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Review

Review: NIR Spectroscopy as a Suitable Tool for the Investigation of the Horticultural Field

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Abstract: The last 10 years of knowledge on near infrared (NIR) applications in the horticultural field are summarized. NIR spectroscopy is considered one of the most suitable technologies of investigation worldwide used as a nondestructive approach to monitoring raw materials and products in several fields. There are different types of approaches that can be employed for the study of key issues for horticultural products. In this paper, an update of the information collected from the main specific International Journals and Symposia was reported. Many papers showed the use of NIR spectroscopy in the horticultural field, and the literature data were grouped per year, per product, and per application, such as studies of direct (chemical composition) and indirect (physical and sensorial) properties (P), process control (PC), and authenticity and classification studies (AC). A mention was made of a recent innovative approach that considers the contribution of water absorption in the study of biological systems.

Keywords: NIR spectroscopy; review; nondestructive techniques; horticultural products

1. Introduction

The application of near infrared (NIR) spectroscopy to the horticultural field still attracts considerable attention. The three last dedicated reviews, available in the literature [1–3], in books relating to the spectroscopic sector, were published before 2010, focusing their attention on adequate ways to analyze fresh horticultural products, and scheduling big tables to highlight the product category, the considered parameters, and the used instrumentation. In particular, Saranwong and Kawano [2] reported exhaustive information on the basic components (light source, detector, etc.) of NIR spectroscopy setup, illustrating several commercially available solutions to reach specific objectives, which are still useful. A short paper [4], published in 2016, while containing traditional and innovative concepts on the trend of NIR applications in the horticultural sector, also mentions bibliographic documents prior to 2010. For this reason, it is time to also update our knowledge of NIR spectroscopy in journals more dedicated to the agronomic field with the aim to help scientists and technicians, operating at both the public and private level, in the collection of useful information about the application of this fast technology, its ability to detect several quality attributes, and for a rapid online sorting of products into quality categories. Today, the development of small portable NIR systems, the improvement of acquisition and processing software, and the progresses in miniature electronics allow an easier approach to NIR spectroscopy more than in the past. In this context, this paper was assembled to update information about the new developments and uses of NIR spectroscopy as a useful tool for measuring internal quality characteristics of horticultural products (fruit and vegetables) in the field, during postharvest and storage, at the market, while also exploring some new applications and including practical experiences and outcomes from an industrial perspective. Seeds, trees, and other specific classes were not considered. The literature data were grouped per year, per product, and per application, such as studies of direct and indirect properties (P), process control (PC), and authenticity and classification studies (AC).

2. Collection of Literature Data

The update of the information reported here was done by checking the scientific papers published since 2009 in the main specific International Journals and Symposia, while some papers were also recovered in International Journals focused on food science. Unfortunately, the proceedings of the Asian Symposia and Conferences could not be added to this review because they are written in their original language, which is very difficult to translate. The aim of this paper was to make available a robust list of papers for a rapid consultation, allowing a simple recovery of dedicated references. Table 1 reports the list of the total papers reviewed; references were grouped by product of interest/assigned class on the basis of the type of determinations made; year of publication (as total references/year and reference/class); total number of papers; and the reference number, as reported inside the "References" paragraph, shown in the last column. In this way, the whole set of information can be checked using Table 1, as a summary table for easy consultation. A first analysis of the data reported in Table 1 allowed us to observe how, out of 160 bibliographic references [5–30,30–165], 80% concerned investigations and studies on fruit [5,7,13,15–30,33–38,40–43,45–59,64,67–93,102–104,106,108,111–121,123–135,141–143,145–162], of which 30% were carried out on apples, with a total of 41 referred papers [21–27,33,38,46,58,59,80–82,84–92,113,123–134,146,150,153,155]. Thus, it appears that many groups of researchers have considered the apple as a model fruit, suitable for testing the applications of NIR spectroscopy in the horticultural sector. About 50% of the papers were focused on the use of NIR for process monitoring and authentication and classification studies [64–145,157–161]. Although olive is a fruit, there is usually a tendency to consider it as a vegetable because olives are not consumed after a meal but as a side dish or appetizer. Using this meaning, olives have been, among vegetables, the most studied species [94–96,136–140], with papers classified in class groups (PC) and (AD); the last dedicated review for this kind of vegetable was published in 2015 [96]. The available literature has been growing from 2013 to today, and 20 papers have been published already in 2019, indicating a parallel growth of interest for this kind of technology in the horticultural field.

Table 1. List of papers reporting near infrared (NIR) applications in the horticultural field.

Product/Class	Year of Publication											# of Papers	Reference Number
	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019		
acerola							1	2	1			4	
P							1	1				2	[5,41]
PC								1				1	[64]
AC								1				1	[104]
apple	3	3		2	4	3	4	2	2	8	10	41	
P	2			1	1	1	1	2	1	1	4	14	[21–27,33,38] 46,58–59,146,151
PC		2			2	1	2			3	3	13	[80–82,84–92] [153]
AC	1	1		1	1	2	1		1	4	2	14	[113,123–134] [155]
apricot	1											1	
P	1											1	[42]
asparagus											1	1	
AC											1	1	[107]
avocado	1		1									2	
P	1											1	[7]
AC			1									1	[108]
bananito								1		1		2	
P										1		1	[8]
PC								1				1	[68]
blueberry	1					1	1					3	
P						1	1					2	[16,28]
AC	1											1	[135]
cassava					1							1	
P					1							1	[20]
cherry										2		2	
P										2		2	[43,148]
cherry tomato	1											1	
P	1											1	[31]
citrus	1				1		1	1	2		1	8	
PC					1							1	[74]
AC	1			1			1	1	2		1	7	[106,114–118,162]

Table 1. *Cont.*

Product/Class	Year of Publication											# of Papers	Reference Number
	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019		
cynar								1				1	
AC								1				1	[109]
fruit	2		1		3	4		2	2	1	1	16	
P	1		1			4		1	2			9	[10,11,13,45,47,49,51,128,147]
PC	1				2			1			1	5	[69–72,83]
AC					1					1		2	[111,112]
fruit and vegetables						1			1	1		3	
P										1		1	[14]
PC						1						1	[97]
AC									1			1	[163]
garlic								1				1	
P								1				1	[6]
grape	2	1		1	1	1		2		1	1	10	
P	2	1		1		1					1	6	[34–37,151,152]
PC								2		1		3	[102,103,154]
AC					1							1	[145]
kiwi	1								1			2	
P	1											1	[52]
PC									1			1	[73]
macadamia											1	1	
PC											1	1	[93]
mandarin	2					1		1				4	
P	2							1				3	[17,53,149]
AC						1						1	[158]
mango	6	1		1	2	1		1	3	1	1	17	
P	1				1			1	3			6	[18,19,54–57]
PC	2	1		1	1					1	1	7	[67,75–79,161]
AC	3					1						4	[119–121,159]
eggplant										1		1	
AC										1		1	[122]
olive		1		1		1	3		1	1		8	
PC							2			1		3	[94–96]
AC		1		1		1	1		1			5	[13–140]
onion										1		1	

Table 1. *Cont.*

Product/Class	Year of Publication											# of Papers	Reference Number
	2009	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**	**2019**		
P										1		1	[44]
orange										1		1	
P										1		1	[40]
palm fruit				1								1	
P				1								1	[29]
papaya										2		2	
P										1		1	[30]
passion fruit						1				1		2	
P						1				1		2	[15,50]
peach									1	1		2	
AC									1	1		2	[142,143]
pear	1				1					1		3	
P										1		1	[12]
PC					1							1	[160]
AC	1											1	[141]
pineapple							1					1	
P							1					1	[165]
pomegranate										2		2	
P										1		1	[48]
AC										1		1	[156]
potato								1				1	
P								1				1	[60]
rape											1	1	
P											1	1	[32]
spinach										1	1	2	
P										1		1	[62]
PC											1	1	[100]
strawberry								1		1		2	
P										1		1	[9]
AC								1				1	[157]
summer squash									1			1	
PC									1			1	[164]
tapioca											1	1	

Table 1. *Cont.*

Product/Class	**Year of Publication**											**# of Papers**	**Reference Number**
	2009	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**	**2019**		
PC											1	1	[101]
tomato									1	1	1	3	
P									1			1	[61]
PC										1		1	[98]
AC											1	1	[144]
vegetable						1		1		2		4	
P						1						1	[63]
PC										1		1	[99]
AC								1		1		2	[105,110]
watermelon							1	1				2	
PC							1	1				2	[65,66]
zucchini					1							1	
P					1							1	[39]
	22	6	2	6	14	15	11	18	14	31	20	159	

P: Direct and indirect properties, PC: Process control, AC: Authenticity and classification studies.

2.1. Direct and Indirect Properties

The Application of NIR spectroscopy within the horticultural field goes back to the late 1920s [2]. As with other food and feed applications, the traditional methods for determining the quality of fruit and vegetables are time-consuming and expensive. To overcome these disadvantages, the potential of NIR spectroscopy for monitoring the quality of fruit and vegetables has been evaluated by different research groups. Several papers have been published, dealing mainly with the determination of Brix (a measure of soluble solids content) and dry matter contents, using quantitative calibration models, and ascribable to (P) categories. Unlike in the past, today, the determination of the main composition parameters, which is useful for describing the quality according to the product category, is carried out with portable instrumentation to be used in field and/or in process. Figure 1 shows the microNIR1700 (VIAVI Solutions, CA, USA), instrumentation owned by the Research Centre for Engineering and Agro-Food Processing—CREA-IT in Milan (Italy).

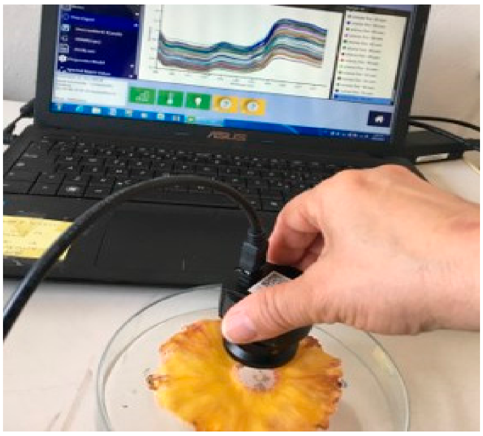


Figure 1. The microNIR1700 (VIAVI Solutions, CA, USA) at work.

The chemical and physical parameters that define intrinsic quality are often determined simultaneously thanks to the use of multicomponent calibrations. For this reason, various works report both data relating to direct index measurements (quantitative parameters) [5–39] and indirect indices (pH, titratable acidity, texture characteristics, and sensory parameters) [40–63]: They are reported in Table 1 with the same legend group (P) [30,128,146–152]. In order to get an idea of the predictive ability of a model, a number of statistical measures were used. These can be applied to the calibration set (the group of samples that were used to build the model parameters), the cross-validation set (samples temporarily excluded from model development but still ultimately involved in the development of the model), and the independent set (samples that have no input in the development of the model). Among the main important statistics figures, RPD (ratio of standard error of performance to standard deviation) and RER (range error ratio) cover an important role because their values are dimensionless, meaning that they can be compared on the same basis between models for different constituents/properties. In 1999, AACC (American Association of Cereal Chemists) International [166] published guidelines containing general information on NIR model development, performance evaluation, and calibration transfer to instruments of a similar brand, solely focused on useful statistics. The interest of researchers during the last decade has already moved towards the study of nutritional compounds and microcomponents, such as pigments [31], lutein [38], total phenolic content [39], carotenoids [15,65,66], nitrate [164,165], and sulfur dioxide [30].

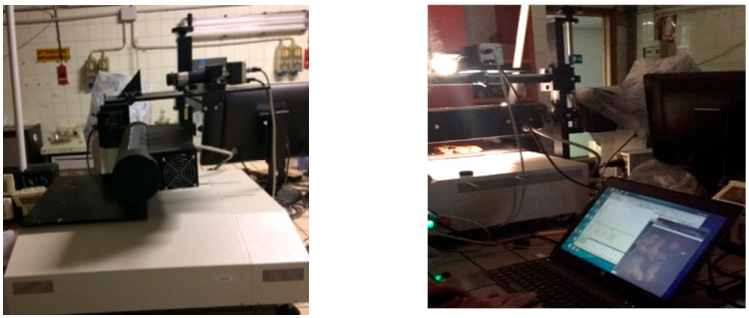
2.2. Process Control, Authenticity, and Classification Studies

Within the food production and processing industry, the requirements of quality control have received much focus recently. In parallel, modern near infrared (NIR) technology offers fast and cost-effective analyses that can afford quality control in both the laboratory and factory environments.

In this paper, the term "process" has been used in the widest sense, classifying in this group of studies in-line, at-line, and online industrial applications as well as research concerning the conservation, storage, and shelf-life of horticultural products. Often, the monitoring of a transformation process is related to the control of authenticity and final quality, so papers ascribable to PC and AC applications, shown in Table 1, were reported in this paragraph. The application of NIR spectroscopy in evaluating the internal and external quality of citrus fruit has been reported in a recent review [162], where the research progress and future prospects in this field were highlighted. The authors concluded that one of the challenges facing future applications of NIRS technology is the inherent variability in fruit and similar biological products, taking into account that the choice of NIR settings and analytical frameworks could affect both the model accuracy and robustness, and this deserves attention for future research. Just as an example, a study [65] focused on the carotenoids determination on intact watermelon using an online NIR probe was mentioned. Authors concluded that lycopene, β-carotene content, and the Brix degree of watermelon could be satisfactorily predicted using an online NIR spectrometer. Even though carotenoids and sugars are located in the flesh, the presence of rind did not seem to interfere with quantitative calibration. The possibility to monitor and analyze each single fruit could represent a step forward for valorizing nutritional characteristics of agri-food products and repositioning them on the market. Furthermore, the availability of small and compact instrumentation allowed the easy checking of fruit quality along the supply chain, from harvest, to storage, to retail distribution, in order to track the product history and to identify fruit that were not managed according to the product specification, suggesting the use of NIR spectroscopy for product traceability. Predictive models based on the NIR spectra could also be developed in order to monitor product quality along the supply chain [85]. Portable devices have been also used for on-field monitoring of the ripening degree of climacteric fruits. The possibility to estimate this feature directly on the tree, through the setup of portable devices, allowed a more precise definition of the optimum time for the fruit harvest and thus improved the final quality. A recent review [163], published in *Critical Reviews in Food Science and Nutrition*, gave a detailed summary about the influence of physical and biological variability, as well as the correction and compensation methods for eliminating or reducing the effects in fruit and vegetable quality nondestructive inspection using imaging and spectroscopy techniques. In fact, a great variety of physical and biological properties of agricultural products influence the optical propagation properties and interaction behaviors with incident light, thus decreasing the quality inspection accuracy.

The NIR technique associated with chemometrics (PLS algorithm) allowed us to elaborate predictive models for the conventional ripening parameters [45]. Particular mention has to be made in this paragraph to the use of hyperspectral imaging systems (HSI) and scanner cameras [5,8,60,67,81,109,112,126,129,143,144,148]. Hyperspectral imaging is a complex, highly multidisciplinary field that can be defined as the simultaneous acquisition of spatial images in many spectrally contiguous bands. Each pixel in the hyperspectral image contains a complete spectrum. Therefore, hyperspectral imaging is a very powerful technique for characterizing and analyzing biological and food samples. The strong driving force behind the development of hyperspectral imaging systems in food quality evaluation is the integration of spectroscopic and imaging techniques for discovering hidden information nondestructively for direct identification of different components and their spatial distribution in food samples. As a result, hyperspectral imaging represents a major technological advance in the capture of morphological and chemical information from food and food products [167]. Whether fruit or vegetables (e.g., apples, tomatoes, onions or berries), products can be quickly and reliably identified using NIR technology HSI to detect impurities such as wood, paper, plastics, stones or insects. As a result, this technology is ideally suited for usage in optical sorting systems. In contrast to conventional RGB (red-green-blue) sensor systems, differences in color and shape between product and impurity are not necessary for a successful sorting process. Identification using NIR technology is based on differences in chemical composition. Therefore, leaves, branches, stems and shells of the same color can be distinguished. Hyperspectral imaging NIR technology can also be used for semiquantitative analysis of carbohydrates and to determine water content.

HSI technology can be integrated directly into the production process. The measurement is contact-free, e.g., installed above a conveyor belt. Such systems will be applied for (i) the analysis of quality class in the respective product, (ii) determination of the optimal degree of the maturity or (iii) early detection of bruises. The analysis result can be visualized for each location point. The results can be used for a monitoring solution or a sorting process. A spatially resolved quantitative analysis of carbohydrates as well as the determination of water content on a laboratory scale can be quickly and easily performed with the hyperspectral scanning system. The measurement is carried out contact-free without any extensive sample preparation. The analysis result of the whole sample is available within seconds either as a false color image to evaluate the homogeneity or displayed as a statistical object-related analysis result. The identification routines are customized and calibrated towards the results of the reference analytics. From the literature published in the last 10 years, the strong development of HSI and MSI applications in the food industry steadily emerges with considerably wider applications in the future. Different algorithms are available for data processing, and these systems are useful for several kinds of applications: traceability, origin, online and in-line studies, and determination of physical and chemical properties. However, the cost of instrumentation is still high, and in general, no training is available for industry operators. Figure 2 shows the spectral scanner system (DV Srl, Padova, Italy) owned by the Research Centre for Engineering and Agro-Food Processing–CREA-IT in Milan (Italy).



(**a**) (**b**)

Figure 2. The DV spectral scanner (DV Srl, Padova, Italy). (**a**) System turned off; (**b**) system turned on, coupled with dedicated software.

2.3. *Advantages and Limitations of Different NIR Technologies*

When choosing a spectrometer technology, the required applications offer a good guide [168–170]. Different applications have different requirements for the spectrometer, and the preferred spectrometer technology is always application-dependent [171]. The major distinctions between spectrometer technologies (scanning grating monochromators, fixed grating detector diode array, FT-NIR) and their preferred use are reported in Table 2.

Table 2. Major distinctions between spectrometer technologies and their preferred use.

Technology	Advantages	Limitations	Applications
Scanning Grating	Signal/noise ratio Wavelength range	Measures needed to improve Wavelength accuracy Lower resolution	Quantitative measurements
Fixed Grating DDA	Robustness	Signal/noise ratio	Process control [172]
FT-NIR	Wavelength accuracy Resolution	Sample heating Vibration sensitive Sample heating	Portable instrumentation [173] Qualitative measurements at lab Authentication, identification, discrimination

2.4. *Aquaphotomic Approach*

Since 2007 [174], a new approach has taken hold, with a holistic view, where water and its NIR absorption bands are the leading actor. Distinct water configurations, for example, dimers, trimers, and solvation shells, are known to contribute very specifically to its NIR spectrum. These are very sensitive to the configuration and charges of the solvated molecules or clusters. Therefore, the NIR spectrum of the solvent (i.e., water) has been found to contain significant information about its solutes. Aquaphotomics has been developed using a deductive approach. It has two main goals: (1) to expand knowledge about the interaction between water and electromagnetic radiation, knowing all possible bands and spectral regions (water matrix coordinates, WAMACS) where water interacts with light and, thus, could be monitored; and (2) to use the water absorbance patterns (WAPS), based on WAMACS and related to water structure and functionalities in various systems, in order to deduce information about water/system peculiarities [175]. Recently, in addition to a "water vocabulary", useful chemometrics information has also been published [176] in order to correctly translate findings about water among different disciplines. Updated information on this interesting area of investigation is available online at https://www.aquaphotomics.com/.

3. Conclusions

The use of NIR spectroscopy in the horticultural sector is surely too large to be reported only in this review. For this reason, this paper did not have the ambition to be exhaustive and complete but to provide good suggestions in order to be able to apply NIR spectroscopy to reach personal and corporate objectives, taking into account experimental data already available and updated. Often, for scientists working in the agricultural sector, it may be difficult to consult articles published in specialized journals of other research fields; thus, the main objective of this paper was to make a large table coupled with the full list of references available, useful for a personal check of a single scientist or a team of scientists, who could then select, on the basis of product, application, year of publication, only the studies strictly related to their research area and easily uncover papers of interest. This collection of literature data showed that most of the research was developed on fruit, using portable and/or online instrumentation for the evaluation of total quality, the determination of macroconstituents and nutritional markers, as well as the presence of defects. The last decade was also characterized by a great improvement of mathematic algorithms able to solve problems related to 'apparent differences' among samples and sets that could increase the risks of misunderstanding the significance of analyzed and processed data. Near infrared technologies offer fast solutions for organic compound discrimination and quantification. With the instrumental market in constant growth and development, cheaper and yet more accurate instruments will probably offer opportunities to explore new applications and fields of work.

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