, 6-metil-5-hepten-2-one, linaloon, 3,7-dimethyl-1,6-octadiene, β-ionone, and γ-decalactone) identified by GC-MS were recognized to be useful for the classification of the varieties. Similarly, Parpinello et al. (2007) applied the e-nose to analyze the headspace of 10 different apricot cultivars, and, by the application of a single hidden layer ANN with 35 neurons, a correlation index higher than 80% on test data set was achieved.

E-nose was applied on sweet cherries to assess the differences among four cultivars and to evaluate their ripening stage (Benedetti et al., 2010). In this work, CA was applied on maturity indices (color, TA, and total soluble solids) in order to categorize cherries into three clusters on the basis of their maturity level, then LDA was performed on e-nose data in order to categorize fruit into the three ripeness stages, and a correct classification percentage of about 95% was obtained.

Two works concern cultivar and genotype discrimination of vegetable products: Abbey et al. (2005) investigated the use of an e-nose to discriminate among eight spring onion genotypes and to evaluate the effect of sulfur nutrition and soil type on headspace volatile compounds, considering also the interaction between these factors; Trirongjitmoah et al. (2015) developed an e-nose method to classify garlic cultivars, and the performance of the e-nose system was confirmed by GC-MS analysis. These studies demonstrate the e-nose ability to discriminate among garlic cultivars and onion genotypes in relation to variations in growing conditions.

Shelf life assessment

Since the most important changes in fruit are experienced during the shelf life period, it is important to monitor the ripening process from harvest until consumption. Traditionally, shelf life is assessed by the evaluation of chemical and physical properties; firmness, color, SSC, and TA are the parameters commonly used by researchers and industry to evaluate fruit shelf life. For the consumers, aroma is an important aspect in defining fruit quality. Thus, measuring and evaluating post-harvest decay of fruits and vegetables through the evaluation of changes in volatile compounds by e-nose is market-oriented. In literature there are several studies reporting the e-nose application to assess the shelf life of fresh fruits evaluated at room temperature (Benedetti et al., 2008; Berna et al. 2004; 2005; Brezmes et al., 2001; Gómez et al., 2008; Guohua et al. 2012; 2013; Messina et al., 2012) or during cold storage (Defilippi et al., 2009; Gómez et al., 2007; Infante, Farcuh & Meneses, 2008; Oshita et al., 2000; Rizzolo et al., 2013; Zhang et al., 2011). In some works, the aroma development during fruit storage was also evaluated by GC-MS analysis (Berna et al. 2004; 2005; Defilippi et al., 2009; Guohua et al., 2012; Oshita et al., 2000; Rizzolo et al., 2013; Saevels et al., 2004; Zhang et al., 2011). In the paper of Saevels et al. (2004) a commercial e-nose and a mass spectrometry e-nose (MSE-nose), based on GC/MS measurements without separation of volatiles, were applied in combination in order to monitor changes in volatile profile of apples during shelf life. E-nose and MSE-nose data were used to build PLS calibration models for firmness and for the number of days in shelf life. The model for firmness based on MSE-nose data had a high correlation between predicted and measured values, while e-nose measurements contained information about the number of days in shelf life.

Peaches are climacteric and particularly perishable during storage; in the work of Benedetti et al. (2008) e-nose data collected on peaches from harvest until senescent were elaborated by PCA, and the loading analysis identified one MOS sensor (W5S) as the most relevant in the discrimination of fruit on the bases of their shelf life. The sensor responses were plotted against time and fitted with sigmoid transition function allowing the definition of the ripening stages based on first and second derivative trends. Classification and regression tree analysis was applied to classify peach samples into three defined ripening stages: unripe, ripe, and over-ripe.

Sanaeifar et al. (2016) applied a low-cost MOS-based e-nose to predict banana quality indices such as total soluble solids, TA, pH, and firmness during 4 days storage at different temperatures (20, 18, and 11°C). PLS, MLR, and support vector regression (SVR) techniques were applied. All models for firmness and total soluble solids showed a good prediction performance; however, for TA and pH there were a poor correlation with the signals of e-nose in MLR and PLS models. The results proved that the performance of SVR models for the prediction of quality indices of banana were better than the others.

Many researches have been carried out to monitor and extend the shelf life of ready to eat fruits and vegetables. The degradation of fresh-cut fruits and vegetables is a complex process concerning both microbial spoilage and physico-chemical and biochemical modifications that mainly affect the sensorial properties, like appearance and flavor. It is well known that aging affects the flavor characteristics by producing off-odors due to bacterial activity or to anoxic conditions that limit the shelf life of fresh-cut products (Rico et al., 2007). In literature there are some works about the application of e-nose in monitoring changes in volatile compounds of fresh-cut fruits (Bai et al., 2004; Correa, Quicazan & Hernandez, 2015; Siroli et al., 2014; Torri, Sinelli & Limbo, 2010) and vegetables (Giovenzana et al., 2014a; Odumeru et al., 2003; Riva, Benedetti & Mannino, 2001) during storage. Siroli et al. (2014) applied a commercial e-nose to evaluate changes in the aromatic profile of fresh-cut apple slices, packaged in modified atmospheres and treated with natural antimicrobials such as hexanal, citral, 2-(E)-hexenal, citron EO, and carvacrol, alone or in combination, to prolong their shelf life. By PCA analysis the e-nose data grouped samples on the basis of their storage time showing that the olfactory profiles perceived by the instrument were quite unaffected by the added antimicrobials. Torri, Sinelli, and Limbo (2010) used the e-nose in order to monitor the changes in volatile compounds of minimally process fresh-cut pineapple during storage at different temperatures. Riva, Benedetti, and Mannino (2001) applied an e-nose equipped with MOSFET and MOS sensors to evaluate the shelf life of fresh-cut "cicorino" and carrots. The results of these works showed the effectiveness of e-nose in modeling the aroma change of fresh-cut products as a function of storage time and temperature.

An e-nose was employed by Giovenzana et al. (2014a) to investigate the applicability in monitoring the shelf life of fresh-cut *Valerianella locusta* L. at different temperatures. Quality indices such as pH, water content, total phenols, and chlorophyll were evaluated, and the results were elaborated by CA in order to categorize *Valerianella* samples according to their freshness; four main groups were identified as "fresh", "acceptable", "spoiled", and "very spoiled". A LDA model was developed to test the performance of e-nose to classify samples into four classes of freshness. Results demonstrated that e-nose was able to support the conventional methods in shelf life assessment providing useful information for a better management of the product along the distribution chain.

Defects and diseases detection

Safety and quality of food products is currently one of the topics of interest to the consumer, and the ability to recognize the presence of deteriorated products during storage or packaging is certainly desirable. Damaged or deteriorated fruits and vegetables are often characterized by off-flavor, and they can have negative implications on consumer's health. According to recent studies, the e-nose can be a useful tool to monitor in a simple and rapid way the presence of internal defects and diseases in fruits such as apple (Di Natale et al., 2001b; Li, Heinemann & Sherry, 2007), orange (Di Natale et al., 2001b; Pallottino et al., 2012), blueberry (Demir et al., 2011; Li et al., 2010), strawberry (Pan et al., 2014), and tomato (Concina et al., 2009; Zhao et al., 2010) and vegetables such as onion (Konduru, Rains & Li 2015a; 2015b; Li, Schmidt & Gitaitis, 2011) and potato (Biondi et al., 2014; de Lacy Costello et al., 2000; Rutolo et al., 2016).

Di Natale et al. (2001b) measured the quality of post-harvest apples and oranges by using e-nose technology as a promising application for defects detection. Defects due to post-harvest treatment are particularly important, and among them mealiness (due to post-harvest overripening), skin damage (due to mechanical or temperature stresses), and infections affect strongly the consumer's perception. In this paper changes of orange and apple aroma due to the presence of mealiness and skin damage were evaluated by thickness shear mode quartz resonators-based e-nose. Results evidenced that in the case of oranges the e-nose was able to measure the aroma evolution occurring during a storage period of 1 month; in the case of apples e-nose was able to detect defect induced by post-harvest overripening (mealiness) and skin damage (such as cuts). A qualitative analysis by PLS-DA showed that the increase of mealiness does not change the nature of volatile compounds but their concentration; in skin cuts the oxidation process produced different compounds in the headspace.

E-nose was applied for the detection of *Penicillum digitatum* in Valencia oranges (Pallottino et al., 2012). Three hundred oranges were analyzed and the collected results screened by PLS-DA in order to investigate whether the e-nose could distinguish between infected and non-infected samples. Highest percentages of correct classification (100%) were obtained at low level of infection (2–5% infection in an independent test).

A conducting polymer sensor array was applied for detecting and classifying three common post-harvest diseases of blueberry fruit: gray mold caused by *Botrytis cinerea*, anthracnose caused by *Colletotrichum gloeosporioides*, and Alternaria rot caused by *Alternaria* sp. (Li et al., 2010). PCA of volatile profiles revealed distinct groups corresponding to the inoculated diseases; CA identified two clusters of non-inoculated fruits (control cluster) and inoculated fruits (pathogen cluster); GC-MS was used to characterize volatile compounds of inoculated blueberry, and six compounds (styrene, 1-methyl-2-(1-methylethyl) benzene, eucalyptol, undecane, 5-methyl-2-(1-methylethyl)-2-cyclohexen-1-one, and thujopsene) were identified as contributing most in distinguishing infected fruit. In a similar work (Li, Schmidt & Gitaitis, 2011), a conducting polymer e-nose was applied to onions inoculated with *Botrytis allii* and *Burkholderia cepacia* pathogens for botrytis neck rot and sour skin, respectively. CA dendrogram illustrated that the e-nose profiles of the two pathogen inoculated bulbs were much closer to each other and separated from the healthy onion bulbs. In the GC-MS experiments, 24 major volatiles were identified in pathogen inoculated bulbs, and the majority of them were sulfur and aliphatic compounds; moreover, in the pathogen inoculated bulbs the volatiles were one or two orders of magnitude higher than in the control healthy bulbs.

Soft root is a widespread potato tuber disease that causes substantial losses each year to the potato industry. In the work of Rutolo et al. (2016); the possibility to early detect and monitor this disease was explored using a commercial e-nose. Potato tubers were inoculated with *Pectobacterium carotovorum*, which causes soft root. The results obtained by the application of various classification models (linear and non-linear methods) showed that selected MOS sensors were suitable for early disease evaluation and for the detection of disease progression to a symptomatic stage.

Process monitoring

In the last decade, consumer's demand for processed products that keep their original characteristics is increased. Today every type of treatment should have as its goal the preservation of the sensorial and nutritional characteristics that are an important aspect of the processed food. Among processes that minimize the changes of the original characteristics, osmotic dehydration has gained an increased interest mainly as a pre-treatment in combined techniques (Torreggiani & Bertolo, 2004). In two works, a commercial e-nose was applied to evaluate changes of volatile profile during osmotic dehydration of strawberry slices (Buratti et al., 2006) and tomato slices (Pani et al., 2008).

Strawberry is one of the most used fruits for osmodehydration processing (Torreggiani & Bertolo, 2004) especially for its characteristic flavor, which is a very complex mixture of esters, aldehydes, alcohols, furans, and sulfur compounds (Azodanlau et al., 2004; Douillard & Guichard, 1989; Forney et al., 1996). In the work of Buratti et al. (2006) strawberry slices were subjected to osmotic dehydration at 30°C for 1, 2, 4, and 6 h using either 60% sucrose or 60% sorbitol solutions, and the e-nose was applied to evaluate the strawberry aroma changes. Nine major volatile compounds of fresh and processed strawberry slices were identified by GC. The results demonstrated that the e-nose was able to reveal changes in the strawberry aroma profile during processing and permitted the differentiation between dehydrated strawberry samples obtained with different osmotic treatments.

Pani et al. (2008) studied the influence of the osmotic pre-treatment on chemico-physical properties, drying kinetics, structure collapse, and color changes of air-dried tomato slices. In this work the e-nose was able to follow the aromatic profile evolution during air dehydration process, useful to understand and parameterize the degradative events caused by dehydration.

Post-harvest dehydration by solar irradiation and tunnel drying are two of the most widely used techniques to obtain dried grapes for consumption as raisins or for production of dessert wines. The parameters that winemakers use to control the drying time are the sugar concentration and the water loss. Anyway, the volatile compounds formed during drying are of great importance since excessive drying could compromise the aromatic quality of grapes. In this contest, the electronic nose is a rapid tool that can help the winemaker to decide the optimum drying time by assessing the aromatic evolution of grapes during dehydration. Lopez de Lerma et al. (2012) and Lopez de Lerma, Moreno, and Peinado (2014) employed the e-nose to establish the optimum sun drying time for *Vitis vinifera* L. cv Tempranillo grapes and Pedro Ximenez grapes; in the paper of Santonico et al. (2010) the e-nose was applied to study the post-harvest air dehydration of Montepulciano grapes.

Vis/NIR and NIR spectroscopy applications

An overview of spectroscopy applications on fruits and vegetables is shown in Table 3. Works were grouped based on instrumental characteristics of the NIRs devices employed for the studies.

Table 3: Selection of applications of vis/NIR and NIR spectroscopy on fruit and vegetables.

Instrument type	Common Name	Species	Spectral range (nm)	Response variable	References
Fixed system	Apple	*M. domestica* Borkh.	380–2000	SSC, Streif index, acidity, and firmness	Peirs et al. (2001)
	Apple	*M. domestica* "Idared" and "Golden delicious"	400–1100	SSC and firmness	Zude et al. (2006)
	Apple	*M. domestica*	300–1100	Chlorophyll	Zude-Sasse, Truppel, and Herold (2002)
	Apple	*M. domestica*	400–800	Chlorophyll, carotenoid, and anthocyanin content	Merzlyak, Solovchenko, and Gitelson (2003)
	Apple	*M. domestica*	400–2100	Texture and flavor	Mehinagic et al. (2003)
	Apricot and cherry	*P. armeniaca* L. and *Prunus serotina* L.	400–2500	SSC	Carlini, Massantini, and Mencarelli (2000)
	Banana	*Musa cavendishii* L.	220–2700	Glucose, fructose, sucrose, and chlorophyll *a*	Zude (2003)
	Carrot	*D. carota* L.	800–1700	Sugar content, αβ carotenes, chlorophyll *a*, vitamin C	Zude et al. (2007)
	Chicory	*C. intybus* L.	350–2500	Sensory parameters: (sweetness, bitterness, and crunchiness) crunchiness, sugar content, and bitter compounds	François et al. (2008)
	Kiwifruit	*Actinidia deliciosa*	300–1140	Dry matter and SSC	McGlone et al. (2002)
	Lamb's lettuce	*V. locusta* L.	400–1000	Glucose, fructose, sucrose, ascorbic acid, and chlorophyll content	Jacobs et al. (2014)
	Mango	*M. indica* L.	1200–2400	Firmness, SSC, and acidity	Schmilovitch et al. (2000)
	Pear	*P. communis* L.	350–2500	SSC and firmness	Paz et al. (2009)
	Pineapple	*comosus* L.	800–2560	SSC, TA, and pH	Di Egidio et al. (2009)
	Table grape	*V. vinifera* L.	833–2500	SSC	Parpinello et al. (2013)

	Tomato	*L. esculentum* L.	400–1500	Color, firmness, lycopene, SSC, TA, pH, and electrical conductivity	Clément, Dorais, and Vernon (2008)
Portable/hand-held	Apple	*M. domestica*	400–1000	SSC, chlorophyll, TA, flesh firmness, total phenols, carotenoids, and ascorbic acid	Beghi et al. (2013a)
	Apple	*M. domestica*	400–1000; 1000–2000	Quality decay during shelf life	Beghi et al. (2016)
	Apricot	*P. armeniaca* L.	650–1200	SSC, total acidity and firmness	Camps and Christen (2009)
	Blueberry	*Vaccinium corymbosum*	400–1000	SSC and firmness, total anthocyanins, total flavonoids, total polyphenols, and ascorbic acid	Guidetti et al. (2009)
	Grape for wine	*V. vinifera*	400–1000	SSC, TA, and pH, and anthocyanins and polyphenols content	Guidetti, Beghi, and Bodria (2010)
	Lamb's lettuce	*V. locusta* L.	400–1000	pH, water content, total phenols, and chlorophyll *a* fluorescence	Giovenzana et al. (2014a)
	Lamb's lettuce	*V. locusta* L.	400–1000; 1000–2000	Quality decay during shelf life	Beghi et al. (2016)
	Mandarin	*C. reticulata* L.	310–1100	SSC, TA	Antonucci et al. (2011)
	Mango	*M. indica* L.	1000–2200	SSC	Saranwong, Sornsrivichai, and Kawano (2003)
Simplified system	Apple	*M. domestica*	Different sets of few individual wavelengths	SSC, water content, and firmness	Qing, Ji, and Zude (2007)
	Blueberry	*V. corymbosum*	680, 740, 850	Ripeness index	Beghi et al. (2013b)
	Dye solutions (preliminary lab-scale tests)	/	630, 690, 750, 850	Different foreseeable applications	Civelli et al. (2015)
	Grape for wine	*V. vinifera*	670, 730, 780	SSC and polyphenols	Giovenzana et al. (2014b)
	Grape for wine	*V. vinifera*	375, 470, 516, 635	Anthocyanin content	Ghozlen et al. (2010)
	Kiwifruit	*A. deliciosa*	670, 720	Fruit maturity stage index	Costa et al. (2011)
	Apple	*M. domestica*	670, 720	Fruit maturity stage index in pre-harvest and during the storage life	Nyasordzi et al. (2013)
	Apricot,	Orange red, Bergarouge	670, 720	Fruit maturity stage index	Costa et al. (2009)
	Peach	*P. persica* (L.) *Batsch*	670, 720	Fruit maturity stage index	Bonora et al. (2013)

Lamb's lettuce	*V. locusta* L.	520, 680, 710, 720	pH, moisture, and total phenols content	Beghi et al. (2014)
Mango	*M. indica* L.	826, 882, 906, 954	Starch and dry matter	Saranwong, Sornsrivichai, and Kawano (2004)
Orange juices	Eight commercial brands	410, 520, 640, 930, 990	SSC and pH	Cen, He, and Huang (2006)
Pear	*P. communis* L.	18 selected wavelengths in the range 200–1100	SSC	Xu et al. (2012)
Wine grape	*V. vinifera* L.	630, 690, 750, 850	SSC and TA	Giovenzana et al. (2015)

Bench top full spectra devices

Many applications of NIRs spectroscopy as rapid tools for the prediction of the concentration of specific chemical constituents in agro-food products can be found in literature using bench top laboratory systems and sorting instruments for applications in research centers or in industry laboratories and warehouses. For example, NIRs have been successfully used to measure a wide range of apple fruit quality attributes, such as SSC (Zude et al., 2006), TA (Peirs et al., 2001), chlorophyll content (Zude-Sasse, Truppel & Herold, 2002), phytonutrients (Merzlyak, Solovchenko & Gitelson, 2003), and firmness (Mehinagic et al., 2003). The SSC is the most studied index using NIRs spectroscopy, since calibration of sugar and moisture contents, as indices of fruit maturity stage or quality in post-harvest, particularly show high potential for these products. For example, SSC was measured in apple (Peirs et al., 2001), table grape (Parpinello et al., 2013), pear (Paz et al., 2009), mango (Schmilovitch et al., 2000), apricot and cherry (Carlini, Massantini & Mencarelli, 2000), kiwifruit (McGlone et al., 2002), orange juice (Cen, He & Huang, 2006), banana (Zude, 2003), and carrot (Zude et al., 2007). An experiment was conducted to simultaneously measure various quality parameters of tomato (lycopene content, firmness, internal quality such as pH, soluble solids, TA, and electrical conductivity) in a non-destructive way by using vis/NIR reflectance spectroscopy and chemometrics (Clément, Dorais & Vernon, 2008). Results indicated that lycopene content and firmness were accurately predicted ($R^2 = 0.98$ and 0.75, respectively), while the prediction of internal quality was less accurate, partly due to a low variability of these parameters among samples. Several applications of NIRs spectroscopy are noticeable specifically for monitoring the evolution of physical, chemical, and sensorial characteristics of packaged minimally processed fruits and vegetables, thus ensuring the eating quality during the entire production chain. NIR spectroscopy was used by Di Egidio et al. (2009) to investigate the loss of freshness of fresh-cut pineapple samples, stored at different temperatures. The FT-NIR spectra were acquired in reflectance mode directly on the fresh-cut pineapple slice. PCA was applied to the second derivative of the spectra to uncover molecular modifications occurring over the storage time. Good results with a clear discrimination between samples classified as "fresh" (pineapple stored up to 5 days, 4 days, and less than 1 day at 5.3°C, 8.6°C, and 15.8°C, respectively) and "old" (samples stored for longer than 6 days, 5 days, and 2 days at 5.3°C, 8.6°C, and 15.8°C, respectively) were obtained for the studied storage temperatures (5.3, 8.6, and 15.8°C). The applicability of vis/NIR spectroscopy was recently tested on lamb's lettuce (*V. locusta* L.). Jacobs et al. (2014) developed a fast non-destructive methodology that used vis/NIR reflectance spectroscopy to give an estimation of the remaining potential shelf life of lamb's lettuce during storage. The vis/NIR spectra were correlated to the storage time and to the quality of the samples evaluated by colorimetric measurements and a panel of experts at the end of shelf life, by using PLS regression algorithm. Authors demonstrated that vis/NIR reflectance spectroscopy was a valid, fast, and non-destructive method for determining and quantifying the storage period of lamb's lettuce. François et al. (2008) tested a bench top NIR system for rapid prediction of sensory parameters in chicory like crunchiness, sugar content, and bitter compounds, obtaining good results.

Portable full spectra devices

The requirement to investigate fruit and vegetable quality and monitoring ripeness directly in the field resulted in the development of NIRs portable devices.

Research and innovations enabled NIRs devices to further decrease their physical size while increasing complexity and amount/size of collected data. Therefore, the availability of low-cost miniaturized spectrophotometers allows new NIRs instrumentation to be more compact and portable (McClure & Tsuchikawa, 2007; Wang & Paliwal, 2007) opening new possibilities for field use. A few portable spectrophotometers, for example, the Fruit Tester 20 (FANTEC, Germany) tested by Saranwong, Sornsrivichai, and Kawano (2003) on intact mango fruit for the SSC determination, or the Jaz Modular Optical Sensing Suite (Ocean Optics, the Netherlands), and the QS_300 (Unitec SpA, Italy) were proposed for different agro-food applications.

The employment of portable devices suitable for field use is more complex than laboratory applications, due to the uncontrolled environmental conditions such as temperature fluctuations, uncontrolled lighting conditions, and power source. These phenomena should be minimized by appropriate data processing (Nicolaï et al., 2007).

On fruits, a portable vis/NIR instrumentation, in controlled laboratory conditions, was applied by Antonucci et al. (2011) for prediction of TA on two cultivars of mandarin getting R^2 that ranged 0.66–0.77, while for the SSC R^2 ranged 0.71–0.72; on apricot, Camps and Christen (2009) estimated the SSC, the total acidity, and the firmness achieving R^2 in cross-validation that ranged 0.77–0.92, 0.53–0.94, and 0.72–0.85, respectively. Beghi et al. (2013a) tested a portable vis/NIR device on "Golden Delicious" apples for the prediction of SSC, chlorophyll, TA, flesh firmness, and apples nutraceutic properties as total phenols, carotenoids, and ascorbic acid, obtaining R^2 equal to 0.72, 0.86, 0.52, 0.44, 0.09, 0.77, and 0.50, respectively. Other studies were performed in field conditions to evaluate grape quality parameters (Guidetti, Beghi & Bodria, 2010) and by the same authors to predict ripening indices of blueberry (Guidetti et al., 2009). Regarding vegetables, Giovenzana et al. (2014a) investigated the applicability of portable vis/NIR spectroscopy in monitoring the freshness decay of fresh-cut *V. locusta* L. during storage at 4, 10, and 20°C. The shelf life of samples was evaluated by quality parameters (pH, water content, total phenols, and chlorophyll a fluorescence). PLS-DA models were developed to classify samples in four classes, based on the above mentioned parameters. The results obtained from PLS-DA models, in validation, gave a positive predictive value (PPV) of classification between 74% and 96%. Moreover, predictive models were performed applying PLS regression algorithm to study the correlation between quality indices and vis/NIR spectra. Very good results were obtained for total phenols with R^2 and RPD equal to 0.89 and 3.19 and for chlorophyll a fluorescence with R^2 and RPD equal to 0.92 and 3.22, respectively.

Finally, NIRs were applied through the packaging film by Beghi et al. (2016). The authors investigated the capability of NIRs spectroscopy to perform useful optical measurements not only directly in contact with the samples but even from the outside of the pack through the packaging film on fresh-cut *Valerianella* leaves and fresh-cut Golden Delicious apple slices. PCA and PLS-DA were applied on spectral data, and the expiration date was chosen as the freshness threshold to reach the objective. Results showed that the packaging presence had only a slight effect on the classification capability. Moreover, the results on Golden Delicious were also satisfactory even if the classification performances were lower than those obtained for *Valerianella*; however, overall collected PPVs ranged from 86.7% to 100.0%. These findings would be useful in the development of freshness decay assessment tools using these optical techniques along products' post-packaging chain.

Simplified devices

The above mentioned applications rely on wide spectral ranges (thousands of wavelengths) and thus require multivariate techniques for data processing to build calibration and prediction models (Cen & He, 2007; Williams & Norris, 2001). Complex chemometric techniques have to be applied to explain chemical information encoded in spectral data (Cogdill & Anderson, 2005). Recently, a general challenge of the research in the field of NIRs instruments is the setting up, design, and testing of innovative simplified optical devices dedicated to a specific chain of the fresh and fresh-cut product sector. In this case chemometrics is used for the selection of a small number of relevant wavelengths, highly representative of the useful information contained in the full spectra (Sun, 2010; Xiaobo et al., 2010). This approach allows to reduce to negligible values the spectral noise and to eliminate the variables containing redundant information. Moreover, a reduced cost for potential miniaturized devices, built to work at only these selected wavelengths, can be foreseen.

The development of simplified optical system for the rapid monitoring of fruit and vegetable parameters directly in field (e.g. ripeness evaluation, diseases and disorders detection, chemicals and physical properties prediction, freshness level or shelf life analysis) could be based on light-emitting diode (LED) technology. In particular, the evaluation of the ripening level of fruits showed several application cases (Beghi et al., 2013b; Civelli et al., 2015Costa et al., 2011; Giovenzana et al., 2014b).

The identification of the most significant bands can be used as starting points for the selection of a few highly informative wavelengths. The selection can maintain the predictive ability of the models by reducing the bias introduced by the uninformative wavelengths (Xu et al., 2009). To reach this goal, considerable efforts have been recently directed towards developing and evaluating different procedures for an objective identification of a few spectral variables containing most of the useful information and to reject redundant or useless variables (Zou et al., 2010). In order to assess the performance of the envisaged simplified prototypes, comparative tests were performed using commercial devices using the full spectral range (Beghi et al., 2014; Giovenzana et al. 2014b; 2015).

In a view of simplified optical systems, different approaches for variables selection were applied on wine grapes (Giovenzana et al., 2014b) and on blueberries (Beghi et al., 2013b), resulting in a selection of a very limited number of highly informative variables. The same authors identified and analyzed freshness parameters (pH, polyphenols, water content, and chlorophyll *a* fluorescence) of fresh-cut *Valerianella* leaf for the setting up of a simplified device (Beghi et al., 2014). Through partial least squares regression analysis (PLS-RCA), standardized regression coefficients from PLS models were used to select the relevant variables, representing the most useful information into the full spectral region, and the four selected wavelengths were 520 nm, 680 nm, 710 nm, and 720 nm. In order to highlight the innovative features, a scheme of a future device was proposed adopting four LEDs as illumination sources at the specific wavelengths, with filtered photodiodes for the readout signal. In order to study the efficiency of the wavelengths selection, the MLR technique was applied. The overall calibration and prediction results of the MLR models were satisfactory, although the performance of the MLR models was slightly worse than the good PLS models. RPD value for pH decreased from 2.54 for PLS to 1.83 for MLR; regarding the moisture content, RPD showed a slight decrement from 2.25 to 2.08, and for total phenols from 3.19 to 2.48 for PLS and MLR, respectively.

Xu et al. (2012) studied four different variable selection methods, namely, stepwise MLR, genetic algorithm (GA)-PLS, interval PLS, and successive projection algorithm (SPA)-MLR combined with GA (GA-SPA-MLR) to on-line determination of sugar content in pears. The results derived by these techniques were then compared. The calibration model built using GA-SPA-MLR on 18 selected wavelengths (2% of the total number of variables) exhibited higher $R^2 = 0.880$ and RMSEP = 0.459° Brix for the validation set.

Qing, Ji, and Zude (2007) tested GAs for the wavelength selection for predicting SSC, firmness, and water content in apple fruit; different sets of individual wavelengths were tested for the identification of the most informative for each studied parameter. Saranwong, Sornsrivichai, and Kawano (2004) selected four effective wavelengths (826, 882, 914, and 954 nm) usable for the prediction of the ripe-stage eating quality (starch content and dry matter) of mango fruit starting from NIR spectra, achieving correlation coefficients of $r = 0.93$ and $r = 0.96$ for starch and dry matter, respectively.

A limited number of already built prototypes of simplified systems based on the analysis of a few variables can be found in literature. Civelli et al. (2015) designed and tested a simplified, LED-based, modular system to be used for the rapid evaluation of fruit and vegetable quality, and preliminary tests performed on lab scale using dye solutions gave encouraging results. The designed LED-based vis/NIR system was tested by the same authors (Giovenzana et al., 2015) for rapid ripeness evaluation of white grape (*V. vinifera* L.). In order to prove the effectiveness of the simplified system, a portable commercial vis/NIR spectrophotometer was used as reference instrument for performance comparison (Figure 2). Correlations between the optical data matrix and ripening parameters (total SSC and TA) were carried out using PLS regression for spectra and using MLR for data from the simplified device (Table 4). Moreover, classification analysis was also performed with the aim of discriminate ripe and unripe samples. Finally, simple equations for SSC and TA prediction were calculated.

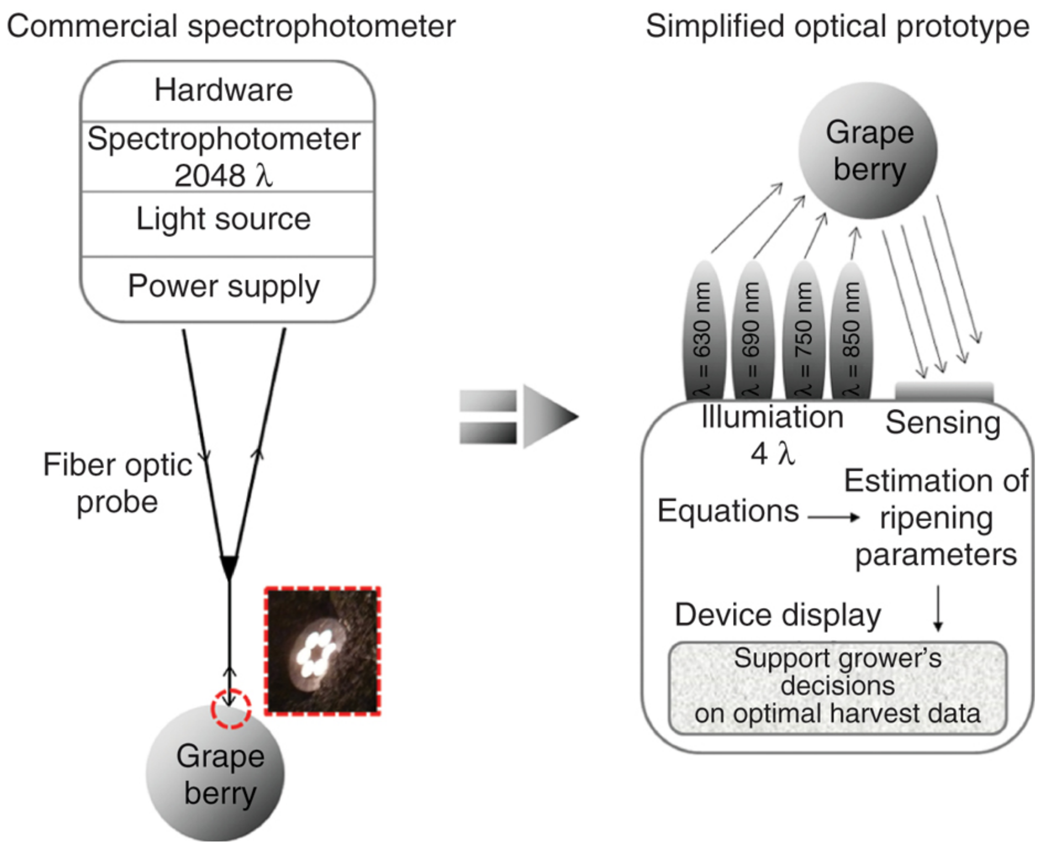

Figure 2: Functional scheme of (A) a portable full range vis/NIR device and (B) a simplified optical device working at four selected wavebands for supporting decisions on optimal harvest date (Giovenzana et al., 2015).

Table 4: Descriptive statistics and statistics of the PLS models elaborated on VIS-NIR spectra and of the MLR models, based on data of the simplified device (four wavelengths 630, 690, 750, and 850 nm) to predict the ripeness parameters of white grapes (Giovenzana et al., 2015).

Ripeness parameters	**Cross-validation PLS**					**Cross-validation MLR**				
	N	R^2_{cv}	**RMSEC**	**RPD**	**RER**	**N**	R^2_{cv}	**RMSECV**	**RPD**	**RER**
SSC (°Brix) *on berries*	475	0.71	1.8	1.94	8.72	433	0.66	1.9	1.74	8.26
SSC (°Brix) *on bunches*	95	0.80	1.3	2.13	8.77	89	0.65	1.8	1.67	7.31
TA (g/dm^3) Umidity	95	0.81	1.9	2.32	10.14	89	0.85	1.8	2.50	12.40

A few examples of commercial non-destructive devices based on a small number of wavelengths are already available on the market. These applications are mainly dedicated to fruits. For example, the University of Bologna patented innovative and simplified NIRs equipments, namely, DA-Meter for peaches (Bonora et al., 2013) and Kiwi-Meter for kiwi (Costa et al., 2011). These systems are used for the analysis of the ripeness level of the fruit through indices based on differences in absorbance between specific wavelengths. This type of instrument, simple and portable, can be used directly on the fruit on the trees and can help growers in making decisions regarding the best cultural management practices (such as pruning, thinning, and nutrition). In this way, the heterogeneity of the product can be reduced and, therefore, the management of product lots can be simplified during pre- and post-harvest. Moreover, the DA-Meter was used also on apricot to verify the applicability of the device in monitoring ripening-related changes (Costa et al., 2009) and to sort apples both at harvest for different quality classes and after storage at removal from storage rooms for different marketing classes (Nyasordzi et al., 2013).

Another commercial hand-held fluorescence sensor equipped with nine LEDs (six UV and three RGB) and filtered-photodiode detection (Multiplex®, FORCE-A, Orsay, France) was tested for the analysis on anthocyanin content in grape samples (Ghozlen et al., 2010). Simplified devices based on the measurement of the normalized difference vegetation index are also available (Garrity, Vierling & Bickford, 2010; Sankaran et al., 2010); these instruments are used for remote sensing application for the study of the relationships between spectral reflectance at specific wavelengths and the characteristics of the vegetation canopies.

Future perspectives

As summarized in this review, e-nose and NIRs devices have been used for many applications to analyze and evaluate the quality of fruits and vegetables. The availability of non-destructive instruments that allow to evaluate changes during shelf life or to estimate quality parameters may have a wide number of practical applications in the product chain: during ripening, in the production process, in the storage period, and during the distribution. Furthermore, a future perspective could be the implementation of these devices, both e-nose and NIRs systems equipped with more robust predictive models, directly at the point of sale as a guarantee, for the consumers, of fresh and minimal processed product quality. New researches should be performed in view of a general simplification of the devices and higher user-friendly utilization.

E-nose and NIRs can be mutually complementary, and their combined application could be assumed; sensors-fusion approach could allow a comprehensive analyses of physico/chemical and sensorial features through the simultaneous use of both these technologies in simplified systems based on a few e-nose sensors and NIRs variables, thus providing rapid information about the appearance, the chemical composition, and the aromatic profile of fruits and vegetables.

These two techniques could be applied as non-destructive tools to classify fruits and vegetables in homogeneous lots with the purpose of a better management of their destination during postharvest life in order to avoid fruit and vegetable wastage.

Regarding NIRs, important drivers for a further success of these optical systems for evaluating fresh and minimally processed fruits and vegetables will be (i) the spectral analysis through the packaging and (ii) the design of compact-sized LED technology-based devices and of customized optical hardware to be coupled with smart phones and related applications, making mobile devices able to classify products on the bases of their quality. These devices are in fact increasingly complex, computationally powerful, sensor-rich, and integrated with social networking. The development of smart phones has led to a proliferation of software applications (apps) which are able to run the execution of the optical measurements, using also the embedded camera of the device. Of course, further studies are needed to determine the best operating conditions and the engineering phases to perform the measurement directly at the retail site. Researchers need to better investigate the measurement through the packaging considering the potential influence of the headspace between the film and product surface, which can affect the spectroscopic signal sensitivity.

Considering the e-nose, the challenges for the future are a further development of e-nose technologies for smaller, simplified, portable, and low-cost devices to be used from field to retail site. The development of new sensor types more effective for gas detection and discrimination and the execution of new algorithms for data elaboration are required to improve the applicability of this device.

In future, the availability of simpler and low-cost compact tools, also combining different technologies, will allow a big impact at different levels of the supply chain, with a real possibility of wide diffusion of these devices up to the consumers. Producers and retailers could take advantage of the application of these non-destructive devices for better management of the products in order to share with customer quality information about fruits and vegetables on sale, maximizing transparency and ensuring consumer loyalty.

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