ABSTRACT

Nowadays it is increasing the needs to know the quality and safety of the food products. These requirements call for on-line detection techniques which have the advantages of be assembled in the production line and take place under realistic environment, know early detection of possible failures, have permanent monitoring of the conditions and know assessment of conditions at any desired time.

This study evaluated the feasibility of using a spectral scanner VIS-NIR (DV Srl, version 1.4., Italia) with a detector in the region between 400-1000 nm to predict quality and characterize local varieties of artichoke: “Violetto” and “Catanese” located respectively in the area of San Ferdinando di Puglia and Brindisi (Puglia Region, Italy). The samples were harvested during years 2009/10 from 20 plants for each field, randomly-chosen and labelled in order to reduce field variability among different harvest dates.

Artichoke heads were harvested from December to May (7 harvest dates) for “Violetto foggiano” and from January to April for “Catanese” (4 harvest dates).

Artichokes were processed and cut into quarters. One quarter for each artichoke was analyzed during storage at day 0, day 2, day 5 and day 7 acquiring hyperspectral images using a hyperspectral imaging system.

Spectral data were analyzed using the Unscrambler packing software version X (CAMO ASA, Oslo, Norway) and PLS toolbox in Matlab (version 2014a). The data set included 736 samples (400 for “Violetto” and 336 for “Catanese”). All the reflectance measurements were firstly transformed to absorbance values using log(1/R) according to the law of Lambert-Beer.

Classification models were built with the aim of discriminate among cultivars, harvest times and day after cut. Two methods were compared: SIMCA (Soft Independent Modelling of Class Analogy) and PLS-DA (Partial least squares discriminant analysis), defining a Training set of 308 samples for “Violetto” and 244 for “Catanese” and a Test set of 92 samples for “Violetto” and 76 for “Catanese”.

In the classification by cultivar (“Violetto” and “Catanese”) the discriminant approach is superior to the class-modeling, mostly because of the two classes have a very similar general profile of the spectrum and one of them (“Violetto”) have an inner variability which encloses the one of the other class (“Catanese”).

Forcing the discrimination, the differences between the two classes are exalted, and the classification is obtained with very interesting results.

For the classification by harvest time, the SIMCA model was developed building individual PCA models for the spectra of each harvest time. Comparing the result coming from the

analysis made with SIMCA and PLS model, it is evident how the PLS-DA is the most performing method for this application giving a "non error rate" of 80% on the external test set.

For the classification by days of storage the PLS-DA model has for all the classes high value of specificity, and for some classes low values of sensibility.

The results suggest that is possible to discriminate samples just cut from samples cut and stored for some days, but that is more difficult to exactly separate samples depending on the days of storage. Most likely this is not due to a low efficiency of the model but to the changing proprieties of the samples that are not so dissimilar between 2 and 7 days of storage, but becoming more evident with the passing of the time.

For these analysis "Non Error Rate" values increased reducing the number of classed from 4 to 3: the model performance improved.

Calibration model for phenols content and antioxidant activity was built analyzing for day 0 several pre-treatment (9 for antioxidant activity and 8 for phenols).

Particularly the data of "Harvest Time 1" showed a different behavior compared to the remaining harvest times and for this reason the prediction models were tested on 3 classes: "All Harvest Time", "Harvest Time 1" and "Other Harvest Time". The efficiency of the model was always higher when using only sample from "Harvest Time 1", suggesting that other sources of variation were included in the data set for the following samplings.

The classes "All Harvest Times" and "Other Harvest Times", for PLS-calibration model, had higher values of R2C and R2CV and low values of RMSEC and RMECV in the wavelength range of 400-1000 nm for both phenols content and antioxidant activity. "Harvest Time 1", instead, carried out the best value for both (phenols content and antioxidant activity) in the range 650-1000nm (R2pred 0.62 and RMSEP of 72 for phenols, and R2pred 0.67, and RMSEP of 126 for antioxidant activity).

Starting from this considerations and from obtained results it may be interesting to further investigate the effect of the harvest time on the phenolic and antioxidant activity prediction to try to improve prediction results. Moreover also the instrumental setting can be improved, trying to standardize as much as possible the acquisition conditions.

Generally results of this thesis explored new area of research developing tools that may be used to increase the value of local productions, by mean of a better characterization and identification and by providing innovative non destructive-tools to be used online during the minimally processing operations for selecting raw material based also on its internal composition.

Key words: *Artichoke, SIMCA, PLS-DA, VIS-NIR, phenols, antioxidant activity, classification*

PART ONE – GENERAL

1.1 NUTRITIONAL PROPERTIES OF ARTICHOKES

1.1.1 General information

Artichoke, Cynara cardunculus L. subsp. scolymus (L.) Hayek, (Scientific name: Cynara scolymus L.) is an ancient herbaceous perennial plant (Figure 1.1), originating from the Mediterranean area, which today is widely cultivated all over the world (Bianco, 2005). Artichoke is one of the popular winter season, edible flower bud. It is used as a vegetable and it is well known since ancient times for its medicinal and health benefiting qualities.

The plant grows up to 1.5-2 m tall, with arching, deeply lobed, silvery-green leaves about 0.5 m long. Beautiful light pink flowers develop in a large head from the edible buds.

Each artichoke globe measures about 6-10 cm in diameter and weighs about 150 g. These are not edible anymore if the flower become old, and large in size.

Seed-propagated plants have hypogeous seed germination and produce a conspicuous, thick, fleshy tap-root apparatus. During the vegetative growth, the plant produces a rosette of large, deeply lobed or divided pubescent green-grayish leaves attached to a compressed stem. Leaves differ sensibly among cultivars for their margin, color, shape, length, presence/absence of spines. The base of the stem produces auxiliary buds from which offshoots (suckers) can grow in a variable number, depending both on the variety and on its attitude to the vegetative propagation. Each offshoot produces adventitious roots that initially are mostly fibrous and thick and, during the first year of growth, differentiate fleshy storage organs (rhizomes). In the spring, above the rosette of leaves, an apical or primary bud appears and a floral stem can elongate above 1 m of height. Floral stem induction is influenced both by temperature and photoperiod and the cultivars differ in their requirements of low-temperature and day length. Secondary, tertiary, and higher-order buds develop on branching stems from leaf axis of the primary stem; the primary terminal bud achieves the largest size, this decreasing sequentially for secondary, tertiary and higher-order flower buds. Each vegetative offshoot produces an erect flower-bearing stem (Jacoboni, 1958). The head or *capitulum* is composed by many florets crowded onto a fleshy receptacle and surrounded by a whorl of multiple rows of bracts, thick and fleshy in basal parts and progressively thinner in upper portions; the outermost bracts are large and fibrous while the inner ones are progressively smaller and tender. The inner tender portions of the receptacle form the ‘heart’ of the globe artichoke (Figure 1.2).

Several cultivars of artichoke grown and are categorized based upon size, color, and presence of the spines.

Figure 1.1. Globe artichoke - From http://www.science.howstuffworks.com

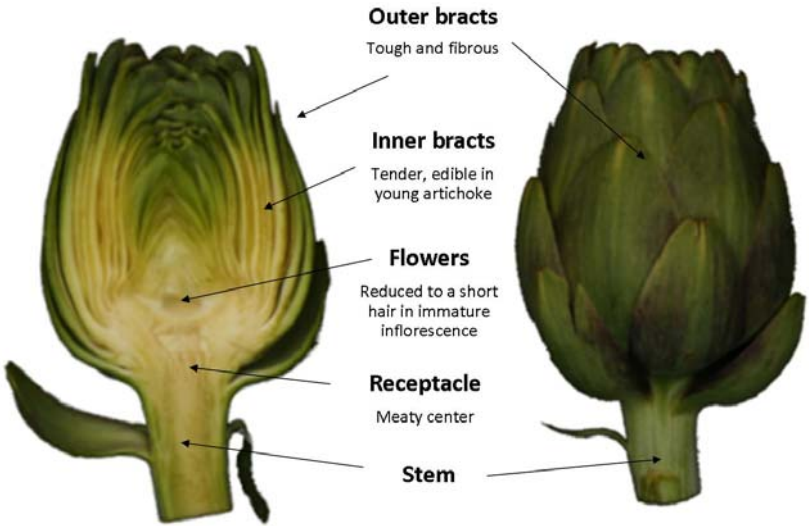


Figure 1.2 – Artichoke section.

The number of globe artichoke cultivars grown in the Mediterranean basin and in other parts of the word cannot be easily determined. A cultivar grown in one location is frequently known by other names in other localities (about 14 to indicate "*Catanese"* globe artichoke) (Bianco, 1990). Therefore, the number of names exceeds that of the actual cultivars. The cultivar composition in Italy, Spain, and France has been extensively studied but it is much less known in other Mediterranean countries. Thirty-seven economically important globe artichoke types have been examinated by Dellacecca et al. (1976). Only 11-12 of them can be considered as being of major

commercial importance (Basnizki and Zohary, 1994). The artichoke world collection in Bari (Italy) was subjected to a detailed study of cultivar divergence by multivariate analysis (Porceddu et al., 1976; Vannella et al., 1981), this showed that the majority of the accessions analyzed fall into the following four main groups (Figure 1.3):

A) *"Spinoso"* (long sharp spines on the bracts and leaves);

B) *"Violetto*" (medium-sized, violet-colored and less spiny heads);

C) "*Romanesco"* (spherical or sub-spherical non-spiny heads);

D) "*Catanese"* (small, elongated and non-spiny heads).

Figure 1.3 – Typologies of globe artichoke cultivated in Italy (Lo Bianco, 2009)

1.1.2 Nutritional aspects and health benefits of artichoke

Artichoke is widely cultivated for its large immature inflorescences, called capitula or heads, which represent an important component of the Mediterranean diet and is a rich source of health-promoting compounds, mainly bioactive polyphenols, flavonoids and also inulin, fibres and minerals (Lattanzio, 1982; Lattanzio et al., 2005; Lattanzio et al., 2009; Llorach et al., 2002; Orlovskaya et al., 2007).

Artichoke is low in calories and fat; 100 g of this flower bud just carries 47 calories. Nonetheless, it is a rich source of dietary fiber and anti-oxidants (Table 1.1.). It provides 5.4 g per 100 g, about 14% of RDA fiber. Dietary-fiber helps control constipation conditions, decreases badly or "LDL" cholesterol levels by binding to it in the intestines and help cut down colon cancer risks by preventing toxic compounds in the food from absorption.

Fresh artichoke is an excellent source of vitamin, folic acid; provides about 68 µg per 100 g (17% of recommended daily allowance). Folic acid acts as a co-factor for enzymes involved in the synthesis of DNA. Scientific studies have proven that adequate levels of folates in the diet during pre-conception period, and during early pregnancy, help prevent neural tube defects in the newborn baby (Kronenberg et al., (2009).

Fresh globes also contain moderate amounts of anti-oxidant vitamin; as-C (about 20% of recommended levels per 100 g). Regular consumption of foods rich in vitamin C helps the body develop resistance against infectious agents and scavenge harmful, pro-inflammatory free radicals from the body.

It is also one of the very good vegetable sources for *vitamin K*; provide about 12% of DRI. Vitamin K has potential role bone health by promoting osteotrophic (bone formation) activity. Adequate vitamin-K levels in the diet help limiting neuronal damage in the brain; thus, has established role in the treatment of patients suffering from Alzheimer's disease (Parris, 2005).

It is also rich in B-complex group of vitamins such as niacin, vitamin B-6 (pyridoxine), thiamin, and pantothenic acid that are essential for optimum cellular metabolic functions.

Moreover, artichoke is rich source of minerals like copper, calcium, potassium, iron, manganese and phosphorus. Potassium is an important component of cell and body fluids that helps controlling heart rate and blood pressure by countering effects of sodium. Manganese is used by the body as a co-factor for the antioxidant enzyme, superoxide dismutase. Copper is required in the production of red blood cells. Iron is required for red blood cell formation (Horacio et al., 2014).

Additionally, it contains small amounts of antioxidant flavonoid compounds like carotene-beta, lutein, and zea-xanthin.

Depending on the cultivar and harvest time, head weight ranges from 150 to 600 g. The ratio of edible parts to the total weight head is 10–18% for the lower part (receptacle), and about 40% for the core parts (receptacle and inner bracts). Since only the central portion of the capitula is consumed, the ratio of edible fraction/total biomass produced by the plant is very low, being less than 15–20% of total plant biomass. This ratio decreases further if the contribution to the total biomass represented by offshoots, removed from the field by common cultural procedures, is also considered (Marzi and Lattanzio, 1981; Lattanzio, 1982; Lattanzio et al., 2009).

Artichokes are a popular winter season vegetables across Europe. Small or baby artichokes can be eaten completely without removing the inside spiny choke.

Table 1.1 – Analysis of nutrients: Artichoke (Cynarascolymus), raw, Nutrition value per 100 g. ORAC value 6552 TE/100 g.
(Source: USDA National Nutrient data base)

Principle	Nutrient Value	Percentage of RDA
Energy	47 Kcal	2%
Carbohydrates	10.51 g	8%
Protein	3.27 g	6%
Total Fat	0.15 g	0.5%
Cholesterol	0 mg	0%
Dietary Fiber	5.4 g	14%
Vitamins		
Folates	68 µg	17%
Niacin	1.046 mg	6.5%
Pantothenic acid	0.338 mg	7%
Pyridoxine	0.116 mg	9%
Riboflavin	0.066 mg	5%
Thiamin	0.072 mg	6%
Vitamin C	11.7 mg	20%
Vitamin A	13 IU	0.5%
Vitamin E	0.19 mg	1%
Vitamin K	14.8 µg	12%
Electrolytes		
Sodium	94 mg	6%
Potassium	370 mg	8%
Minerals		
Calcium	44 mg	4%
Copper	0.231 mg	27%
Iron	1.28 mg	16%
Magnesium	60 mg	15%
Manganese	0.256 mg	11%
Phosphorus	90 mg	13%
Selenium	0.2 µg	<0.5%
Zinc	0.49 mg	4.5%
Phyto-nutrients		
Carotene-alpha	8 µg	
Crypto-xanthin	0 µg	
Lutein-zeaxanthin	464 µg	

The edible part is widely consumed raw, boiled, steamed or fried and as a component of many recipes. Within the capitulum only the receptacle is usually considered fully edible, but the bracts, if properly prepared, are edible as well (Lattanzio et al., 2005).

In respect of this chemical composition, the globe artichoke combines good sensory properties with a healthy image, known since Roman times which are linked to their high content of inulin and polyphenolic compounds (Robertfroid, 2005; Holst and Williamson, 2008), which are phytontrients not included in the composition Table 1.1. and that dispite to their minor content are very important for a nutritional point of view.

Inulin is a highly water-soluble carbohydrate, which serves as an alternative storage carbohydrate in the vacuole of approximately 15% of all flowering plant species (Lattanzio et al., 2009). Inulin belongs to a group of fructose-based polysaccharides called fructans, which are not digested in the small intestine because humans lack the enzymes required for hydrolysis of fructans. A reason for the recent interest in inulins is due to the publication of data showing the positive influence on the composition of the gut microflora, and there are indications of beneficial effects on mineral absorption, blood lipid composition, and prevention of colon cancer. In addition, inulin is a low-calorie fiber that has potential for use in the production of low-fat foods (Frehner et al., 1984; Pollock, 1986; Darwen and John, 1989; Pontis, 1990; Carpita et al., 1991; Rapaille et al., 1995; Hellwege et al., 1998; Roberfroid and Delzenne, 1998; Van Loo et al., 1999; Hellwege et al., 2000).

Phenolic are heterogeneous group of phytochemicals normally synthesized both during regular plant grown and development and are prominent in fruit and vegetables, where they are important in determining color, appearance, flavor, and taste (Lattanzio, 2003). Polyphenols synthesis and accumulation in plants may be stimulated in response to biotic and abiotic stresses (Beckman, 2000), modifying qualitatively and quantitatively the composition (Falleh et al., 2008). Phenolic compounds form one of the main classes of secondary metabolites, with a large range of structures as shown in Table 1.2: (Harborne, 1980).

Table 1.2 – The major classes of phenolic compounds (from Lattanzio, 2003).

Basic skeleton	Class
C_6	Simple phenols, Benzoquinones
C_6-C_1	Phenolic acids
C_6-C_2	Acetophenones, Phenilacetic acids
C_6-C_3	Hydroxycinnamic acids, Phenylpropenes, Coumarins, Isocoumarins, Chromones
C_6-C_4	Naphtoquinones
C_6-C_1-C_6	Xanthones
C_6-C_2-C_6	Stilbenes, Anthraquinones
C_6-C_3-C_6	Flavonoids, Isoflavonoids
$(C_6$-$C_3)_2$	Lignans, Neolignans
$(C_6$-C_3-$C_6)_2$	Biflavonoids
$(C_6$-$C_3)_n$	Lignins
$(C_6)_n$	Catechol melanins
$(C_6$-C_3-$C_6)_n$	Proanthocyanidins

The importance of these compounds seems to be linked to their well-established role as a protective pool against oxidative damages caused by free radicals (Racchi et al., 2002; Rice-Evans and Miller, 1996). The action of phenolic as strong antioxidants is due mainly to their redox properties, which allow them to act as reducing agents, hydrogen donators and single oxygen quenchers (Rice-Evans and Miller, 1996). The most abundant phenolic substances reported in artichoke heads belong to the class of hydroxycinnamic acids, such as coumaric (4-hydroxycinnamic acid), ferulic (3-methoxy-4-hydroxycinnamic acid) and caffeoylquinic acid derivatives, particularly chlorogenic acid (5-O-caffeylquinic acid), the most abundant single component (39% of total caffeoylquinic acid contents), 1,5-di-O-caffeoylquinic acid (21%) 3,4-O-dicaffeoylquinic acid (11%), 1,3-O-dicaffeoylquinic acid (Cynarin) (about 1.5%) and 3,5-di-O-caffeoylquinic acid (Lattanzio et al., 1994).

About flavonoids, apigenin and luteolin glycosides have been detected in both leaves and artichoke heads, while anthocyanin pigments are present only in capitula. Anthocyanin pigments are responsible for most of the blue, purple, red and intermediate hues of plant tissues. From a quantitative viewpoint, these compounds are considered minor constituents of the total phenolic content (about 10% or less) of artichoke tissue (Lattanzio et al., 2009).

Due to the high content of phenolics compounds artichoke heads might, therefore, be regarded as a source of dietary antioxidants. (Lattanzio and Linsalata, 2005; Lattanzio 2009). In addition, leaves and outer bracts of artichoke heads can be considered as a cheap, as yet unused, source of natural non toxic antioxidants for use in industrial processes (to preserve and stabilize the freshness, nutritive value, flavour and colour of foods.

Phenolic content, profiles of polyphenols and minerals may significantly vary among artichoke plant parts, genotype, and are affected by several physiological and environmental factors. Some studies reported that, in some artichoke cultivars, single polyphenols accumulate preferentially in the edible parts of the heads (Lattazio et al., 2009). Phenolic content decreases during capitula development and content at commercial maturity stage is about half of the content at the early development (Fratianni et al., 2007; Di Venere et al., 2009; Lombardo et al., 2009, 2010, 2011; Pandino et al., 2011a, 2011b).

Several authors reported a different phenol content and composition, and antioxidant activity among heads or leaves of artichoke varieties (Gorny et al., 1999; Fratianni et al, 2007); several studies are available on phenolic components and antioxidant activity of artichokes (Lattanzio et al., 1994; Alamanni et al., 2003; Wang et al., 2003; Brecht et al., 2004; Fratianni et al., 2007, Lattanzio et al., 2009; Lombardo et al., 2010, Coinu et al., 2007; Lutz et al., 2011; Di Venere, personal communication).

Phenolic content of artichoke heads is strictly related to winter or spring harvest and is dependent from the climatic conditions (temperature, rainfall, light, etc.) (Lombardo et al., 2010; Di Venere et al., 2005a). Lombardo et al. (2009) found that the different environmental and weather conditions influenced the phenolic bio-synthesis for some artichoke genotypes, and also that there is an inverse relationship between phenol content and tissue age. Some authors reported that the profiles of polyphenols and minerals of some artichoke varieties were significantly different amongst genotype and plant parts (Lombardo et al., 2009, 2010; 2011; Pandino et al., 2011a, 2011b) and some authors reported that phenol content of artichokes harvested in sping decreased compared to artichokes harvested in winter (Massignan et al., 2005; Bianco and Pace, 2009).

1.1.3 Storage condition

Artichoke production is essentially continuous throughout the year, although about 70% of the crop is harvested in a specific part of the year. Fields with winter-spring cycles produce the highest yields, and are continuously harvested from September through May (Lo Bianco, 2009).

Highest quality heads show no violet discoloration on the inner bracts, a short pappus and outer bracts tightly closed and are free of blemishes (Miccolis et al., 1988; Mencarelli et al., 1993). Bract opening, external and internal blackening and wilting are the main factors limiting quality of artichokes during distribution (Escriche et al., 1982).

Artichokes harvested in early production are, normally used for the fresh market, whereas the last part of the late production is industrially processed (canned or frozen).

Delays between harvest and consumption or processing can result in losses of flavor and nutritional quality. Keeping intact fruits and vegetables within their optimum ranges of temperature and relative humidity is the most important factor in maintaining their quality and minimizing postharvest losses during the entire postharvest handling system. Storage temperature and relative humidity are the most important factors in postharvest quality maintenance of fresh produce. Atmospheric modification can be a very useful supplement to providing the proper temperature and relative humidity (Kader, 1990; 2002e; 2004).

Temperature management is the most effective tool for extending the shelf-life of fresh horticultural commodities (Kader, 2002a). Low temperatures (between 0°C and 5°C) together with high relative humidity (90–95% RH) during storage are recommended to maintain quality of artichokes for longer durations (Mencarelli et al., 1993; Suslow and Cantwell, 1997). The storage potential of artichokes is generally less than 21 days as visual and sensory quality deteriorate rapidly (Suslow and Cantwell, 1997), and depend on temperature of storage; some authors have reported even shorter storability that does not exceed 2 weeks at 1–2°C, 10 days at 5°C and 5 days at 10°C

with RH > 90% (Saltveit, 1991). Gil et al. (2001) reported that visual quality of artichoke heads decreased considerably during storage at 9°C and 17°C; after 16 days, visual quality was considered acceptable only for artichokes stored at 0°C or 6°C. Another study showed that 'Blanca de Tudela' artichokes stored at different temperatures showed significant changes in total phenol contents (Gil-Izquierdo et al., 2001).

Currently, no other postharvest technologies beside temperature and humidity control are applied when storing artichoke heads, and also because they are generally consumed close to the production area.

Relative humidity (RH) can influence water loss, decay development, incidence of some physiological disorders, and uniformity of fruit ripening. The optimum relative humidity during storage of fresh non-fruit vegetables ranges between 95-98% (Kader, 2002b).

The physiological activity of plant tissue continues after harvest inducing wilting phenomena of tissue, a phenomenon primarily due to transpiration, i.e. the transfer of water contained within the plant tissue to the surrounding atmosphere. The dehydration depends on many factors including the temperature and relative humidity of the storage room, the air movement and the packaging material. The decrease in weight may be attributed to respiration and other senescence-related metabolic processes during storage (Watada and Qi, 1999); Agamia (1984) has shown that the weight loss of artichoke heads is due to both respiration and transpiration. Water loss is not only results in direct quantitative losses (loss of salable weigh), but also in losses in appearance (wilting and shriveling), textural quality (softening, flaccidity, limpness, loss of crispness and juiciness) and nutritional quality. The commodity's dermal system (outer protective coverings) governs the regulation of water loss. The transpiration rate (evaporation of water from the plant tissues) is influenced by internal factors (morphological and anatomical characteristics, surface-to-volume ratio, surface injuries, and maturity stage) and by external, or environmental, factors (temperature, relative humidity, air movement, and atmospheric pressure) (Kader, 2002b). Condensation of moisture on the commodity (sweating) over long periods of time is probably more important in enhancing decay than is the RH of ambient air. Management of relative humidity is very important for storage of artichoke heads, in fact values RH> 95% assure a low weight loss avoiding the loss of turgidity of the outer bracts and of the stem and the wilting of the leaves (Lipton and Stewart, 1963; Suslow and Cantwell, 1997). A study of Leroy et al. (2010) showed that weight loss increased significantly during storage for artichokes stored at 4°C (60% RH) and 18°C (80%RH), while dry matter increased.

Relative humidity can be controlled by one or more of the following procedures: adding moisture (water mist or spray, steam) to air by humidifiers, regulating air movement and ventilation in relation to produce load in the cold storage room, maintaining the refrigeration coils within about

1 °C of the air temperature, providing moisture berries that insulate storage room and transit vehicle walls, wetting floors in storage rooms, adding crushed ice in shipping containers or retail displays for commodities that are not injured by the practice, sprinkling produce with water during retail marketing (Kader, 2002b).

One final method to extend storability of fresh produce is the modification of the storage atmosphere by reducing oxygen and increasing carbon dioxide partial pressure (Zhang et al., 2011).

In modified atmospheres (MA) or controlled atmospheres (CA), gasses are removed or added to create an atmospheric composition around the commodity that is different from that of air (78.08% N_2, 20.95% O_2, and 0.03% CO_2). Usually this involves reduction of oxygen (O_2) and/or elevation of carbon dioxide (CO_2) concentrations. The use of modified or controlled atmospheres should be considered as a supplement to proper temperature and relative humidity management (Table 1.3). The potential for benefit or hazard from using MA depends on the commodity, cultivar or variety, physiological age, atmospheric composition, temperature and duration of storage (Amanatidou et al., 1999; Kader, 2002c; Gorny, 2004; Colelli and Elia, 2009). CO_2 is the most important gas in the modified atmosphere packaging of foods, due its bacteriostatic and fungi static properties. It inhibits the growth of the many spoilage bacteria and the inhibition rate is increased with increased CO_2 concentrations in the given atmospheres. CO_2 is highly soluble in water and fat, and the solubility increases greatly with decreased temperature (Sivertsvik et al., 2002). Atmospheres with low O_2 levels inhibit the growth of most aerobic microorganisms, also this contributes to the maintenance of metabolic activities of the product (Farber, 1991; Klieber et al., 1996; Beaudry, 1999; Saltveit, 2003; Soliva-Fortuny et al., 2004).

MAP produces benefits by extending appearance and sensory quality, increasing overall marketability (Table 1.3).

Table 1.3 – Modified Atmosphere Packaging (Gorny, 2004)

Can	**Cannot**
Increase shelf-life	Substitute for Temperature Control
Slow Microbial Growth	Stop Microbial Growth
Maintain Nutritional Quality	
Slow Browning	

It aims to the creation of an ideal gas composition within the packaging, which can be directly generated by the commodity respiration, or actively created by flushing a gas mixture within the packaging before sealing it. Once the package is closed, no further control is possible and the gas composition will inevitably change due to produce metabolism and to film barrier properties (Sivertsvik et al., 2002; Gorny, 2004).

However, differences between beneficial and harmful atmosphere combinations may be small. One of the mayor problems encountered in using MAP is the accumulation of anaerobic metabolites (i.e. ethanol and acetaldehyde) in the packages: if the O_2 level decreases below the fermentation threshold, anaerobic respiration is triggered leading to the production of off-flavors and stimulating the growth of some anaerobic psychotropic pathogens (Oms-Oliu et al., 2009); similarly, high CO_2 concentrations can be harmful for vegetal tissues. Also, in some leafy green vegetables, increases in ammonia were observed with high CO2 atmospheres and were associated with darkening of tissues (Cantwell et al., 2009).

A reduction in browning of the outer bracts is the major benefit from CA storage when artichoke buds are stored at temperatures higher than 0°C. However, the effectiveness of CA storage is dependent on bud maturity, cultivar, temperature and the particular atmosphere used (Andre et al., 1980; Rappaport and Watada, 1958; Ryder et al., 1983). Optimal CA conditions vary widely among cultivars, ranging between 1 to 6% O_2 and 2 to 7% CO_2 (Andre et al., 1980; Escriche et al., 1982; Ryall and Lipton, 1979; Saltveit, 1997). Little or no beneficial effect on quality retention can be obtained by CA storage when artichoke buds are stored at 0°C (Miccolis and Saltveit, 1988). Therefore, no general recommendation can be made for CA storage; studies reported that conditions of 2-3% O_2 and 3-5% CO_2 delay discoloration of bracts and the onset of decay by a few days at temperatures around 5°C, while atmospheres below 2% O_2, fixed as the fermentation threshold, may result in internal blackening of artichokes (Suslow and Cantwell, 1997; 1998). In MAP, the levels of O_2 and CO_2 within a package depend on the interaction between commodity respiration and the permeability properties of the packaging film and/or microperforations. Yommi et al. (1996; 2001) indicate that packing with HDPE reduced weight loss and extended postharvest life of artichoke heads.

1.2 POTENTIAL USE OF THE ARTICHOKE FOR THE FRESH-CUT PROCESSING

1.2.1 General information on fresh-cut artichokes

Processing of fruit and vegetables has ever had as its principal objective to extend the shelf-life for a long time, allowing the consumption even during periods of absence of fresh produce. Artichoke heads are traditionally processed as canned (in oil or in brine) or frozen. However, fresh-cut vegetables market has grown rapidly in recent years as a result of changes in

consumer attitudes. Currently, consumer needs are principally focused on added-value products, in terms of quality, convenience, nutritional value and ease of preparation (Colelli and Calabrese, 2009). For these reasons, there is a real need to find methods for preservation of minimally processed food products that can gain widespread acceptance by the industry.

Artichoke is a very important crop in Southern Italy, but its use is limited because trimming is time-consuming and complex. In addition, the edible portion is the inner part of the head which is about 15–20% of its fresh weight, and about 50% of the whole head (Lattanzio et al., 2009).

The high percentage of discarded plant waste, together with complex and time-consuming trimming operation, make artichoke processing as a fresh-cut product desirable. The presentation of this vegetable as a minimally processed product, ready to use, would be very convenient for its commercialization, reducing transport costs, storage space and preparation time (Yommi et al., 2001). A potential flow diagram of the operations for fresh-cut artichoke processing is showed in Figure 1.4.

However, fresh-cut artichokes suffer several degradative reactions (especially enzymatic and non-enzymatic browning) mainly related to phenolic compounds, which limit their marketability and the technological transfer of this process.

The shelf-life of fresh-cut of artichoke is, in fact, linked with reference to some operation listed in the flow diagram, in particular the cooling and temporary storage, the antibrowning treatment and the packaging (with particular references to the MAP: Modified Atmosphere Packaging).

Some of these operation have been widely studied in other to find optimal solutions for the implementation of a fresh-cut process.

Few authors studied how to develop the step of antibrowning treatment and packaging in order to improve the fresh-cut artichokes. In general, the major enzyme responsible for the browning reactions is polyphenol oxidase (PPO), a copper containing enzyme which also catalysis the orthohydroxylation of monophenols and the oxidation of o-diphenols to o-quinones (Lee and Whitaker, 1995).

Lattanzio et al. (1989) investigated the use of citric and ascorbic acids to delaying browning of stored artichokes heads; more recently, Giménez et al. (2003) and Del Nobile et al. (2009) tested ascorbic acid dipping and edible coatings containing citric acid, respectively, on minimally processed artichokes. However the use of ascorbic acid and citric acid provides only temporary prevention of browning (Özoglu and Bayindirli, 2002). Recently Amodio et al. (2011), in a study where different compounds were tested, reported that ascorbic acid had little effect on delaying browning of cut artichokes, which could be observed only up to 3 h after cutting, whereas

citric acid had a postcutting effect not different from control samples. On the other hand, these authors reported that cysteine at 0.5% was the most effective treatment to prevent browning and its effectiveness was improved by increasing the pH of the solution from 2.2 to 3. On a further study Amodio et al. (2012) observed that fresh-cut artichokes treated with l-cysteine at pH 7 showed best appearance and lowest changes in color attributes, due to the higher inhibition of PPO activity.

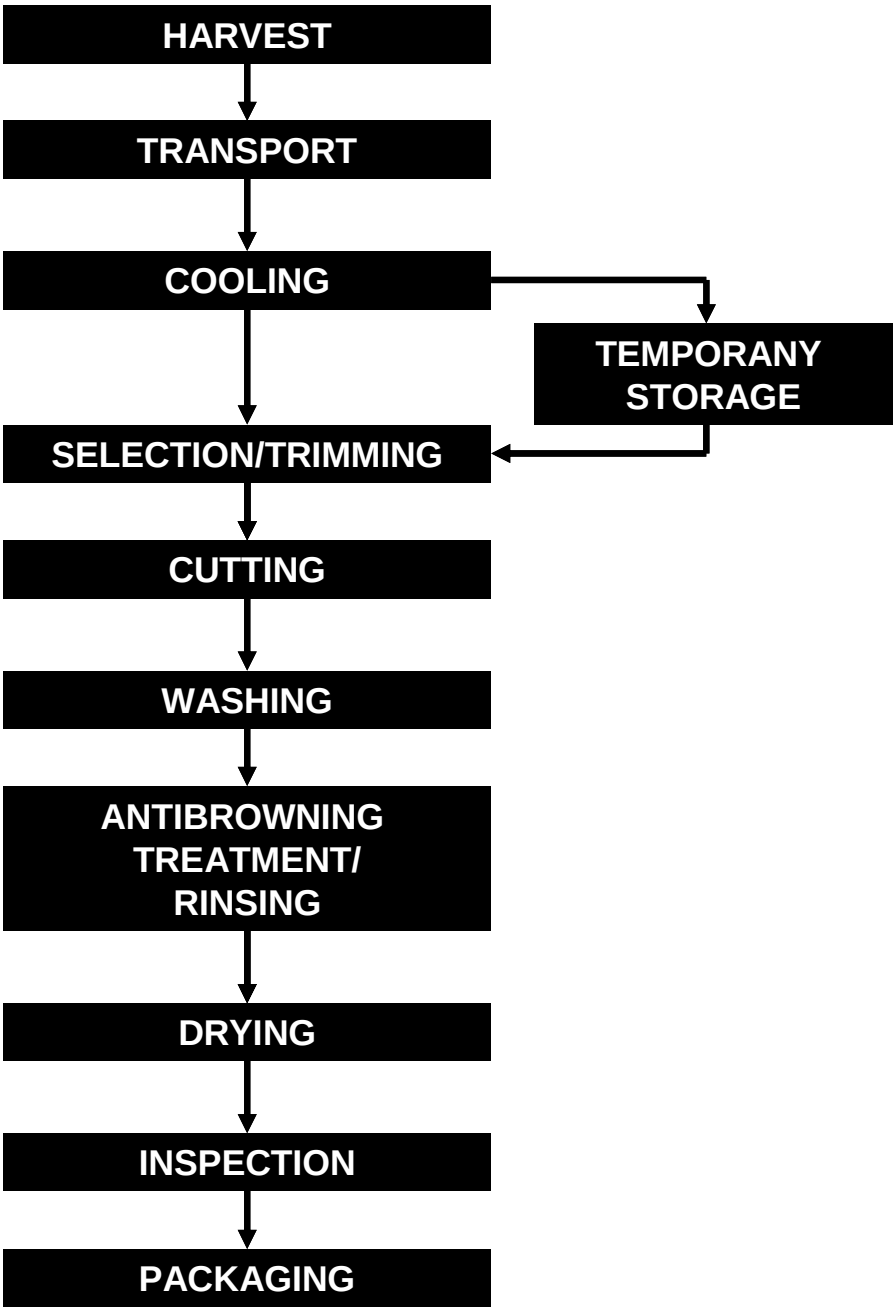


Figure 1.4 – Flow diagram of the operations for fresh-cut artichokes(Colelli, 2010)

Non-enzymatic browning reactions are caused by iron-polyphenol complexes: chlorogenic acid, the most representative phenolic compound of artichoke heads, in presence of oxygen forms dark colored complexes with Fe^{3+}, while the same substrate in anoxic conditions forms colorless complexes with Fe^{2+}, but after exposure to air the complex Fe^{2+} is quickly oxidized to Fe^{3+} to give colored compounds (Lattanzio, 2003). Also, mechanical wounding enhances a diverse array of enzymatic pathways, many of which are associated with volatile accumulation, such as ammonia, ethanol and acetaldehyde, which leads to darkening of tissues and onset of off-flavors (Salunkhe and Do, 1976; Rolle and Chism, 1987).

The use of modified atmospheres can promote or, otherwise, inhibit this degradative reactions, and differences between beneficial and harmful effects of gas mixtures may be small. Increased levels of CO_2 are used in combination with low O_2 concentrations to maintain the visual quality of several fresh-cut produce. Carbon dioxide is considered a competitive inhibitor of PPO, but increases in ammonia were observed in leafy tissues stored in high CO_2 (Cantwell et al., 2010); similarly, if the O_2 level in the package decreases below the fermentation threshold, anaerobic respiration is triggered leading the accumulation of anaerobic metabolites (i.e. ethanol and acetaldehyde) and stimulating the growth of some anaerobic pathogens (Oms-Oliu et al., 2009). The presence of a very high CO_2 concentration (25%) in the storage atmosphere have been proved to be deleterious for fresh-cut artichokes (la Zazzera et al., 2012), while only slight beneficial effects were observed for lower concentrations (5 and 15%). Therefore, the avoidance of extreme conditions in terms of CO_2 and O_2 concentrations within the package should be the main objective when designing a modified atmosphere packaging (MAP) system for fresh-cut artichokes.

Giménez, (et al. 2002) studied the impact of modified atmosphere packaging (MAP), on sensory quality (weight losses, color, texture and sensory acceptability) and on the growth of indicator micro-organisms (mesophiles, psychrotrophs, anaerobic micro-organisms, spore formers, fecal coliforms, Salmonella and Escherichia coli) in minimally processed artichokes packaged with five different films (two PVC and three P-Plus).

The atmospheres obtained, together with the different permeability to water vapor of the films under study, determined the evolution of the visual and microbiological quality of the artichokes.

For most of the batches, no correspondence was found between microbial growth and changes in appearance. Those batches where the equilibrium atmosphere was clearly anaerobic showed microbial counts below the legally established microbiological limits but also showed a rapid loss of sensory quality. On the other hand, some batches with an acceptable sensory evaluation had microbial counts higher than those allowed by the legislation. This last situation is particularly

dangerous from a health point of view since it allows the growth of micro-organisms (even pathogens) although the product may seem to be acceptable for consumption.

This lack of correspondence constitutes an important point to be attended to on the microbiological safety of these foods, since the preservation technologies applied allow the prolonging of their sensory characteristics but, at the same time, may favor the growth of micro-organisms.

Moreover the final results may be affected by the thermical history of the product as well as by the harvest date. It has been reported that time and temperature of storage before cutting influenced quality attributes of cut artichokes, but to a different extent depending on the cultivar. "Violetto Foggiano" artichokes benefited from pre-cutting low storage temperature (0°C), whereas "Catanese" showed physiological injuries on outer bract surfaces, where brown spots occurred. In both cases low temperatures during pre-cutting storage (5°C and 0°C) reduced the browning rate of the cut surface which maintained a higher L* value, compared to artichokes stored at 12°C. Moreover, pre-cutting storage at 12°C resulted in a reduction of quality of artichokes due to growth of floral primordial in the form of reddish tissues at the base of the receptacle for both cultivars. Management of storage conditions before cutting is therefore critical in fresh-cut processing operations of artichokes (Ricci et al. 2013).

On the same cultivar, Ricci (et al.2013) studied the effect of harvest date on post-cutting. quality of artichokes. Heads were harvested from December 2009 to May 2010 in 7 harvest dates (for "Violetto") and from January to April 2010 in 4 harvest dates (for "Catanese"). For both the cultivar harvested in February and analyzed after 7 days of storage, the lowest color variation for bracts and receptacle was observed compared with the other harvesting date. Visual quality of fresh-cut quarters decreased with the progress of the season, and for "Violetto foggiano", with the decrease of the antioxidant activity. Total phenolic content and antioxidant activity were different among harvest dates for both cultivars studied, and for "Violetto foggiano" showed a significant polynomial trend, denoting 2 phases of antioxidant accumulation from December to February and then from middle of March to May. The natural decline of plants at the end of production may be the reason of the poor quality of cut-artichokes in the last sampling date, and in general, considering the average temperatures at harvest, quality of fresh-cut artichokes could be positively affected by the lowest temperatures occurring in February.

1.3 ANALYTICAL METHODS FOR THE MEASURE OF PHENOLS AND ANTIOXIDANT ACTIVITY

1.3.1 Phenols

The most common methods to analyse total phenolic contents is the Folin–Ciocalteu method (1927), better known as Folin–Ciocalteu reagent (FCR) or also called Gallic Acid Equivalence method (GAE). This method is a colorimetric in vitro assay of phenolic and polyphenolic antioxidants based on the reaction with a mixture of phosphomolybdate and phosphotungstate (Singleton et al., 1999).

The F-C reagent is prepared by first dissolving 100 g of sodium tungstate ($Na_2WO_4*2H_2O$) and 25 g of sodium Mo ($Na_2MoO_4*2H_2O$) in 700 mL of distilled water. Then, the solution is acidified with 50 mL of concentrated HCl and 50 mL of 85% phosphoric acid. The acidified solution is boiled for 10 h, cooled, and 150 g of $Li_2SO_4*4H_2O$ is added. The resultant intense yellow solution is the F-C reagent (Huang et al, 2005; Singleton et al., 1999). Although the chemical nature of the F-C reagent has not been elucidated, it is believed to be composed of heteropoly – phosphotungstates – molybdates (Huang et al, 2005). Likewise, the exact chemical nature of the F-C reaction that leads to blue species [possibly $(PMoW11O40)^4$] is unknown and likely to remain so due to its complexity (Singleton et al., 1999). However, it is assumed that the F-C reaction involves sequences of reversible one or two electron reduction reactions (Huang et al, 2005; Singleton et al., 1999; Ainsworth and Gillespie, 2007). From the components of the FC reagent, molybdates are more easily reduced than tungstates, and thus it is suggested that most of the electron-transfer reactions in the assay are between the reductants and the molybdates. During the F-C assay, the reaction between PC and the F-C reagent takes place at a pH of ~ 10, which is reached by adding sodium carbonate. Under those basic conditions, dissociation of a phenolic proton leads to the formation of a phenolate ion, which is capable to reduce the F-C reagent (Huang et al, 2005; Singleton et al., 1999). The intensity of the blue color is than measured spectroscopically at 765 nm.

The reagent does not only measure phenols, since it reacts with any reducing substance. It therefore measures the total reducing capacity of a sample, not just phenolic compounds. This reagent is part of the Lowry protein assay, and will also react with some nitrogen-containing compounds such as hydroxylamine and guanidine (Ikawa et al., 2003). The reagent has also been shown to be reactive towards thiols, many vitamins, the nucleotide base guanine, the trioses glyceraldehyde and dihydroxyacetone, and some inorganic ions. Copper complexation increases the reactivity of phenols towards this reagent (Everette et al., 2003). Due to these reason Sánchez - Rangel et al. (2013) proposed a revisited method to simultaneously quantify TPC value and the

ascorbic acid reducing activity in plant food extracts, allowing to correct the value of TOC by subctraticng the contribution of ascorbic acid.

One of the problems about measuring total phenols is that of extraction, since exhaustive treatment with alcoholic and aqueous-alcholic solvent can still leave behind much tannin and other phenolic bound at the cell wall. Measurement of total phenol is therefore often confined in practice to the soluble fraction, which after concentration in vacuum, is made up to a standard volume.

A second problem is that, many different classes of phenol are going to be present in the extract and any method of measurement will be a compromise, since each class of phenol is likely to react differently with any given color reagent. This is also the reason why direct spectrophotometric measurement is usually ruled out, since it is impossible to select only one wavelength for such determinations. Spectrophotometry is only applicable if one class of phenol is predominant.

The development of HPLC techniques has to a large extent provided the means of quantitatively analysis plant of phenolics, since with HPLC it is now possible to determine very accurately the amounts of individual compounds. Although HPLC does not directly provide a determination of total phenol, it is often possible to do this by summation.

The HPLC conditions mainly include the use of C18 reversephased (RP) columns, a binary solvent gradient, and diode array detector or tandem mass spectrometry. The mobile phase usually consists of an aqueous solution of acid and an organic solvent (acetonitrile or methanol). HPLC-mass spectrometry (MS) combines the separation of LC with the selectivity and sensitivity of the MS detector to permit the identification of individual compounds from the complex matrices (Pyrzynska and Sentkowska, 2015). Mass spectrometry (MS) can often be applied directly to a small (0.1 mg) sample of phenolic and is especially useful for determining the molecular weight, preferably in an apparatus which provides precise mass measurement. In the case of labile or involatile phenolics, the method to be preferred is fast atom bombardment (FAB)-MS, where the sample is dissolved in glycerol or thioglycerol before measurement. MS and FAB-MS cause breakdown of the sample, so that a “fragmentation” pattern is usually obtainable, which will give additional structural information.

1.3.2 Antioxidant activity

ABTS is an analytical method that uses a type measure spectrophotometrically to determine the antioxidant capacity of a sample. Using a spectrophotometer UV-Vis is measured the absorbance of a solution containing the radical $ABTS^{+}$, generated by oxidation dell'ABST (2,2'-azinobis (3-etilbenzotiazolin-6-sulfonate), a colorless substance that in a chemical configuration of

radical is colored absorbing at characteristic wavelengths of the visible range. The addition to the solution of $ABTS^{+}$ (Figure 1.5 of antioxidant molecules, that may acts transferring or hydrogen or an electron, cause the reduction of the radical to form colorless and the discoloration of the reaction mixture. This discoloration, proportional to the quantity of antioxidant present, can be measured as decrease of absorbance during a fixed period and at a specific wavelength (734 nm). The antioxidant capacity is expressed by comparison with the absorbance values measured with known amounts of an antioxidant molecule selected as the reference standard, which is usually ascorbic acid or Trolox, a cell-permeable, water-soluble derivative of vitamin E, (in this case we speak of antioxidant activity TEAC Trolox Equivalent antioxidant Capacity), (Re et al., 1998).

The measure of the antioxidant based on the use dell'ABTS has the advantage to be simple and rapid. Moreover, ABTS allows the measurement of both hydrophilic and lipophilic antioxidants in a wide pH range. However, it is necessary to remember that the radical employed ($ABTS^{+}$) is not physiological and is not present in biological systems and often it is highlighted issues of repeatability of the measurement due to the reaction kinetics of the different antioxidants involved.

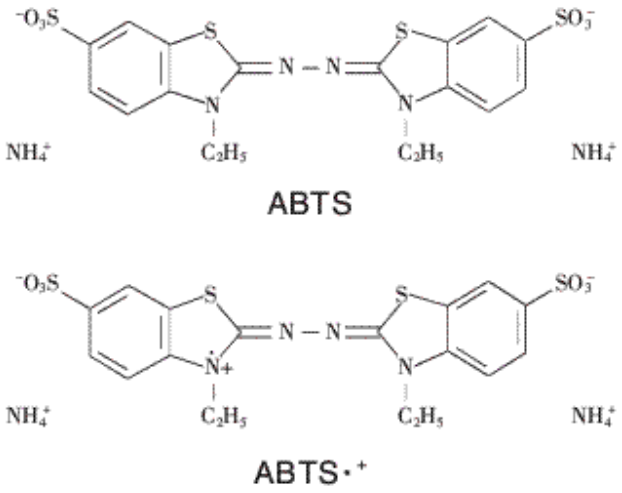


Figure 1.5 – ABTS and Oxygen Radical

The FRAP test measures the reducing capacity of antioxidants against the Iron ions. It is a method based on the transfer of electrons, in which iron ions pass from $Fe3^{+}$ to $Fe2^{+}$. In certain conditions of pH (3.6) and with the availability of TPTZ (2,4,6-tris (2-pyridyl) -s-triazine), these ions form complexes with different characteristics, in particular the derivative reduced ($Fe2^{+}$-TPTZ) takes on a blue color that has an absorption maximum at 593 nm measured by spectrophotometry (Figure 1.6). The reducing ability of an antioxidant can then be measured as a variation in

absorbance of the solution containing the oxidant to the wavelength established for comparison with the variation relative to a standard (for example Ascorbic acid).

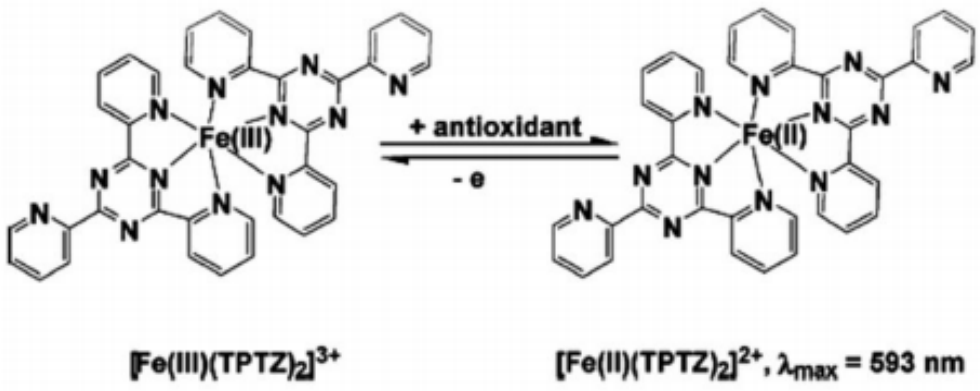


Figure 1.6 – TPTZ (2,4,6-tris (2-pyridyl) -s-triazine)

The FRAP test has been created for the measurement of the reducing power of the plasma, (Benzie and Strain, 1996) but it was then adapted to test the antioxidant capacity of pure mixtures and complex matrices. Since this method allows to evaluate only the reducing capacity through the transfer of electrons, completely ignoring the action of antioxidants that act via hydrogen transfer, it does not allow to measure the contribution of molecules, such as thiols and proteins that have a role antioxidant fundamental in biological fluids (for example blood). The advantage coming from the use of this method is that it is one of the most simple, quick and less expensive for the determination of antioxidant capacity in vitro.

The 2,2-diphenyl-1-picrilidrazile (DPPH), Figure 1.7, is a nitrogen radical very stable and commercially available, characterized by an intense red-purple coloring, which loses color when reduced in the presence of a molecule with antioxidant capacity. Using spectrophotometric measurement at 517 nm of the absorbance variation of the DPPH solution after reaction with an antioxidant mixture, it is possible to quantify the reducing capacity of the substance tested if it is acting with the transfer of hydrogen or if it is acting with the transfer of electrons. The result is generally expressed as IC50: the quantity of antioxidant able to reduce of 50% the initial concentration of DPPH.

It is a quick, simple and economical. The limits of this analytical technique are given by the possibility that the results of the analysis are distorted in the case in which the molecules under consideration absorb in the same range of the wavelength of the DPPH radical or in the presence of large molecules that do not sterically bulky arrive to react with the reactive part of the radical. This determines that the DPPH reacts with antioxidants up to 1000 times more slowly than peroxyl radicals (Borset et al., 1994).

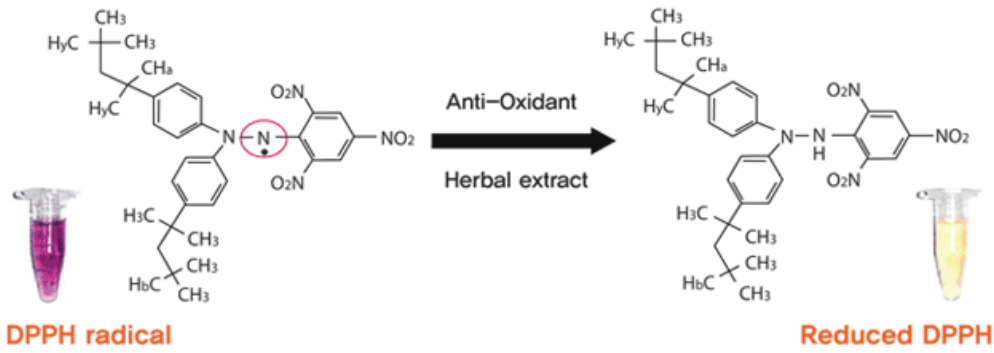


Figure 1.7 – DPPH reduction

1.4 NOT DESTRUCTIVE QUALITY EVALUATIONS

Generally, for determination of fruits and vegetables maturity index and composition, analysis are destructive and involve a considerable amount of manual work and can require sophisticated equipment. In recent years, quality and safety are the key factor in modern food industry, so researches have been focused on the development of non-destructive techniques suitable to increase the number of fruit pieces that can be analyzed, which can be repeated more times on the same sample during its physiological evolution, and can allow to achieve real-time information (Costa et al., 2009).

1.4.1 Overview of the most common techniques

Optical sensing technologies have been investigated as potential tools for non-destructive evaluation and inspection for food quality and safety. In particularly, hyperspectral imaging (or imaging spectroscopy) (Sun, Da-Wen, 2010), which is based on two mature technologies of imaging and spectroscopy (Sun, Da-Wen, 2008), have been widely studied and developed, resulting in many successful applications in the food industry.

There is also other imaging techniques as Magnetic resonance imaging, Soft X-ray imaging, Ultrasound imaging, Thermal imaging and Fluorescence imaging.

Nuclear magnetic resonance (NMR) is a unique technology that measures the magnetic properties of spins that can then be related to the physical or chemical properties of subjects. With the NMR technique applying an external magnetic field the physical process of radiation aborbtion by the nucleus, whose magnetic moment is not zero, is studied. Detectors receive the NMR signals

released as electromagnetic radiation; these signals can then be sent to the computer and be converted into the image through data processing. Magnetical Resonance Image (MRI) machines make use of the fact that food tissue contains lots of water which gets aligned in a large magnetic field. Each water molecule has two hydrogen nuclei or protons. When food is put in a powerful magnetic field, the average magnetic moment of many protons becomes aligned with the direction of the field. A radio frequency transmitter is briefly turned on, producing a varying electromagnetic field. This electromagnetic field has just the right frequency, known as the resonance frequency, to be absorbed and flip the spin of the protons in the magnetic field. After the electromagnetic field is turned off, the spins of the protons return to thermodynamic equilibrium and the bulk magnetization becomes re-aligned with the static magnetic field. During this relaxation, a radio-frequency signal is generated and can be measured with receiver coils. Information about the origin of the signal in 3D space (Koeckenberger et al., 2004) can be learned by applying additional magnetic fields during the scan. A 3D image is compiled from multiple 2D images, which are produced from any plane of view. The image can be rotated and manipulated to be better able to detect tiny changes of structures within the food object. These fields, generated by passing electric currents through gradient coils, make the magnetic field strength vary depending on the position within the magnet. Because this makes the frequency of the released radio signal also depend on its origin in a predictable manner, the distribution of protons in the food can be mathematically recovered from the signal, typically using the inverse Fourier transformation. In the images, each pixel value reflects the NMR-signal intensity of a voxel in the measured material, which relates with the resonance density and the two main parameters (i.e., relaxation time: T1 and T2).

MRI shows the image of the object structure making its physical and chemical information visible. In brief, the MRI system includes (Mariette, 2004):

- the magnet and power-supply equipment that can produce a wide range of uniform, stable and constant magnetic field;
- a set of gradient magnetic field coil, a controller and power-driven equipment;
- a radio-frequency (RF) system;
- a computer system with large storage capacity for data collection and processing;
- some auxiliary equipment.

MRI being a non-invasive technique, find application to retrieve structural information from plants and fruits (Gruwel et al., 2013), as for example to study growth and ripening of grapes since it allows to obtain the volume and the soluble solids distribution within a cluster (Andaur et al., 2004) and for detecting fluid flow (Scheenen et al., 2002; 2007) in typical vascular structures such as xylem and phloem.

X-ray, also called roentgen ray, is electromagnetic radiation with a wavelength range of 0.01–10 nm. The photon energy of an X-ray is in the range of 0.1–120 keV, which leads to strong penetrability.

X-ray, similar to other electromagnetic waves, can show the following phenomena: reflection, refraction, scattering, interference, diffraction, polarization and absorption. Usually, X-rays whose photon energy is up to about 10 keV (10–0.10 nm wavelength) are classified as ‘‘soft’’ X-rays, and those of 10–120 keV (0.10–0.01 nm wavelength) are ‘‘hard’’ X-rays, due to their penetrating abilities. As hard X-rays pollute food, only the soft XRI technique is used in food inspection.

The principle of soft XRI inspection is based on the density of the product and the contaminant, as shown in Figure 1.8 (a). As an X-ray penetrates a food product, it loses some of its energy. A dense area, such as contaminant, will reduce the energy even further. As the X-ray exits the product, it reaches a sensor. The sensor then converts the energy signal into an image of the interior of the food product. Foreign matter appears as a darker shade of grey that helps to identify foreign contaminants. The soft X-ray inspection system, as shown in Figure 1.8 (b), mainly comprises a computer-controlled X-ray generator (i.e. X-ray source tube), a line-scanning sensor for X-ray detection, conveying belt, stepping motor, image-acquisition card and computer. As a rapid, non-invasive assessment technique, XRI also produces 3D information that can be manipulated numerically.

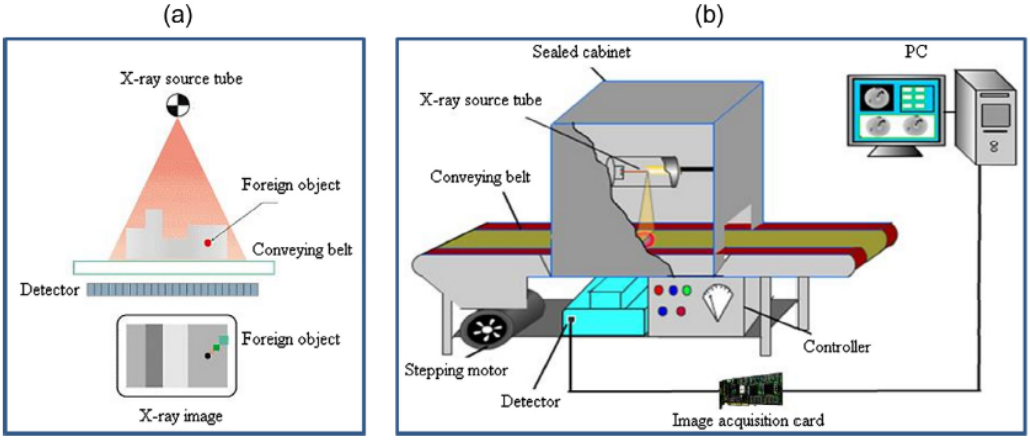


Figure 1.8 – Principle of soft X-ray imaging (a) and the soft X-ray inspection system (b), Chen et al., 2013

XRI is relatively cheap to use and simple in accessibility. Unfortunately this technique has material restrictions, such as for ferromagnetic metals (Bischof et al., 2007), difficulty to recognize objects whose density is similar to that of water and cannot detect hair, paper and plastics. On the other side, X-ray is very effective for investigating the internal condition of foods (Morita et al.,

2003). X-rays have strong penetration ability, so the image can directly reflect internal defects of food and agriculture products, and structural organization changes in quality.

There are several application on food industry. Mousavi (et al., 2005; 2007) demonstrated the capability of an X-ray as a non-destructive technique to characterize the ice-crystal microstructure of mycoprotein products after freezing; Mendoza (et al., 2010), studied the shelf-life of frozen products, while many applications have been developed for the detection of foreign materials in foods (deboned poultry, packaged dry foods and fish bones in fish fillets (Tao et al., 2001; Kwon et al., 2008; Narvankar et al., 2009; Mery et al.; 2011).

Ultrasound Imaging implies mechanical waves at frequencies above 20 kHz, which is beyond the upper limit of the human auditory acoustic frequency range (viz 20–20000 Hz). They are propagated by vibration of the particles in the medium and may be reflected and transmitted when they pass from one medium to another (Cho et al. 2003). Detailed information about the different physical properties of materials can be acquired through the amount of energy reflected or transmitted through the objects depending on their relative acoustic impedances. In addition, the time-of-flight and the speed can also indicate a material property or changes in material characteristics, since ultrasound velocity depends on the density and the elastic property of the medium (Povey et al. 1988). Like light waves, incident ultrasound captures objects, and ultrasound energy attenuation differs for the internal structure of an object to produce a different echo, which leads to a series of points of light displayed on the screen, that is, the ultrasound image. Primarily, the image contrast depends on differences in densities and speeds of the sound, because these properties determine the scattering and the reflectivity of tissue.

Thermal Imaging (TI) is an emerging, non-invasive analytical tool suitable for the food industry. The basic principle of TI is that all materials, above the absolute zero temperature (0 K), emit IR radiation, which is a band of invisible light with wavelengths of 0.75–100 μm. IR radiation can be divided into five regions: near (0.75–2.5 μm), short wave (1.4–3 μm), mid (3–8 μm), long wave (>8 μm) and extreme (15–100 μm).

TI is not only a non-invasive, but also a non-contact system of recording thermal distribution by measuring IR radiation emitted by a body surface to produce a pseudo image of the temperature distribution of the surface (Arora et al., 2008).

Thermal images can be obtained using passive or active TI systems. Passive thermography refers to TI without applying any external energy to the object; the features of interest are naturally at a higher or lower temperature than the background. Active thermography requires the application of thermal energy to produce a thermal contrast between the feature of interest and the background.

TI systems typically comprise the following components: camera, an optical system (e.g., focusing lens, collimating lenses, and filters), detector array (e.g., microbolometers), signal

processing, and image-processing system. TI does not require an illumination source, but integrated systems for active thermography measurements contain a heating or cooling unit to provide a thermal differential. In TI cameras, the IR energy emitted from an object under investigation is converted into an electrical signal via IR detectors and displayed as a monochrome or color thermal image. The image-acquisition speed of the approach may be high enough (e.g., 50–60 images/s) to explore rapidly changing thermal conditions (Rahkonen and Jokela, 2003).

TI, originally developed for military applications and for surveillance in night vision, was used in various fields, including medicine, materials science and fire safety. Actually is a system suitable also for the food industry, due to their portability, real-time imaging, and non-contact temperature-measurement capability (Goedeken et al., 1991; Ibarra et al., 2000; Varith et al., 2003; Vereycken et al., 2003; Fuller et al, 1998; Gariepy et al., 1989; Nanni Costa et al., 2010; Wang et al., 2006; FIto et al., 2004; Manickavasagan et al., 2006; Manickavasagan et al., 2008; Meinlschmidt and Maergner, 2002).

Limitations and disadvantages of thermography are the price higher than visible-spectrum counterparts, the difficulties to interpret accurately when based upon certain objects, specifically objects with erratic temperatures, the accuracy of the camera (±2% in most case) that is lower than the contact methods and the thermal influence on the test of the ambient.

Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation. It is a form of luminescence. In most cases, the emitted light has a longer wavelength, and therefore lower energy, than the absorbed radiation. Fluorescence will disappear immediately without the incident light. There are two kinds of fluorescence, which are autofluorescence and fluorescence with the help of fluorescent pigment.

1.4.2 Techniques VIS -NIR

Visible and near infrared (VIS-NIR) spectroscopy is widely used for rapid, low-cost and non-destructive analysis of inner properties of fruits. The use of VIS-NIR technology have been extensively used for prediction of SSC, pH, acidity, phenols and antioxidant activity of fruits and vegetables (Cozzolino et al., 2004; 2006; Nicolai et al., 2007).

Near infrared radiation was discovered by Friedrich Wilhelm Herschel in 1800 (Davies, 2000) and covers by definition the wavelength range from 780 to 2500 nm. When radiation hits a sample, the incident radiation may be reflected, absorbed or transmitted, and the relative contribution of each phenomenon depends on the chemical constitution and physical parameters of the sample.

Reflection is due to three different phenomena. Specular reflection causes gloss, whereas external diffuse reflection is induced by rough surfaces. Both only provide information about the surface of the sample. Scattering results from multiple refractions at phase changes inside the material. The main scattering elements in fruit and vegetables are the cell wall interfaces since they induce abrupt changes in refractive index (McGlone et al., 1997), but suspended particles, such as starch granules, chloroplasts and mitochondria may also induce scattering caused by diffraction at the particle surface where the refractive index is different from that of the surroundings (Il'yasov and Krasnikov, 1991). The scattering is also dependent on the size, the shape and microstructure of the particles. Scattering may also appear due to heterogeneities, such as pores, openings, capillaries that are randomly distributed through the sample. Multiple scattering events largely determine the intensity of the scattered light that is emitted (McGlone et al., 1997). The scattering process affects the intensity level of the reflected spectrum rather than the shape; the latter is more related to the absorption process.

Most of the absorption bands in the near infrared region are overtone or combination bands of the fundamental absorption bands in the infrared region of the electromagnetic spectrum, which are due to vibrational and rotational transitions. In large molecules and in complex mixtures, such as foods, the multiple bands and the effect of peak-broadening, result in NIR spectra that have a broad envelope with few sharp peaks. The spectra are clearly very similar and are dominated by the water spectrum with overtone bands of the OH-bonds at 760, 970 and 1450 nm and a combination band at 1940 nm (Polessello and Giangiacomo, 1981). This similarity is the reason why sophisticated multivariate statistical techniques are essential to extract useful information from an NIR spectrum.

The equipment to perform the NIR analysis is the NIR spectrophotometer that consists of a light source (usually a tungsten halogen light bulb), sample presentation accessory, monochromator, detector, and optical components, such as lenses, collimators, beam splitters, integrating spheres and optical fibers. Spectrophotometers are conveniently classified according to the type of monochromator.

NIR spectroscopy was first used in agricultural applications by Norris (1964) to measure moisture in grain. Since then it has been used for rapid analysis of mainly moisture, protein and fat content of a wide variety of agricultural and food products (Davies and Grant, 1987; Gunasekaran and Irudayaraj, 2001). Early applications in horticulture focused on dry matter content of onions (Birth et al., 1985), soluble solids content (SSC) of apples (Bellon-Maurel, 1992) and water content of mushrooms (Roy et al., 1993), but then many other applications have followed. As the propagation of NIR radiation in fruit and vegetable tissues is affected by their microstructure, it was soon discovered that NIR spectroscopy could also be used to measure microstructure-related attributes, such as stiffness (Lammertyn et al., 1998), internal damage (Clark et al., 2003a,b), and

even sensory attributes (Mehinagic et al., 2004). Recent developments which extend the potential of NIR spectroscopy further include multi- and hyperspectral imaging techniques which also provide spatial information (Martinsen and Schaare, 1998; Lu, 2003) and time-resolved spectroscopy which allows measurement of absorption and scattering processes separately (Cubeddu et al., 2001).

The increasing importance of NIR spectroscopy in postharvest technology is linked with the fact that many manufacturers of on-line grading lines have now implemented NIR systems to measure various quality attributes.

1.4.3 Hyperspectral images

Hyperspectral imaging, known also as chemical or spectroscopic imaging, is an emerging technique that integrates conventional imaging and spectroscopy to attain both spatial and spectral information from an object (Gowen et al., 2007), which are both critical to the detection of food safety and to the evaluation of food quality attributes. A typical hyperspectral system consists of a light source, a wavelength dispersion device, and detector. The images are acquired over the visible and near-infrared (or infrared) wavelengths to specify the complete wavelength spectrum of a sample at each point in the imaging plane. These images are then combined and form a three dimensional hyperspectral cube, with two dimensions for describing spatial information (X and Y) and the third one for spectral information. In this hypercube, each spectral pixel corresponds to a spectral signature (or spectrum) of the corresponding spatial region, recording the entire measured spectrum of the imaged spatial points (Figure 1.9). Therefore the measured spectrum indicates the ability of the sample in absorbing or scattering the exciting light, representing the inherent chemical properties of a sample. As a result, the technology provides us with unprecedented detection capabilities, which otherwise cannot be achieved with either imaging or spectroscopy alone, providing information on where is what (Sun, Da-Wen, 2010).

When a fruit is exposed to light, the reflected radiation can be measured and recoded as a reflectance spectrum. This spectrum is related to chemical composition of the fruit, and spectra collected from fruit at different quality levels can therefore be quite different (Elmasry et al., 2007).

Hyperspectral imaging techniques have received much attention for food quality and safety evaluation and inspection. Many approaches and applications have shown the usefulness of hyperspectral imaging in the food industry (Sun, Da-Wen, 2008).

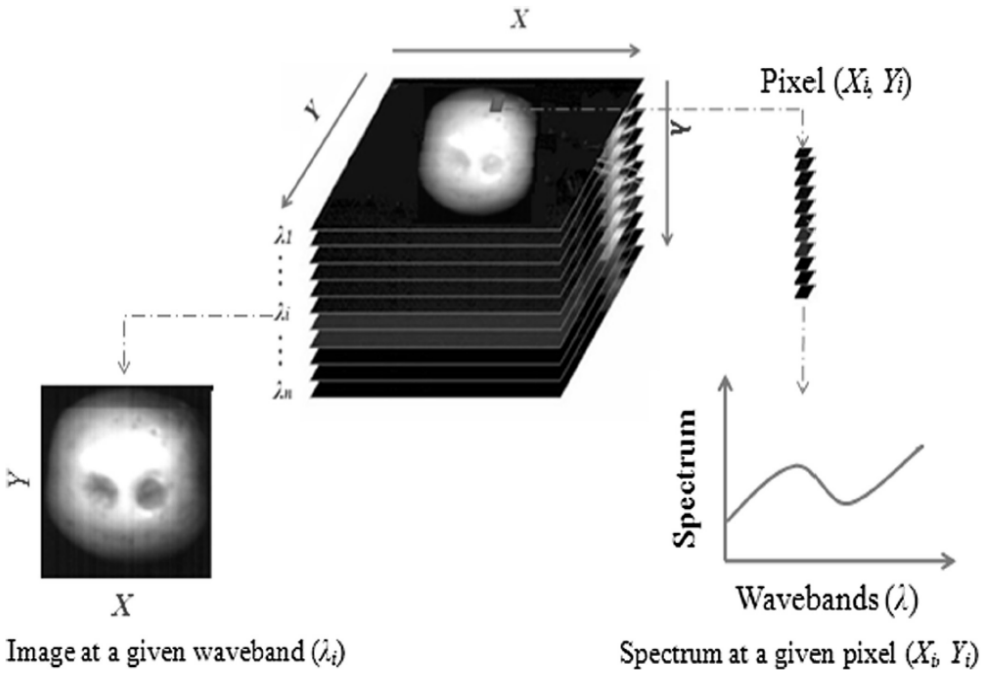


Figure 1.9 – Hypercube showing the relationship between spectral and spatial dimensions - Chen et al., 2013

Hyperspectral imaging technique has been for soluble solid content, bitter pit, bruise and surface defects and contaminations in apple fruit, (Mehl et al., 2004; Peri et al., 2005; Xing et al., 2005; Nicolaï et al., 2006), for the citrus fruit inspection (Moltó et al., 2010.), to predict the sugar content distribution in melons (Sugiyama and Tsuta, 2010), for measuring ripening of tomatoes (Polder and van der Heijden, 2010), for quality evaluation of mushroom (Gowen et al., 2010.), to detect defects of pickling cucumber (Ariana and Lu, 2010), to measure soluble solid content and firmness of strawberries and blueberries (Nagata et al., 2005; Leiva-Valenzuelaa et al., 2013), to monitor ripening on peaches and on banana (Lleó et al., 2011; Rajkumar et al, 2012) and to identify hidden bruise on kiwifruits (Qianga and Mingjie, 2012).

Sometime it is necessary quantify the presence of substance and monitor the changes (increase or decrease) function of the epoch. Figure 1.11 shows the possibility to analyze the sugar distribution in a fruit like melon; the output from of the analysis is a map of the brix grade. The concentration of the substance defines univocally a color in the scale of color; so it is possible define a scale of color for each degree of Brix degree.

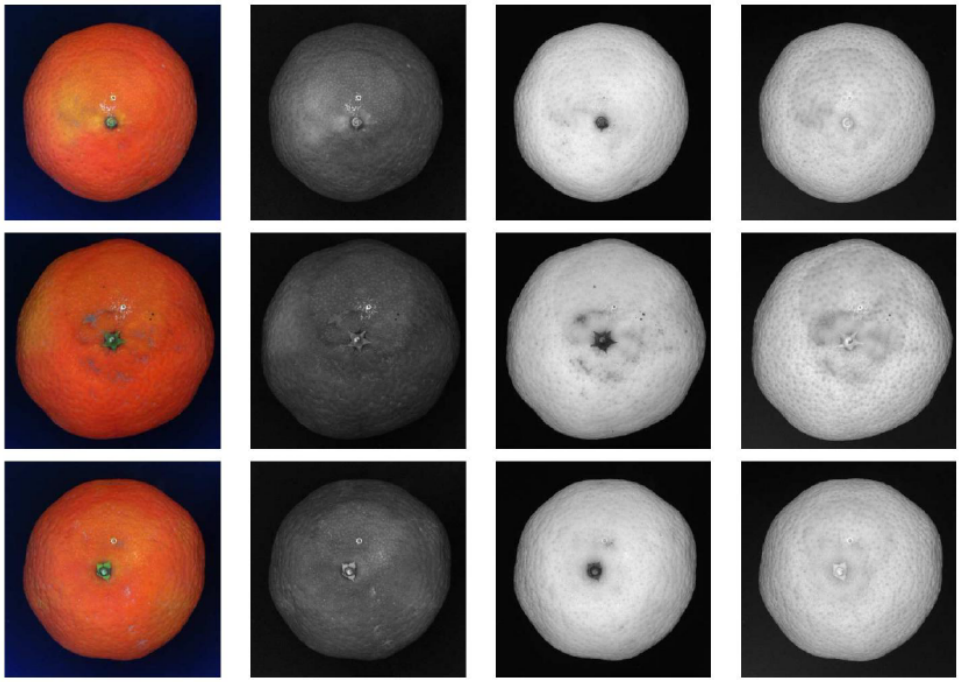


Figure 1.10 – RGB and monochromatic images (550 nm, 660 nm and 950 nm) of various mandarins (cv. Clemenules) - (Moltó, et al., 2010.)

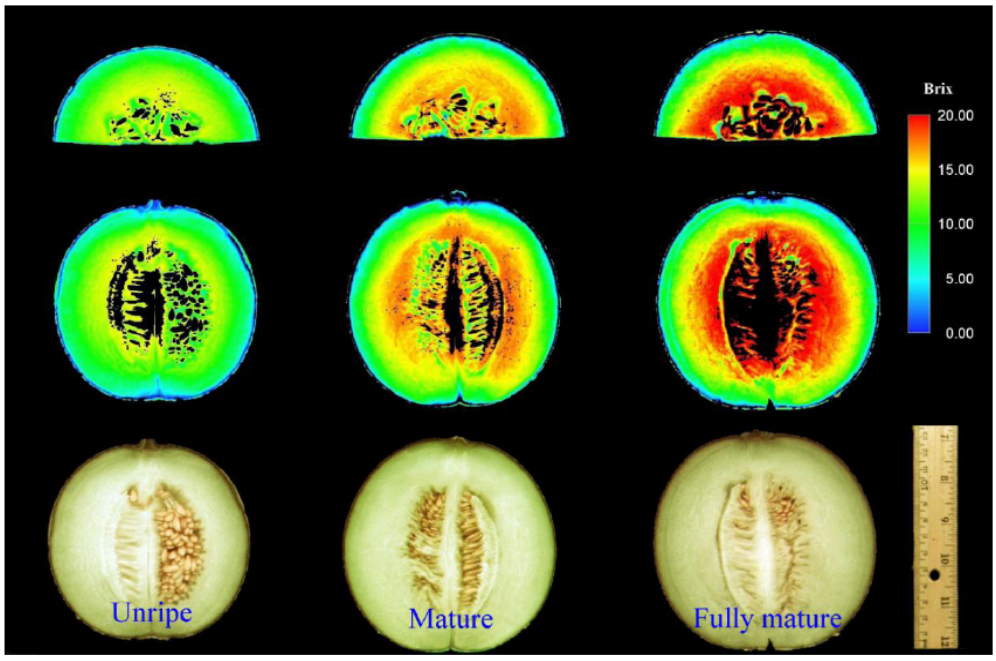


Figure 1.11 – Sugar distribution map for unripe, mature and fully mature melons - (Sugiyama, J., Tsuta, M. 2010)

1.5 CHEMIOMETRIC TECHNIQUES

NIRS prediction models relate the spectral information of collective learning samples to quality parameters as measured using a reference method. Once developed, the model can be used to predict the content of other samples similar to those in the training (or calibration) group. Generally to extract relevant information from spectra, mathematical pre-treatments of spectral signals are needed, allowing to separate chemical information from merely physical variations (due to texture, size, geometry of the particles). In the spectroscopic signals, in facts, unwanted effects are normally included, also known as 'noise'. These have different origins or causes and affect the spectrum differently. The components of the instrumentation used to record the spectrum (instrumental noise), variations of temperature, humidity or other environmental conditions during registration (environmental noise) or variations in the signal due to the nature of the sample can be some of the causes of noise. Among most used pretreatments we count "scatter" or scattered radiation called multiplicative correction of the effect of scatter, Standard Normal Variate (SNV), and Detrend (DT) (Shenk and Westerhaus, 1995a; Heise and Winzen, 2002; Naes et al., 2002; Nicolaï et al., 2007). Other pre-treatments are the Derivatives described by Savitzky and Golay (1964). Generally, by using the derivative (first and second), the scatter effects of spectra is reduced. The first derivative spectrum is the slope at each point of the original spectrum; it has peaks where the original has maximum slope, and crosses zero in correspondence of original peaks. The second derivative is the slope of the first derivative. It is more similar to the original spectrum in some ways, having peaks in roughly the same places, although they are inverted in direction (Naes et al., 2002).

Previous studies are advisable before applying techniques of preprocessing, as these may remove a fraction of the stored information.

After signal pretreatment, necessary steps are directed to develop a calibration equation that can predict quality parameters of other unknown samples, but with similar characteristics to those belonging to the calibration sample (Shenk and Westerhaus, 1995b, 1996, Williams and Sobering, 1996). Available techniques are: Principal Component Analysis (PCA), methods of linear regressions (belonging to quantitative analysis) that are available for developing a calibration (Martens and Naes, 1989; Burns and Ciurczak, 1992, 2001), like Multiple Linear Regression (MLR), the Principal Component Regression (PCR) and the Partial Least Squares (PLS) (Shenk and Westerhaus, 1995b; Pérez-Marín et al., 2007).

Qualitative analysis are based on the spectral characteristics of samples and are aimed to the development of classification models in response to those characteristics, grouping samples with similar spectra, which are separated from other with different spectra (Downey, 1994, 1996). This

applications is useful in the quality control of food products to identify unknown samples as for instance for distinction between varieties, shape, or dimensions. (Paz et al., 2009a and b; Sánchez et al., 2009).

Most analytical methods relate similarity between the spectral characteristics of a group of samples. Such similarity can be expressed based on different tools such as spectral correlation, logical operations or calculating distances (Pérez-Marín, 2005). The most common methods of classification are: Linear discriminant analysis (LDA), Soft Independent Modelling of Class Analogy (SIMCA), and PLS-Discriminant Analysis (PLS-DA) (Naes and Indahl, 1998; Vandeginste et al., 1998; Vigneau et al., 2000; Naes et al., 2002).

1.5.1 PCA: Principal Component Analysis

Principal Component Analysis (PCA) is a technique used at any stage of the data processing to study the spectra population in order to achieve information on the variables (wavelengths) and on the sample distribution and to detect abnormal samples. This technique is used to find the principal components (PC's) explaining maximum variability of the samples and use them as new coordinate axes.

Each main component contains different relevance information describing the most important source of variation data.

PCA is used to detect those samples with different behavior, called ‘outliers’, whose malfunction can be caused by both physic-chemical and spectroscopic features. Normally the outlier detection is based on the distances between the spectra of the various samples in a n-dimensional space which is generally, calculated applying the Mahalanobis distance (Shenk and Westerhaus, 1995b, 1996). Mahalanobis distance is defined by a distance measure based on a set of multivariate data (the training data) that are used to describe it and whose Euclidean length varies according to the direction in the space in which it is being measured. The equivalent Euclidean length is large in the direction (dimension) where the data are spread out and small in the direction in which the data are compact.

A detailed description of possible causes of abnormal spectra, was performed by Williams and Norris (2001) which suggested that detection, interpretation and possible elimination of these anomalous samples is a critical step in the development of prediction models, due to the great influence of their presence on the results.

These procedures are performed prior to define the collective calibration either for the construction of calibration equations (quantitative analysis) or for classification models (qualitative analysis).

Different methods of linear regressions are available for developing a calibration (Martens and Naes, 1989; Burns and Ciurczak, 1992, 2001), the most common methods being the Multiple Linear Regression (MLR), the Principal Component Regression (PCR) and the Partial Least Squares (PLS) (Shenk and Westerhaus, 1995b; Pérez-Marín et al., 2007).

1.5.2 Quantitative Analysis

Research in science and engineering often involves the use of controllable and/or easy-to-measure variables (factors) to explain, regulate, or predict the behavior of other variables (responses). When the factors are few in number, are not significantly redundant (collinear), and have a well-understood relationship to the responses, then multiple linear regression (MLR) can be a good way to turn data into information. However, if any of these three conditions breaks down, MLR can be inefficient or inappropriate. In such so-called soft science applications, the researcher is faced with many variables and ill-understood relationships, and the object is merely to construct a good predictive model.

Partial least squares (PLS) is a method, introduced almost 30 years ago by Wold (et al., 2001), for constructing predictive models when the factors are many and highly collinear, taking into account, for the calculation of these variables, not only spectral information but also the reference value of the parameter measured for each sample (Westerhaus et al., 2004). Note that the emphasis is on predicting the responses and not necessarily on trying to understand the underlying relationship between the variables.

MLR can be used with many factors; however, if the number of factors gets too large (for example, greater than the number of observations), you are likely to get a model that fits the sampled data perfectly but that will fail to predict new data well. This phenomenon is called over-fitting. In such cases, although there are many manifest factors, there may be only a few underlying or latent factors that account for most of the variation in the response. The general idea of PLS is to try to extract these latent factors, accounting for as much of the manifest factor variation as possible while modeling in a good way the responses. For this reason, the acronym PLS has also been taken to mean “projection to latent structure”. It should be noted, however, that the term ‘‘latent’’ does not have the same technical meaning in the context of PLS as it does for other multivariate techniques. In particular, PLS does not yield consistent estimates of what are called ‘‘latent variables’’ in formal structural equation modelling (Dykstra, 1983; 1985).

The extracted factors X-scores are used to predict the Y-scores, and then the predicted Y-scores are used to construct predictions for the responses. This procedure actually covers various techniques, depending on which source of variation is considered most crucial.

Interpretation of the relationship between X-data and Y-data (the regression model) is then simplified as this relationship is concentrated on the smallest possible number of latent variables. The method performs particularly well when the various X-variables express common information, i.e., when there is a large amount of correlation, or even co-linearity, which is the case for spectral data of intact biological material. PLS regression can be easily extended to simultaneously predict several quality attributes. In this case the algorithm is called PLS2 (Næs et al., 2004).

The use of these techniques presents, among many others, the advantage of not having to select the wavelengths with which the model is developed, (Mark and Workman, 1991; Workman, 1992). As indicated by Shenk and Westerhaus (1995a), the PLS algorithm for food products is more accurate and stable on the base of the number of factors selected by cross validation regression (Shenk and Westerhaus, 1995a). Cross-validation is an algorithm that selects different groups of calibration and validation spectra within a specific population. The procedure consists of dividing the collective calibration sample in several groups (depending on the number of samples); once the equation is developed each validation group is predicted from other groups. This procedure also prevents model overfitting (Shenk and Westerhaus, 1995a; Williams, 2001), which would give poor results with external calibration.

Some statistical indices are used to select the best models for regression model: coefficient of correlation for calibration (R), coefficient of determination for calibration (R^2) and coefficient of determination for cross-validation (r^2). In addition, there are the standard error of calibration (SEC) which is defined as the standard deviation of residuals (difference between the value provided by the reference method and the value estimated by the equation) for the group of calibration (Williams, 2001); while the standard error Prediction (SEP) is known as the standard deviation of the differences, for a validation group, between the value determined by the reference method and the value estimated by NIRS analysis and is the statistical more used to estimate the predictive ability of a calibration equation NIRS (Mark and Workman, 1991; Shenk and Westerhaus, 1995b; Williams, 2001; Wise et al., 2006). Finally, there is the standard error of cross-validation (SECV) which together SEC defines the error of a model of regression. A good model should have a low SEC, a low SECV and high determination coefficients, but also a small difference between SEC and SECV (Shenk and Westerhaus, 1995b; Williams, 2001).

Several software packages are available for multivariate calibration. The Unscrambler package (http://www.camo.com) it is a menu-driven, very easy to use and offers a range of preprocessing techniques. The Grams Suite is a general purpose software package for handling spectroscopic data including chemometrics and is distributed by the Thermo Scientific company (http://www.thermo.com). The Matlab PLS toolbox of Eigenvector Research (software.eigenvector.com) offers the flexibility of Matlab for applications in which programming is

required. Many statistical packages, such as SAS (http://www.sas.com) and statistica (http://www.statsoft.com) also provide multivariate calibration but are less convenient to use for processing spectral data.

1.5.3 Qualitative analysis

Classifying means, in a general sense, to assign an individual (sample) to one or more categories based on a set of measurements used to describe or characterize the object itself. From a geometrical standpoint, this corresponds to identifying regions in the hyperspace of the variables corresponding to the different classes (Marini, 2010).

Specifically, the term class or category indicates a collection of objects sharing similar characteristics; it is very important to highlight that the definition of these characteristics is problem-dependent, so that the same set of samples can be grouped in different ways, according to the final scope of the modelling.

Classification methods can be grouped in different ways depending on the properties of interest.

A first fundamental differentiation can be made between those methods which are focused on discriminating among different categories (discriminant classification) and those which are rather directed towards modelling classes (class-modelling) (Albano et al., 1978).

The discriminant techniques are focused on the differences between samples coming from different classes; the class-modelling methods are based on capturing the similarities among samples from the same category.

Geometrically, the discriminant techniques produce as result hypersurfaces (multidimensional surfaces), dividing the variable space in as many regions as the number of available categories. The class-modelling methods identifies a volume in the multidimensional space enclosing the class, so that if a sample falls within that volume it is accepted by the particular category, while if it falls outside, it is rejected by that class model.

A second distinction is based on the mathematical form of the functional relationship representing the classification rules in terms of the measured variables (or, alternatively, on the geometrical shape of the decision boundaries in the multidimensional space). The main differentiation is made between linear and non-linear methods (that can be subdivided according to the kind of non-linearity).

Lastly, it is possible to further differentiate classification methods, based on whether they explicitly assume a probability distribution of the data or not.

Starting from similarity between the spectral characteristics of a group of samples, classification methods can be applied to discriminate among different groups. Such similarity can be expressed based on different tools such as spectral correlation, logical operations or calculating distances (Pérez-Marín, 2005). The most common methods of classification are: artificial neural networks (ANN), Soft Independent Modelling of Class Analogy (SIMCA), and PLS-Discriminant Analysis (PLS-DA) (Naes and Indahl, 1998; Vandeginste et al., 1998; Vigneau et al., 2000; Naes et al., 2002).

LDA and PLS belong to discriminant classification methods, instead SIMCA belong to the class-modelling methods.

Linear discriminant analysis (LDA), is the oldest and most studied supervised pattern recognition method. It was originally proposed by Fisher in 1936. It is a linear technique, that is the decision boundaries separating the classes in the multidimensional space of the variables are linear surfaces (hyperplanes). From a probabilistic standpoint, it is a parametric method, as its underlying hypothesis is that, for each category, the data follow a multivariate normal distribution.

PLS (Partial Least Squares) algorithm was originally introduced to build calibration models, and then reformulated to solve the classification problem in terms of a regression equation (PLS discriminant analysis, PLS-DA).

The model seeks to correlate spectral variations (X) with defined classes (Y), trying to maximize covariance between the two types of variables. In this type of approach, the variables are artificial or fictitious categorical variables ("dummy"), created by assigning the value 0 to the sample of category A and the value 1 to the sample of category B (Heise and Winzen, 2002; Naes et al., 2002; Kramer et al., 2004).

When there are only two classes to discriminate PLS1 algorithm can be applied since there is one independent variable to each outlet collective learning sample giving a value of 0 or 1. The criteria for classification unknown samples in either category will depend on if the predicted value is nearer to 0 or to 1, respectively. If more than two classes need to be discriminated, the use of the algorithm PLS2 multivariate regression would be advisable. However, this algorithm can be also used when there are only two classes (Naes et al., 2002). The significance of the dummy variables changes slightly when applying PLS2. In this approach, the independent variable becomes a vector of classes, so that each sample has a value of 1 in the class to which it belongs, and a value of 0 for the other classes (Vandeginste et al., 1998; Heise and Winzen, 2002; Naes et al., 2002). Meanwhile, for the prediction of unknown samples, we obtain a value of the discriminatory variable for each of the classes provided, so a value of 1 in the categories represent a perfect assignment thereof, while a value of 0 would indicate no such class membership. For the same sample, if the dummy variable values used are 0 and 1, the predicted values obtained for each class must give a sum of 1.

As PLS is a component-based technique, even when it is used for classification, in the model building phase, it is necessary to estimate the optimal complexity in terms of the number of latent variables leading to the best results. Usually, this choice is made based on some sort of internal or external validation procedure.

The SIMCA classification (Soft Independent Modelling of Class Analogy), proposed by Wold et al. (1976), has been extensively described in the chemiometric literature (Wold et al., 1983; Sharaf et al., 1986; Beebe et al., 1998). SIMCA is a method based on disjoint PCA modelling realized for each class in the calibration set. Unknown samples are then compared to the class models and assigned to classes according to their analogy with the calibration samples. Each class is modelled using separate PCA models. A number K of principal components is used to build the model. These K components define the inner space, the space of the structure, and the other principal components are the outer space, the space of the noise. The SIMCA model is a hyper volume in the space of the significant components, delimited by the range of the scores (normal range). The sensitivity of a class model is the fraction of the objects belonging to that class accepted by the model. The specificity of a model is the fraction of objects belonging to other classes rejected by the studied class model. An unknown sample is compared with each group in turn by computing two distances: the Euclidean distance from the spectrum to its projection into the model for that group (distance from the model) and the Mahalanobis distance from the projected spectrum to the group mean (distance within the model), and comparing these distances with thresholds derived from the training data. If both distances are less than the threshold, the unknown is a possible member of that group. After all the comparisons have been made, the unknown sample may be identified as a possible member of none, one, or more than one of the groups.

PART TWO – EXPERIMENTAL

2.1 OBJECTIVE

Nowadays it is increasing the needs to know the quality and safety of the food products. These requirements call for on-line detection techniques which have the advantages of be assembled in the production line and take place under realistic environment, know early detection of possible failures, have permanent monitoring of the conditions and know assessment of conditions at any desired time.

Hyperspectral imaging is an innovative technique that integrates conventional imaging and spectroscopy to attain both spatial and spectral information from an object (Gowen et al., 2007)..The images are acquired over the visible and near-infrared (or infrared) wavelengths to specify the complete wavelength spectrum of a sample at each point in the imaging plane. These images are then combined and form a three dimensional hyperspectral cube, with two dimensions for describing spatial information (X and Y) and the third one for spectral information. In this hypercube, each spectral pixel corresponds to a spectral signature (or spectrum) of the corresponding spatial region, recording the entire measured spectrum of the imaged spatial points The choice of this type of analysis is dictated by reduction in analysis time and the possibility to analyze several attributes on the same sample, also at different times, since it is a non destructive method.

Scope of the present work was to use hyperspectral images of artichoke quarters acquired in the VIS-NIR range to classify samples by cultivar ("Violetto" and "Catanese"), by harvest time and days of storage and to predict the internal content of phenols and antioxidant activity in artichoke "Violetto".

2.2 CULTIVAR CLASSIFICATION: "VIOLETTO" vs "CATANESE"

2.2.1 Experimental design

Artichoke heads were harvested from December to May (7 harvest dates) for "Violetto foggiano" and from January to April for "Catanese" (4 harvest dates) from commercial fields located respectively in the area of San Ferdinando di Puglia and Brindisi (Puglia Region, Italy). Harvest dates during years 2009/10, together with data on mean temperatures (°C) and days of rainfall (in days) during the 15 days preceding harvest are reported in Table 2.1. At the first harvest 20 plants for each field were randomly-chosen and labelled in order to reduce field variability

among different harvest dates. Artichokes were directly transported to the postharvest laboratory at the University of Foggia and processed on the same day.

Artichokes were processed in a cold room 10 °C under suitable hygienic conditions. Heads were hand trimmed using sharp stainless steel knives in order to remove external bracts, leaves and stalks and then washed in a NaClO solution (0.01%, w/w of free chlorine) to eliminate soil and insect residues. After washing, head trimming was completed in a cold room by further removal of external greener and tougher bracts (inedible fraction) so as to retain just the inner most tender bracts. The upper portion of artichokes was removed and then hearts were cut into quarters and immersed for 1 minute in a 0.01 % NaOCl solution, rinsed with tap water and dried with paper.

Table 2.1 – Harvest dates, mean temperature (°C) and rainfall (in days) recorded during 15 days before harvest for "Violetto foggiano" and "Catanese" artichokes.

Cultivar	Harvest dates (2009/10)	Temperature (°C)	Rainfall (Days)
Violetto foggiano	Dec-15	10	5
	Jan-18	8	4
	Feb-3	6	4
	Mar-1	12	6
	Mar-15	9	5
	Apr-21	14	4
	May-3	19	0
Catanese	Jan-11	11	4
	Feb-1	8	5
	Mar-17	10	8
	Apr-21	14	5

Each artichoke replicate was cut into quarters and then placed in plastic trays and stored in humidified flow of air at 5 °C. One quarter for each artichoke was analyzed during storage at day 0, day 2, day 5 and day 7.

2.2.2 Hyperspectral image acquisition

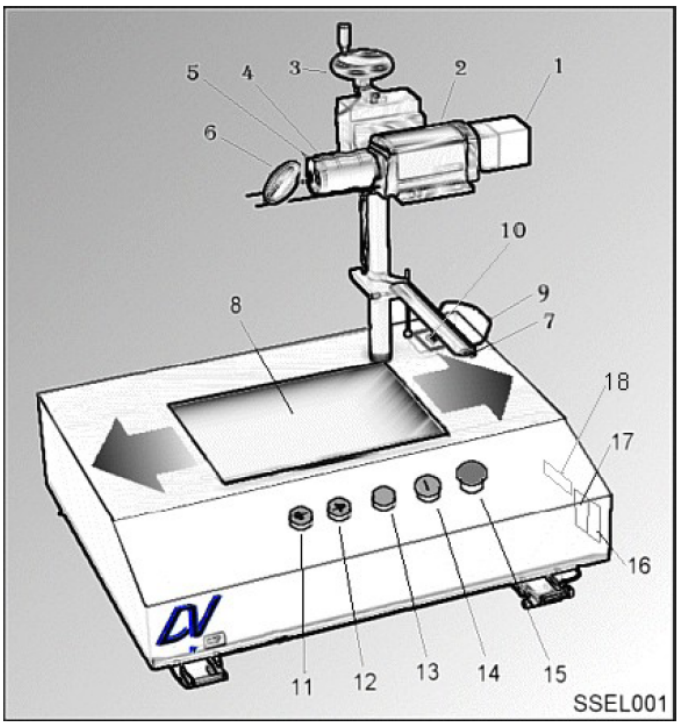
Hyperspectral images were acquired using a hyperspectral scanner (version 1.4, DV srl, Padova, Italy) consisting in a charge-coupled device (CCD), a 12-bit camera connected to a spectrograph (ImSpector V10, Specim Ltd., Haarlem, The Netherlands) coupled with a standard C-mount f16 mm lens (Figure 2.1). The optics of this imaging system allowed to study the sample properties associated to the spectral range 400-1000 nm of reflectance with 5 nm of resolution. The light source consisted of a 150W halogen lamp (EKE 21V150 W, Japan) mounted at a 45°angle

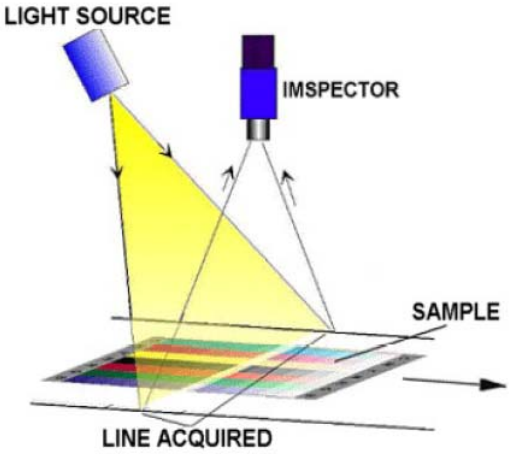
respect to the horizontal plane, and of an optic fibre that transfer the radiation to a linear light diffuser. The camera spectrograph assembly was supplied with a stepper motor to move the unit through the field of view of the camera and line-by-line scan the sample (Figure 2.2). The spectral images were collected in a dark room where only the halogen light source was used The hyperspectral images were firstly corrected with a white and a dark reference. The dark reference was used to remove the effect of dark current of the CCD detectors, which are thermally sensitive.

Figure 2.1 – Hyperspectral scanner (version 1.4, DV srl, Padova, Italy)

Two scan per samples, were acquired, the first for the external surfaces of the outer bracts and the second for the cut surfaces of all artichoke quarters. On the external surfaces of each artichoke quarter (per replicate) a region of interest corresponding to the maximum inscribed rectangle was manually selected, while for the cutting surfaces, two individual regions, corresponding to the receptacle and the cut inner bracts were selected.

1 – CCD Camera
2 – ImSpector
3 – Regulator optic high
4 – Junction C objective
5 – filter 80 A (optional)
6 – Mirror
7 – Fiber optic light line
8 – Translation table
9 – Fiber optic
10 – Light source
11 – Carriage switch back
12 – Carriage switch ahead
13 – Switch on pilot light
14 – Ignition - key
15 – Emergency stop button
16 – 220VAC tension
17 – Main ignition switch
18 – Parallel PC connection





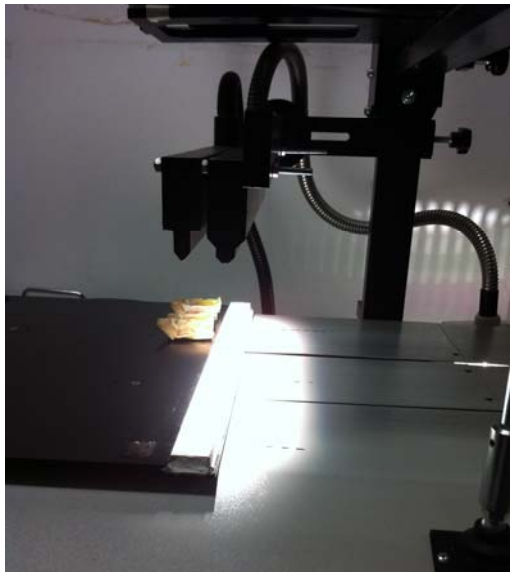


Figure 2.2 – Spectral Scanner acquisition process

2.2.3 Data analysis

Spectral data were analyzed using the Unscrambler packing software version X (CAMO ASA, Oslo, Norway) and PLS toolbox in Matlab (version 2014a).

Spectral data set included 736 samples (400 for “Violetto” and 336 for “Catanese”).

All the reflectance measurements were firstly transformed to absorbance values using log(1/R) according to the law of Lambert-Beer. Then different pretreatments were applied, smoothing of second polynomial order, Multiplicative Scatter Correction (MSC), II derivative and Mean Center.

The spectra were firstly analyzed with a PCA (Principal component analysis) for a first exploration of the data and to identify and eliminate defective spectral outliers (Massart et al., 1998; Naes et al., 2002).

As for classification, SIMCA and PLS-DA analysis were carried out using the SIMCA (Soft Independent Modelling of Class Analogy), defining a Training set of 308 samples for “Violetto” and 244 for “Catanese” and a Test set of 92 samples for “Violetto” and 76 for “Catanese”. The external set of data was used to test the model in prediction.

The SIMCA model was developed by building PCA models for each “variety”, which were subsequently used to classify external spectra. The PCA scores represent the weighted sums of the original variables without significant loss of useful information, whereas loadings (weighting coefficients) allow to identify major variables responsible for specific features appearing in the scores.

The PLS-DA model was developed applying the PLS2 algorithm- Briefly, PLS-DA uses a training set to develop a qualitative prediction model which may subsequently be applied for the classification of new unknown samples. This model seeks to correlate spectral variations (X) with defined classes (Y), attempting to maximise the covariance between the two types of variable. In this type of approach, the Y variables used are not continuous, as they are in quantitative analysis, but rather categorical “dummy” variables created by assigning different values to the different classes to be distinguished (Naes *et al.*, 2002). Spectral variations were correlated with the 2 established categories, corresponding to the two varieties. All models were constructed using full cross-validation (leave-one-out), suitable for small sample sets (Naes *et al.*, 2002).

The goodness of a model can be defined with the evaluation of the capacity to individuate, among different samples or classes of samples the ones with the expected characteristics for the model class; this evaluation was driven by two parameters: sensibility and specificity. These parameters can be measured physically as probabilistic percentage and they are not complementary and there is no proportion between them.

Sensibility of a test is the probability that the sample, effectively with the characteristic awaited, is positive to the test.

Specificity of a test is the probability that the sample, effectively without the characteristic awaited, is negative to the test.

If we define:

- A: samples belonging to class A and correctly classified in class A;
- B: samples belonging to class B and incorrectly classified in class A;
- C: samples belonging to class A but incorrectly classified in class B;
- D: samples of class B correctly not classified in class A.

Sensibility = A/(A+C).

Specificity = 1-B/(B+D).

Another important aspect or characteristic that confirms that the model is robust is the accuracy of a measurement: the degree of closeness of measurements of a quantity to that quantity's true value.

In our analysis the prediction error of a calibration model is defined as the root mean square error for calibration (RMSEC), cross validation (RMSECV) when cross validation is used and for prediction (RMSEP) when external validation is used (Naes et al., 2004).

$$\text{RMSEC or RMSECV or RMSEP} = \sqrt{\frac{\sum_{i=1}^{n_p} (\hat{y} - y_i)^2}{n_p}}$$

with np the number of validated objects, and ŷi and yi the predicted and measured value of the i^{th} observation in the test set, respectively. This value gives the average uncertainty that can be expected for predictions of future samples. The number of latent variables in the calibration model is typically determined as that which minimizes the RMSECV or RMSEP.

Another useful statistic parameter is the R^2 value. In the analysis performed it essentially represents the proportion of explained variance of the response variable in de calibration (R^2_c) or validation (R^2_v) set.

Calibration models are called robust when the prediction accuracy is relatively insensitive towards unknown changes of external factors.

2.2.4 PCA explorative analysis

The spectra were pretreated applying MSC, and then the data were mean centered before PCA analysis. PCA model with three components described 97.39% of the variation in the experimental data (PC1: 76.42%; PC2: 16.21%; PC3: 4.85%). Figure 2.3. shows the plot of PCA scores using the first two components. It can be observed that a high degree of overlapping between the two varieties is present, with a tendency for Catanese samples to occupy the left part of PC1.

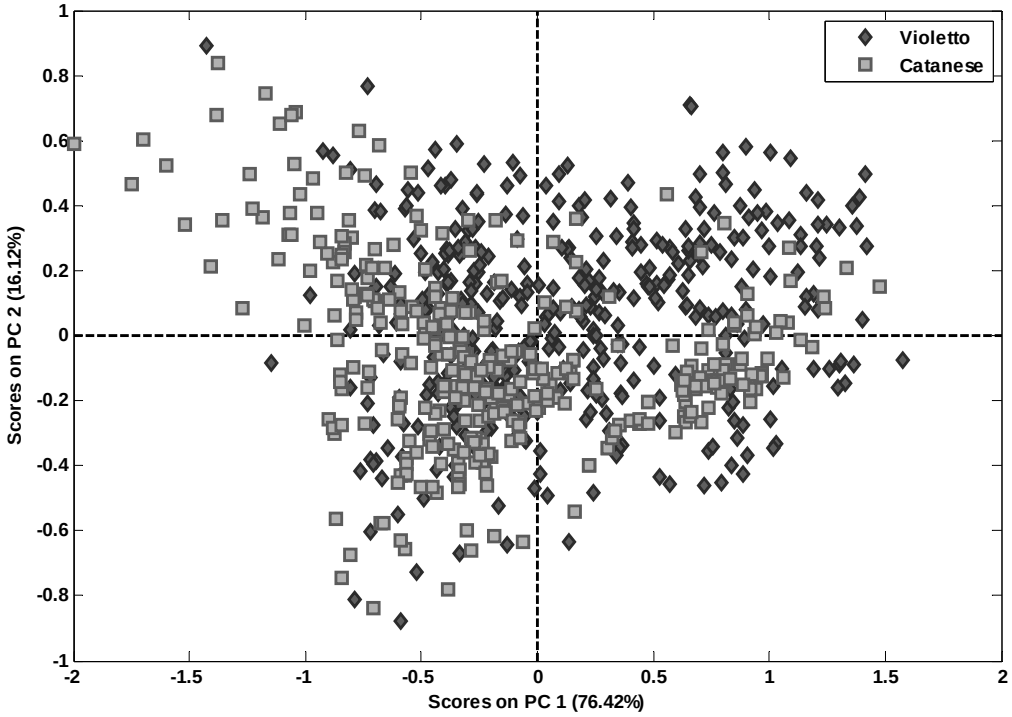


Figure 2.3 – PCA analysis based on 2 PCs on spectra of "Violetto" and "Catanese" cultivars on the spectra preprocessed with the Second Derivative and the Mean Center

Figure 2.4 reports the scores of the first three principal components. The dashed line divides "Violetto" from "Catanese" samples (on the right). Continuous lines define the harvest times (7 for "Violetto" and 4 for "Catanese"). There is no clear differentiation of the spectra, but it is evident how some samples are grouped, particularly for days of storage.

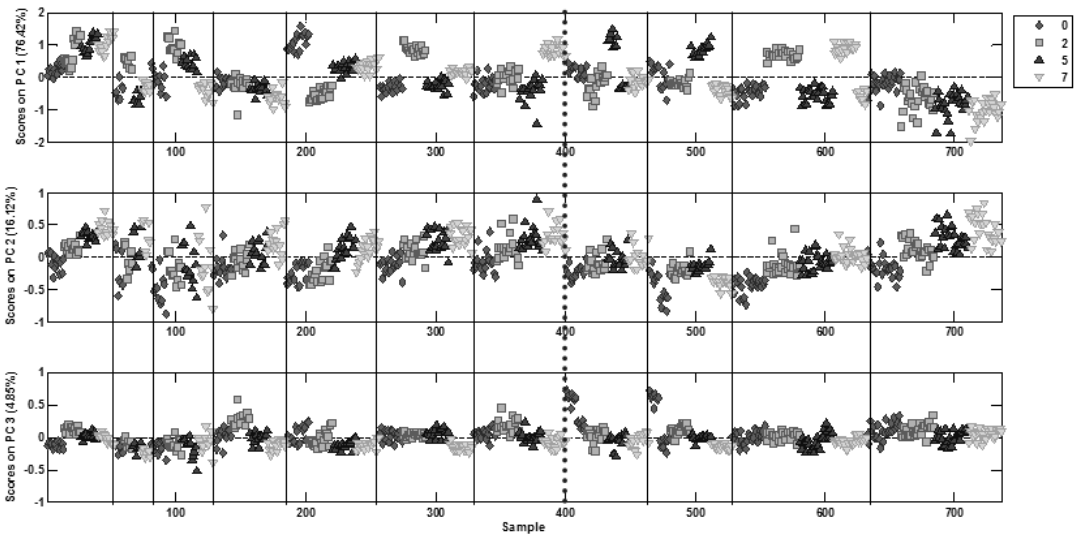


Figure 2.4 – Scores of PC1, PC2 and PC3 for all the samples

When using a different signal pretreatment prior to PCA analysis, some differentiation between the two varieties becomes clearer Figure 2.5 shows the results of the PCA made on spectra transformed using the second derivative using 4 principal components, and the scores of PC1 vs PC4 are here reported. In spite of the high overlapping, "Violetto" samples (red points), takes mainly positive values and "Catanese" (green points), takes mainly negative ones on PC4.

In Figure 2.6 the loadings on PC4 suggest a modification (which appears in the form of sign changes in the contribution to PC4) of the absorption band in the range 650-900 nm with a positive contribution peak (at 720 nm) surrounded by two negative ones. Looking at the signal (Figure 2.7a) we can see that a big peak of different shape is present for the two cultivars, suggesting that the main difference, which appears as a sign change in the loadings, is related to a different convolution effect of the peaks underlying the highlighted absorption area. In Figure 2.7b the zoom allows to observe the different structure of the peaks for the two cultivars: "Violetto" appears to have a sharper absorption peak, with an additional absorption after 750 nm.

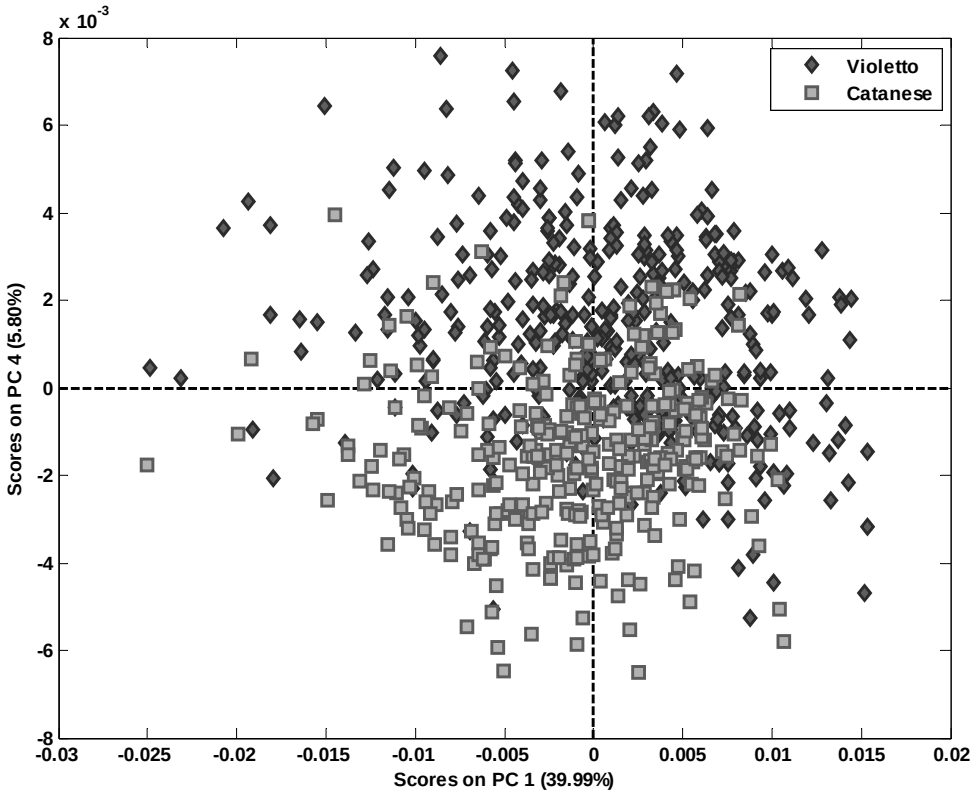


Figure 2.5 – PCA analysis based on 4 PCs on spectra of "Violetto" and "Catanese" cultivars on the spectra preprocessed with the Second Derivative and the Mean Center

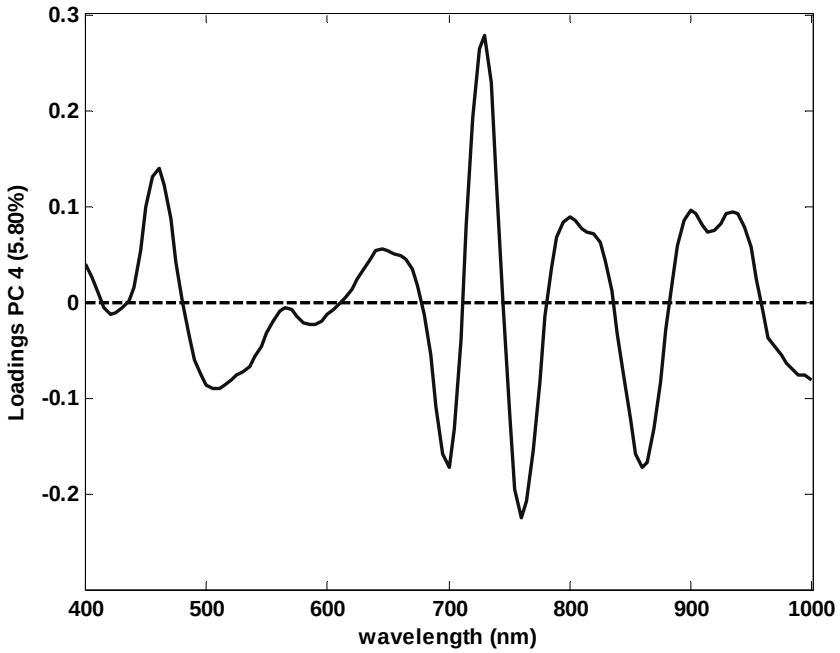


Figure 2.6 – Loadings on PC4 by wavelength

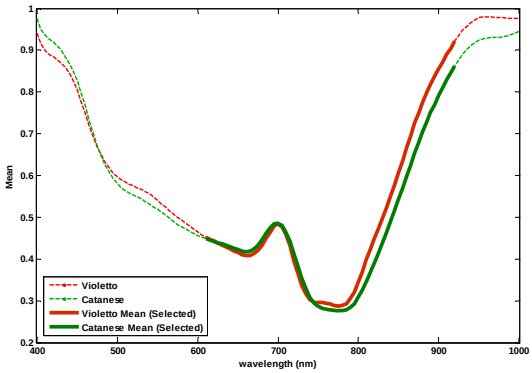


Figure 2.7a – Comparison of signal for the "Violetto" and "Catanese" cultivar

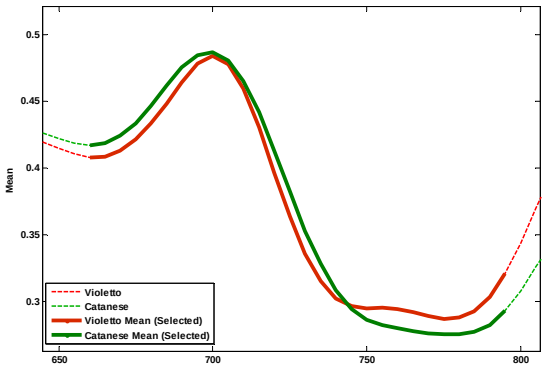


Figure 2.7b – Zoom Figure 2.7a for the range 650-800 nm

2.2.5 SIMCA Classification

In order to evaluate the classification of the two cultivars on the basis of the Vis-NIR spectrum, a two-class Soft Independent Model of Class Analogies (SIMCA) was computed. The two classes were modeled separately by computing a PCA model, choosing the dimensionality on the basis of the best sensitivity and specificity in cross-validation on a training set. Prediction capability was evaluated in the same terms on a set of left-out samples, selected in order to represent the most of the variability of the complete dataset.

"Violetto" PCA model was built considering nine Principal Components, while "Catanese" was modeled by means of six Principal Components. Figures 2.8 and 2.9 show the distances to the model for "Violetto" and "Catanese" class respectively. The results in terms of sensitivity and specificity are reported in Table 2.2 for the training set and 2.3 for the external test set: the sensitivity for each class is satisfactory, but low specificity is quite low, especially for "Catanese" vs. "Violetto".

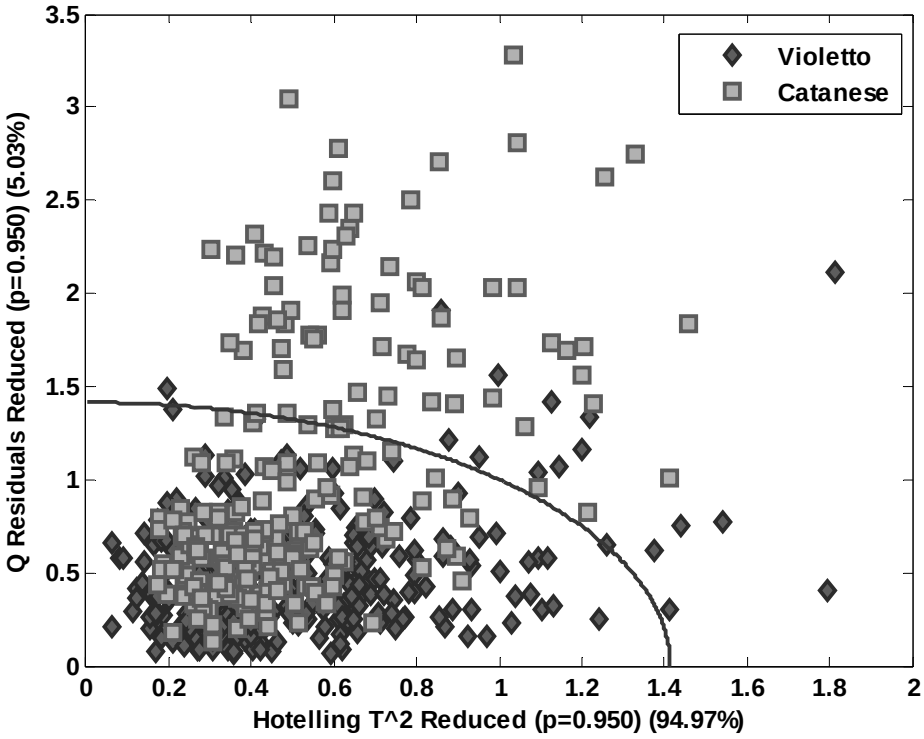


Figure 2.8 – "Violetto" PCA model: 9PC

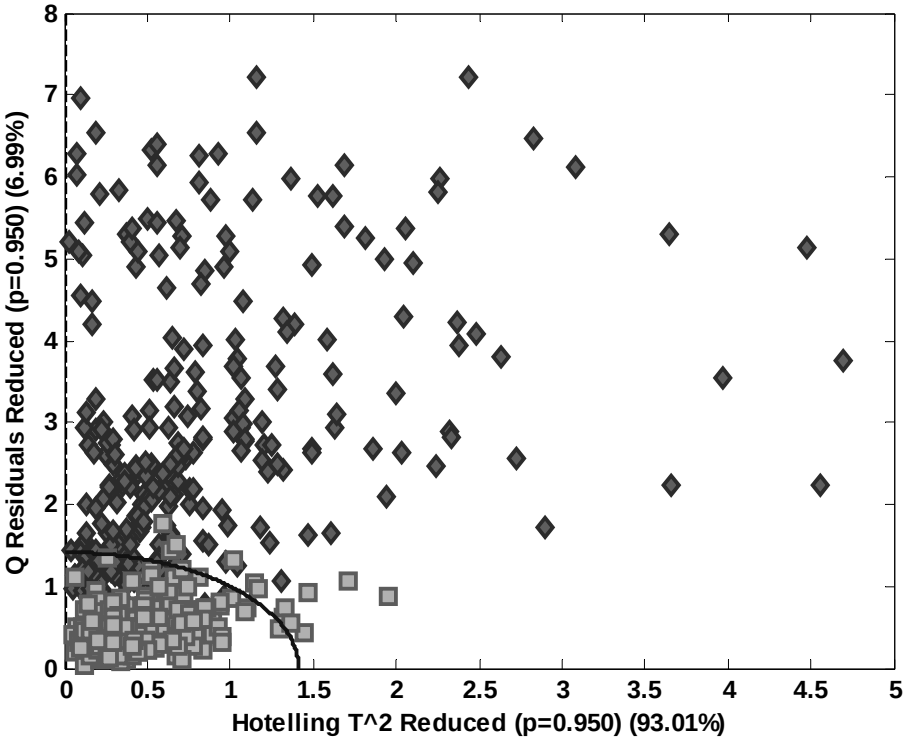


Figure 2.9 – Catanese PCA model: 6PC

Table 2.2 – SIMCA results of classification between "Violetto" and "Catanese" samples of the training set

TRAINING SET		Real class:	
		Violetto	Catanese
Predict as:	Violetto	291	176
	Catanese	77	231
	TOT	308	244
SENS Violetto: 95% SPEC Violetto vs Catanese: 68%			
SENS Catanese: 95% SPEC Catanese vs Violetto: 43%			

Table 2.3 –SIMCA results of classification between "Violetto" and "Catanese" samples of the external test set

TEST SET		Real class:	
		Violetto	Catanese
Predict as:	Violetto	90	54
	Catanese	22	70
	TOT	92	76
SENS Violetto: 98 % SPEC Violetto vs Catanese: 71%			
SENS Catanese: 92% SPEC Catanese vs Violetto: 41%			

These results are confirmed in prediction, when the left-out samples are projected onto each model (Figures 2.10 and 2.11 and Table 2.2 and 2.3).

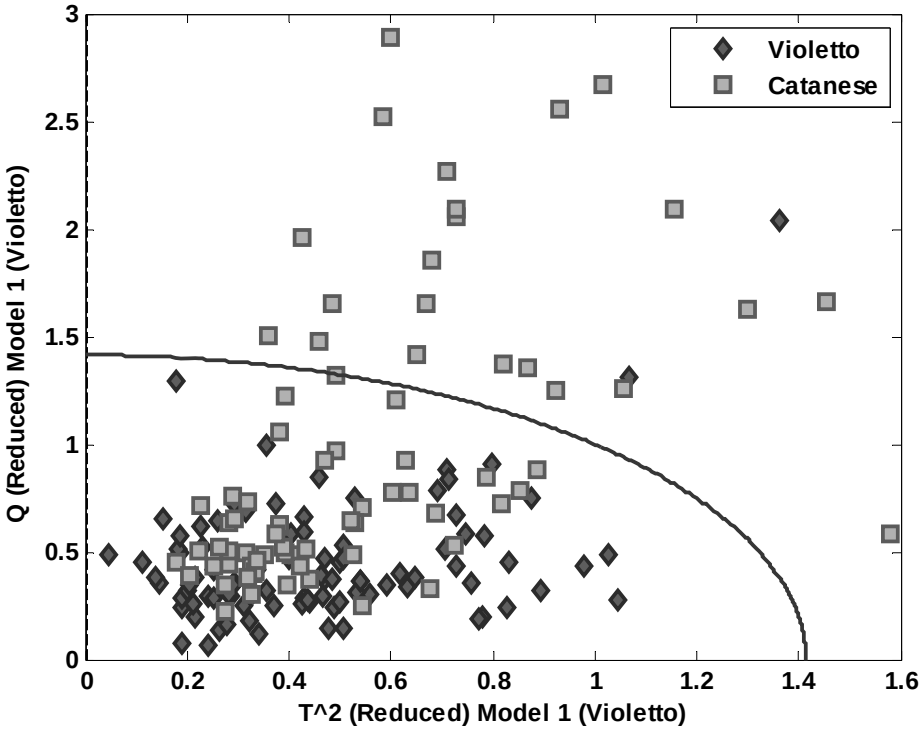


Figure 2.10 – Result of prediction of external set plotted on the model of "Violetto". Red curve denote the threshold of classification between the two cultivars.

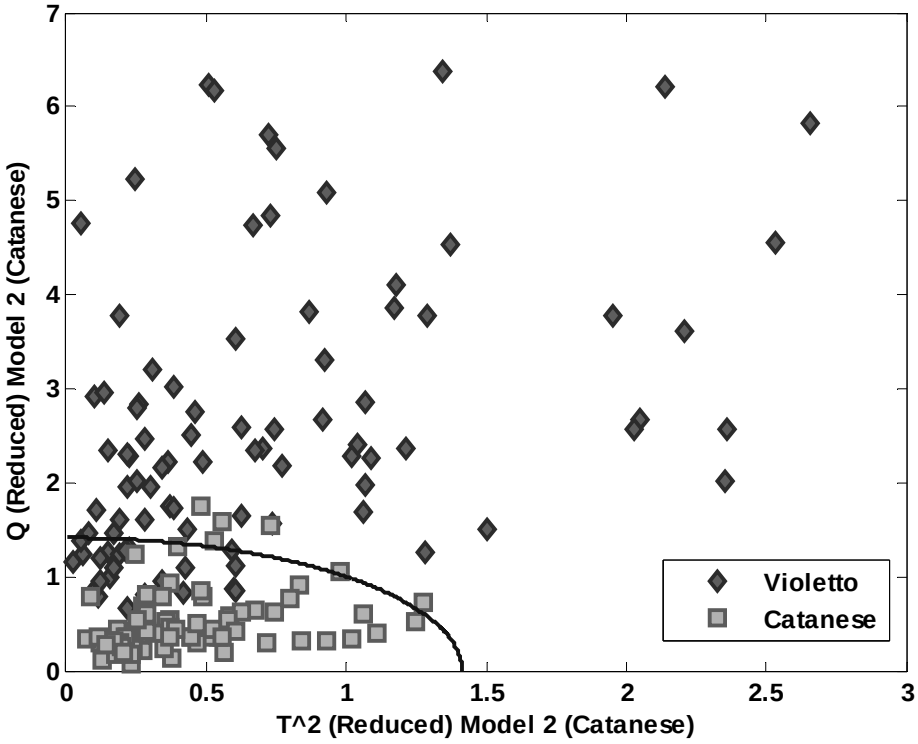


Figure 2.11 – Result of prediction of external set plotted on the model of "Catanese". Red curve denote the threshold of classification between the two cultivars.

SIMCA results show that, to some extent, it is possible to classify the two varieties, although this method shows a great degree of overlapping of the two. The great differences in terms of specificity suggest that the variability of the signal Vis-NIR recorded on the internal part of "Catanese" artichoke is included in the variability of the signal recorded on the internal part of "Violetto" artichoke. To evaluate which are the spectral regions mainly responsible for the differentiation of "Violetto" samples from the "Catanese" model, it is possible to focus the attention on the PCA model built on "Catanese" artichokes and evaluate the contributions to Q (Distance from a class model) and T^2(Distance in score space inside class model) distances both for class samples and for the "Violetto" projected samples.

Figure 2.12 and 2.13 show in black the profiles of the contributions to the distance Q and T^2 for all samples of "Violetto" projected on the PCA model calculated on "Catanese". The same contribution profiles can be computed for "Catanese" samples projected onto the model (test set): these samples should represent the variability "compatible" with the model, therefore they can be used as an evaluation of random variability for contributions. Yellow and red lines represent the percentile limits, corresponding respectively to 95 and 99% confidence limit. It can be observed (especially for Q distance) that almost all samples present significant contribution in the range

between 630 and 800 nm, which corresponds to the loadings of PC4 already analyzed for the PCA global model previously assessed.

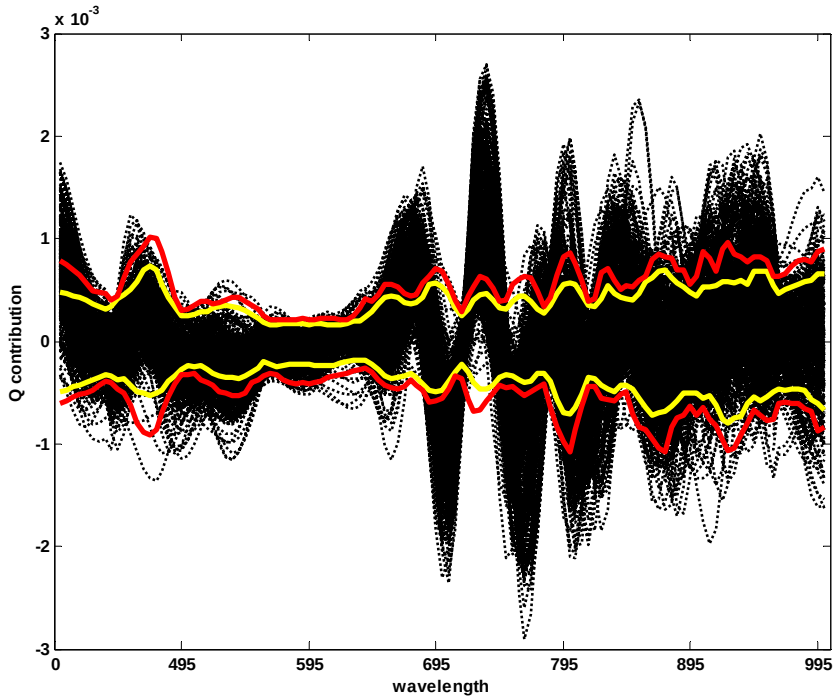


Figure 2.12 – Q distance for all samples of "Violetto" projected on the PCA model calculated on "Catanese"

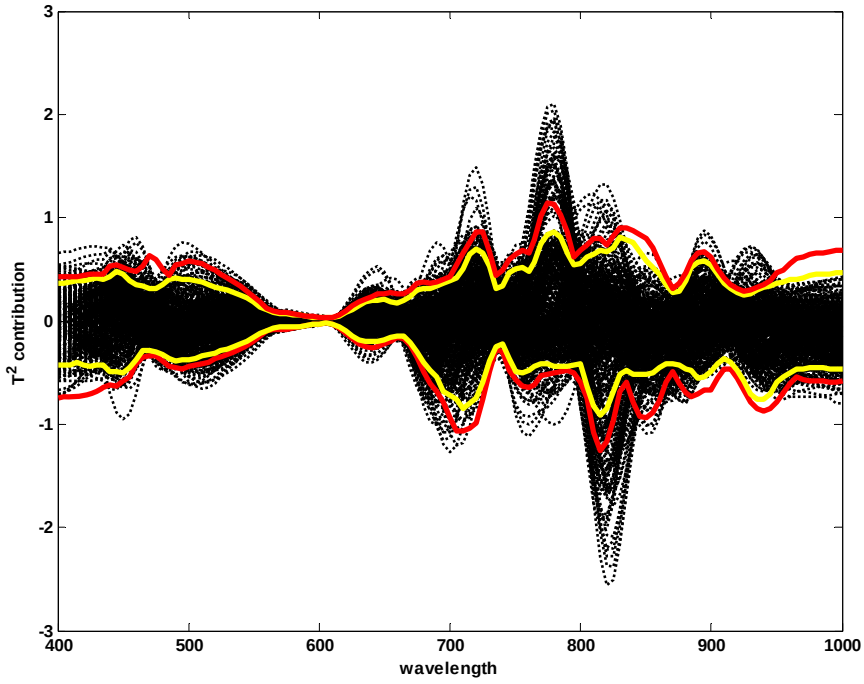


Figure 2.13 – T2 distance for all samples of "Violetto" projected on the PCA model calculated on "Catanese"

2.2.6 PLS-DA Classification

The same datasets analyzed with SIMCA whit the same chosen pretreatment where elaborated also by means of a Discriminant Analysis method, Partial Least Squares – Discriminant Analysis. Since SIMCA focuses on the variability which, independently, characterizes each class, it is possible that specificity results might be poor when the two classes have very similar variability, such as in the case of the two cultivars here discussed. A discriminant method, which exalts the sources of differentiation among the classes, might therefore be more suitable for the purpose of distinguishing the two cultivars.

Cross-Validation results for Training set, as showed in Figure 2.14 are very satisfactory. In the figure the blu line define all the predict values for all the samples assigned to "Violetto" grade and the green one the one to "Catanese".

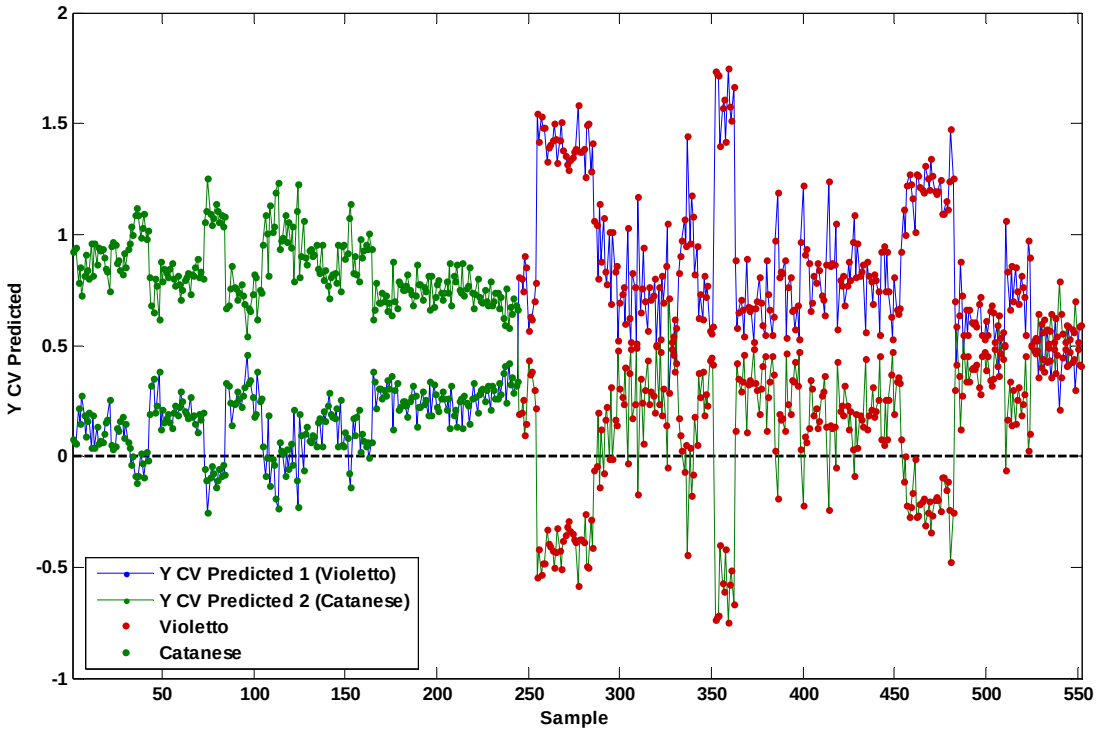


Figure 2.14 – Cross-validation results for training set (4LV)

Applying the rules of assignment based on the biggest value, the result are reported in Tables 2.4 and 2.5:

Table 2.4 – PLS-DA result of classification between "Violetto" and "Catanese" samples of the training set

TRAINING SET – FIT		Real class:	
		Violetto	Catanese
Predict as:	Violetto	297	0
	Catanese	11	244
	TOT	308	244
SENS Violetto: 96% SPEC Violetto vs Catanese: 96%			
SENS Catanese: 100% SPEC Catanese vs Violetto: 100%			

Table 2.5 – PLS-DA results of classification between "Violetto" and "Catanese" samples of the training set in cross validation

TRAINING SET – CV		Real class:	
		Violetto	Catanese
Predict as:	Violetto	284	0
	Catanese	24	244
	TOT	308	244
SENS Violetto: 92% SPEC Violetto vs Catanese: 90%			
SENS Catanese: 100% SPEC Catanese vs Violetto: 100%			

These results are confirmed in prediction (Table 2.6):

Table 2.6 – PLS-DA results of classification between "Violetto" and "Catanese" samples of the external test set

TEST SET		Real class:	
		Violetto	Catanese
Predict as:	Violetto	92	0
	Catanese	0	76
	TOT	92	76
SENS Violetto: 100% SPEC Violetto vs Catanese: 100%			
SENS Catanese: 100% SPEC Catanese vs Violetto: 100%			

The results show a good discrimination of the two classes and a reduced overlap (good specificity) of each one towards the other. These findings are confirmed in prediction on the left-out samples in the test set: for both classes, sensitivity and specificity reach 100%, as shown in Figure 2.15.

By evaluating the regression coefficients and Variance Importance in Prediction (VIP) scores, shown in Figure 2.16, it is possible evaluate which part of the signal is more relevant for the discrimination among the two classes. It is clear that the main area is around 700 nm and is made by four peaks: 680 nm, 705 nm, 730 nm and 755 nm. Due to the fact that we are analyzing a second derivative of the original signal, the peaks must be considered altogether and correspond to changes of shape of original signal.

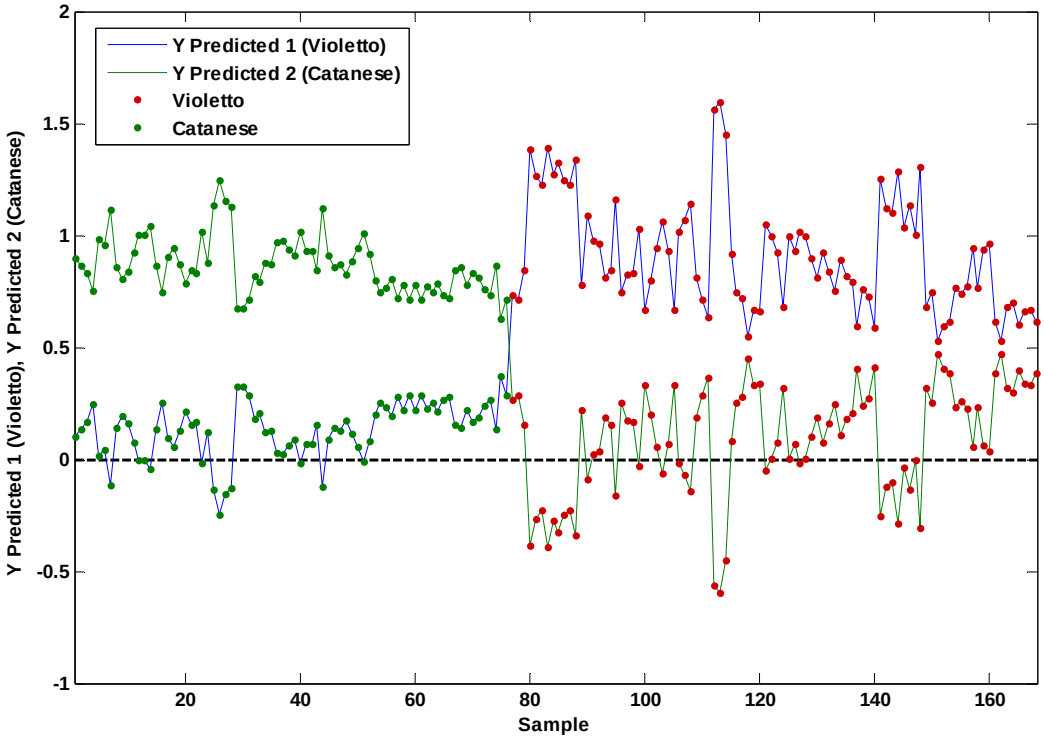


Figure 2.15 – Prediction test set

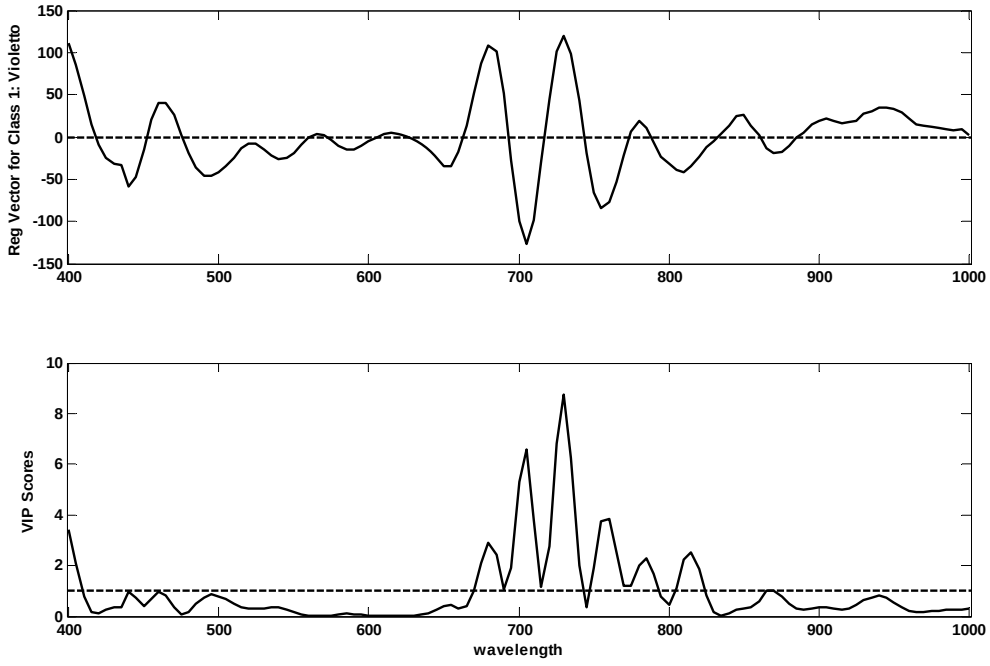


Figure 2.16 – Regression coefficients and VIP scores by wavelength

2.2.7 Conclusions

In this experimental classification example, the ability of the Vis-NIR signal acquired on the internal part of artichokes to distinguish two cultivar ("Violetto" and "Catanese") has been evaluated. After a preliminary exploration of the data, which allowed understanding the variability of the two sets and suggested the use of a derivative pretreatment to enhance the differentiation, two classification methods were tested: a class-modeling / pattern recognition method (SIMCA) and a discriminating method (PLS-DA). The results show that, for this set of data, the discriminant approach is superior to the class-modeling, mostly because of the two classes having a very similar general profile of the spectrum and one of them ("Violetto") having an inner variability which encloses the one of the other class ("Catanese"). When forcing the discrimination by means of PLS-DA, the differences between the two classes are exalted, and the classification is obtained with very interesting results. Since the region of the spectrum all the methods insist to find as most important for the differentiation corresponds to an absorption of the red portion of the Vis region, the main distinction between the two varieties must be due to a different shade of green.

2.3 CLASSIFICATION BY HARVEST TIMES AND DAYS OF STORAGE FOR EACH CULTIVAR

2.3.1 Classification Models

The same spectra of "Violetto" used in the paragraph 2.2 were used for the classification by harvest times and days of storage, after cutting.

Classification models for harvest times were constructed comparing 2 classification methods: SIMCA (Soft Independent Modelling of Class Analogy) using the Unscrambler X software, and PLS-DA (Partial least squares discriminant analysis) using the toolbox in Matlab (version 2014a). A training set (308 spectra) and an external test set (92) were used for both the analysis.

For the classification by days of storage only the PLS-DA model was used. The analysis was made on 4 classes: day 0, day 2, day 5 and day 7 after harvest time, using 75 samples for each day as Training set and 25 samples for Test set.

2.3.2 Classification by harvest times: results

SIMCA (Soft Independent Modelling of Class Analogy)

The SIMCA model was developed by building PCA models for each harvest time for all the samples. In order to find the mathematical transformation which best allowed to differentiate among spectra from different harvest dates, different pre-treatment methods were tested. Transformed data were used to build PCA models. After data pre-treatments it was found that the Smooting (Second Derivative) plus MSC allowed the complete separation of the PC1 score among harvest dates.

Table 2.7 – SIMCA classification results by harvest times on the training and test set.

Training set		TOT	Predicted Value							Specificity
			HT1	HT2	HT3	HT4	HT5	HT6	HT7	
Observed data	HT1	10	10	5	10	7	0	0	0	95
	HT2	5	0	5	1	3	0	1	0	30
	HT3	9	3	7	9	3	0	0	1	71
	HT4	11	0	11	4	11	0	8	9	41
	HT5	13	0	0	0	0	13	0	0	100
	HT6	13	0	13	3	12	0	13	11	69
	HT7	14	0	13	1	13	0	10	14	66
Test set		**TOT**	**Predicted Value**							**Specificity**
			HT1	HT2	HT3	HT4	HT5	HT6	HT7	
Observed data	HT1	3	0	3	1	3	0	3	3	100
	HT2	2	0	1	1	1	1	1	1	43
	HT3	3	0	0	0	0	3	0	0	71
	HT4	3	0	0	0	0	3	0	0	64
	HT5	5	0	0	0	0	5	0	0	100
	HT6	5	0	4	1	3	1	4	3	70
	HT7	4	0	4	1	4	0	4	3	71

Comparing the predicted value with the observed one, sensibility and specificity for each class can be observed by table (Table 2.7) sensibility is 100% for all the class. Specificity was high for HT1 (95% in Training set and 100% in Test set) and HT5 (100% in Training set and 100% in Test set) and particularly low for HT2 (30% in Training set and 43% in Test set), since its samples were also predicted in HT3, HT4 and HT7 and for HT4, which was also confused with HT2, HT3, HT6 and HT7 (Table FFF). Specificity for HT 3, HT6 and 7 ranged between 66 and 71% with similar value in Training set and Test set.

PLS-DA model

The PLS-DA model was developed applying the PLS2 algorithm and using the toolbox in Matlab (version 2014a). Briefly, PLS-DA uses a training set to develop a qualitative prediction model which may subsequently be applied for the classification of new unknown samples. This model seeks to correlate spectral variations (X) with defined classes (Y), attempting to maximise the covariance between the two types of variable. In this type of approach, the Y variables used are not continuous, as they are in quantitative analysis, but rather categorical "dummy" variables created by assigning different values to the different classes to be distinguished (Naes et al., 2002). Particularly The independent variable becomes a vector of classes, so that each sample has a value of 1 in the class to which it belongs, and a value of 0 for the other classes (Vandeginste et al., 1998; Heise and Winzen, 2002; Naes et al., 2002). Meanwhile, for the prediction of unknown samples, we obtain a value of the discriminatory variable for each of the classes provided, so a value of 1 in the categories represent a perfect assignment thereof, while a value of 0 would indicate no such class membership. Spectral variations were correlated with the 7 established categories.

In the Table 2.8 are shown the result for the calibration model using a Training set of 73 samples and the prediction model using a Test set of 25 samples. On the right side the values of Sensibility and Specificity are reported.

Table 2.8 – PLS-DA classification results by harvest times on the training and test set.

Training set	***CV***	***Predicted Value***							***TOT***	**Global**	
		HT1	***HT2***	***HT3***	***HT4***	***HT5***	***HT6***	***HT7***		**SENS**	**SPEC**
Observed data	***HT1***	10	0	0	0	0	0	0	10	100	100
	HT2	0	3	0	1	0	1	0	5	60	99
	HT3	0	0	9	0	0	0	0	9	100	100
	HT4	0	0	0	10	0	0	0	10	100	98
	HT5	0	0	0	0	13	0	0	13	100	100
	HT6	0	1	0	0	0	11	1	13	85	98
	HT7	0	0	0	0	0	0	13	13	100	98
TOTAL									**73**	Non error rate = 92	
Test set	***CV***	***Predicted Value***							***TOT***	**Global**	
		HT1	***HT2***	***HT3***	***HT4***	***HT5***	***HT6***	***HT7***		**SENS**	**SPEC**
Observed data	***HT1***	3	0	0	0	0	0	0	3	100	95
	HT2	0	1	0	0	0	1	0	2	50	100
	HT3	0	0	3	0	0	0	0	3	100	100
	HT4	1	0	0	1	0	1	0	3	33	100
	HT5	0	0	0	0	5	0	0	5	100	100
	HT6	0	0	0	0	0	5	0	5	100	85
	HT7	0	0	0	0	0	1	3	4	75	100
TOTAL									**25**	Non error rate = 80	

It is evident how the Sensibility is high (100%) for all harvest times, except HT2 and HT6, when values of 60 and 85%, are respectively obtained However for the test set 100% of sensibility is observed only for HT1, HT3, HT5 and HT6 and a very low value of 33% is observed for HT5, followed by HT 2 (50%) and HT7 (75%).Specificity was a value generally high, above all for HT1, HT3, and HT5 in Training set and in Test set, generally higher than 95% except than for the HT6 in the test set when a value of 85% has been obtained.

The best result for Sensibility and Specificity is carried out by HT3 and HT5 that confirm the 100% of the value in Training and Test set.

Another parameter that can be calculated for the PLS-DA is the "Non Error Rate" that is the average of the sensibility calculated over the classes. This calculation was not assessed on SIMCA since in SIMCA the same sample could be assigned to more than one class each time. In Training test the "Non Error Rate" is 92%, instead in the Test set is 80% .

The discussed value recorded in the Table 2.8, are plotted in the diagram of 2.17 and 2.18 were is possible to see graphically what discussed.

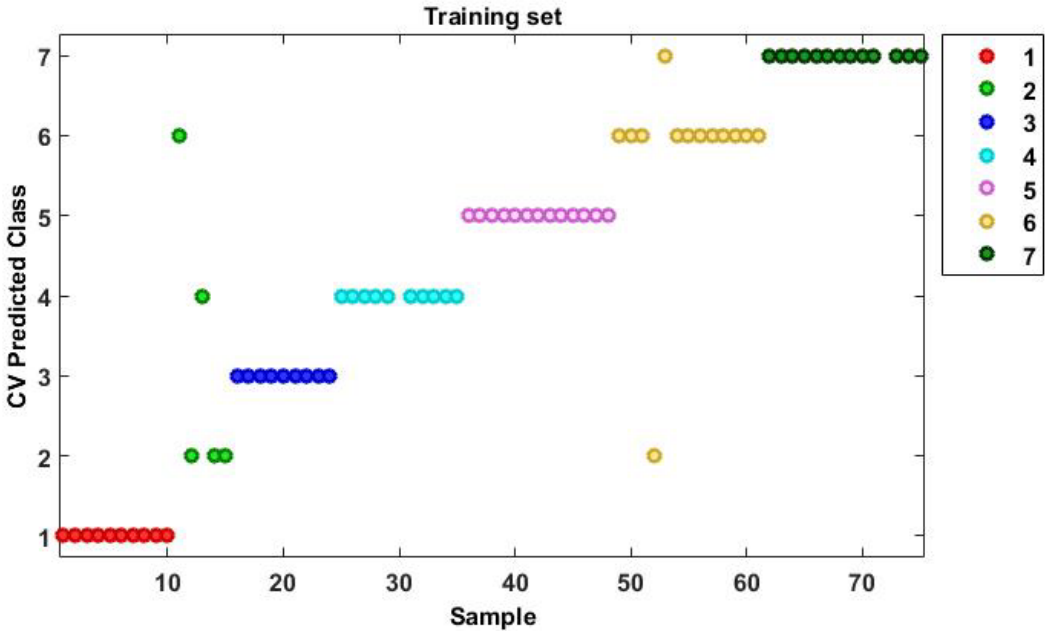


Figure 2.17 – PLS-DA classification results by harvest times on the training set.

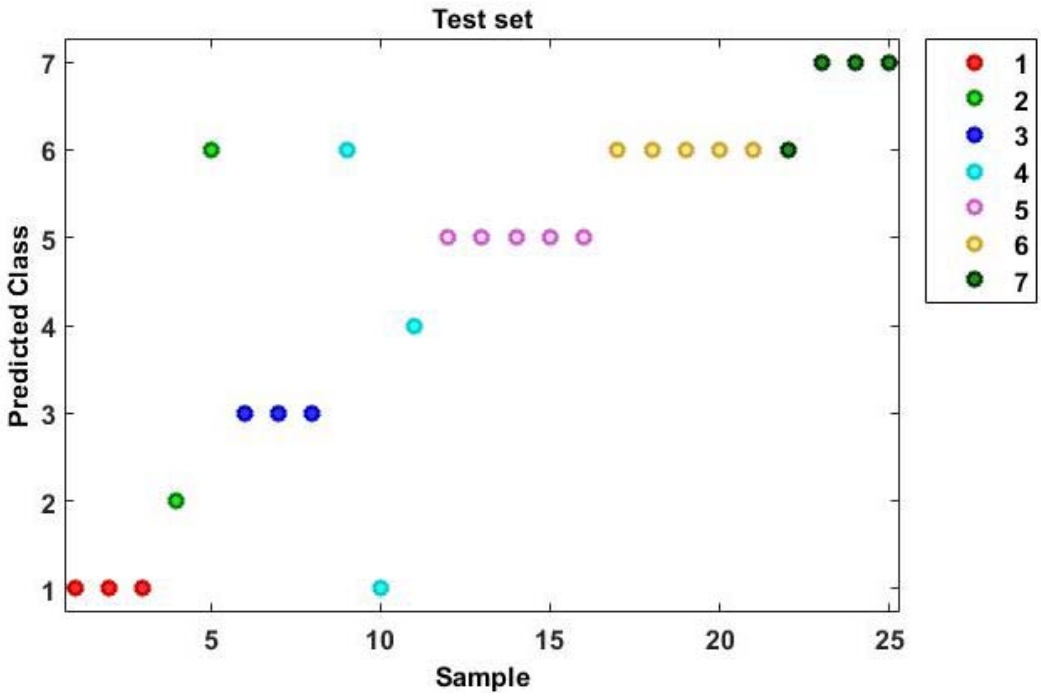


Figure 2.18 – PLS-DA classification results by harvest times on the test set

2.3.3 Conclusion

Comparing the result coming from the analysis made with SIMCA and PLS model, it is evident how the PLS-DA is the most performing method for this application. Both model gave 100% of sensibility and Specificity for HT5 and few point percentage less for the HT1 for specificity; SIMCA allowed to obtain always 100 % of sensibility but generally with a very low specificity; PLS-DA on the other side gave higher values for specificity compared to sensibility. It should be noticed that while PLS-DA is a true discriminating method, always classifying one sample in one and only one class, SIMCA is here used in its class modelling original formulation. Therefore, SIMCA model can, and do assign one sample to more classes which can have similar variability, thus giving poor specificity values.

2.3.4 Classification by days of storage: results

In the table 2.9 classification results are shown. It is evident how the highest sensibility and specificity of the training set was obtained for day 0.

Concerning Day 2, 5 and 7, we find specificity values higher than the sensibility for both Training and Test set. Moreover for class 5 days the lowest value of sensibility were found for both

training (55%) and test set (52%), with most of the sample being classified in class 7, and some in class 2. This confusion between class 5 and 7 is not necessary due to the low power of classification of the model, but is possible that samples after 5 days were very similar to samples after 7 days. Intermediate value in Training set and Test set are recorded for day 2 and 7. Generally for this classification a "Non Error Rate" of 74% and 79% was obtained, for the training set and the test set, respectively.

Table 2.9 – PLS-DA classification results by days of storage on training an test set (4 classes).

Training set	***CV***	***Predicted Value***				***TOT***	**Global**	
		0	***2***	***5***	***7***		**SENS**	**SPEC**
Observed data	***0***	72	3	0	2	77	94	91
	2	18	50	5	4	77	65	92
	5	0	10	42	25	77	55	92
	7	2	5	13	57	77	74	87
TOTAL						308	Non error rate = 72	
Test set	***CV***	***Predicted Value***				***TOT***	**Global**	
		0	***2***	***5***	***7***		**SENS**	**SPEC**
Observed data	***0***	23	0	0	0	23	100	96
	2	3	18	1	1	23	78	98
	5	0	4	12	7	23	52	99
	7	0	1	2	20	23	87	97
TOTAL						92	Non error rate = 79	

Standing to these consideration a second analysis was aimed to reduce the number of classes to 3, by grouping day 5 and 7 in one class. From the result carried out with these three classes it is evident how the sensibility and specificity for the days higher than 5 increased in Training and Test set. The classification for samples (Table 2.10) at day 0 maintained the highest values in Training set (sensibility 95% and specificity 95%) and Test set (sensibility 96% and specificity 96%), whereas as before, the worst results were obtained for day 2 in Training set (sensibility 62% and specificity 97%) and Test set (sensibility 74% and specificity 98%). Most of these samples for the training set were classified as class >5 (19) and some as class day 0 (10).

The results can be explained by the fact that the event of cutting has a strong impact soon after day 0 and that there are less differences due to the time after cutting (from 2 to 7 days).

Specificity values are higher than sensibility for all the classes in Training and Test set and the "Non Error Rate" increased compared to the classification based on 4 classis to 84 and 87% for training and test set, respectively.

Table 2.10 – Classification by days of storage with PLS-DA model (3 classes)

Training set	CV	Predicted Value			TOT	Globali	
		0	2	5		SENS	SPEC
Observed data	0	73	3	1	77	95	95
	2	10	48	19	77	62	97
	> 5	1	5	148	154	96	87
TOTAL					308	Non error rate = 84	
Test set	**CV**	**Predicted Value**			**TOT**	**Globali**	
		0	2	5		SENS	SPEC
Observed data	0	22	1	0	23	96	96
	2	3	17	3	23	74	98
	> 5	0	4	42	46	91	99
TOTAL					92	Non error rate = 87	

2.3.5 Conclusion

For the classification by days of storage the PLS-DA model has for all the classes high value of specificity, and for some classes low values of sensibility. Particularly in the model with 4 classes lower value were obtained for day 2 (65% for the Training set and 78 for the Test set), and day 5 (55% in the Training set 55 and 52% in the Test set). For results with 3 classes lower values were obtained for day2 (62% in the Training set and 74% in the Test set), indicating at the same time that eventually the time after cutting is not impacting to much artichoke quality and spectra- than 95% except for the day7 and days >5 in Training set. For both models the best value of sensibility and specificity are recorded for day 0: model with 4 classes, sensibility 94% and specificity 91% in Training set and sensibility 100% and specificity 96% in Test set; model with 3 classes, sensibility and specificity 95% in Training set and sensibility and specificity 96% in Test set.

These results suggest that is possible to discriminate samples just cut from samples cut and stored for some days, but that is more difficult to exactly separate samples depending on the days of storage. Most likely this is not due to a low efficiency of the model but to the changing proprieties

of the samples that are not so dissimilar between 2 and 7 days of storage, but becoming more evident with the passing of the time.

As indicated by the "Non Error Rate", the model performance improved, in fact, reducing the number of classed from 4 to 3.

2.4 PREDICTION OF THE CONTENT OF PHENOLS AND ANTIOXIDANT ACTIVITY IN ARTICHOKE "VIOLETTO"

The same spectral data set of "Violetto" artichoke utilized for the classification have been used with the intent to build a model able to predict the content of phenols and antioxidant activity.

Spectral data were analysed using the Unscrambler packing software version X (CAMO ASA, Oslo, Norway). All the reflectance measurements were firstly transformed to absorbance values using log(1/R) according to the law of Lambert-Beer and then spectra were pre-treated by different mathematical methods: Smoothing, Normalization, Multiple Scatter Correction, Noise, Norris Derivative, Savitzky-Golay Derivative and Baseline.

The analysis to be carried out was a function of a relevant number of variables below listed and quantified:

- Harvest period (7),
- Days of storage (4),
- Sequence number of the artichoke (18),
- Wavelengths (400-1000 nm),
- Type of transformation (9 for antioxidant activity and 8 for phenol),
- Setting parameters of the transformations.

All the possible combinations of variables, generated a high source of variation which is added to the instrumental noise and to other variation related to acquisition.

Therefore we decide to use the spectra obtained at Day 0, in order to test the model before including the variation due to the time of storage.

Moreover to test the contribute of different wavelength ranges to the antioxidant prediction the following spectral ranges were tested:

- Ranges of wavelengths: (400-1000 nm, 400-800 nm, 400-650 nm, 650-800 nm, 650-1000 nm).

Finally the effect of 8 different mathematical transformations on the final ability of the model to predict phenols and antioxidant activity were applied.

The spectra were analyzed with a PCA (Principal component analysis) central model to identify and eliminate defective spectral outliers (Massart et al., 1998; Naes et al., 2002).

A Partial least squares (PLS) algorithm was applied on transformed spectra for each of the measured chemical parameters (phenols measured as gallic acid/100 g and antioxidant activity measured as trolox equivalents) with the aim of developing predictive models based on spectral information. The analysis was performed first only in cross validation and then also in prediction using a training (308 spectra) an external test set of data (92 spectra).

2.4.1 Analytical determination of total phenolic content and antioxidant activity

Samples, after spectra acquisition, were frozen in liquid nitrogen and stored at -80 °C until use for chemical analysis. On frozen samples total phenol content (inner bracts and receptacle) and antioxidant activity (inner bracts and receptacle) were measured.

The same extraction was carried out for analyses of total phenolic content and antioxidant activity. Five grams of artichoke tissues were homogenized in an Ultraturrax (IKA, T18 Basic; Wimington, NC, USA) for 1 min with 20 mL of extraction medium, 2 mM NaF methanol: water solution (80:20) (Tomás-Barberán et al., 2001) The homogenate was filtered through 2 cheesecloth and then centrifuged at 5 °C at 9000 rpm for 5 minutes. The pellet was discarded and the supernatant was retained and used as extract, which was further diluted (1:20). Total phenolic contents were determined according to the method of Singleton and Rossi (1965). Each diluted extract (100 μL) was mixed with 1.58 mL distilled water, 100 μL of Folin–Ciocalteu reagent and 300 μL of sodium carbonate solution (200 g L−1). After 2 hours standing in darkness, the absorbance was read at 725 nm against a blank using a spectrophotometer (UV-1700, Shimadzu, Jiangsu, China). Total phenolic content was calculated on the basis of the calibration curve of chlorogenic acid and was expressed as grams of chlorogenic acid equivalents per 100 g of fresh weight (f.w.).

The antioxidant assay was performed following the procedure described by Brand-Williams et al. (1995) with minor modifications. The diluted sample of 50 μL, was pipetted into 0.95 mL of DPPH (diphenylpicrylhydrazyl) solution to initiate the reaction. The cuvettes were closed with a stopper and secured with parafilm to prevent evaporation during 24 hours in darkness. The absorbance was read, spectrophotometrically, after 24 hours in darkness, at 515 nm. Trolox (6-Hydroxy-2, 5, 7, 8-tetramethylchromane-2-carboxylic acid) was used as the standard of the measurement and the antioxidant activity was reported as g of Trolox equivalents (TE) per 100 g of fresh weight (f.w.).

2.4.2 Explorative Analysis of analytical variables

For the internal part of the samples it has been prepared the below reports Box-Whiskers (Figures 2.19 and 2.20) in order to display the distribution of phenols and gallic acid content for the different combination of harvest period with days after the harvest period. Through the report it is possible to estimate, based on the distribution of the values, the variability of the sample, comparing in a non-parametric way groups corresponding to different conditions. The rectangular shape defines the interquartile range (75^{th} and 25^{th} percentile) and contains the 50% of the measure of a defined group. The internal line of the box is the median (50^{th} percentile), the red point instead is the average. The lines that extend from the box (whiskers) can be used to obtain an indication of the dispersion of the values around the central tendency (in this case the median), in analogy to what is the confidence interval for the mean for a distribution normal (the more the values follow a normal distribution, the higher the symmetry of the box-plots than the median). Points beyond the whiskers are reported as outliers.

Harvest period 1-3 has a different trend compared with the 4-7. Inside each harvest period there are more or less obvious trend of progressive variation in correspondence of the increase of days after harvest period. It is evident as the variability of results tends to make quite similar to each other the different days by cutting (for harvest period 4-7 the trend is highly absent and the values appear constants). For some samples there are particularly high and outside the box-whisker representation, which may indicate the presence of outliers.

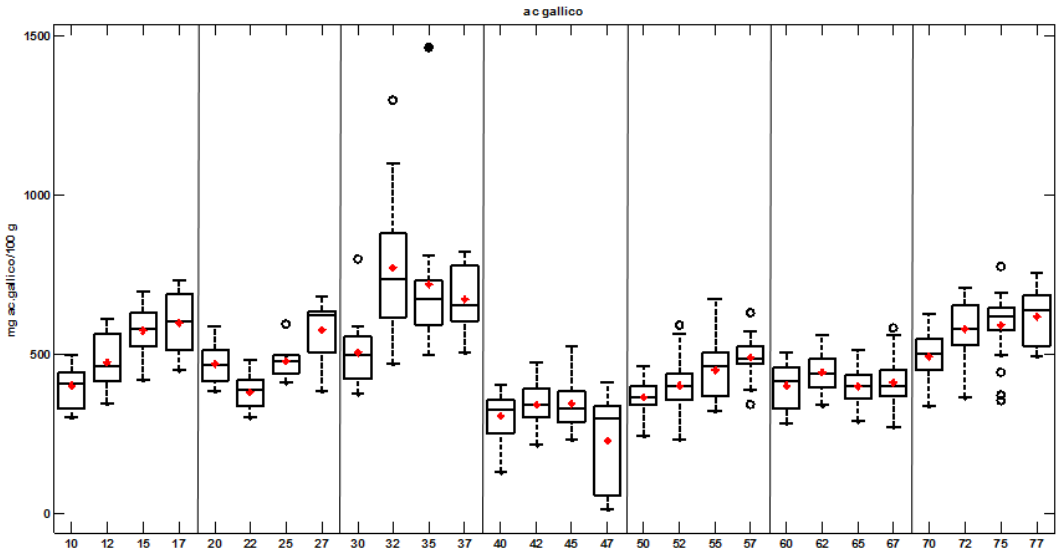


Figure 2.19 – Distribution of phenols with Box-Whiskers representation

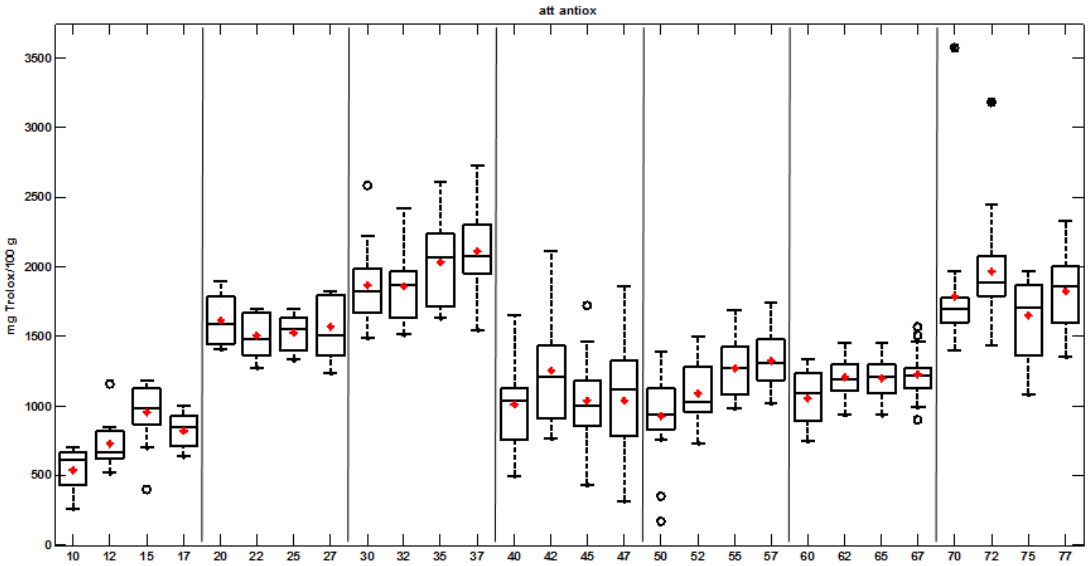


Figure 2.20 – Distribution of antioxidant activity with Box-Whiskers representation

In the Figure 2.21 is displayed the relationship between the antioxidant activity on y axis and the phenol on x axis.

It is evident the presence of two different groups: the sample of the harvest period 1 that at a fix range of phenols have antioxidant activity lower than the one of the other harvest period. The sample of the harvest period 4 and 5 show a variability as phenol concentration higher than the other harvest period, with a tendency of the samples of the time 4 to have lower values than other one. For the harvest period 7 there are two value that we can consider like outlier for the antioxidant analysis.

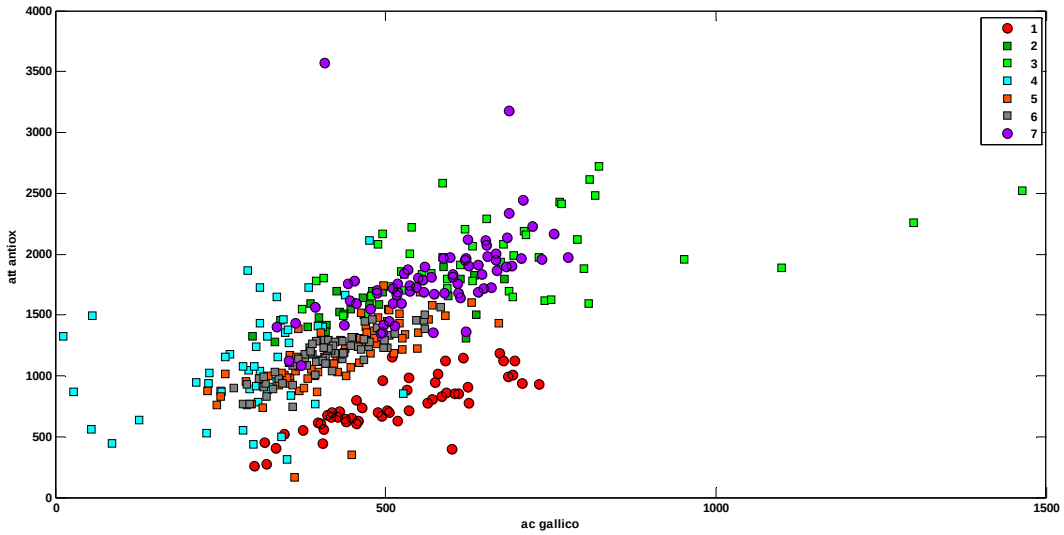


Figure 2.21 – Report relationship antioxidant activity with gallic acid

2.4.3 Explorative Analysis on Vis-NIR spectra

Spectral image of artichoke quarters acquired by VIS-NIR technique with reflectance, plotted in the Figure 2.22 A, were transformed in absorbance Figure 2.22 B. In the figure it is evident the presence of noise, above all at the extreme part of the wavelength range, that we tried to attenuate processing the dates with a smoothing filter Savisky-Golay (polynomial 2° order with 13 point), as per Figure 2.22 C. Other transformation has been applied in the Figures 2.22 D and E, respectively Normalization (MSC) setting of main center (MC) by column and Derivate II with the setting of main center (MC) by column.

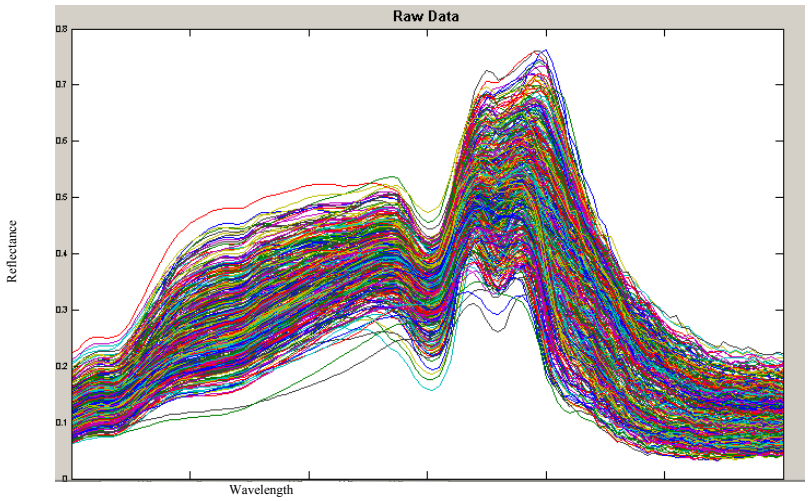


Figure 2.22 A – Wavelength-Reflectance

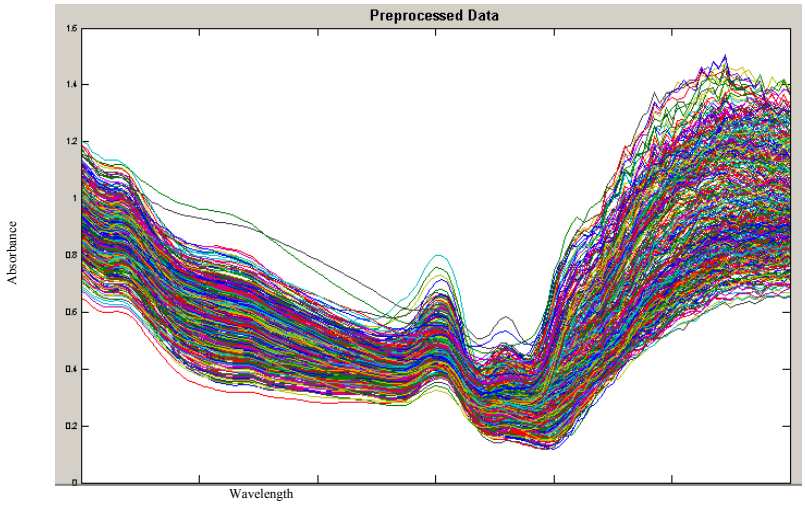


Figure 2.22 B – Wavelength-Absorbance

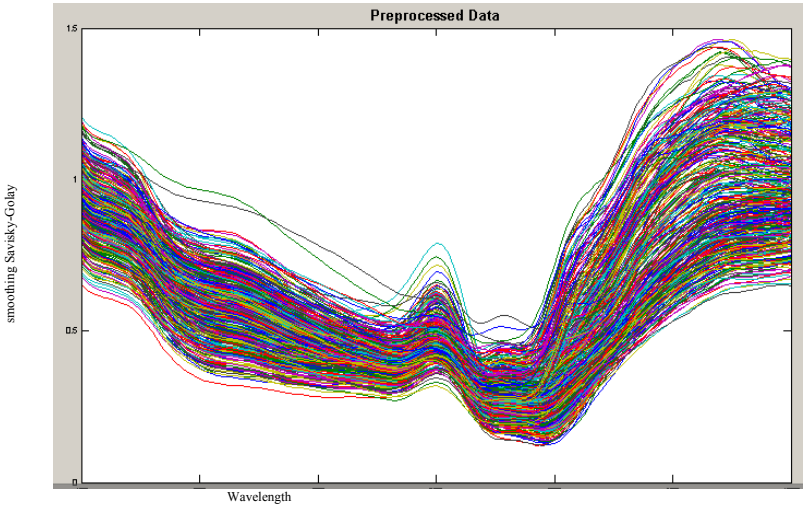


Figure 2.22 C – Wavelength-smoothing Savisky-Golay

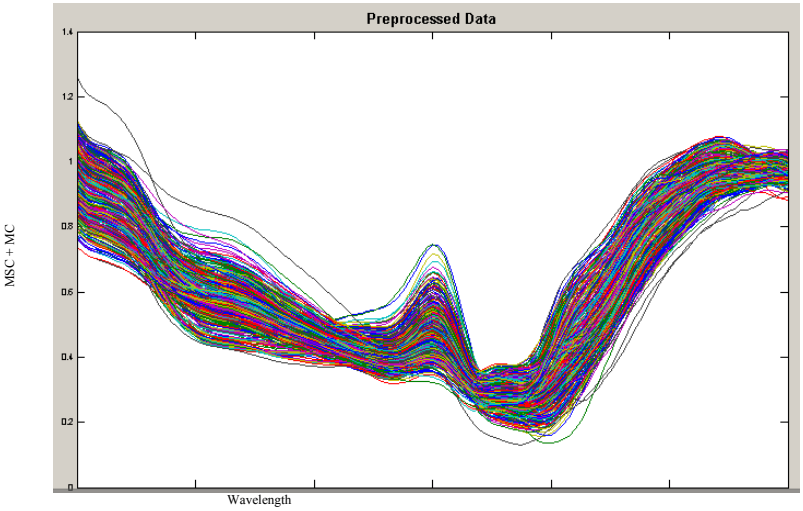


Figure 2.22 D – Wavelength- MSC + MC

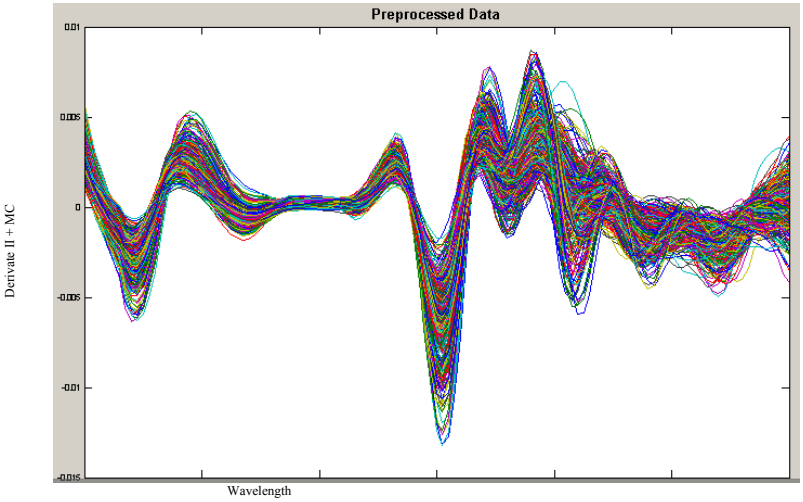


Figure 2.22 E – Wavelength-Derivate II + MC

2.4.4 PLS-calibration models

The first analysis was carried out using only samples of Day 0, in order not to include many sources of variability in the model and to find the optimal preprocessing. In the following tables (2.11 to 2.12) 8 different preprocessing were compared for 5 different spectral ranges. The best result of the analysis, based on the highest R and the lowest RMSE in calibration and in cross validation were obtained when out Smoothing (Polynomial second order with 13 point selected) was combined with MSC. Before to run the PLS for all analysis spectra were also mean centered.

Table 2.11 – PLS results for phenols content prediction after mathematical preprocessing and for selected wavelength range (day 0 for all harvest times)

PHENOLS									
	CALIBRATION				CROSS-VALIDATION				Factor
	SLOPE	OFF SET	RMSEC	R^2	SLOPE	OFF SET	RMSECV	R^2	
ANALYSIS DAY 0 - WAVELENGTH 400-1000									
SMOOTING	0.209	333.0	87.02	0.209	0.155	356.6	92.91	0.106	4
MSC	0.031	408.0	96.32	0.031	0.010	416.7	98.38	0.023	1
1° DERIVATIVE GOLAY	0.110	374.6	92.29	0.110	0.082	386.5	95.25	0.065	2
BASELINE	0.182	344.4	88.49	0.182	0.135	364.6	93.66	0.108	3
DETREND POL 1	0.194	339.6	87.87	0.194	0.156	354.3	92.48	0.119	3
DETREND POL 2	0.110	374.7	92.30	0.110	0.068	392.2	96.86	0.051	3
2° DERIVATIVE GOLAY	0.389	257.2	76.47	0.389	0.230	321.2	99.16	0.022	5
SMOOTING+MSC	0.424	240.8	73.18	0.424	0.276	302.8	90.40	0.135	7
ANALYSIS DAY 0 - WAVELENGTH 400-800									
SMOOTING	0.121	370.2	91.75	0.121	0.096	380.7	95.36	0.080	2
MSC	0.271	306.9	83.53	0.271	0.122	370.4	94.08	0.073	3
1° DERIVATIVE GOLAY	0.230	324.1	85.84	0.230	0.168	349.6	94.10	0.097	4
BASELINE	0.170	349.7	89.17	0.170	0.126	368.1	93.92	0.093	3
DETREND POL 1	0.255	313.6	84.44	0.255	0.202	337.2	91.90	0.127	4
DETREND POL 2	0.278	303.9	83.12	0.278	0.205	335.7	92.24	0.141	4
2° DERIVATIVE GOLAY	0.411	248.1	75.10	0.411	0.350	272.6	85.07	0.262	6
SMOOTING+MSC	0.465	223.9	70.57	0.465	0.368	263.8	84.23	0.243	8
ANALYSIS DAY 0 - WAVELENGTH 400-650									
SMOOTING	0.356	271.0	78.50	0.356	0.270	306.7	89.56	0.169	7
MSC	0.444	234.0	72.94	0.444	0.312	290.9	88.79	0.200	7
1° DERIVATIVE GOLAY	0.208	333.4	87.07	0.208	0.175	346.6	90.71	0.163	2
BASELINE	0.219	328.7	86.46	0.219	0.174	347.9	92.21	0.141	4
DETREND POL 1	0.425	242.0	74.17	0.425	0.303	294.6	89.22	0.176	7
DETREND POL 2	0.178	346.2	88.72	0.178	0.136	363.9	93.77	0.087	3
2° DERIVATIVE GOLAY	0.422	243.5	74.42	0.422	0.350	274.7	82.81	0.292	5
SMOOTING+MSC	**0.511**	**129.1**	**53.58**	**0.691**	**0.511**	**202.9**	**78.69**	**0.351**	**20**
ANALYSIS DAY 0 - WAVELENGTH 650-800									
SMOOTING	0.347	274.8	79.05	0.347	0.26	311.6	92.19	0.101	7
MSC	0.393	255.6	76.23	0.393	0.292	298.4	92.42	0.149	7
1° DERIVATIVE GOLAY	0.248	316.4	84.82	0.248	0.196	339.2	92.04	0.131	5
BASELINE	0.410	248.4	75.15	0.410	0.330	281.8	88.02	0.205	7
DETREND POL 1	0.231	323.6	85.78	0.231	0.186	343.4	90.47	0.147	3
DETREND POL 2	0.337	279.3	79.69	0.337	0.278	304.0	87.21	0.213	6
2° DERIVATIVE GOLAY	0.350	273.6	78.87	0.350	0.282	301.4	87.41	0.223	5
SMOOTING+MSC	0.445	231.9	71.82	0.445	0.368	264.5	81.91	0.305	8

ANALYSIS DAY 0 - WAVELENGTH 650-1000									
SMOOTING	0.130	366.2	91.25	0.130	0.100	378.6	94.67	0.081	2
MSC	0.443	234.5	73.02	0.443	0.262	308.8	93.19	0.104	5
1° DERIVATIVE GOLAY	0.080	387.2	93.83	0.080	0.060	395.9	95.76	0.060	1
BASELINE	0.181	345.0	88.57	0.181	0.133	364.1	94.14	0.087	3
DETREND POL 1	0.204	335.1	87.29	0.204	0.152	357.2	93.02	0.118	3
DETREND POL 2	0.062	394.9	94.76	0.062	0.036	405.7	97.49	0.03	1
2° DERIVATIVE GOLAY	0.379	261.6	77.13	0.379	0.221	326.9	95.15	0.051	5
SMOOTING+MSC	0.398	251.9	74.84	0.398	0.262	308.6	91.06	0.113	7

Table 2.12 – PLS results for antioxidant activity content prediction after mathematical preprocessing and for selected wavelength range (day 0 for all harvest times)

ANTIOXIDANT ACTIVITY									
	CALIBRATION				CROSS-VALIDATION				Factor
	SLOPE	OFF SET	RMSEC	R^2	SLOPE	OFF SET	RMSECV	R^2	
ANALYSIS DAY 0 - WAVELENGTH 400-1000									
SMOOTING	0.520	595.902	380.73	0.520	0.454	666.955	433.32	0.393	6
NORMALIZZATION	0.513	605.000	383.62	0.513	0.416	736.016	439.06	0.368	5
MSC	0.673	406.363	314.40	0.673	0.501	611.811	444.68	0.358	6
1° DERIVATIVE GOLAY	0.574	528.670	358.61	0.574	0.511	614.017	429.59	0.393	7
BASELINE	0.420	720.744	418.71	0.420	0.345	810.334	473.27	0.284	5
SNV	0.627	465.315	334.83	0.627	0.516	601.443	419.73	0.408	5
DETREND POL 1	0.618	476.530	338.84	0.618	0.491	632.016	426.01	0.419	6
DETREND POL 2	0.634	457.245	331.91	0.634	0.519	608.825	404.28	0.459	5
2° DERIVATIVE GOLAY	0.674	407.074	313.17	0.674	0.557	559.791	413.71	0.441	7
SNV + DETREND POL 1 + 2° DERIVATIVE GOLAY	0.701	373.231	299.87	0.701	0.579	528.078	408.16	0.450	7
SNV + DETREND POL 2 + 2° DERIVATIVE GOLAY	0.70	374.556	300.40	0.700	0.574	537.657	410.75	0.459	7
MSC + DETREND POL 1 + 2° DERIVATIVE GOLAY	0.686	389.656	307.87	0.686	0.583	523.815	410.95	0.462	7
MSC + DETREND POL 2 + 2° DERIVATIVE GOLAY	0.549	559.764	369.00	0.549	0.464	658.884	428.47	0.411	4
SMOOTING +MSC	0.707	353.468	255.79	0.707	0.629	447.844	307.33	0.584	7
ANALYSIS DAY 0 - WAVELENGTH 400-800									
SMOOTING	0.492	630.671	391.68	0.492	0.403	740.787	483.81	0.218	7
NORMALIZZATION	0.597	500.053	348.76	0.597	0.518	599.942	436.00	0.385	7
MSC	0.536	576.822	374.58	0.536	0.472	657.300	447.12	0.368	5
1° DERIVATIVE GOLAY	0.366	787.569	437.69	0.366	0.304	864.435	501.12	0.213	5
BASELINE	0.390	758.300	429.48	0.390	0.340	817.878	469.70	0.293	5
SNV	0.586	516.518	352.77	0.586	0.505	632.702	445.71	0.364	5
DETREND POL 1	0.596	504.373	348.60	0.596	0.528	587.885	434.11	0.371	7
DETREND POL 2	0.586	517.029	352.94	0.586	0.520	605.807	441.79	0.348	7
2° DERIVATIVE GOLAY	0.600	499.097	346.77	0.600	0.540	567.178	412.42	0.464	7
SMOOTING +MSC	0.805	234.944	208.54	0.805	0.739	314.858	284.27	0.642	14
ANALYSIS DAY 0 - WAVELENGTH 400-650									
SMOOTING	0.440	695.220	411.23	0.440	0.379	768.415	455.69	0.327	6
NORMALIZZATION	0.626	465.199	336.39	0.626	0.506	604.67	419.93	0.421	7
MSC	0.469	659.636	400.57	0.469	0.412	729.265	458.35	0.311	6
1° DERIVATIVE GOLAY	0.500	625.475	390.06	0.497	0.430	727.288	449.02	0.348	7
BASELINE	0.558	549.261	365.52	0.558	0.465	664.159	445.06	0.354	7
SNV	0.638	452.403	330.15	0.638	0.560	550.199	436.88	0.382	7
DETREND POL 1	0.607	490.743	343.85	0.607	0.523	596.814	415.42	0.444	7
DETREND POL 2	0.446	691.985	408.31	0.446	0.397	747.325	456.57	0.320	5
2° DERIVATIVE GOLAY	0.565	543.567	361.89	0.565	0.495	625.29	441.97	0.378	7
SMOOTING +MSC	0.761	287.871	230.83	0.761	0.709	349.077	297.3	0.614	12

ANALYSIS DAY 0 - WAVELENGTH 650-800									
SMOOTING	0.496	626.286	390.31	0.496	0.442	693.273	445.31	0.369	7
NORMALIZZATION	0.578	524.571	357.21	0.578	0.533	581.108	408.20	0.442	6
MSC	0.583	517.500	354.80	0.583	0.528	587.126	426.96	0.390	6
1° DERIVATIVE GOLAY	0.473	654.308	398.95	0.473	0.383	768.194	474.11	0.263	7
BASELINE	0.613	480.501	341.88	0.613	0.534	582.390	444.36	0.364	7
SNV	0.617	478.027	339.37	0.617	0.584	538.816	415.57	0.448	6
DETREND POL 1	0.624	446.649	328.04	0.642	0.621	458.929	401.33	0.484	7
DETREND POL 2	0.577	528.800	356.94	0.577	0.524	582.176	419.44	0.417	7
2° DERIVATIVE GOLAY	0.540	574.474	372.03	0.54	0.496	618.468	423.35	0.437	7
SMOOTING +MSC	0.754	296.612	234.31	0.754	0.715	348.18	276.10	0.669	10
ANALYSIS DAY 0 - WAVELENGTH 650-1000									
SMOOTING	0.607	488.236	344.62	0.607	0.517	599.870	430.44	0.398	7
NORMALIZZATION	0.653	431.457	323.96	0.653	0.514	602.510	420.26	0.424	6
MSC	0.686	390.554	308.22	0.686	0.539	568.715	409.84	0.473	6
1° DERIVATIVE GOLAY	0.515	602.544	382.84	0.515	0.449	684.930	432.02	0.396	6
BASELINE	0.610	484.988	343.47	0.610	0.452	682.361	452.47	0.338	6
SNV	0.691	385.740	304.85	0.691	0.554	553.254	390.69	0.501	6
DETREND POL 1	0.708	364.969	296.53	0.708	0.542	571.524	410.10	0.464	7
DETREND POL 2	0.700	375.061	300.61	0.700	0.562	551.002	402.01	0.48	6
2° DERIVATIVE GOLAY	0.582	522.721	354.88	0.582	0.503	620.112	420.31	0.426	5
SNV + DETREND POL 1 + 2° DERIVATIVE GOLAY	0.569	538.490	360.19	0.569	0.512	603.138	403.79	0.459	4
SNV + DETREND POL 2 + 2° DERIVATIVE GOLAY	0.569	537.942	360.01	0.569	0.504	611.473	412.60	0.432	4
MSC + DETREND POL 1 + 2° DERIVATIVE GOLAY	0.579	523.169	356.74	0.579	0.532	654.839	402.71	0.473	4
MSC + DETREND POL 2 + 2° DERIVATIVE GOLAY	0.579	523.184	356.74	0.579	0.534	587.338	408.66	0.459	4
SMOOTING +MSC	0.813	225.173	204.16	0.813	0.738	322.669	284.97	0.644	14

Based on the highest R^2 of calibration and validation and on the lowest RMSEC and RMSECV, the transformation Smooting + MSC was the optimal transformation to predict the phenols in the range 400-650 nm and antioxidant activity in the range 650-800 nm, value highlighted in the tables in grey.

Considering all days of storage, new models were generated applying the best transformation obtained for day 0 (Smoothing plus MSC) on all considered spectral range. It is possible in fact that the time of storage affects different part of the spectra compared to day 0. Moreover since explorative analysis highlighted the presence of difference between artichoke from HT1 and the artichokes from other harvest times, three models were developed for each spectral range corresponding to “Hall Harvest Times”, “Harvest Time 1” and “Other Harvest Times” (from HT2 to HT7).

In the Tables 2.13 and 2.14 are reported the statistics of the analysis for each spectral range and sample grouping highlighting for each group the best model.

Table 2.13 – PLS results for phenols content prediction after mathematical preprocessing and for selected wavelength range (all days of storage grouped by different harvest times)

PHENOLS - SMOOTING+MSC									
	CALIBRATION				CROSS-VALIDATION				Factor
	SLOPE	OFF SET	RMSEC	R^2	SLOPE	OFF SET	RMSECV	R^2	
WAVELENGTH 400-1000									
HALL HARVEST TIMES	**0.461**	**257.266**	**106.882**	**0.461**	**0.403**	**285.382**	**119.435**	**0.331**	**14**
HARVEST TIME 1	0.555	227.665	74.461	0.555	0.529	240.330	78.942	0.493	1
OTHER HARVEST TIMES	**0.483**	**244.222**	**107.555**	**0.483**	**0.434**	**268.447**	**120.699**	**0.353**	**14**
WAVELENGTH 400-800									
HALL HARVEST TIMES	0.422	276.107	110.726	0.422	0.391	290.495	117.579	0.352	11
HARVEST TIME 1	0.631	189.675	65.053	0.631	0.565	223.150	75.994	0.489	4
OTHER HARVEST TIMES	0.403	280.140	123.454	0.403	0.366	297.208	131.738	0.322	11
WAVELENGTH 400-650									
HALL HARVEST TIMES	0.329	320.663	119.326	0.329	0.288	339.231	126.997	0.242	14
HARVEST TIME 1	0.637	186.385	64.487	0.637	0.554	227.744	79.187	0.497	5
OTHER HARVEST TIMES	0.316	322.771	123.648	0.317	0.277	341.181	131.556	0.232	10
WAVELENGTH 650-800									
HALL HARVEST TIMES	0.417	278.500	111.205	0.417	0.396	288.835	116.556	0.362	10
HARVEST TIME 1	0.562	225.100	70.868	0.562	0.524	243.412	76.626	0.533	3
OTHER HARVEST TIMES	0.362	299.003	127.542	0.362	0.331	314.345	134.345	0.297	10
WAVELENGTH 650-1000									
HALL HARVEST TIMES	0.412	280.786	111.661	0.412	0.371	299.881	120.230	0.324	14
HARVEST TIME 1	**0.755**	**125.998**	**53.021**	**0.755**	**0.646**	**182.311**	**74.796**	**0.560**	**6**
OTHER HARVEST TIMES	0.409	279.175	114.994	0.409	0.365	300.056	124.603	0.312	13

Table 2.14 – PLS result for antioxidant activity by harvest time and wavelength range (all days of storage grouped by different harvest times)

ANTIOXIDANT ACTIVITY - SMOOTING+MSC									
	CALIBRATION				CROSS-VALIDATION				Factor
	SLOPE	OFF SET	RMSEC	R^2	SLOPE	OFF SET	RMSECV	R^2	
WAVELENGTH 400-1000									
HALL HARVEST TIMES	**0.531**	**620.778**	**313.950**	**0.531**	**0.484**	**681.722**	**345.177**	**0.438**	**14**
HARVEST TIME 1	0.499	379.919	158.136	0.499	0.421	437.694	182.879	0.328	4
OTHER HARVEST TIMES	**0.513**	**687.129**	**293.968**	**0.513**	**0.464**	**7575.04**	**326.668**	**0.403**	**11**
WAVELENGTH 400-800									
HALL HARVEST TIMES	0.464	708.909	335.496	0.464	0.436	746.277	354.116	0.406	10
HARVEST TIME 1	0.382	469.097	175.718	0.382	0.351	492.173	185.068	0.295	1
OTHER HARVEST TIMES	0.522	674.675	291.292	0.522	0.4896	721.739	313.089	0.449	12
WAVELENGTH 400-650									
HALL HARVEST TIMES	0.426	760.270	347.442	0.426	0.360	842.113	389.597	0.281	20
HARVEST TIME 1	0.375	474.707	176.766	0.375	0.340	500.689	187.142	0.353	2
OTHER HARVEST TIMES	0.346	922.474	340.610	0.346	0.315	962.975	359.238	0.275	10
WAVELENGTH 650-800									
HALL HARVEST TIMES	0.464	709.894	335.729	0.463	0.427	757.314	358.200	0.393	14
HARVEST TIME 1	0.435	429.098	168.060	0.435	0.383	468.996	184.288	0.343	3
OTHER HARVEST TIMES	0.425	810.661	319.301	0.425	0.409	832.638	331.407	0.389	9
WAVELENGTH 650-1000									
HALL HARVEST TIMES	0.528	624.190	314.812	0.528	0.477	694.594	352.472	0.414	19
HARVEST TIME 1	**0.484**	**391.534**	**160.536**	**0.484**	**0.417**	**443.935**	**177.795**	**0.423**	**3**
OTHER HARVEST TIMES	0.487	724.551	301.867	0.487	0.437	791.252	340.403	0.351	14

For phenols the classes “All Harvest Times” and “Other Harvest Times” gave better results in the wavelength range of 400-1000 nm showing high values of R^2_C 0.46 and 0.48 and R^2_{CV} 0.33 and 0.35 respectively and low values of RMSEC and RMECV: 106.88 and 119.44 for “All Harvest Time” and 107.56 and 120.7 for “Other Harvest Time”. Phenol content for “Harvest Time 1” instead is better predicted in the range 650-1000nm with R^2_C 0.76, R^2_{CV} 0.56, RMSEC 53.02 and RMECV 74.8.

For Antioxidant activity is confirmed that for the classes “All Harvest Times” and “Other Harvest Times” the best results were obtained in the wavelength range 400-1000 nm with value of R^2_C 0.53 and 0.51 and R^2_{CV} 0,44 and 0.40 respectively and value of RMSEC and RMECV: 313.95 and 345.18 for “All Harvest Times” and 293.97 and 326.67 for “Other Harvest Times”. “Harvest Time 1”, as for phenols content is better predicted in the range 650-1000nm with R^2_C 0.48 and R^2_{CV} 0.42 and values of RMSEC 160.54 and RMECV 177.8.

2.4.5. PLS prediction models

After having defined the PLS-calibration model (paragraph 2.4.4), the model is used to predict, starting from a Training set (calibration value), a Test set of unknown samples (calibration value).

Considering the fact that for harvest period 1 all the samples showed lower concentration of antioxidant activity with the same phenols concentration, this harvest period was modeled separately.

Starting with this consideration, the analysis for gallic acid and antioxidant activity were carried out considering three model: “All Harvest Times”, “Harvest Time 1” and “Other Harvest Times” on the spectral range individuated in 2.4.4. and particularly the whole range 400-1000, except that “Harvest Time 1” was also modeled in the range 650-1000. Table 2.15 and 2.16, respectively for phenols and antioxidant activity record the statistical value of the Cross-Validation model.

As obtained in cross validation phenols content was well modeled in the wavelength range 400-1000 nm for the classes “All harvest Times” and “Other Harvest Times” with high value of R^2pred and low value of RMSEP, respectively 49% and 94 (“All Harvest Times”), and 37% and 166 (“Other Harvest Times”). Figures 2.23 and 2.24 show the results of the prediction for ”All harvest times”, both for the training and the test set, respectively. For “Harvest Time 1” the range 650-1000 was also tested. In this range R^2pred was 62% with an RMSEP of 72, compared to the 33% and 95 obtained in cross validation.

Table 2.15 – PLS results for prediction on phenol content on the external test set by wavelength range (all days of storage grouped by different harvest times)

N	Model Name	# LV"s	RMSEC	RMSECV	R^2fit	R^2CV	RMSEP	R^2pred
WAVELENGTH RANGE 400-1000								
1	ALL HARVEST TIMES	14	86	97	54%	43%	94	49%
2	HARVEST TIME 1	6	63	95	68%	33%	85	46%
3	OTHER HARVEST TIMES	14	110	124	45%	32%	166	37%
WAVELENGTH RANGE 650-1000								
4	HARVEST TIME 1		78	81	51%	46%	72	62%

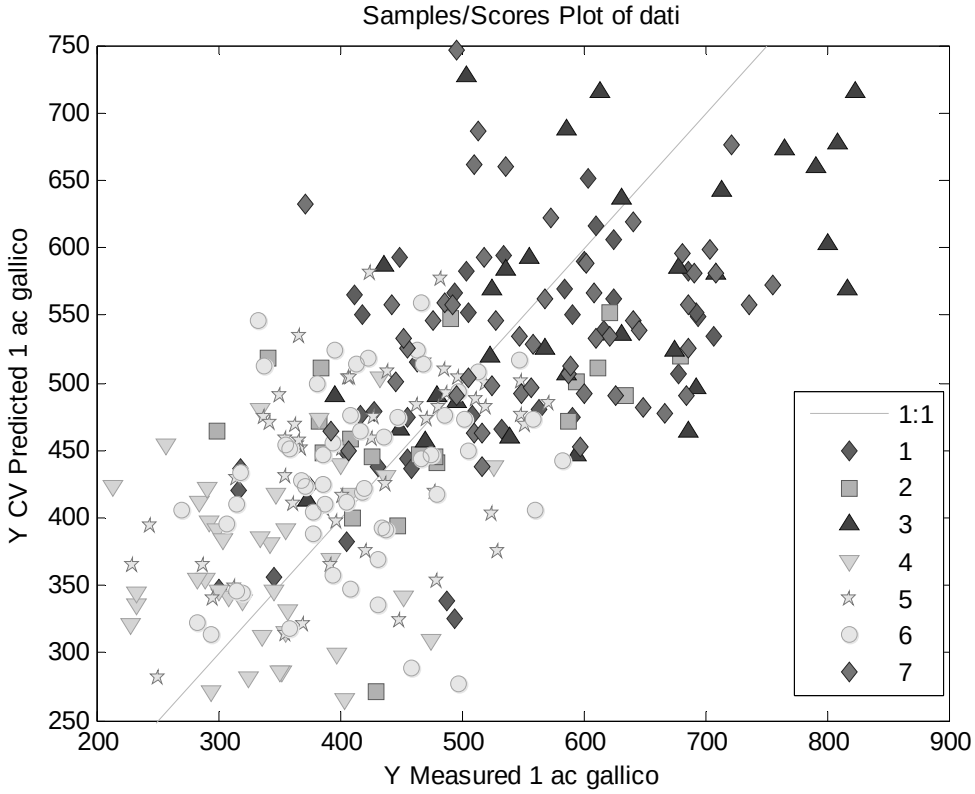


Figure 2.23 – Prediction results on the Training set for phenols content (All Harvest Times, spectral range400-1000 nm)

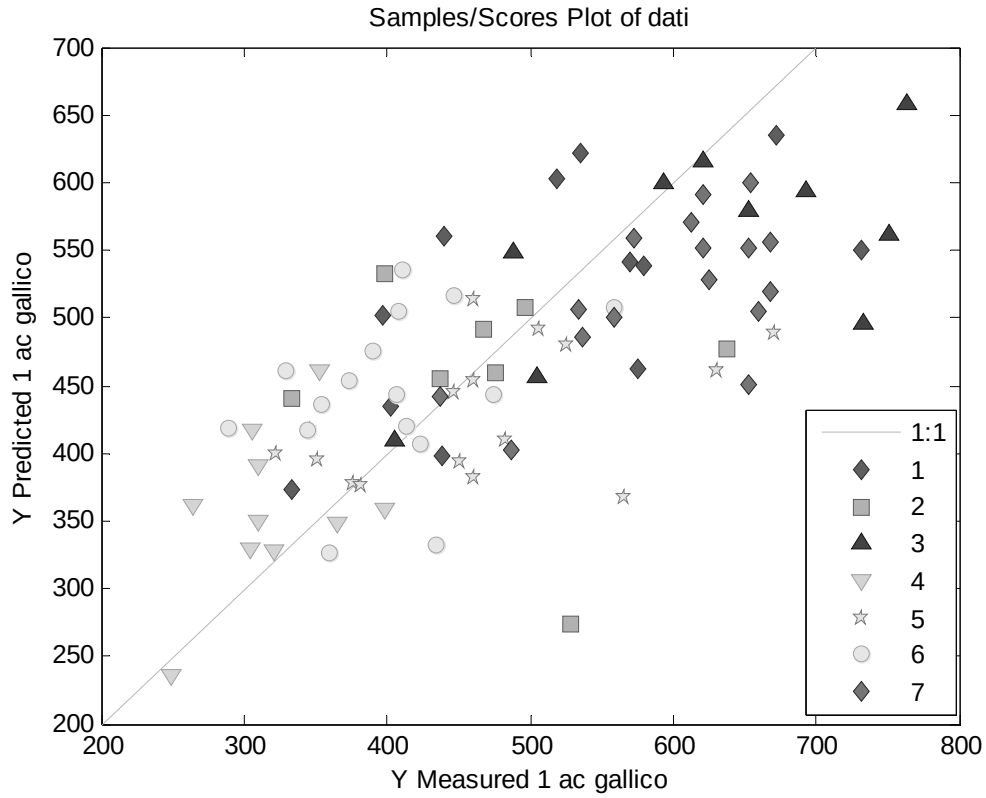


Figure 2.24 – Prediction results on the test set for phenols content (All Harvest Times, spectral range 400-1000 nm)

The antioxidant activity was also better modeled in the range 400-1000 nm for the classes "All harvest Times" and "Other Harvest Times" with R^2pred and RMSEP, respectively 46% and 356 (All Harvest Times), and 44% and 340 (Other Harvest Times). The class HT1 was better modeled in the range 650-100 nm than 400-1000 nm, showing R^2pred of 67% and RMSEP of 126 versus R^2pred 60% and RMSEP 140 obtained in the range 400-1000 nm. Figures 2.25 and 2.26 show the results of the prediction (for the training and the test set) for the "Harvest Time 1" in the wavelength 400-1000 nm, whereas the Figures 2.27 and 2.28 show the prediction results for the "Other Harvest Times", respectively for the training and the test set. Generally for both considered spectral ranges, using artichokes only for "Harvest Time 1" allowed to have much higher results for the prediction of phenols and antioxidant activity, suggesting that part of the variance of the data when considering all the samples. was due to other variables not directly related to changes in composition. It may be also possible that some of this variance could be generated by instrumental noise or changed conditions during the acquisition. Further studied may be therefore needed to validate these models.

Table 2.16 – PLS results for prediction on antioxidant activity on the external test set by wavelength range (all days of storage grouped by different harvest times)

N	Model Name	# LV"s	RMSEC	RMSECV	R^2fit	R^2CV	RMSEP	R^2pred
WAVELENGTH RANGE 400-1000								
1	ALL HARVEST TIMES	14	356	396	47%	36%	356	46%
2	HARVEST TIME 1	4	125	151	65%	48%	140	60%
3	OTHER HARVEST TIMES	11	284	321	53%	41%	340	44%
WAVELENGTH RANGE 650-1000								
4	HARVEST TIME 1	13	163	197	48%	28%	126	67%

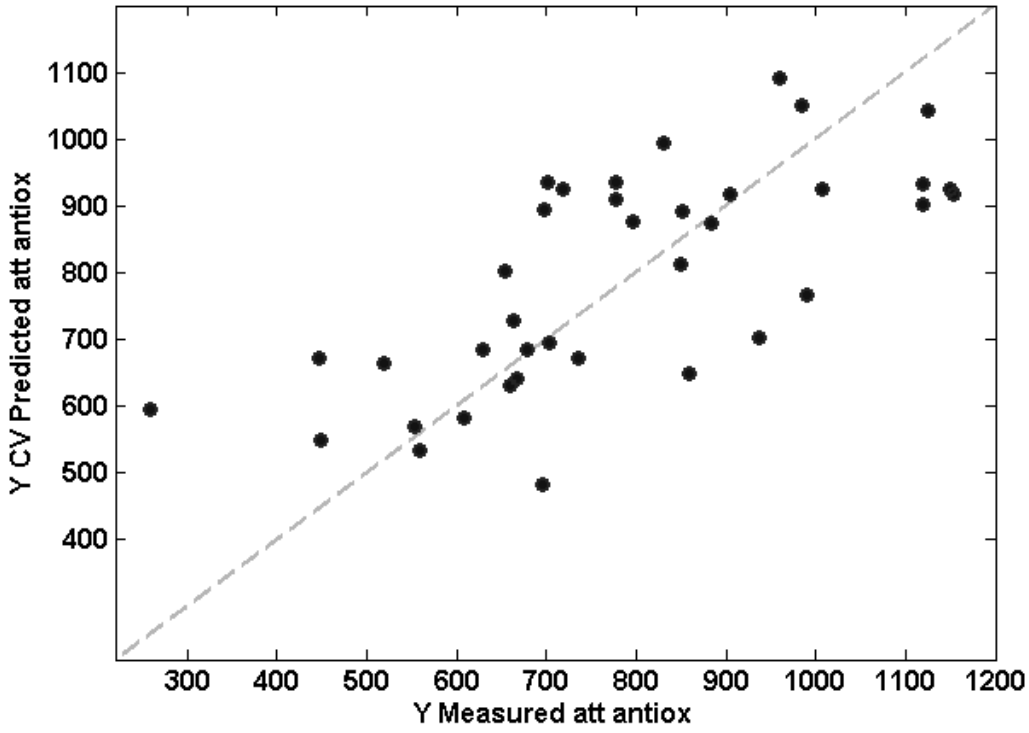


Figure 2.25 – Prediction results on the Training set for antioxidant activity (HT1, spectral range 400-1000 nm)

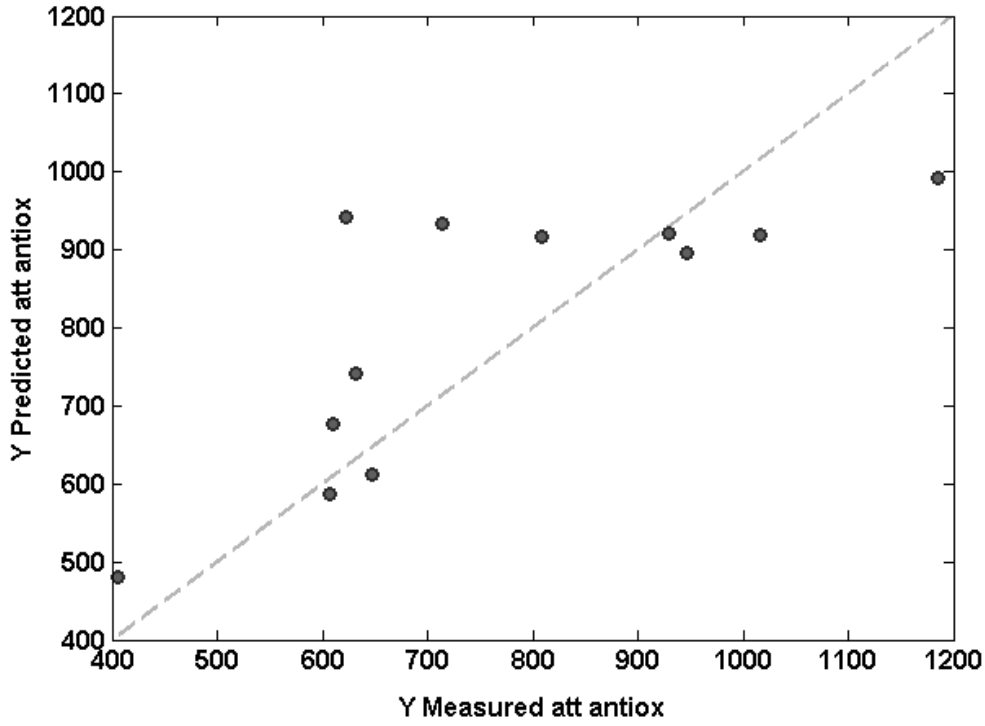


Figure 2.26 – Prediction results on the Test set for antioxidant activity (HT1, spectral range 400-1000 nm)

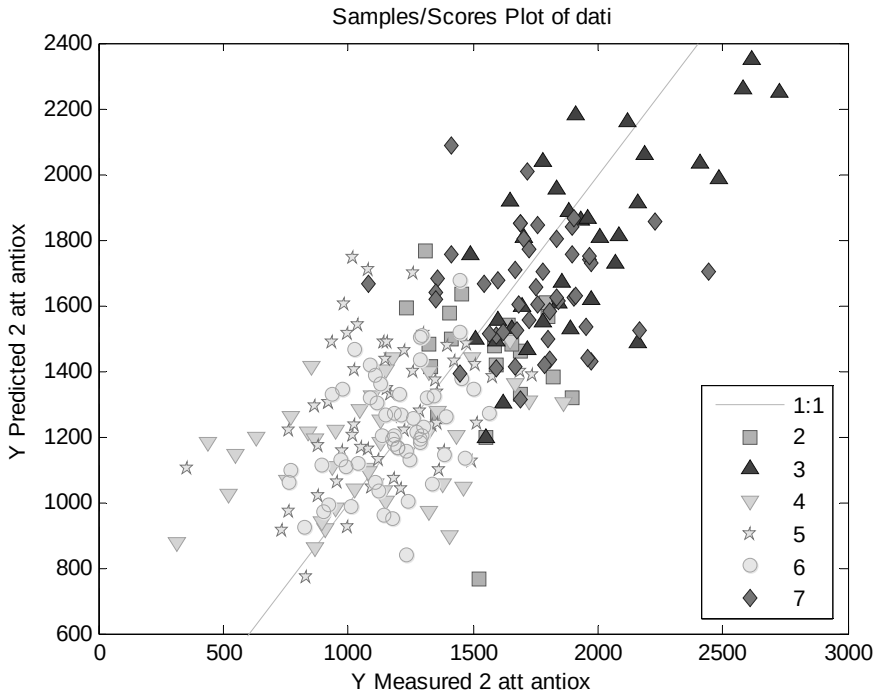


Figure 2.27 – Prediction results on the Training set for antioxidant activity (Other Harvest Times, spectral range 400-1000 nm)

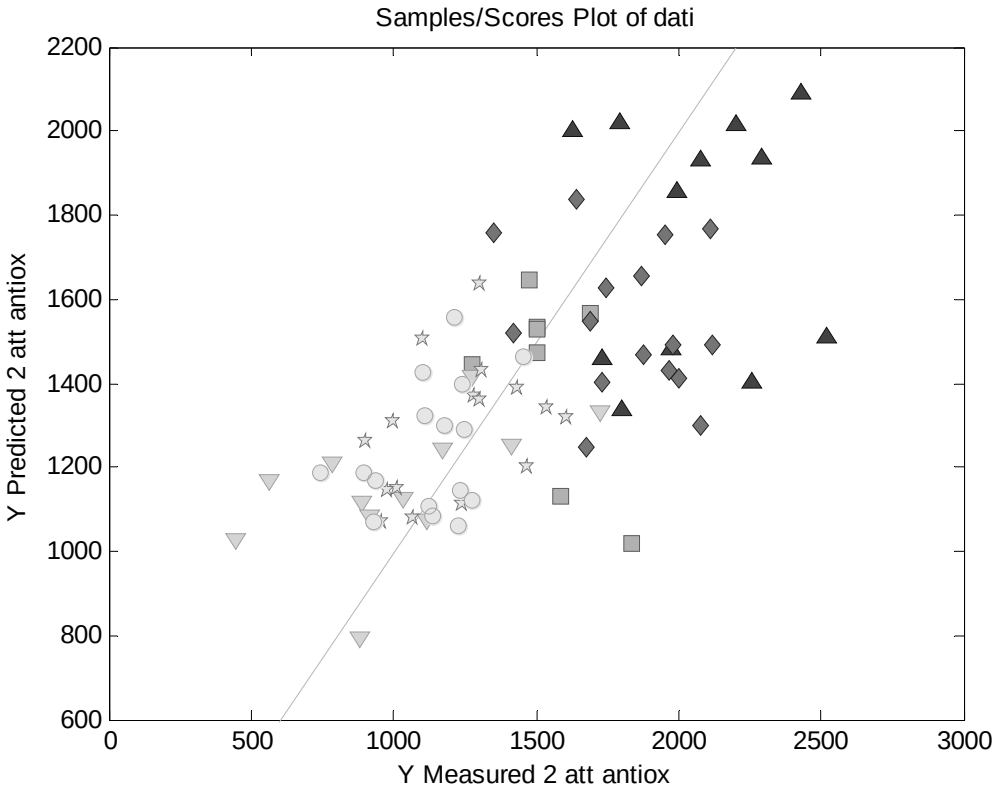


Figure 2.28 – Prediction results on the test set for antioxidant activity (Other Harvest Times, spectral range 400-1000 nm)

2.4.6 Conclusions

Results of these work allowed to test the feasibility of using spectral information generated by hyperspectral imaging to predict phenols and antioxidant activity of cut artichokes. Among all the pre-processing techniques Smooting + MSC gave the best results for the further prediction of both phenols and antioxidant activity content. Since some variation due to the harvest time was noticed both on spectral data and analytical analysis and particularly that data of "Harvest Time 1" showed a different behavior compared to the remaining harvest time, 3 models were generated-: "All Harvest Time", "Harvest Time 1" and "Other Harvest Time". Generally using the whole spectral range 400-1000 could be predicted phenol content and antioxidant activity for the classes "All Harvest Time" and Other Harvest Time", whereas a more accurate prediction for "Harvest Time 1" was obtained using the spectral range from 650 to 1000.

Moreover the efficiency of the model was always higher when using only sample from "Harvest Time 1" suggesting that other source of variation were included in the data set for the following samplings.

Starting from this considerations and from obtained results it may be interesting to further investigate the effect of the harvest time on the phenolic and antioxidant activity prediction to try to improve prediction results. Moreover also the instrumental setting can be improved, trying to standardize as much as possible the acquisition conditions.

PART THREE – CONCLUSIONS AND REFERENCES

3.1 CONCLUSION

Fresh-cut vegetables market has grown rapidly in recent years as a result of changes in consumer attitudes that prefer added-value products, in terms of quality, convenience, nutritional value and ease of preparation for which they are even willing to pay a higher price.

Artichoke heads are traditionally processed as fresh, canned (in oil, vinegar or in brine) or frozen but the high percentage of discarded plant waste, together with complex and time-consuming trimming operation, make artichoke processing as a fresh-cut product desirable, allowing to maintain the high nutritional value due to its composition very high in phenol and antioxidant activity.

On the other hand, due to the dual role of phenols, they are also the substrates of oxidative reactions which nowadays limit the possibility of the production and commercialization of fresh-cut artichokes. For these reason it may be important to monitor the concentrations of phenols and antioxidant activity in artichokes, as one of the key factors to monitor in order to produce high quality ready-to-use-products.

Moreover since phenols and antioxidant activity varies with the cultivar and that it has been widely shown that cultivar selection is the first key step in the implementation of the whole process for fresh-cut artichokes, the cultivar identification is demonstrated to be another step to monitor. In addition since the "Violetto" cultivar grown in the area of Brindisi (Puglia region) known as "Cariciofo Brindisino" received the Protected Geographical Indication (IGP) having a tool to identify the cultivar once the artichoke is cut may be very valuable.

To this aim, a system for the classification of two artichoke cultivars, "Violetto" and "Catanese" was implemented. Two classification methods were tested (using a derivative pretreatment): a class-modeling / pattern recognition method (SIMCA) and a discriminating method (PLS-DA). The discriminant approach gave best performance compared to the class-modeling, mostly because having observed a very similar spectral profile for the two classes, forcing the discrimination by means of PLS-DA, allowed to highlight the difference between the two classes.

A second aim of the classification analysis was also to discriminate artichokes from different harvest times and days of storage. Also for the classification by harvest period PLS-DA was the most performing method, allowing to separate classes with high sensibility and specificity. Results of the classification by days of storage after cutting (0, 2, 5 and 7) suggested that is possible to discriminate samples just cut from samples cut and stored for some days, but that is more difficult to exactly separate samples depending on the days of storage. Most likely this is not due to a low efficiency of the model, but to the changing proprieties of the samples that are not so dissimilar between 2 and 7 days of storage. As indicated by the "Non Error Rate", the model performance

improved, in fact, reducing the number of classed from 4 to 3, corresponding to day 0, day 2 and days from 5 to 7.

Finally the part aimed to test the feasibility of using spectral information generated by hyperspectral imaging to predict phenols and antioxidant activity of cut artichokes gave interesting results which encourage further studies. Some variation not directly correlated to the antioxidant content, was in fact detected. Particularly the data of "Harvest Time 1" showed a different behavior compared to the remaining harvest times and for this reason the prediction models were tested on 3 classes: "All Harvest Times", "Harvest Time 1" and "Other Harvest Times". The efficiency of the model was always higher when using only sample from "Harvest Time 1", suggesting that other sources of variation were included in the data set for the following samplings.

Starting from this considerations and from obtained results it may be interesting to further investigate the effect of the harvest time on the phenolic and antioxidant activity prediction to try to improve prediction results. Moreover also the instrumental setting can be improved, trying to standardize as much as possible the acquisition conditions.

Generally results of this thesis explored new area of research developing tools that may be used to increase the value of local productions, by mean of a better characterization and identification and by providing innovative non destructive-tools to be used online during the minimally processing operations for selecting raw material based also on its internal composition. These methods may be in fact be extended to other crops, and may be improved and adapted to increase quality of raw and processed products.

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