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TITOLO TESI

Electric techniques for the assessment of quality parameters of foodstuffs

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…ogni volta come se fosse la prima volta,
senza nessuna estrema certezza,
perché il dubbio è l'inizio della sapienza…
Cartesio
"Discorso sul metodo", 1637

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1.Introduction

In food industry, quality assurance requires low cost methods for the rapid assessment and preferably on-line measurement of the parameters that affect product stability. Chemical and physical properties of raw material, process streams and end products are the main aspects which define the level of product quality and stability. Quality parameters in foodstuffs define the degree of excellence of a product or suitability for specific applications (Soltani et al., 2011).

Foodstuffs are complex in their structure, mainly composed by gaseous, liquid and solid phases which often coexist in the same product (Rogers, 2001). For example, within the liquid portion fat and water may be combined and the result is called emulsion.

These structural characteristics include physical, mechanical and chemical properties that could undergo modification induced by the industrial process or storage.

Special attention is given to water, concerned as natural component of the major food product or as added ingredient of a production process, which assumes a great importance on technical and economical levels. Particularly water is structurally present in the matrix and not completely available. In this way, water can be present in foodstuff in many different states: as water of crystallization, bound to protein or starch molecules, entrapped in biopolymer networks or adsorbed on solid surfaces of porous food particles. Only this parameter can be exhaustive to well describe the variability of samples belonging from food industry.

Moreover foodstuffs change as a function of the season, the region of origin, the harvesting, the storage conditions as well as the processing step.

The traditional and most widely used technique for the assessment of food quality give reliable information but are destructive, time consuming and unsuitable for on line application (Barbosa-Canovas et al. 2006). The principal problem of an off-line measurement is the limitation to destructive disposal, time dispersant and the acceptance of not being able to correct the production process in real time (Rogers, 2001).

In particular technologies for non-destructive internal properties assessment are very limited. Therefore, investigation of the dielectric behavior of major food components and processing effects are needed to provide useful information to well understand the different

material for more solid design or better monitor of manufacturing process for quality control (Agilent.com, 2006).

The techniques proposed to monitor the quality parameters of foodstuff answer to the limited disposition of time and could be able to characterize the main compositional parameters. Dielectric interaction response is mainly related to water and could be useful not only to provide information on the total content but also on the degree of mobility of this ubiquitous molecule in different complex food matrix.

New development technologies are being introduced to provide selective analysis and adaptation to changing market structure, process procedures and variability of raw material. In this way the proposal of this thesis is to answer at this need. Dielectric and electric tool can be used for the scope and led us to describe the complex food matrix and predict food characteristic.

The thesis is structured in three main part, in the first one some theoretical tools are recalled to well assess the food parameter involved in the quality definition and the techniques able to reply at the problem emerged. The second part explains the research conducted and the experimental plans are illustrated in detail. For convenience this part is divided for kind of food considered and relative technique applied. Finally the last section is left for the practical application and rapid method easily implementable in an industrial control protocol or monitoring process.

1.1 Dielectric behavior of food

Biological materials, as food, act as non-ideal capacitor for their ability to store and dissipate energy from an external electric field. When a foodstuff is placed in an electric field, part of the electric charge does not pass through the material but only shift from their equilibrium causing a dielectric polarization (Britannica, 2009). In this way, food products have the ability to store energy when an external fields is applied and for this reason can be defined as a dielectric. The author has found that the capacity of a capacitor was dependent on the nature of the material separating the conducting surface. The properties related to the electrical capacitance and resistance are defined as dielectric properties. Every foodstuff has a characteristic pool of electrical properties that depend on its dielectric behavior. The complex quantity that describes the interaction of a material with the electric field is the permittivity ($\mathcal{E}_r$).

Permittivity is composed by a real and an imaginary part and it is expressed by the following theoretical equation:

$$\varepsilon_r = \varepsilon'_r - j\,\varepsilon''_r$$

Where $\mathcal{E}_r$ is the complex permittivity, $\mathcal{E}'_r$ is the real part called also dielectric constant and $\mathcal{E}_r''$ is the imaginary part named loss factor.

The storage capacity of a material is related to the real part of permittivity, the dielectric constant. The dissipation of energy represents the imaginary part and can be classified as loss factor. The effects that contribute on this parameters are loss and conductivity.

When complex permittivity is considered, the relative losses of a material is the ratio of the energy lost to the energy stored and is called the loss tangent (tan ϱ).

$$\tan\varrho = \frac{\varepsilon''_r}{\varepsilon'_r}$$

This parameter provides a measure of the material's loss angle which is complementary to the phase angle between the voltage and current related to material's impedance and conduction (Mudgett, 1986).

1.2 Electric polarization

At atomic level, every material is primarily made of negative and positive charges. In the presence of an electric field these charges are distorted and this interactions result from dipole polarization (Collie et al., 1948). When the electric field is removed the atoms return to the original state after a period of time called relaxation time (Mudgett, 1995).
Five main polarization mechanism are resume and show in figure 1.

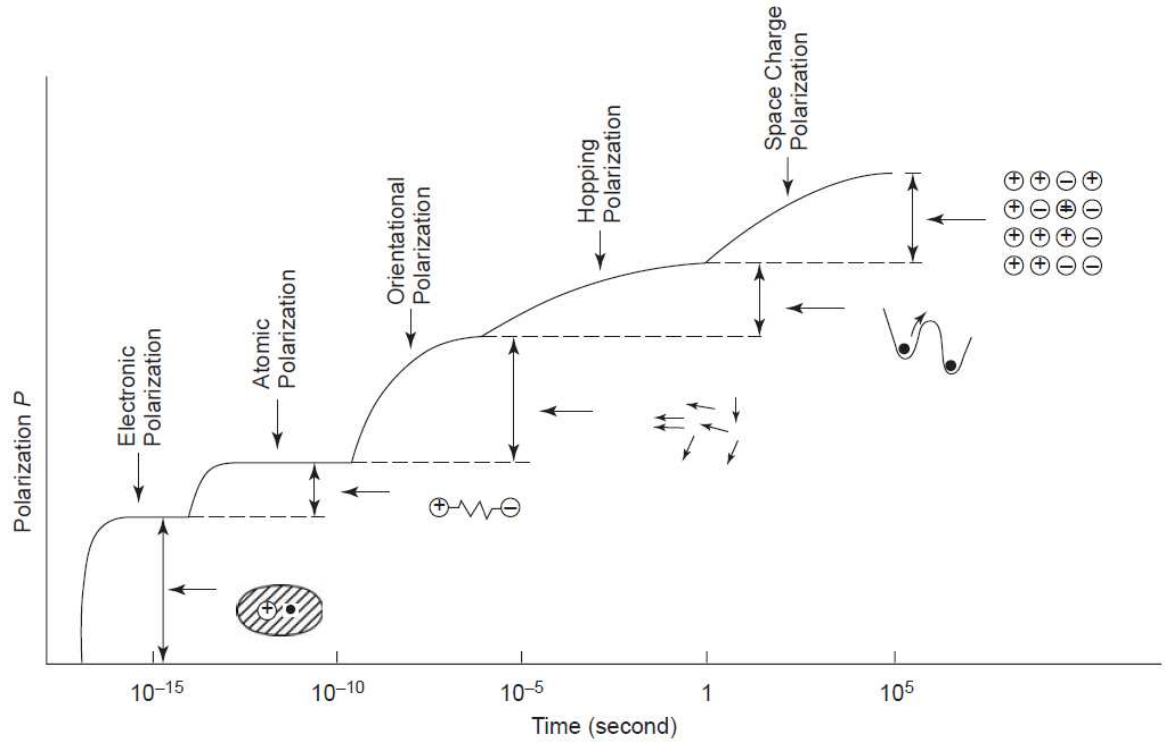

Fig. 1 Polarization effects (de Loor and Meij-boom, 1966).

The first polarization that occur is the “electronic polarization” caused by the deformation of the electron around the molecule. It occurs in neutral atoms when the electric field displaces with respect to negative charge.

The “atomic/ionic polarization” is due to the shift between two atoms belonging to different molecules. The atoms acquire charges of opposite polarity and the external field will tend to change the equilibrium positions of the atoms themselves, leading to atomic polarization.

The “dipolar/orientational polarization” is indication of a permanent dipole moment and its due to the re-orientation of the electric dipole which would line up with the electric field applied. This occurs only in dipolar materials possessing permanent dipole moment.

The last polarization that can occur is the “space charge polarization” involving free or fix charge of the material. It is present in dielectric materials which contain charge carries which can migrate through the bulk of the material creating a macroscopic field distortion.

Space charge polarization can be classified into hopping polarization and interfacial polarization. In dielectric materials, localized charges (ions and vacancies, or electrons and holes) can hop from one site to another site, which creates the hopping polarization. Similarly the separation of the mobile positive and negative charges under an electric field can produce an interfacial polarization (Sudheendran et al., 2011).

Usually in foodstuff this last polarization is less frequent than the other. Nerveless every kind of polarization requires time to manifest which create a displacement between the material polarization and the electric field applied.

To simulate the permittivity of the dielectric materials and therefore the relaxation phenomenon were developed many models as Debye, Cole-Cole, Davidson-Cole o Havriliak-Negami.

Among all, however, the only model of Debye (shown in figure 2) was born from an observation of the physical system, while all the others are originated from a parametric fitting. Debye model described the dielectric behavior of polar molecules in terms of permittivity as function of frequency. Different mechanism of polarization in biological materials are associated at different electromagnetic spectrum regions (de Loor and Meijboom, 1966).

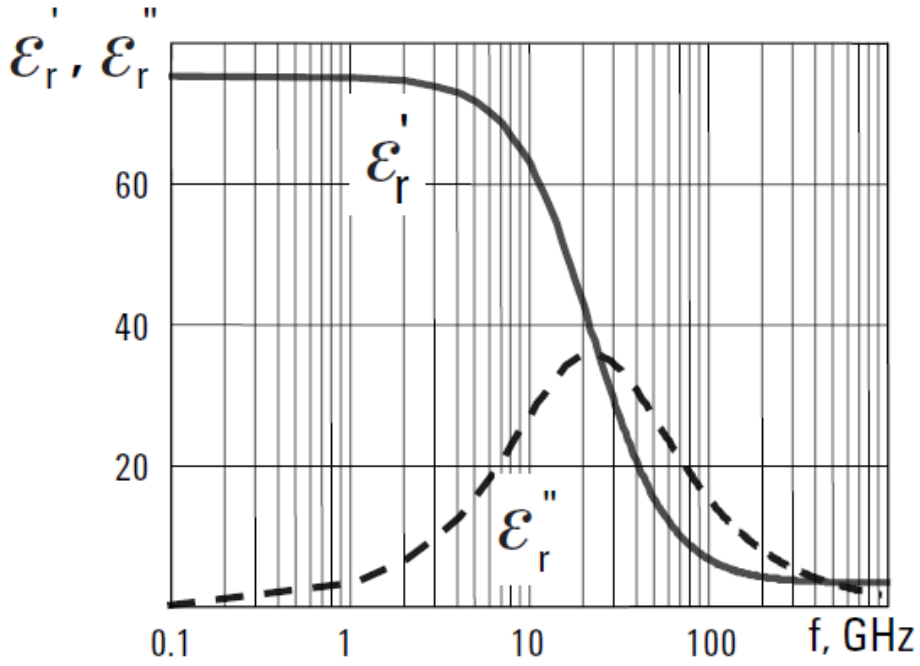

Figure 2 Debye model of the relaxation of water at 30°C.

The dipole rotation process persists until the relaxation phenomena occurs. The time of relaxation is the time required by molecule dipoles to become electric field oriented and it is strictly frequency dependent (Mudgett, 1986). At radiofrequencies the dipoles follow the external field and do not oscillate so fast to produce significant heat generation. Otherwise at higher frequency the dipoles are reacting to the electric field, but they are unable to follow the rapid field and relaxation phenomena occur. Moreover at high frequency the dielectric constant has a value of $\varepsilon_{r,\infty}$ and loss factor reaches its maximum at the relaxation frequency. This Debye interpretation of the variation of dielectric constant and loss factor with frequency has limitations and large deviations can occur, in terms of dipolar rotation against frictional forces in the medium. Despite this, Debye equation is the best for describing the variation of dielectric properties with frequency of liquid water, as the best example of polar material.

In particularly when food is taken into account for an absorption of energy some mechanism occurs and are dependent on the shape, volume, surface area, dielectric properties and equipment configuration (Nelson and Datta 2001). Otherwise, the two mechanisms primarily involved are dipolar relaxation and ionic conduction. Considering a foodstuff, the main component affect by these two mechanisms is water. Collie et al. (1948) well

described that dipole rotation in biological materials is associated with positive and negative charge on the hydrogen and oxygen atoms of water molecules. Water characterized by its dipolar nature tries to follow the electric field and such rotational movement of molecules produce heat and migration of ions under the influence of the electric field. These mechanisms are all energy losses and are all considered in the loss factor parameter. Furthermore, the decrease and increase in loss factor has been related to ionic conductivity at lower frequencies, to bound water relaxation, and to free water relaxation near the top of frequency range (Nelson and Datta, 2001).

1.3 Dielectric properties of food

In food, permittivity is related to chemical composition, physical structure, frequency and temperature, with moisture being the dominant factor (Barbosa- Cànovas et. al 2006; Ohlsson *et al.*, 1974; Kent and Jason, 1975; Engelder & Buffler, 1991; Nelson, 1961 and Nelson S O, 1992; Nelson & Kraszewski, 1990; Sipahioglu et al., 2003).
Subsequently, these main parameters are discussed.

Frequency

The dielectric properties of the foods may be determined in frequency intervals from direct current to optical frequencies by various measuring techniques (von Hippel, 1954).
The principal contribute of the frequency is polarization of molecules. With the increase of the frequency, the polar molecules follow the changes of the electric field up to the point where the orientation of the dipoles cannot keep up of the electric field and the dipoles relaxed. The dipoles relaxing assume a random orientation and as a result, the dielectric constant decreases or remains constant with the increase of the frequency (Içıer and Baysal, 2004). Spectroscopic techniques get information about the food matrix belonging from the emitted spectrum of the food propagation parameters. Food properties are more often detected in radio or microwave frequencies. Between 1 and 100 GHz, the microwave region, it can be possible to obtain different information compared to the radio frequency region. In the microwave range, the conductivity effects on the dielectric properties of the material can be ignored. Physical contact between sample and equipment is not required so does not alter or contaminate the material under test. Furthermore in microwave region at around 20 GHz, free water relaxes and allowing the detection of very small amounts of water (De los Reyes Canovas 2010).
A brief review of the main work showed the frequency influence is subsequently reported.
Thermal denaturation of liquid egg whites and whole eggs influenced the dielectric constant and dipole loss component of eggs, as reflected by changes in loss factor of egg yolk. As expected ionic conductivity was considered a dominant factor determining the dielectric

loss behavior of egg products at radiofrequencies, whereas dipole water molecules played an increasing role with an increase in microwave frequencies (Wang et al., 2009).

Wang et al. (2008) observed the differences in the dielectric properties of anterior, middle, tail, and belly portions of Alaska pink salmon (*Oncornynchus gorbuscha*) fillets. Dielectric constant and loss factor were determined in the frequency range between 27 and 1800 MHz from 20 to 120 C to provide insights for improving the modelling of microwave and radio frequency commercial sterilization processes of salmon products. Different part of salmon fillet contributed to observe little differences in the dielectric properties. At radio frequencies of 27 and 40 MHz, the dielectric constant decreased with increasing temperature. Although at microwave frequencies (e.g. 915, 1800 MHz), an opposite trend was observed. Over the tested frequency range, the dielectric loss factor increased with increasing temperature. Dielectric properties at radio frequencies suggest that ionic conductivity was the major contributor to temperature dependence on the electrical conductivity of minced salmon fillets.

Penetration depths are used to assess whether microwave or radio frequency energy at particular frequencies penetrates through a certain thickness of food so that a relatively uniform heating could be achieved during dielectric heating provide important information in pasteurization processes (Al-Holy et al., 2005). The authors determined the dielectric constant, loss factor and penetration depth for salmon and sturgeon caviar at 27 MHz and 915 MHz. The penetration depth was higher at 27 MHz compared to the microwave region.

Temperature

Temperature has a significant influence on the dielectric properties of food. The dependence of dielectric properties on temperature is therefore complex, this can grow or decrease as function of the material taken into consideration. For most reliable measurements of the dielectric properties of food, a control on this parameter must be performed. The influence of temperature on the dielectric properties of the food depends on many factors such as humidity, composition, salt and frequencies involved (Tang, 2005).

The influence of temperature among foodstuff parameters is subsequently reported in a brief literature review. Everard et al. (2006) measured dielectric properties of 16 processed

cheeses over the frequency range 0.3-3 GHz. Authors found that dielectric constant increased at low temperature until reach a minimum at high temperature, while loss factor for medium-high moisture decreased at low temperature and increased at high temperature. In pure water for example, an increase in temperature increases the frequency at which the relaxation phenomena occurs and the loss factor raise (Mudgett, 1995).

Dielectric properties of ground samples of peanuts were measured for several densities, temperatures and moisture content in microwave region from 300 to 3000 MHz. The dielectric properties of peanuts increase with density. At higher moisture content the temperature effect was reduced by the high dependence of dielectric properties on moisture content (Boldor et al. 2004).

The dielectric properties of food at low temperature, particularly below the freezing point are affected by the progressive conversion of liquid water to ice with the concentration of dissolved salt (Mudgett et al.,1995). This phenomena suggest that dielectric properties in frozen foods are related to aqueous ionic environment, characterized by relative motilities of water and ions which can be determined as loss factor variation (Bengtoss and Risman, 1971; Westphal, 1972).

The dielectric properties of foods at high temperature, in specific about non-polar liquids and solids are reported (vonHippel 1954; Chernow et al. 1967; Westphal and Sils, 1972). These measurements indicates that the properties of non-polar food are constant over a wide range of temperatures and are dielectrically inert compared to the aqueous polar substances (Mudgett, 1995).

Wang et al. (2009) studied the effects of cooking on dielectric properties of liquid whole eggs and egg whites in relation to radiofrequencies and microwaves by using an open ended coaxial probe over a wide range of temperature 20-120 °C.

Moreover Coronell et al. (2008) tested ready to eat puddings, soy beverages and avocado paste products. Soy beverages followed the same general trend traduced in a decrease of dielectric constant and an increase of loss factor with temperature raise. For puddings the dielectric properties had similar values, 64 and 52 for dielectric constant and 17.2 and 22.7 for loss factor, respectively which can be used to implement flow applications.

Food compositional constituents

Dielectric constant and loss factor are primarily determined by the chemical composition of foodstuff, such as the presence of mobile ions and permanent dipole moment associated to water and the interaction between other molecules, and only subsequently by their physical structure (Barbosa- Cànovas et. al 2006).

Dielectric properties of food product depend on their major relevant components, such as moisture, salt content, carbohydrate, protein and fat.

Several studies regarding dielectric characterization of agri-food products were carried out in the past 40 years to study the influence on different compositional factors (Nelson, 1996; Venkatesh & Raghavan, 2005). These studies investigated grain and seed (Nelson, 2003), fruits and vegetables (Tran et al., 1984; Nelson, 1992; Nelson et al., 1996; Berbert et al., 2001), beverages (García et al., 2001), baked food and flours (Seras et al., 1987; Zuercher et al., 1990), dairy products (Sone et al., 1970; Kudra et al., 1992), fish and meat (Bengtsson & Risman, 1971; Ohlsson et al., 1974; Lyng et al., 2005).

An extensive analysis was conducted on compositional changes of fruit due to insect pest attack (Wang et al. 2008 and 2009; Ikediala et al. 2002). The authors explored in the first step the fruit dielectric behavior at the radiofrequencies region and then observed an increase in loss factor when the fruit was affected by insects.

Egg constituents were characterized by Ragni et al. (2007) through dielectric properties, to investigate the electrical changes during storage by using an open-ended coaxial probe in the frequency range 20-1800 MHz. Their results indicated R^2 values up to 0.92, 0.60, 0.53 and 0.73 for the air cell height, thick albumen height, Haugh unit and Yolk index, respectively.

The differences in composition of grape juice varieties can be evaluated by using dielectric properties (Garcia et al. 2001). Red wine grape juice samples were used for measuring the dielectric constant and loss factor in the frequency range 0.2-3 GHz. The investigators observed differences among varieties in relation to the value of the total and dipolar losses at 3 GHz but more measurements are necessary to be decisive enough.

Regarding carbohydrates, the principal species present in food system are starches, sugars and gums. Detecting this kind of compounds by using dielectric properties can be difficult

because they do not show appreciable dipolar polarization at microwave frequencies (Ryynanen, 1995). Therefore, for carbohydrate solutions, the effect of free water on dielectric properties becomes significant. Hydrogen bonds and hydroxyl group water interactions also play a significant role in dielectric properties of high sugar, maltodextrin, starch hydrolasate and lactose like disaccharide based foods (Roebuck et al., 1972).

The dielectric properties of thirteen sweet potato cultivars were determined to develop a process for rapid sterilization and aseptic packaging of potato puree by using a continuous flow microwave system operating at 915 MHz (Brinley et al., 2008). Results indicated that temperature, moisture, sugar and starch content had a pronounced effect ($p < 0.001$) on dielectric properties measured from 15°C to 145°C. The authors described as the sugar content of the purees had a negative effect on the dielectric loss factor, as a consequence of the formation of hydrogen bonding with the free water which decreased the polarization of water molecules.

A simple method based on a designed dielectric cell was proposed for determination of dielectric properties of powder grains (Bhargava et al., 2014). Dielectric constant and loss factor of five varieties of wheat have been determined to investigate food nutrients dependence, such as moisture, protein, fat and carbohydrates. In particular, the authors underlined that the value of dielectric constant first increases and then decreases as the % of carbohydrates is increased, it being highest at about 66 % of carbohydrate value for all the grain sizes. The loss factor on the other hand first decreases and then increases, showing lowest value at about 66% of the carbohydrates.

Dielectric properties at 2450 MHz were determined for tapioca, corn, wheat, rice, waxy-maize and amylo-maize starches in granular, at temperatures from 30 to 95°C by Ndife et al. (1998). Dielectric properties were shown to be dependent on temperature, moisture content and starch type. Quadratic equations were developed to show the relationship between the changes in dielectric properties with temperature for starch species. The authors found significant differences in dielectric properties of different types of starches.

Protein are relatively inert and do not interact significantly with microwaves. Proteins are partially soluble and partially insoluble with ionizable surface regions that may bind water or salts to give rise to zeta potential and double-layer effects associated with free surface charge (Mudgett, 1995). The dielectric properties of proteins depend on their chains, which

can be nonpolar with decreasing order of alanine, glycine, leucine, isoleucine, methionine, phenylanine and valine or polar with decreasing order. Free aminoacids are instead dielectrically reactive and contribute to an increase in dielectric loss factor. Since protein dipole moments are a function of their amino acids and the pH of the medium, the dielectric properties and microwave reactivity of cereal, legume, milk, meat and fish proteins are expected to be different. The water absorbed on proteins affects their dielectric properties. The dielectric activity of proteins can be divided into four categories:

- high activity due to charge effects of ionization carboxyl, sulfhydryl's and amines;
- hydrogen and ion binding as affected by pH;
- net charges on dissolved proteins;
- relatively low activity due to relaxation and conductive effects.

Bircan and Barringer (2002) determined the protein denaturation of muscle foods using the dielectric properties. Both the dielectric constant and loss factor increased at a temperature that appeared to match the denaturation temperature for collagen in beef, chicken breast, chicken thigh, perch, cod, and salmon. When the sample was reheated the change did not reoccur, indicating that the dielectric properties were measuring an irreversible change. At lower frequencies the increase in the dielectric properties was larger. When collagen and acto-myosin denature, the muscle shrinks, expelling water and minerals becoming more mobile. The dielectric constant and loss factor measure the mobility of water and ions; therefore they may be able to determine the temperature of protein denaturation.

The dielectric properties of milk protein (whey protein isolate), starch and water were investigated by Tsoubeli et al. (1995) to controlling the cereal product quality. At lower moisture contents, Ca-caseinate has a lower dielectric constant than whey protein isolate or starch. The addition of whey protein isolate in the starch water system could increase the ability of starch to dissipate energy, manifested by the higher dielectric loss at almost all moisture contents. It was evident that although the water environments were similar among the systems studied, their dielectric properties differed. Thus the authors concluded that the dielectric properties do not solely depend on water but are also influenced significantly by the macromolecule present.

Dielectric properties of soy protein isolate dispersions were measured by Ahmed et al. (2007) over the frequency range of 200–2500 MHz by the open-ended coaxial probe

method. Results indicated that the dielectric constant decreased with temperature and frequency while increased with protein concentration. Moreover the significant change in dielectric properties at 90 C was a result of protein denaturation which was identified by differential scanning calorimetry (DSC).

Lipids are hydrophobic compounds, except for ionizable carboxyl groups of fatty acids and do not strongly interact with microwaves (Mudgett, 1995). Therefore, the dielectric properties of fat are very low (Lizhi et al., 2008). The effect of fat on dielectric properties is due to the dilution effect in the system. In this way, the increase in fat content reduces the free quantity of water in the system, which reduces the dielectric properties (Ryynanen, 1995). Dielectric properties were used to study UHT skim, low fat and homogenized whole milk by Nunes et al. (2006). Dielectric constant and loss factor among these products were very similar in the same frequency region considered as a consequence of low fat contribution. Also Coronel et al. (2008) demonstrated the negligible effects of fat content on dielectric properties of skim milk and fat milk in the microwave range.

Dielectric properties of meat products and typical ingredients of meat manufacture in the microwave region are reported by Lyng et al. (2005). The authors found that fat had lower dielectric activity than lean tissue.

Zhang et al. (2007) examined the influence of the level of added water (21–29%), fat (12.4–29.7%) and salt (0.4–2.4%) on radio frequency and microwave dielectric properties. Results revealed that added fat had an influence on thermal properties and a lesser influence than salt on dielectric properties.

One of the major components of food system is salt. Salt is one of the principal factor for ionic conduction. Addition of salt creates a decrease in dielectric constant due to the binding of water in the system which reduces the available water for polarization. On the other hand, addition of salt creates an increase in loss factor since more charged particles are added to the system and charge migration is increased (Mudgett, 1995). Nelson and Datta (2001) showed that in aqueous ionic solution, loss factor decreased with temperature for salt concentration less than 1.0%. On the opposite, loss factor increased as temperature for higher salt concentration in reason to a dominant ionic mechanism.

Ahmed et al. (2007) determined the dielectric properties of salted and unsalted butter in the microwave frequency range. The results showed a significantly dependence of salt among

the explored temperature while for frequency only loss factor decreases with an increase of this parameter.

Water

In order to investigate possible other dependences between dielectric properties and food composition, water content had to be taken as the initial guess (Datta et al.,1995).

Liquid water is a very polar compound and can easily absorb energy because of dipolar rotation. For this reason, moisture content is one of the major determinants of food dielectric properties. The increase in water content produce an increase of the polarization phenomena, raising both dielectric constant and loss factor of food system (Wang et al., 2008).

Moisture measuring, such as electrical conductance and capacitance and microwave interaction, are the most applied (Vlachos et al. 2000).

An on-line monitoring system to determine moisture content of grain during process was develop by Weidong (2007). The dielectric constant was measured with a cylindrical capacitive sensor and the proposed model were built to predict moisture content of wheat and corn. In this direction Rai et al. (2005) developed a moisture meter for grain (wheat, paddy, sunflower, mustard and soybean) by using a parallel plate capacitor as probe. The device works in the moisture range from 5 to 25%, with an accuracy of 1%. A capacitive moisture meter for corn was develop by Jùnior (2008). An alternate voltage, a divisor voltage and a capacitor in a moisture range of 11-27% offered at 10 KHz the best sensibility.

Berbert et al. (2001) predicted the water content of bean seeds by measuring the dielectric properties and proposed three models with low standard errors of calibration. Li et al. (2003) determined moisture content of cookies by using dielectric spectroscopy characterized by three electrodes used as a fringing field sensor. To measure the capacitance of sensor they used a sweep signal from 10 Hz to 10 kHz. At higher frequencies they reported an increase of sensitivity. 10 kHz were selected to calibrate the system. A linear correlation between capacitance and moisture content was determined. Furthermore the dielectric properties were used by Trabelsi et al. (2009) to estimate the moisture content of

shelled peanuts. The experiment was carried out in the frequency range from 8 to 14 GHz and in a temperature range from 1 to 38°C. The best equation for the moisture content prediction as function of temperature was at 10 GHz frequency. Mizukami et al. (2006) measured electrical impedance, resistance, reactance and capacitance by using four stainless steel electrodes and an LCR meter in the frequency range 10 Hz-10 MHz. The purpose of the research was the assessment of the moisture content of tea leaves. Satisfactory results were obtained only by developing a new equation that consider impedance and capacitance together. On the contrary, considering the impedance or capacitance separately, the levels of standard error was higher and low levels of correlation were achieved. An on-line monitoring system to determine moisture content of grain during process was developed by Weidong (2007). The dielectric constant was measured with a cylindrical capacitive sensor and the proposed model was built to predict moisture content of wheat and corn. A non-destructive and on-line moisture meter was proposed by Berbert et al. (2001) for the indirect determination of moisture content in coffee grains. The potential application of the knowledge of relative permittivity of coffee and bulk density of several varieties were determine and analyzed for frequency from 75 kHz to 5 MHz. A loss factor decrease was observed in reason to a frequency increase, but the behavior was less regular and dependent on moisture content.

The electrical properties of wheat bread as function of moisture content and storage time were studied by Bhargava et al. (2014).Various sections of bread were measured and the moisture content was estimated by using a multichannel ring electrodes. The capacitance variations were reported as a function of the moisture content of the bread crust, not only for the water content evaluation but also to further understand the glass transition phenomena.

Dielectric water behavior

Water in its pure liquid state is rarely found in food products. The relationship between water content and water availability plays a key role in the stability factors towards microbial spoilage and water migration (Lewicki, 2004). The influence of water on physical properties of food is dependent on the state. Water can exist in food system either in free form or in a loosely defined state called the bound state. Water in foods is dissolved as

constituents, physically absorbed in food capillaries or chemically bound to other molecules or absorbed on the surface of dry materials. Water can also act as plasticizer making possible movement of the structures (Seow et al., 1999).

The spatial configuration of a water molecule is pictured as a regular tetrahedron, where inside the solid there is an atom of oxygen and in corners there are positive charges and two orbitals of paired electrons (Lewicki, 2004). Partial charges lead to the interaction between other molecules. The water ability to engage in three dimensional hydrogen bounds provides a logical explanation for many of its unusual properties. Its large values of heat capacity, melting point, boiling point, surface tension and enthalpies of various phase transition are all related to extra energy needed to break intermolecular hydrogen bonds (Fennema, 1996). The permittivity of water is also influenced by hydrogen bonding. Hydrogen-bonded clusters of molecules apparently give rise to multi-molecular dipoles, which effectively increase the permittivity of water (Fennema, 1996). So, the dielectric constant and loss factor are affected by the presence of free and bound water surface charges, electrolytes, non-electrolytes and hydrogen bonds in the food product. Unfortunately, hydration of polar molecules cannot be estimated on the number of groups able to form hydrogen bonds since considering that these interactions can alter spatial conformation of a solute and solvent as well (Lewicki, 2004).

The stronger the binding forces among water and proteins or carbohydrates, the smaller is the contribution of the bound water to the dielectric constant or loss factor. In macromolecules such as proteins or polysaccharides intramolecular interaction are able to deform electron cloud and surplus or deficit of electrons occurs. Hence, hydrogen bonds can be formed and water molecules are built in the structure of biopolymers. In this case two states of water can be considered, one in which water molecules are immobilized in the structure of a macromolecule (structure water) and another state in which molecule are not completely restricted (hydration water) (Lewicki, 2004).

Apolar compounds interact with water reducing its degrees of freedom with a consequent stabilization of water molecules in space, in which the liquid acquires a structure of a solid. This phenomenon is called hydrophobic hydration. Hydrophobic interactions lead to the formation of structures in which properties of water differ from those of freezable water.

When water molecules are bound to hydrophilic center and polar groups do not freeze, is not available to chemical reactions and does not serve as solvent (Lewicki, 2004).

On the contrary of the large amount of data for water evaluation only few works showed the dielectric behavior of water in terms of mobility and availability. Furthermore knowledge are needed to definitely verify a strong correspondence between the dielectric behavior and water status.

Castro-Giraldez et al. (2010; 2011; 2012; 2013; 2014) demonstrated in the light of different research that dielectric measurements at microwave frequencies could be used to analyze the interactions between water bound state and different compositional parameters for controlling several industrial processes.

Henry et al. (2003) presented a methodology based on the resonant cavity in microwave domain to obtain dielectric parameters on hydrated material under test. A theoretical approach was useful to calculate the value of water activity on the surface of solid materials.

Protein-water dynamics were studied by using dielectric relaxation spectroscopy. A dielectric relaxation of small polar groups of protein plasticized by water, overlapped by relaxations of un-crystallized water molecules and separate relaxation of water in the crystallized water phase were recorded (Panagopoulou et al., 2011).

DeLoor and Meijboom (1966) collected data on dielectric properties of fruit and vegetable. The authors demonstrated that at moisture contents less than 20%, dielectric properties were almost constant, showing that water was tightly bound form and very limited to move and assumes exiting status. Between moisture contents of 20 and 76% there was a rapid increase in dielectric properties due to the increase in freely available water. However, in frozen state, both dielectric constant and loss factor were small and not much affected by the increase in moisture content. This is attributed to the presence of water in bound form. Thus, since the moisture content of many food is greater than 60%, the free water with high dielectric activity should be the dominant component governing the overall behavior of foods (deLoor and Meijboom, 1966).

The relationship between the organization of cellular water, molecular interactions, desiccation tolerance, dielectric behavior of water and water plasticized biomolecules in red oak seeds were studied by Sun (2000). Three dielectric dispersion were investigated: the relaxation of loosely-bound water and small polar groups, the relaxation of tightly- bound

water, carbohydrate chain, large polar groups of molecules and the freezing in molecular mobility.

1.4 Methods for dielectric properties measurements

Dielectric properties measurement concerns the selection of different techniques depending on the nature of dielectric material, frequency of interest, degree of accuracy required and availability of the measuring equipment (Nelson and Datta et al, 2001). Moreover the choice of the equipment and sample holder should be made upon the dielectric material to be measured, the extent of the research, the device availability and the economic resources for the study (Venkatesh and Raghavan 2005).

Several foodstuff can be explored with improved sensing devices for control and automation, such as the moisture sensing devices that create an absolute possibility to well employ dielectric properties of materials as a consequence of more adaptable characteristic of the equipment (Venkatesh and Raghavan 2005).

Several methods can be used ranging from direct current to microwaves to determine the electrical properties of biological materials by using different devices including parallel plate capacitor, coaxial probe, lumped circuit, waveguide, resonant structure, inductance, capacitance, resistance (LCR) meter, impedance analyzer and scalar and vector analyzer (Nelson, 1999; Içier & Baysal, 2004; Ragni et. al, 2006; Sucher and Fox 1963; De Loor and Meijboom 1966; Bengtoss and Risman, 1971; Thompson and Zachariah, 1971; Metaxas and Meredith 1983; Nyfors and Vainikainen, 1989; Hewlett Packard, 1992).

The challenge in performing accurate permittivity measurements is not only related to the choice of the technique but also concerns designing of the material sample holder and circuit modeling for reliable calculation of permittivity (Nelson 1998). Nelson (1973, 1983, 1984, 1991) used different sample holders with various microwave measurement systems assembled for dielectric parameter evaluation of grain, seed, fruit and vegetable in the frequency range 1 to 22 GHz. For example if a radiofrequency circuit is well designed and it can be possible to register impedance or admittance data and the dielectric properties can be further calculated by using specific equations related to the material. Corcoan et al. (1970) reported dielectric properties of grain with a precision bridge for audio frequencies from 250 Hz to 20 GHz with a coaxial sample holder. Grain and seed samples were also tested by using a Q-meter based on resonant circuit between 1 and 50 MHz (Nelson 1991).

A review of the techniques for permittivity estimation in the low medium and high frequency ranges including the use several bridges and resonant circuits was written by Field (1954).

Software may also be required to convert measured data from the instrument in the most convenient physical quantity, allowing also the extraction of the properties of interest.

Accurate and useful analysis for most food products can be provide by automated network analyzers, but with an application limit due to the high cost of the equipment, such as Time Domain Reflectometry technique. In frequency range near to 915 and 2450 MHz dielectric properties can be performed with cavity perturbation technique by using a dielectric analyzer instead of a network analyzer. A vector analyzer is versatile but expensive and can be adapted for several studies, while scalar network analyzer and impedance analyzers are quite less expensive. For limited studies, more suitable equipment can be radiofrequency or microwave devices if a apposite sample holder is set up.

Economic instrumental chain, such as system using scalar network or impedance analyzers, could be attractive as function of its accuracy, ease of operation, simple sample preparation, convenient temperature control, and the affordability of owning this equipment (Datta et al, 2014). Furthermore impedance analyzers and LCR meter are used to measure the material properties at lower frequencies. Subsequently the principal technique are reported.

Waveguide and coaxial line

Transmission line methods involve placing the material inside a portion of enclosed conveyance system (Nelson 1998). The waveguide is a method belonging from the transmission line that exploits the transport of an electromagnetic wave within a closed cavity for the detection of the dielectric properties of the material (Behlriti et al., 2013).

Each waveguide has endless configurations of electromagnetic field called MODES. The characteristics of MODES depend on size of the section, type of material and frequency used (Green, 1996). The MODES are generally classified according to the nature of the components of the electric field. The MODES most often in use are the TE MODE (transverse electric), TM MODE (transverse magnetic) or TEM MODE (transverse electromagnetic).

The waveguide system required a specific design of the device with particular attention paid to the dimension of the sample holder (vonHippel, 1954). Another critical aspect for a waveguide technique is a precise sample preparation requirement, with constant geometry and no air gaps. Both these factors can compromise the measurements by introducing errors. The geometry of the material influence the electromagnetic wave with course distortions that involved in wrong spectrum acquisition. Air gaps is a very important aspect to take into account as a consequence of very different behavior respect biological material. It is well known that air has a very low dielectric constant determining relevant changes in dielectric properties determination, as a consequence the sample does not have air gaps to avoid possible mistakes.

The values of dielectric constant and loss factor can be derived from the transmission line theory, which indicates that these properties can be calculated by measuring the phase and amplitude of a reflected microwave signal from a dielectric material placed against the end of a transmission line, such a waveguide (Roberts and von Hippel 1946; von Hippel 1954).

The waveguide dimension are: *a* (width), *b* (height) and *d* (length). The cut off wavelength in the guide is $\lambda c=2a$. The cut off frequency (*fc*) of the guide is given by the following expression (Baker-Jarvis et al., 1990):

$$fc = \frac{\sqrt{2c}}{\sqrt{\lambda c^2(\sqrt{\varepsilon_r^2 + \varepsilon_t^2} + \varepsilon_r)}}$$

The formula assumed a waveguide characterized by single mode propagation (mode TE_{10}), completely filled with the material under test.

In agri-food sector this kind of technique is not so common. Hunger et al. (2011) describe path length waveguide setup to obtain accurately measurements of complex permittivity of liquid, such as water and water-ethanol mixtures, in the frequency range 60 to 90 GHz. The authors presented the technique to investigate low-loss as well as high loss liquids. Green (1996) studied the dielectric properties of cheddar cheese at microwave frequency (from 750 MHz to 12.4 GHz). The physical and chemical properties of the cheese were also measured and correlated with dielectric properties.

The waveguide technique was implemented for the evaluation of ripening indices of kiwi fruit (Ragni et al., 2012) and the freshness of the eggs (Ragni et al. , 2010), the composition of the grated Parmigiano Reggiano cheese (Cevoli et al. , 2012).

Parallel plate capacitor

The parallel plate capacitor method involves sandwiching a thin sheet of material between two electrodes to form a capacitor. A typical measurement system using the parallel plate method consists of an LCR meter or impedance analyzer and fixtures. It is an economic method and relatively simple. In a parallel plate capacitor, capacitance is directly proportional to the surface area of the conductor plates and inversely proportional to the separation distance between the plates. A capacitor is a device which is able to store energy and electric charge, made of two isolated conductors at closer distance. These two conductors are called plates where a uniform electric field can be generated. If the charges on the plates are $+q$ and $-q$ respectively, and V gives the voltage between the plates, then the quantity of charge Q is proportional to the voltage applied:

$$Q = CV$$

C is the capacitance and it is measured in Farad (F). The capacitance of the capacitor is dependent only by its structure and dimension, if a dielectric is absent between plates. So the related capacitance is:

$$C = \varepsilon_0 A / d$$

Where A is the plates area, d the distance between plates and $\mathcal{E}_0$ is the dielectric constant of free space (8.85 pF/m). In the real case when an analysis is performed a dielectric is inserted between plates and generates voltage decrease. The capacitance in this case increases and if a saturation of the space between plates is considered, the capacitance raises with an a-dimensional factor $\mathcal{E}_r$, the dielectric constant of the material submitted (Agilent.com).

Capacitive technique is employed for evaluation of water in wheat (Berbert and Stenning, 1996), water and bulk density in safflower (Sacilik et al. 2007), ripening of banana fruits (Soltani, 2005). Afzal et al 2010 estimated leaf moisture content by measuring the dielectric constant of leaf with the variation of capacitance by employing a capacitive sensors in five different types of crops. The dielectric constant of water at room temperature is 80 greater than that of air or solid, 1 and 2-5 respectively. According to their results, the capacitance was affected by the amount of ions and the thickness of the leaf. Campbell at al. (2005) developed a capacitive system for monitoring bees passing troughs a tunnel that was able to recognize between entering and exiting bees and provide information on the size and speed of each bee. They used a ring sensor which has small electrodes respect to a parallel plate sensor and allow a decreased size and precisely position during manufacturing.

Jarimopas et al. (2005) designed an electronic device with a cylindrical capacitive sensor to select vegetables and fruits by volume. Thirty samples were used to calibrate the device and a very good correlation was obtained compared to the water displacement method. Considering watermelons, large cucumbers, wax gourds and guavas were obtained the subsequently R^2 0.999, 0.957, 0.999 and 0.99. Ragni et al. (2006, 2008) used a simple dielectric technique based on a sine wave radio frequency oscillator with a parallel plate capacitor probe to determine the quality of eggs during storage.

Time-Domain Reflectometry method

In the 1980s a new technique, with a high accuracy within a few percent of error was developed for the dielectric food properties assessment and is called Time Domain Reflectometry (TDR) (Afsar et al. 1986).

Time domain spectroscopy utilizes the reflection characteristics of the material under test to compute the dielectric properties. The TDR is a technique based on the generation of an electromagnetic signal and the time-domain analysis of the reflected signal from a generic load (sample). The instrumental chain setup is made of an electric step generator and an oscilloscope for the digital sampling. In this way, an electromagnetic pulse is propagated along the transmission line. The reflected and the transmitted signal are shown on the TDR

oscilloscope. TDR reveals the characteristic impedance of the line and shows the location and the type (resistive, inductive or capacitive) of each discontinuities along the line.

The transmission line consists of a continuous structure of resistors, inductors, and capacitors. Assuming that the line has an infinite length and characteristic, L (inductance), R (resistance), G (conductance) and C (capacitance) are defined per unit of length:

$$Z_{in} = Z_0 \sqrt{\frac{R + j\omega L}{G + j\omega C}}$$

Where Z0 is the characteristic impedance of the line and ω is the frequency of the applied voltage. The impedance is a physical magnitude vector that represents the dipole strength of opposition to an alternating electric current passage. The impedance is expressed as complex number and it takes into account the phenomena of electricity consumption and accumulation of electromagnetic energy.

The impedance is described mathematically by a complex number whose real part represents the dissipative phenomenon and corresponds to the resistance (R); the imaginary part, said reactance (X) is associated with the phenomena of energy accumulation.

$$Z = R + jX$$

A voltage supplied by the generator will require a finite time to walk the line up at the point x. The phase of the voltage that remains along the line will result in a delay with respect to the generator for an amount of β per unit length.

The TDR technique requires a small sample size and homogeneous substances to be analyzed and it is an excellent tool for advanced research on the interaction of electromagnetic energy over a wide range of frequency, despite the high cost (Mashimo et al. 1987; Ohlsson et al. 1974).

TDR was employed for the assessment of soil water content and salinity (Topp et al.,1982; Dalton and Van Genuchten, 1986; Noborio, 2001) and for dielectric permittivity and conductivity measurements of different kinds of liquids such as alcohols (Fellner-Feldegg,

1968), carbohydrate solutions (Van Loon et al., 1995), micro-emulsions (Nozaki and Bose, 1990) and various materials (Pettinelli and Cereti, 2002). Puranik et al. (1991) investigated the dielectric properties of honey-water mixture by using TDR technique in the frequency range 10 MHz-10 GHz at 25°C. Ragni et al. (2012) assessed the water content of EVOO and characterized different content of fatty acids alkyl esters of EVOO (Berardinelli et al., 2014) by using time domain reflectometry technique. TDR technique was able to predict very small water quantities in oil with R^2 value up to 0.984 and a root mean square error of prediction of about 55 mg of water/kg of oil.

Cavity perturbation technique

The cavity perturbation technique is one of the most commonly used techniques for measuring the dielectric properties of homogenous food materials because of its simplicity, ease of data reduction, accuracy, and high temperature capability (Venkatesh and Raghavan, 2005; Sucher and Fox 1963; de Loor and Meijboom 1966; Bengtsson and Risman 1971; Metaxas and Meredith 1983). The technique is also well suited to low-loss materials. It is based on the shift in resonant frequency and the change in absorption characteristic of a tuned resonant cavity due to insertion of a sample of target material. Changes in the center frequency and width due to insertion of the sample, provide information to calculate the dielectric loss. The resonant cavities can be designed in two mode of propagation of the electromagnetic fields, the transverse magnetic (TM) and the transverse electric (TE) which is based on the shift in resonant frequency and the change in absorption characteristic of a tuned resonant cavity. Changes in the center frequency and width due to the insertion of the sample provide information useful to calculate the dielectric constant while changes in the Q-factor are used to estimate the loss factor. The size of the cavity must be designed according to the frequency of interest, higher frequency need smaller cavity. The size of cavity must be designed for the frequency of interest taking into account that the relationship is inverse. It is quite reasonable that each cavity need a calibration, but after that permittivity data of different samples can be rapidly determined. Sample preparation is relatively easy, and the permittivities of a large number of samples can be determined in a short time.

This method can be used to determine the dielectric properties of many agri-food products over a wide range of frequencies, temperatures and compositions (Bengtsson and Risman 1971; Ohlsson and Bengtsson 1975; Venkatesh 1996). The cavity perturbation method was used to investigate dielectric properties of supersaturated a-D-glucose aqueous solutions (45-56% w/w) at 2.45 GHz from 25 to 80°C. Liao et al. (2001) reported the measurement details and the perturbation equations adapted for dielectric constant and loss factor calculation. Moreover Sharma and Prasad (2002) measured the dielectric properties of garlic at selected levels of moisture by using cavity perturbation in the temperature range 35-75°C. The authors determined the transmission characteristic by Hewlett-Packard 5410B Network Analyzer and S-parameter test set (HP 1992) combination.

Open-ended coaxial probe technique

The open ended coaxial probe method can be described as a modification of the transmission line method which calculates from the phase and amplitude of the reflected signal at the end of an open or ended line directly inserted into the sample. Care must be exercised with this technique because errors are introduced at both very low frequencies and very high frequencies, as well as at low values of dielectric constant and loss factor. Interpretation for lower loss materials, such as fats and oils, must be treated with caution.
Nelson et al. (2007) considered the external part and the internal tissue of four cultivars of watermelons over a range of maturities by using an open-ended coaxial line probe and an impedance analyzer. Dielectric constant and loss factor were provided from 10 MHz to 1.8 GHz frequency range improving permittivity data. The analysis of the two main parameter showed the dominance of ionic conduction at lower frequencies and dipolar losses at higher frequencies. A correlation between soluble solids content and dielectric constant and loss factor was obtained with and R^2 of 0.932.
Particularly for liquid and semi-solid food materials open ended coaxial-line probes have been used for permittivity measurements (Grant et al. 1989; Blackham and Pollard 1997), in particular for fresh fruit and vegetables investigation (Ohlsson et al. 1974; Nelson et al. 1994).

Such technique is not free of errors, in fact density variation of the material, air gaps or bubbles between the end of the coaxial probe and the sample can compromise the results. Moreover this tool is not suitable for granular and pulverized samples (Venkatesh and Raghavan 2005). This technique can be efficient in the frequency range from 915 to 2450 MHz (for materials with loss factor greater than 1), but care should be given to errors possible at very low or very high frequencies (Sheen and Woodhead 1999).

Dielectric properties of fruit commodities and four associated insect pests were measured with an open ended coaxial probe device in the frequency range 1-1800 MHz between 20 and 60°C of temperature (Wang et al. 2003).

Ragni et al. (2007) investigated the quality parameters of shell eggs during storage by using an open-ended coaxial probe measurement technique. The frequency explored ranged from 10 to 1800 MHz. R^2 values up to 0.985 and 0.980 were obtained. Low coefficient of determination were determined for yolk index, thick albumen height, and Haugh unit. Moreover the authors investigated the dielectric parameter of fresh hen in the frequency range 20-1800 MHz, on thick albumen and yolk of eggs after 1, 2, 4, 8 and 15 days of storage at room temperature. Dielectric constant and loss factor of yolk raised with the storage time, until to reach a maximum after 15 days of storage (22%).

Free space transmission technique

Free-space transmission technique is a non-destructive and non-contact measuring method (Redheffer, 1966). It does not require special sample preparation, therefore, it is particularly suitable for materials at high temperatures and for inhomogeneous dielectrics (Kraszeski 1980, 1996). In addition, it may be easily implemented in industrial applications for continuous monitoring and control. In a free space transmission technique, a sample is placed between a transmitting antenna and a receiving antenna, and the attenuation and phase shift of the signal are measured (Venkatesh and Raghavan 2005). The results can be used to compute the material dielectric properties. Accurate measurement of the permittivity over a wide range of frequencies can be achieved by free-space techniques. In most systems, the accuracy of dielectric constant and loss factor depends mainly on the performance of the measuring system and on the validity of the equations used for the calculation. The usual

assumption made for this technique is that a uniform plane wave is normally incident on the flat surface of a homogenous material, and that the planar sample has infinite extent laterally, so that diffraction effects at the edges of the sample can be neglected. To enhance the measurement accuracy, special attention must be paid to the choice of the radiating elements, the design of the sample older, the sample geometry and location between the two radiating elements. To avoid disturbances resulting from multiple reflections between samples and antennas and problem caused by diffraction of edges for free space measurements an attenuation through the sample layer should be maintained (Trabelsi et al. 1998). Trabelsi et al. (1997) accounted for multiple reflections, mismatches and diffraction effects at the edges of the sample as the main sources of errors. In this way special attention must be paid to choice of radiating elements, design of sample holder and sample geometry. A free space measurements with a vector analyzer were used to obtain microwave dielectric properties of wheat and corn. The rectangular samples holders were placed between the horn antennas and a similar radiating element (Trabelsi et al., 1997).

Only a brief review, respect the amount of literature available, of the main work conducted on food material by using the free space transmission technique is subsequently reported.

A free space transmission system, including a vector network analyser, horn/lens antennas, holder for grain and oilseed samples was used for measures reliable permittivity data for wheat, shelled corn and soybeans (Trabelsi et al., 2002). Dielectric constant and loss factor for wheat, corn and soybeans are listed for reference at frequencies from 5 to 17 GHz at different densities and moisture levels at about 23 °C.

Free space transmission technique was applied to measure the moisture content of powdered food, such as wheat flour, milk powder and coffee powder. In frequency range from 1 to 15 GHz the microwave attenuation, phase shift and moisture density were measured and correlated with correlation coefficient greater than 0.91 (Kim et al., 2006).

The waste of several agricultural products, such as rice husk, rice straw, and kenaf were studied in the frequency range of 2.2 to 3.3 GHz. The dielectric properties were determine by using microwave free-space transmission measurements technique. From the result obtained, rice husk was found to possess a high dielectric constant compared to rice straw and kenaf, due to the natural properties of rice husk. The large surface area of rice straw has provided the ability to absorb more electromagnetic signal (Wee et al. 2009) .

Micro-strip transmission line

The effective permittivity, represented by a combination of the substrate permittivity and the permittivity of the material above the line, of a micro-strip transmission line is strongly dependent on the permittivity of the region above the line (Venkatesh and Raghavan 2005). This effect has been utilized in implementing microwave circuits and to a lesser extent on the investigation of dielectric permittivity. Furthermore, the measurement of effective permittivity is relatively straightforward, and is well suited for implementation in industrial equipment. Such system could be based on determining the effective permittivity of a micro-strip line covered by an unknown dielectric substance (Datta et al., 1995). Unfortunately its applicability to food and agricultural material processing would still be an anticipatory issue at this stage (Venkatesh and Raghavan 2005).

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2. Extra virgin olive oil (EVOO)


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A capacitive technique to assess water content in extra virgin olive oils

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The evidence reported in this chapter are also object of the reported scientific paper.

Extra virgin olive oil (EVOO) is one of the main Italian product with international recognition. Water content is one of the principal parameters for the quality assessment of this product. Usually commercial extra virgin olive oils (EVOO) ranges from 0.3 to 2.0 g of water/kg of oil. The production process, in particular extraction and filtration procedures, can affects moisture content in EVOO (Cerretani et al., 2010; Lozano-Sánchez et al., 2010). Water in oil is evenly dispersed as micro drops (Petrakis, 2006). The dispersion, in the form of fine or micro emulsions, can be stabilized by aggregation and dissolution of polar substances such as salts, free acids, di-glycerides, phospholipids, alcohols and phenols (Cerretani et al., 2008). Moreover water content is correlated with taste characteristic, such as pungency, bitterness and can play an important role in stability and quality preservation during storage (Lercker et al., 1994; Fregapane et al., 2006; Ambrosone et al., 2007).

The "International Olive Oil Council" (IOOC, 2009) and the "Codex Alimentarius" (CODEX STAN, 1981) recommended moisture values not higher than 0.2% (kg/kg).

For moisture determination the most commonly method in EVOO is the oven method which is based on the loss of weight upon a drying treatment (ISO 662, 1998) (Gradinarsky et al. 2006; Kraszewski et al, 1997). Another tool used to determine water content is Karl Fisher titration (AOAC, 1998). Furthermore moisture determination is rarely absolute moisture

estimating and particularly in EVOO volatile compounds can introduce errors in this kind of moisture estimation system. The traditional methods are destructive, time consuming, require large amount of reagents and are not economically advantageous.

Dielectric techniques can be proposed for such quality parameters assessment. The most widely used are near infrared (NIR) (Armenta et al, 2010) and Fourier transform infrared (FT-IR) spectroscopy (Vlachos et al, 2006; Nunes et al., 2009; Cerretani et al. 2010), often in association with chemiometric statistical analysis such as partial least square regression (PLS). The determination of water content with NIR techniques have been tested on olive fruits (Jimenez et al., 2000), olive pomace (Muik et al., 2004) and in olive oils in production processes (Bendini et al., 2007), but these conditions exhibit a water content much higher than that of commercial EVOO. According to Bendini et al. (2007), R^2 values of 0.913 (RMSE= 1.29%) was obtained for the estimation of moisture content in olive oil samples characterized by a moisture content ranging from 45-73%. Commercial oil analyzers based on NIR technology have been employed to determine moisture content in olive fruit, paste and pomace (Armenta et al., 2010).

Water content ranging from 290 to 1402 mg/kg oil was predicted by FT-IR attenuated total reflectance (ATR) spectroscopy with a R^2 of 0.89 (Cerretani et al, 2010). Better performance was obtained by ^{31}P-NMR spectroscopy in olive oils where the same moisture content (ranging from 204-769 mg/kg oil) was determined with an R^2 value up to 0.98 (Hatzakis and Dais, 2008). The time domain reflectometry (TDR) achieved similar results (R^2 = 0.984) on samples of EVOO with higher water content ranging from 714-2008 mg of water/kg of oil (Ragni et al, 2012). Terahertz time-domain spectroscopy (THz-TDS) has also been used to investigate the water content in synthetic oils (Gorenflo et al., 2006). The goodness of prediction, expressed by the relative root mean square error (RMSE), was up to 24 mg/kg oil in samples where the water content ranged from 430-3280 mg/kg oil.

NMR, FT-IR, TDR and THz-TDS are all expensive techniques which require time and a high level of competence for data manipulation. Capacitive methods could be a rapid and efficient tool as previously reported in this thesis in the dielectric technique paragraph.

A simple capacitive technique based on a discontinued variable capacitor as a probe together with basic statistical analysis is proposed. The same commercial EVOO was tested for moisture content determination and further exploration involved several EVOO samples

to evaluate the prediction for different oils composition. In-fact previously Rudan-Tasik and Klofutar (1999) and Lizhi et al. (2008), revealed that fatty acids composition can affect dielectric properties of edible oils, in particular for the unsaturation level.

The capacitive technique could be a valuable instrument to monitor the filtration process or to perform an approximate classification of the water content in commercial EVOO oil, where the fatty acids composition greatly varies from oil to oil.

2.1 Material and methods

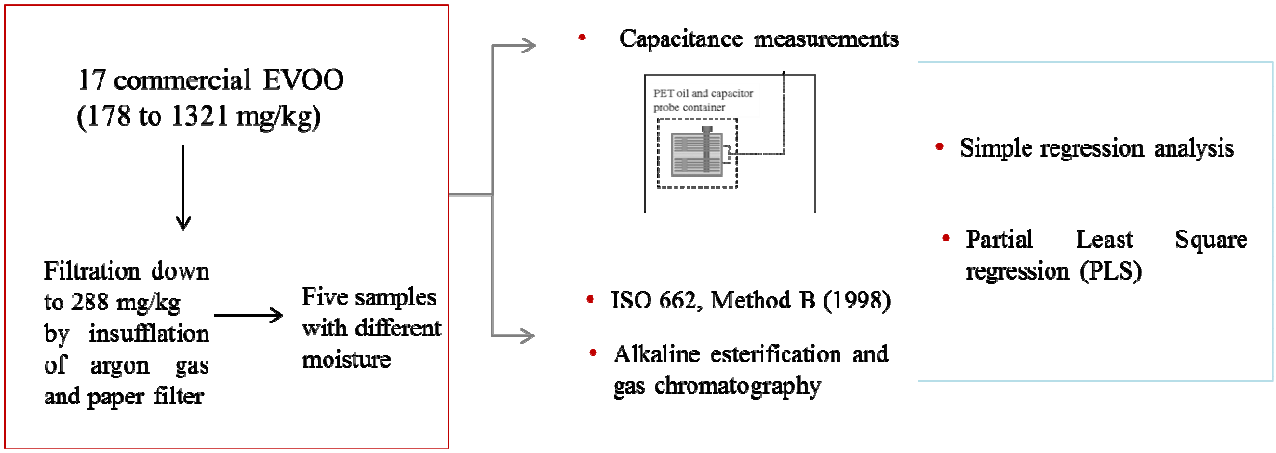

Fig 3. Experimental plan extra virgin olive oil characterized by a moisture content ranging from 178 to 1321 mg/kg.

To assess the water content of an oil matrix seventeen extra virgin olive oils ranging from 178 to 1321 mg/kg oil were selected, as shown by the experimental plan in figure 3. Furthermore to assess the influence of moisture only, the oil with the maximum water content (1321 mg/kg oil) was filtered down to 288 mg/kg by insufflation of argon gas (12 l/min) for 3 h by using the patented method number WO 2009/107096 A2 (Cerretani et al., 2009) and filtrated by gravity with paper sheets (Filter papers 55 mm, Whatman) to reach the minimum content of water. Five samples with different percentages of non-filtered and filtered oils were prepared to obtain oils with intermediate water content.

The amount of water was determined according to the standard ISO 662, Method B (1998), in triplicate by drying 10 g of oil in an oven. This gravimetric method overestimates the water content, including the volatile compounds, but the error should be considered minor and acceptable since they do not exceed 50 mg/kg oil in EVOO (Angerosa et al., 2004).

The fatty acid percentage was determined as the principal oil constituents. For this determination, alkaline esterification producing fatty acids methyl esters and followed by gas chromatography (Bendini et al., 2006) were used. Measurements were carried out in triplicate. The peak retention time was compared to those of the GLC 463 FAME standard mixture (Nu-Chek, Elysian, MN) to identify the peaks. Fatty acid were grouped in the three conventional classes according to their degree of unsaturation: saturated (SFA), monounsaturated (MUFA) and polyunsaturated (PUFA).

Parallel plate capacitor

To perform the dielectric oils behavior capacitance measurements were conducted by using a variable capacitor as a probe together with a LCR meter (LCR-8101G, GW-Instek, Good Will Instrument Co. Ltd, Taiwan) (Fig. 4).

Fig. 4 Instrumental chain and parallel plate capacitor with mobile and fixed plates.

The capacitor has fixed and mobile armatures consist of 12 and 10 plates, respectively and a maximum rated capacitance of 470 pF in air. The capacitance can be manually changed by the rotation of the axis which involves modification in the total plate surface of the capacitor. The probe container was made of PET with the following dimensions: 82 mm (length), 77 mm (width) and 55 mm (high). The container housing the capacitor was filled with 150 g of oil to fully cover the plate armatures, as shown in figure 5.

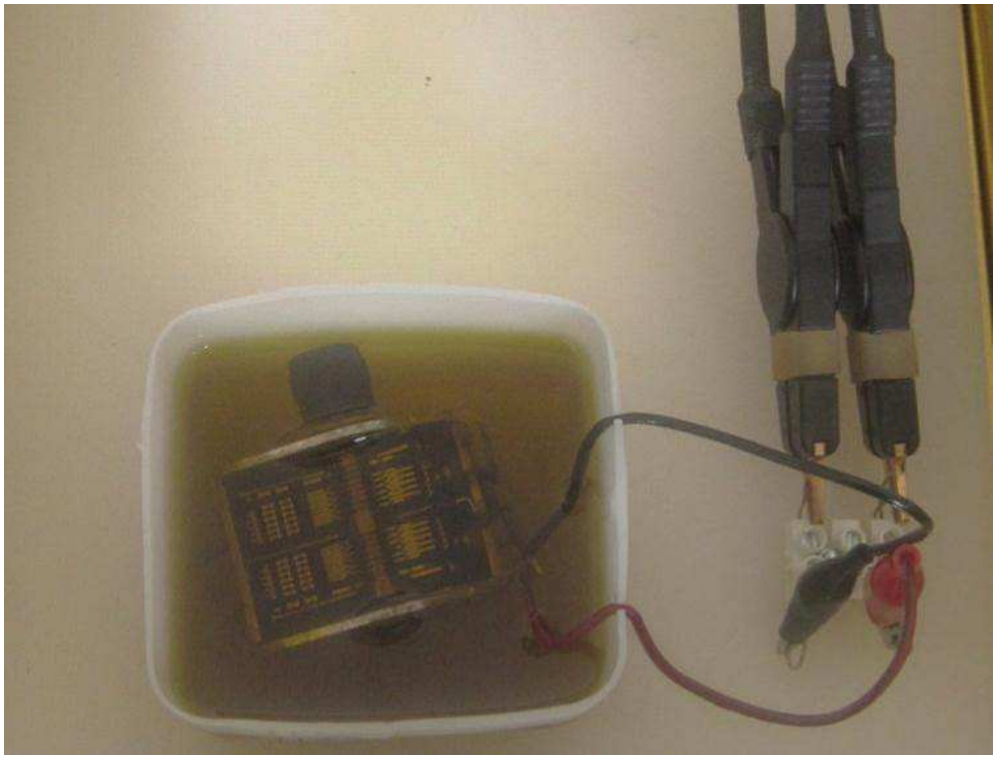

Fig. 5 Parallel plate capacitor covered by EVOO sample.

To avoid electromagnetic interference the container with capacitor and oil was placed in a metal box. In order to shield the retention of bubbles during the oil filling, measurements were made after the rotation of the plates. Rotation of the mobile plate armature with respect to the fixed one also allowed to easily remove the oil between subsequent tests by washing the probe with n-hexane. Measurements of capacitance were carried out at the same temperature of 20°C at frequencies of 500 Hz, 2 kHz, 8 kHz, 32 kHz, 128 kHz and 512 kHz, for the five oil samples with different moisture contents. Each measurement was the average of 50 subsequent measurements and always conducted in triplicate; the averaging process required about 20 s. The voltage was set to 100 mV. Sweep measurements were carried out from 100 Hz to 10 kHz (steps 49.5 Hz) with the capacitor empty and filled with the oil having the maximum water content in order to consider some limits related to the behavior of the system and the consequent oil dielectric constant determination. The capacitance of a parallel plate capacitor (C, in Farads) can be calculated according to the following formula:

$$C = \varepsilon_r \varepsilon_0 \frac{A}{d}$$

where $\mathcal{E}r$ is the relative dielectric constant of the material, $\mathcal{E}_0$ is the dielectric constant of vacuum (8.85 x 10^{-12} F/m), *A* is the area of the plates (m^2), *d* is the distance between the plates (m). If *A* (area) and *d* (distance) remain constant, $\mathcal{E}r$ can be roughly calculated by dividing the capacitance with the material by the capacitance with air. This is a reasonable method to determine the static capacitance with direct current, but it becomes less appropriate with alternating current, because the real capacitor and all the instrumental chain have a behavior that is strictly frequency dependent (Ragni et al., 2013). Some measurements of impedance with air and oil were also made to assess which part of it can be explained by the capacitive reactance. The impedance *Z* contains three different contributors, namely ohmic resistance, reactive capacitance *Xc* and reactive inductance *Xl*. In a real capacitor *Xc* explains most part of the impedance *Z* and can be calculated by:

$$X_c = \frac{1}{2\pi fC}$$

where *f* is the frequency (Hz), and *C*, is the capacitance (F).

Statistical analysis

Filtered oil mixtures

The correlation between capacitance and water were investigated by using simple linear regression. The two frequencies which give the best results in term of coefficient of determination and maximum variation of capacitance between samples were then used for the subsequent measurements on the 17 EVOO.

Commercial oil

Simple regression analysis was performed to investigate the correlation between capacitance, water and fatty acids content of the different EVOO samples. Furthermore calibration and cross validation (leave-one-out method) models were built. The coefficient of determination and the p-level values were reported. The root mean square error (RMSEC) was obtained to assess the prediction power of the models. Cross validation was

performed for the seventeen EVOO samples to predict the water content by using the capacitance values.

2.2 Results and discussion

The extra virgin olive oil with the high water content, 1321 mg/kg was filtered to reduced moisture down to 288 mg/kg oil. Filtered and non-filtered oil were used to obtain five samples with different moisture content of 1321 ± 31, 920 ± 120, 753 ± 24, 513 ± 7.5 and 288 ± 54 mg/kg oil. The mixture were obtained to test only the moisture influence as consequence of a constant chemical composition preserved. Furthermore 17 EVOO commercial samples were selected with a moisture ranging from 178 mg/kg to 1321 mg/kg with a minimum and maximum differences of 10 mg/kg and 266 mg/kg.

The table 1 shows the fatty acid composition and put on light differences between SFA, MUFA and PUFA up to 66.58%, 83.19% and 23.48%, respectively.

Fatty Acids	EVOO											
	1	2	3	4	5	6	7	8	9	10	11	12
C16:0	10.41 (0.40)	10.49 (0.16)	14.10 (0.04)	11.07 (1.16)	11.67 (0.03)	12.61 (0.21)	12.43 (1.03)	10.98 (0.02)	12.57 (0.81)	12.17 (0.22)	12.48 (0.04)	15.22 (0.29)
C16:1 n-9	0.12 (0.00)	0.14 (0.02)	0.15 (0.01)	0.09 (0.01)	0.12 (0.00)	0.13 (0.02)	0.12 (0.02)	0.14 (0.02)	0.14 (0.02)	0.12 (0.02)	0.08 (0.06)	0.13 (0.02)
C16:1 n-7	0.74 (0.00)	0.70 (0.01)	1.31 (0.02)	0.83 (0.07)	0.89 (0.00)	1.08 (0.04)	1.18 (0.14)	0.73 (0.01)	1.11 (0.12)	1.03 (0.04)	0.80 (0.02)	1.10 (0.03)
C17:0	0.05 (0.00)	0.06 (0.01)	0.09 (0.01)	0.05 (0.00)	0.06 (0.02)	0.08 (0.00)	0.08 (0.01)	0.10 (0.01)	0.08 (0.00)	0.07 (0.00)	0.01 (0.01)	0.13 (0.02)
C17:1	0.08 (0.02)	0.13 (0.01)	0.17 (0.02)	0.10 (0.01)	0.10 (0.01)	0.12 (0.00)	0.11 (0.00)	0.18 (0.00)	0.16 (0.01)	0.12 (0.00)	0.05 (0.05)	0.19 (0.00)
C18:0	3.37 (0.12)	3.08 (0.05)	2.24 (0.03)	3.21 (0.06)	2.86 (0.02)	2.76 (0.02)	2.69 (0.06)	3.08 (0.05)	2.51 (0.05)	3.04 (0.01)	2.67 (0.07)	2.52 (0.00)
C18:1 n-9	79.11 (1.77)	75.85 (0.18)	67.96 (0.04)	75.17 (1.47)	74.36 (0.09)	70.45 (0.43)	68.81 (1.22)	73.54 (0.07)	70.58 (0.79)	72.96 (0.54)	71.24 (0.13)	64.25 (0.50)
C18:1 n-7	2.32 (0.14)	2.25 (0.09)	3.17 (0.03)	2.37 (0.33)	2.40 (0.00)	2.55 (0.15)	2.59 (0.19)	2.41 (0.01)	2.84 (0.10)	2.62 (0.09)	2.79 (0.03)	2.81 (0.04)
C18:2	2.33 (2.41)	5.71 (0.01)	9.30 (0.01)	5.45 (0.00)	6.02 (0.04)	8.62 (0.00)	10.39 (0.06)	6.90 (0.02)	8.21 (0.06)	6.25 (0.03)	7.67 (0.06)	11.85 (0.03)
C20:0	0.40 (0.03)	0.40 (0.03)	0.38 (0.01)	0.45 (0.04)	0.39 (0.01)	0.44 (0.02)	0.47 (0.02)	0.44 (0.01)	0.44 (0.08)	0.41 (0.04)	0.43 (0.04)	0.40 (0.03)
C18:3 n-3	0.62 (0.01)	0.68 (0.02)	0.69 (0.02)	0.68 (0.01)	0.67 (0.01)	0.73 (0.02)	0.70 (0.04)	0.74 (0.00)	0.64 (0.02)	0.71 (0.00)	0.73 (0.05)	0.72 (0.00)
C20:1	0.26 (0.01)	0.28 (0.01)	0.31 (0.04)	0.26 (0.05)	0.26 (0.00)	0.30 (0.03)	0.29 (0.05)	0.31 (0.01)	0.30 (0.03)	0.26 (0.01)	0.34 (0.02)	0.26 (0.01)
C22:0	0.13 (0.02)	0.11 (0.00)	0.13 (0.01)	0.13 (0.04)	0.13 (0.01)	0.14 (0.01)	0.14 (0.04)	0.11 (0.05)	0.15 (0.05)	0.17 (0.05)	0.13 (0.02)	0.10 (0.01)
C24:0	0.06 (0.04)	0.11 (0.03)	0.00 (0.00)	0.13 (0.08)	0.07 (0.03)	0.00 (0.00)	0.00 (0.00)	0.34 (0.00)	0.28 (0.01)	0.09 (0.04)	0.00 (0.00)	0.31 (0.10)
SFA	14.42	14.25	16.94	15.04	15.18	16.02	15.81	15.05	16.02	15.93	16.02	18.69
MUFA	82.63	79.35	73.07	78.83	78.12	74.63	73.10	77.30	75.13	77.11	75.30	68.75
PUFA	2.95	6.39	9.99	6.13	6.69	9.35	11.10	7.64	8.85	6.96	8.11	12.57

Table 1. Values of SFA (satured fatty acid), MUFA (mono- unsatured fatty acid) and PUFA (poli- unsatured fatty acids).

Data provided are in accordance with literature and legal limits (Anonymous, 2011) for EVOO category.

Table 2 were summarizes the results of the linear regression analysis conducted between capacitance and water content of the five oil samples characterized by the same fatty acids composition.

Frequency (kHz)	R^2	ΔCabs. (pF)	ΔC%	RMSE (mg/kg of oil)
0.5	0.895	8.350	0.605	111
2	0.959	8.390	0.599	48
8	0.962	7.085	0.536	118
32	0.959	6.030	0.450	73
128	0.781	3.047	0.227	170
512	0.784	6.710	0.500	169

Table. 2 W, water content (mg/kg oil); C, capacitance (pF); ΔCabs, difference between the highest and the lowest capacitance measured values (pF); ΔC%, ratio between ΔCabs and the lowest capacitance value x100; RMSE, root mean square error.

Capacitance and water show a general linear trend for all the frequency explored (500 Hz and 512 kHz) with good determination coefficient values which they ranged from 0.781 to 0.962. The related root mean square error (RMSEC) ranged from 48 mg/kg oil to 170 mg/kg oil.

Considering these results were selected two frequency, in particular 2 and 8 kHz, to measure the capacitance of all EVOO samples.

The impedance (Z) and capacitive reactance (Xc) for the probe with and without oil were calculated and reported for different frequencies in table 3.

Frequency (Hz)	Air		Oil		Z/Xc Air	Z/Xc Oil
	Z (Ohm)	Xc (Ohm)	Z (Ohm)	Xc (Ohm)		
500	693130	693151	235237	235228	0.99997	1.00004
2000	173412	173413	58908	58926	0.99999	0.99970
8000	43389	43389	14806	14806	0.99999	1.00002
32000	10854	10854	3691	3691	1.00000	1.00001
128000	2716	2716	926	926	0.99994	1.00005
512000	678	678	230	230	1.00018	0.99997

Table. 3 Impedance and reactive capacitance of the probe in air and with oil with a water content of 1321 mg/kg oil (n.12, in Tables 1 and 2), at different frequencies. Z, impedance; Xc, capacitive reactance.

As can be see Xc well describe the impedance with a ratio Z/Xc from 0.99997 to 1.00018.
The capacitance and water content of the 17 commercial EVOO were reported in figures 6 and 7, while predicted and observed values are shown in figures 8.
R^2 values of 0.804 and 0.818 were obtained for frequencies of 2 kHz and 8 kHz, respectively.

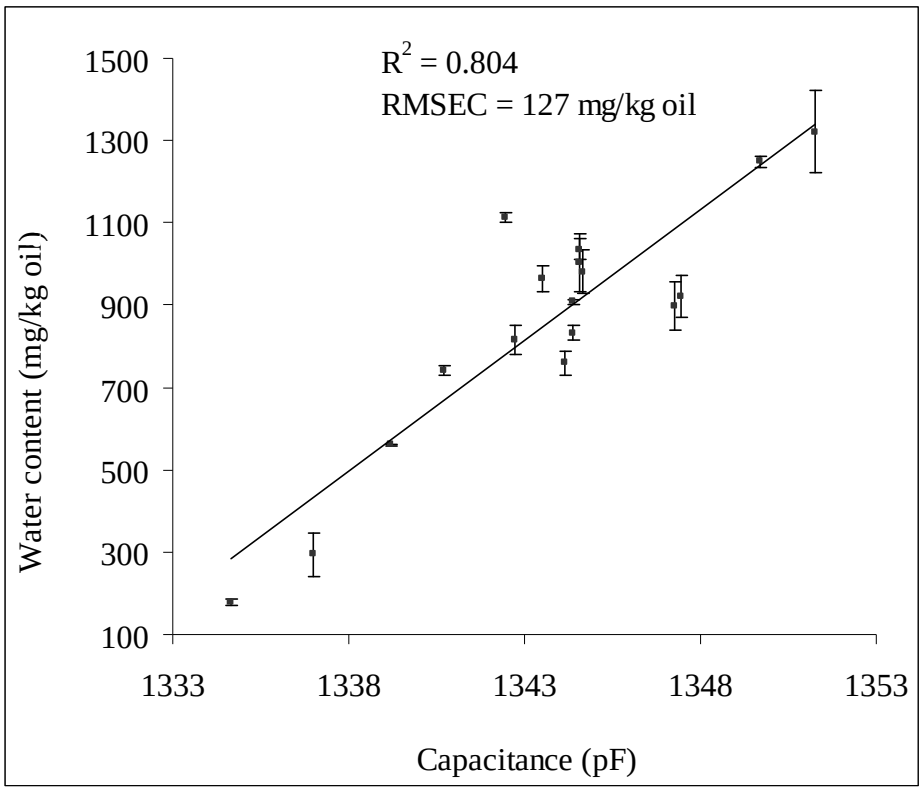

Fig. 6 Correlation between capacitance and water content for all oils at 2 kHz frequency.

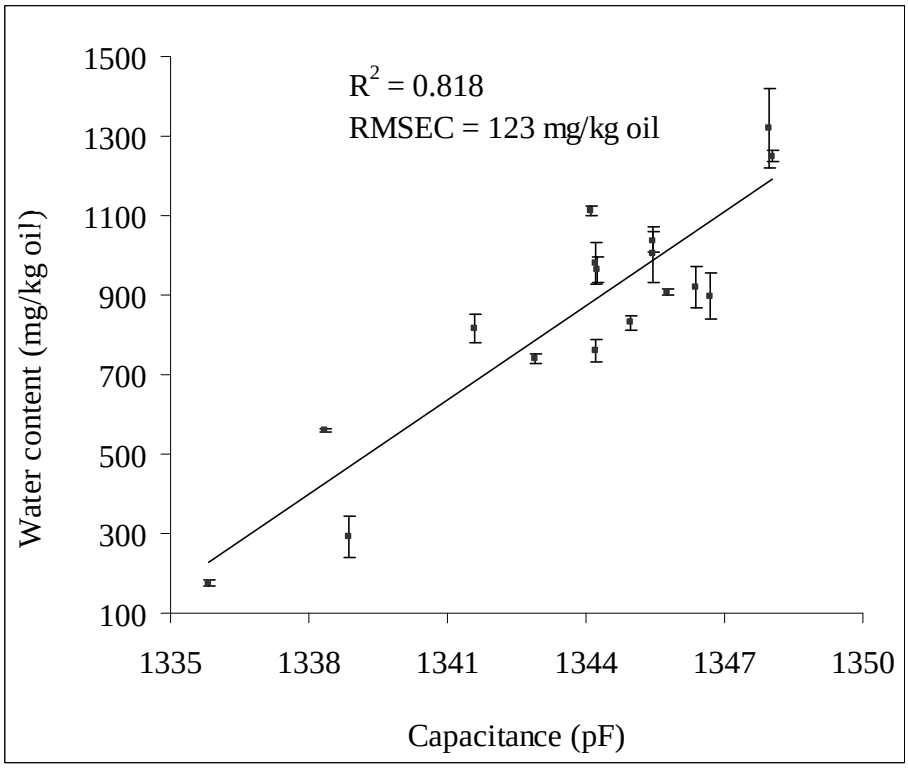

Fig. 7 Correlation between capacitance and water content for all oils at 8 kHz frequency.

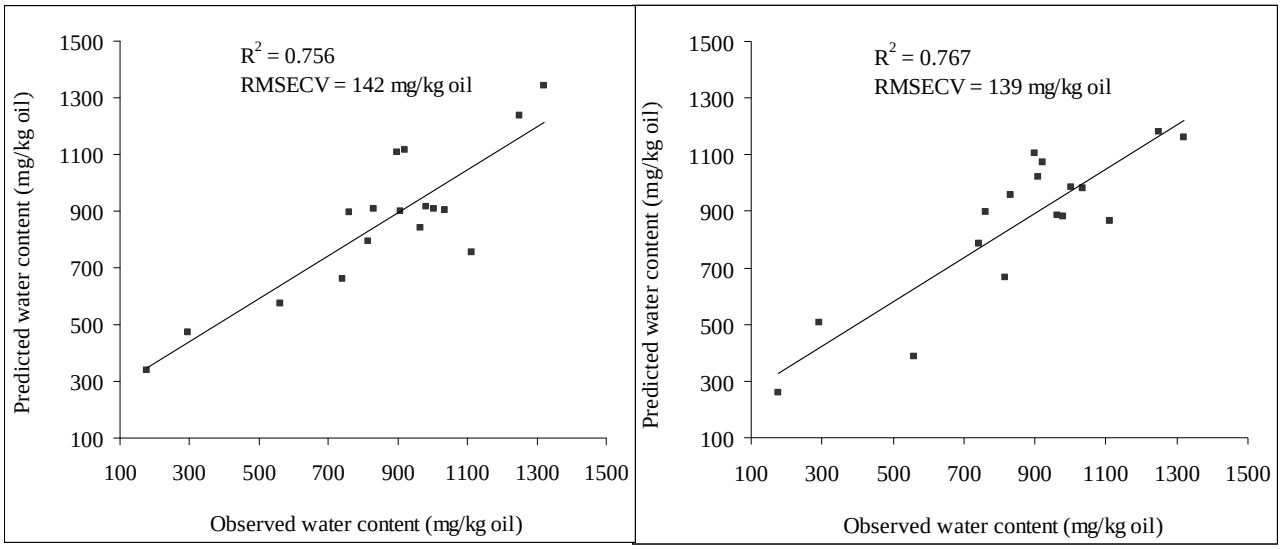

Fig. 8 Predict and observed values for the water content at 2 kHz and 8 KHz (cross validation).

The RMSEC was 127 mg/kg and 123 mg/kg oil, while RMSECV was 142 and 139 mg/kg for the two selected frequencies. The lower coefficient of determination compared to the obtained from the filtered oil are due to the different composition which involves in perturbation of the electrical information. Lizhi et al. (2008) measured the relative dielectric constant of some SFA (saturated fatty acids), MUFA (monounsaturated fatty acids) and PUFA (polyunsaturated fatty acids) in the range of frequency of 100 Hz to 1 MHz and it was roughly invariant up to a frequency of 100 KHz. The values ranged from 2.3 for palmitic to 2.5 for stearic acid. Although water has a dielectric constant so much higher than the fatty acids, the main contribute remain at conductivity level. However despite the little contribution, the different percentages of fatty acids in the matrix involve in changes in moisture retention. A linear correlation between capacitance and MUFA was obtained with a coefficient of correlation of 0.627 (Figure 10).

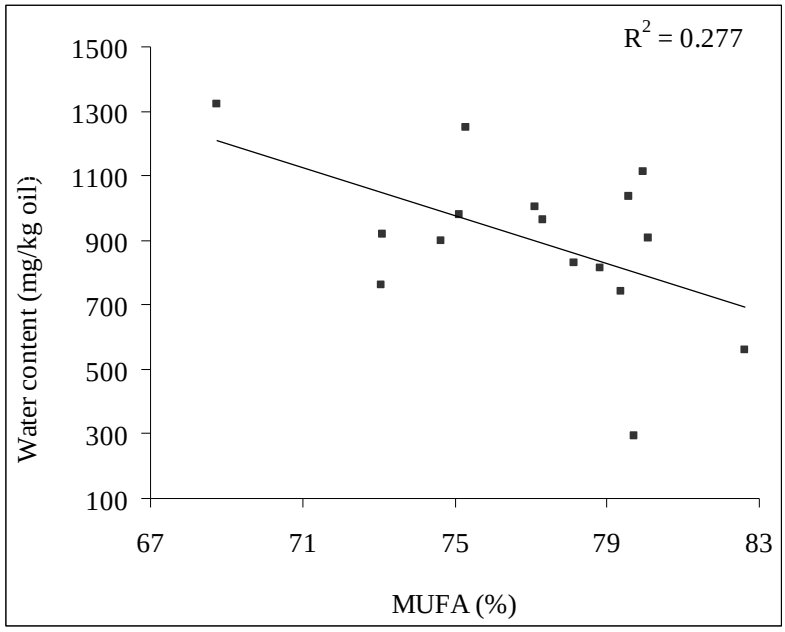

Fig. 9 Correlation between monounsaturated fatty acids (MUFA) and water content for all oils.

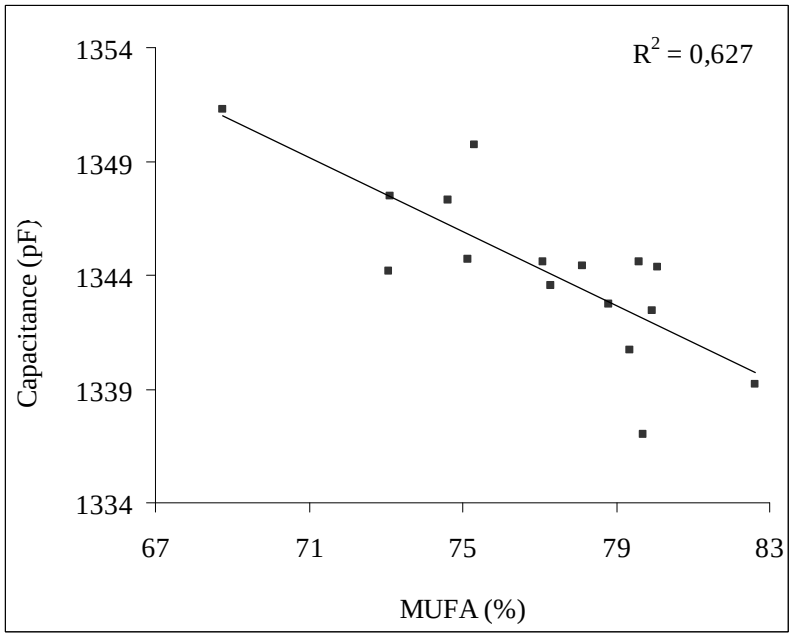

Fig. 10 Correlation between capacitance and monounsaturated fatty acids (MUFA) for all oils at 2 kHz frequency.

This probe did not allowed a dielectric constant calculation through the ratio of capacitance with and without oil at different frequencies. Several regions seems to affect the probe response where the capacitance drops to lower values compared to an ideal capacitor. The mentioned capacitor probe is very distant to an ideal capacitor, in particular it is a complex component characterized by a large metallic armature which show a specific behavior.

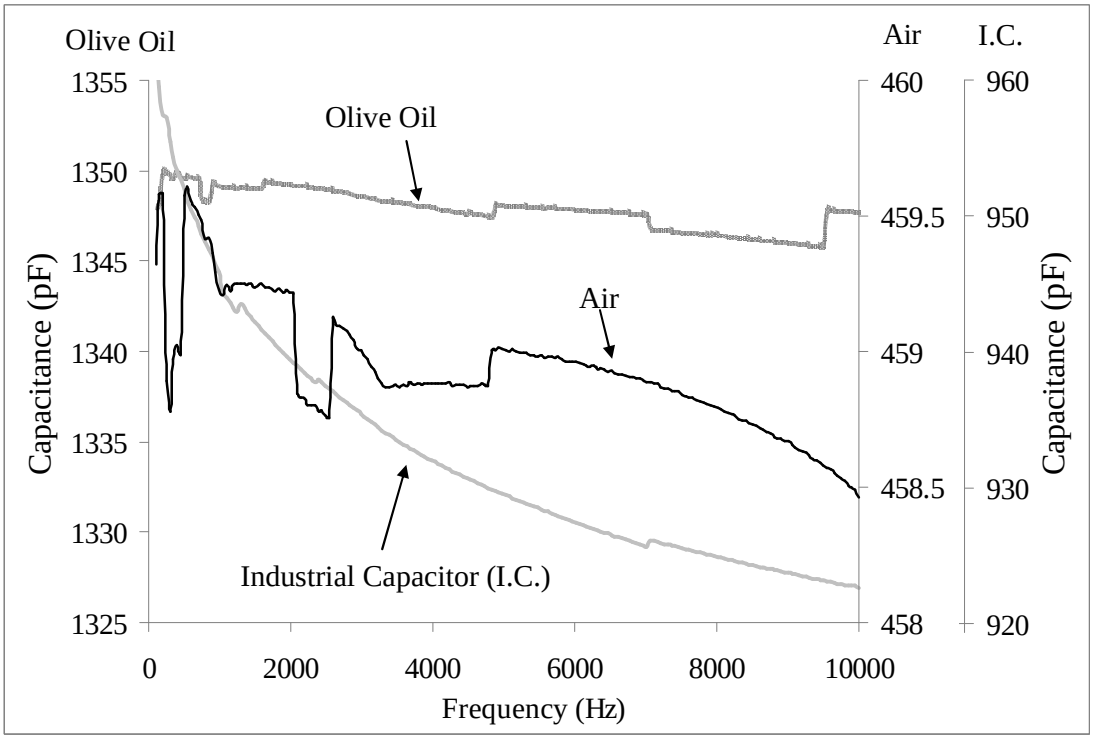

Fig. 11 Capacitance for the probe in air and with an oil having a water content of 1321 mg/Kg oil (n. 12, in Tables 1 and 2), together with an industrial capacitor having a rated capacitance of 1 nF, in the range 100 Hz to 10 kHz.

Antenna effects, reflections and resonances can occur at some frequencies when it is filled with a dielectric such as oil and at other frequency when it is filled with a different dielectric as air (as shown figure 11). For these reasons it can be possible only calculate an approximate relative dielectric constant of oil in the explored frequency range from 2.933 to 2.942. At certain frequency the variation of the relative dielectric constant and the capacitance variation due to different moisture content of the oil are the same (values between 0.227% and 0.605%).

2.3 Conclusion

A multiple parallel plate capacitor was taken into consideration for extremely low water content prediction of EVOO. A water content from 0.03% to 0.13% (kg/kg) can be predicted by using a simple linear regression with an R^2 values ranging from 0.781 to 0.962 for some explored frequencies range (RMSE up to 48 mg/kg for the best model).

Correlations between EVOO with different chemical composition was lower than the oil where only moisture content changed, with a maximum determination coefficient of 0.818.

This study showed that this system can be used to water content prediction if a precision, expressed as root mean square error, not higher than 142 mg/kg is requested. A maximum uncertainty of 50 mg/kg oil as to be added to consider possible contribution of volatile compounds.

Finally, a simple instrumental system demonstrates that is possible to measure voltage and current for the prediction of some chemical oils characteristic.

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3. Orange Juice

Study of a control methodology of orange juice evaporation by dielectric spectroscopy

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InsideFood Symposium, 9-12 April 2013, Leuven, Belgium

The subsequent work was presented as paper reported in the "InsideFood Symposium" congress issue as shown above. The research was carried out in the Institute of Food Engineering for Development Department of Food Technology, Polytechnic University of Valencia, Spain.

Orange juice is the most popular fruit juice with an estimated consumption of around 5 billion liters for year in the European Union (Brown et al, 2004). The challenge of the industrial sector of fruit juice is to obtain a stabilized product by preserving the unique combination of sensory attributes, such as colour, aroma, flavour and nutritional value of the fresh product.

The most common methods used to concentrate the orange juice are: Thermally Accelerated Short Time Evaporator (TASTE) and Waste Heat Evaporator (WHE).

The TASTE is able to pasteurize the juice inactivating the natural enzymes. In this heat exchanger, the juice is pumped through series of inter-stages in which the temperature increases under the effects of vapour. The stages inactivate organisms and stabilize microbiologically the product. At each stage, flash of vapour are distributed in the cones of the heather exchanger and evaporated the water from the juice. The liquid and vapour go out from the bottom and are separated in cyclone to allow the vapour to continue the evaporation process in the subsequent heater. Every heater is created to obtain the same amount of evaporation, because increasing concentration and viscosity and lowering the temperature require a higher exchange surface (Bates, 1984).

The WHE is another citrus processing machine similar to the TASTE and operates along the same basic principles. The evaporator is constructed as a multistage tubular element which communicates to each other. It is created to maximize the heat transfer surface to achieve a

rapid heat transfer and the effect can be implemented with low pressure. The Waste Heat Evaporator has the advantage of both reducing energy costs and heat pollution (US patent, 1989).

The complex part of the industrial plants is the control of the water evolution and the solid soluble level. The sugar level, measured in Brix degree, is one of the most important parameter for the monitoring of orange juice production process. Brix degree explains the percentages by weight of sugar in a solution. In this kind of production process the on-line control of the Brix degrees variation can be difficult as consequence of the low pressure and the big changes in the citrus juice. Barometers and spectrophotomer are the devices actually most often in use.

Both methods showed a low accuracy and do not ensure a right audit of the process that is useful to preserve the natural characteristic of the juice. The evaporation process requires a high level of accuracy in reason why little change in pressure and water content that both can involve in big change of the final product.

For this purpose an innovative control system employing a coaxial probe to check pressure loss and the correct transmission of heat was proposed. Appling this system the most important index of the evaporation process were monitored by detecting the compositional variation of the orange juice, with particular regard to soluble content.

Complex permittivity (ε_r) can enucleate properties of food through the interaction of electromagnetic fields (Castro-Giráldez et al, 2010a). At microwave frequency the main contribution to the loss spectra are the ion conductivity and dipole polarization (Castro-Giráldez et al, 2010b). In the orange juice there is a lot of sugar that also contributes to the dielectric spectra because sugar can make bonds with water. These bonds lead to a reduction of water mobility and a shift of relaxation frequency (Castro-Giráldez et al, 2010b). In this work the high content of solute amplifies this phenomenon that can allow us to distinguish the different state of concentration of citrus juice.

Considering the assumption above, the actually control system of the evaporation process can be improve. A powerful tool to control the quality of citrus juice based in dielectric spectroscopy, in the microwave range, is shown in this work. The aim of this research is quantify the water content and determine the soluble content of citrus juice in order to apply a sensor of electromagnetic fields in an industrial evaporator.

3.1 Material and methods

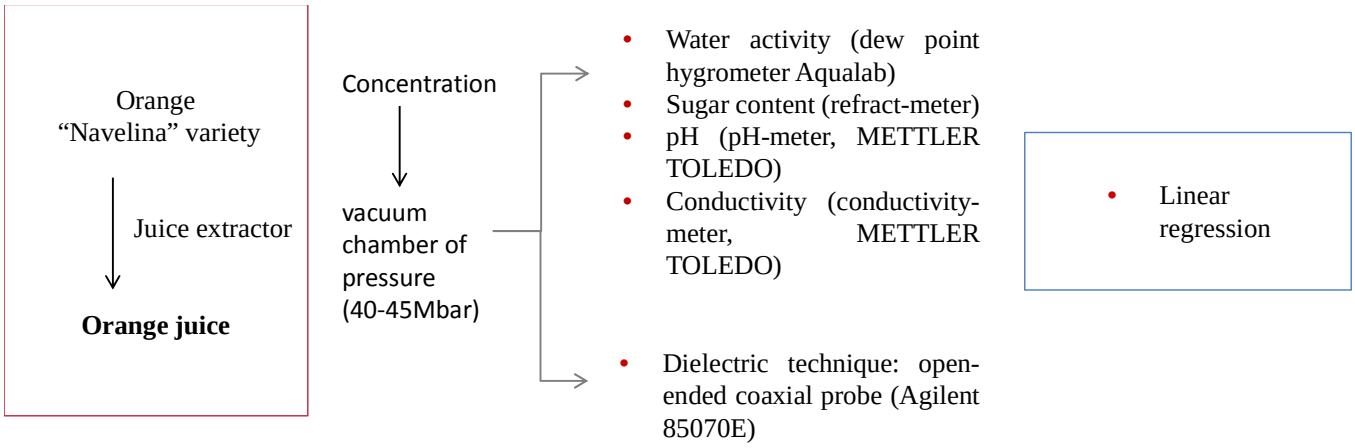

Fig. 12 Experimental plan

The research on the monitoring of concentration process of orange juice was carried out as shown in the experimental plan (figure 12).

Fresh orange, "Navelina" variety, bought from a local supermarket were used to carry out the experiment. The oranges were cut and the orange juice was obtained with a juicer (Orangine Juice extractor 30489. MOD. HA-3171). The orange juice was filtered to remove the pulp. In the industrial process the concentration of orange juice is performed with a low pressure evaporator to preserve the typical characteristic of the product. To simulate this system a vacuum chamber of pressure (Patent P99 02730-5) was used to reach about 40-45 Mbar and at least 55°C of temperature. As the industrial process, the concentration was performed at low pressure, this gives us the possibility to use low temperature and not influence the quality of the citrus juice. Subsequently the atmospheric pressure was restored and all the analyzes were performed at 20ºC.

The water activity was carried out by using a dew point hygrometer Aqualab series 3 TE (Decagon Devices, Inc., Pullman, Washington). The sugar content was determined by a refract-meter (ABBE, ATAGO model 3-T, Japan). The pH was measured with a pH-meter (METTLER TOLEDO GmbH, Analytical CH-8603). The conductivity of the orange juice was determined by a conductivity-meter (METTLER TOLEDO GmbH, Analytical CH-8603) with a conductivity probe (InLab 730, NTC 0.01-1000 mS/cm).

Zetasizer-Nano Zs (Malvern instruments) with the software potential zeta analyzer was performed4. The internal parameters used to conduct the analysis were previously set up, so at different concentration a new dispersant was created to put the right data set: ºBrix, viscosity, dielectric constant and refraction index. All measures were carried out at 20ºC and repeated 5 times for sample.
To take into account the real condition of the technological process the Reynolds number was exploited to calculate the viscosity with a polynomial equation (Lewis, 1987).

Coaxial probe with vector analyzer

The dielectric constant and loss factor of orange juice previously concentrated at different °Brix (up to 45°) were measured with an Agilent 85070E open-ended coaxial probe connected to an Agilent E8362B Vector Network Analyzer. The equipment was calibrated with two different loads: a short circuit and 20ºC Milli-Q water. For these measurements, a stainless steel support is required to fix the probe and an elevation platform was used to bring the sample near the probe to avoid possible phase changes due to cable movements after calibration. The dielectric spectra were carried out by introducing the probe in the sample about 3 or 4 mm. The measurements were conducted from 500 MHz to 20 GHz and repeated in triplicate.
The statistical analysis used to correlate the spectral data point with the quality parameter measured was a simple linear regression. The characteristic investigated with statistical toll were water acitivity (a_w), moisture content (Xw), Reynold's number (ρ/μ) and soluble content (°brix).

3.2 Results and discussion

The physical behavior of different concentration of orange juice are characterized in figure 13.

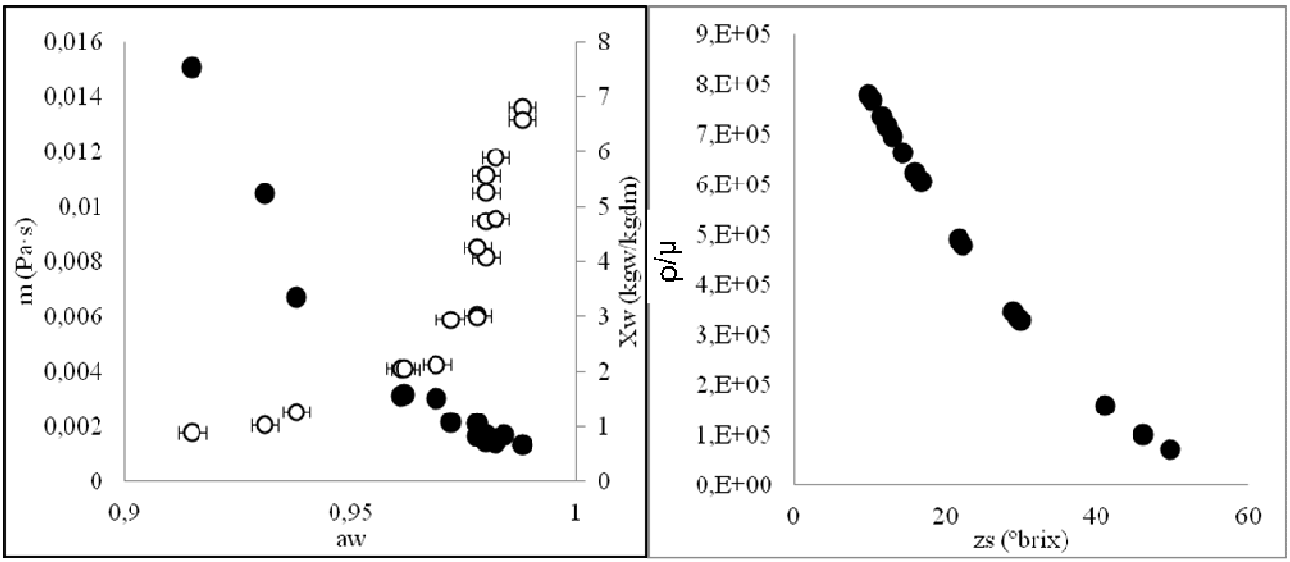

Fig. 13 Physical characterization during the concentration process, the empty dots represent the correlation between aw and Xw; the full dots show the correlation between aw and m.

In the left one, viscosity expressed in Pa*s, aw and Xw are put into relation to describe the sorption profile of the different concentrations of orange juice as function of aw variation that represent a process index. Xw was calculated with this formula:

$$Xw = (1-(°brix/100)-aw)$$

and used to represent the moisture content on dry matter. As expected, it is possible to observe the viscosity decrease as a consequence of a water activity increase.

Furthermore to understand the circulation regime type of the orange juice during process, a parameter expressed as:

$$\rho/\mu$$

ρ, density (kg/m3) and μ = dynamic viscosity (Ns/m2), was calculated and correlated with °brix (Figure 12, right one). An increase in °brix correspond to a decrease in ρ/μ ratio. This ratio is fundamental because is the main part of Reynolds number.

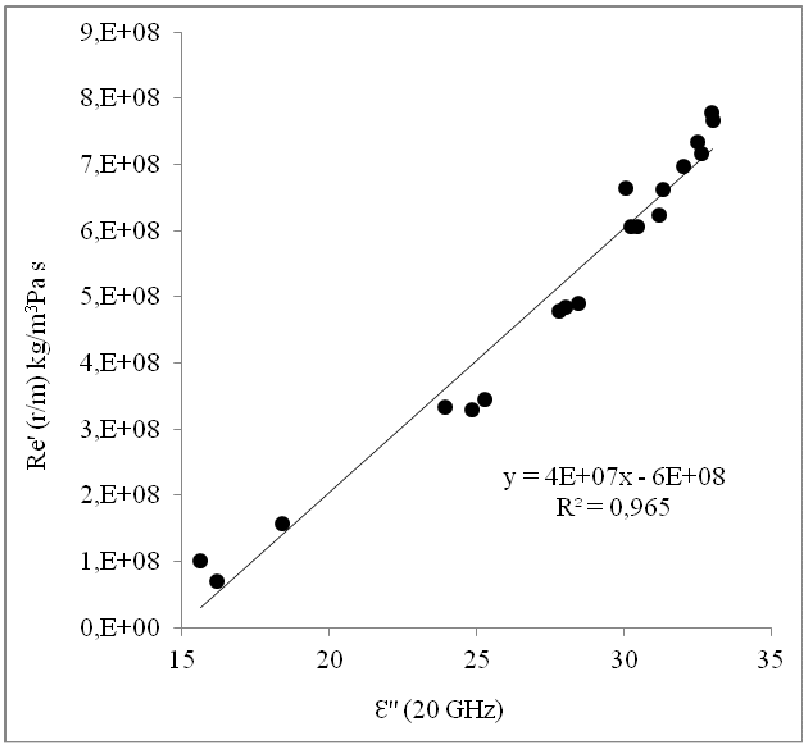

Fig. 14 Correlation between Reynolds number and loss factor spectral data at 20 GHz

A linear correlation between soluble solids content and loss factor at 20 GHz is shown in figure 14. As it was expected, an increase in soluble solids content corresponds with a decrease in loss factor.

Dielectric constant and loss factor spectra of different orange juice concentration are shown in figure 15. A decrease of dielectric constant (from blue to light blue) and loss factor variation (from orange to light orange) as a consequence of a concentration increase is explained by the figure with a reduction of the color tone.

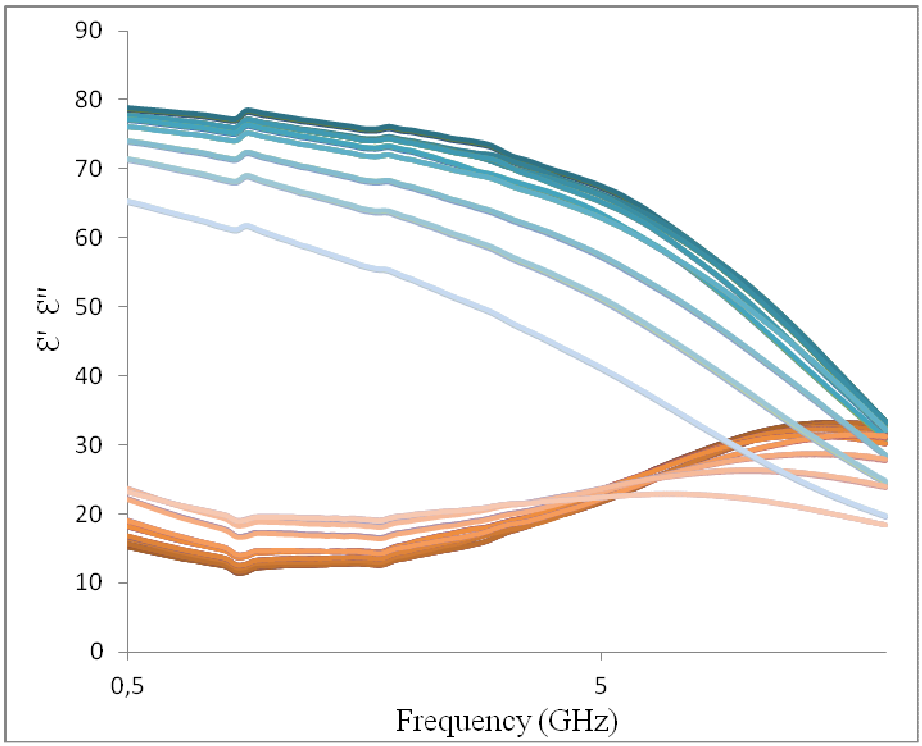

Fig. 15 Dielectric constant and loss factor at different °brix.

A concentration increase is correspondent to a sugar content raise and it can be possible to observe a decrease of the polarization capacity. A reduction of water mobility and polarization capacity is expected in function of increasing formation of hydrogen bonds with water molecules. In this way the reduction of water dipoles involve in a decreasing of dipolar relaxation frequency (Castro-Giraldez et al. 2010). Difference between dielectric constant and loss factor spectra at different concentration are also probably due to the partial removal of water content.

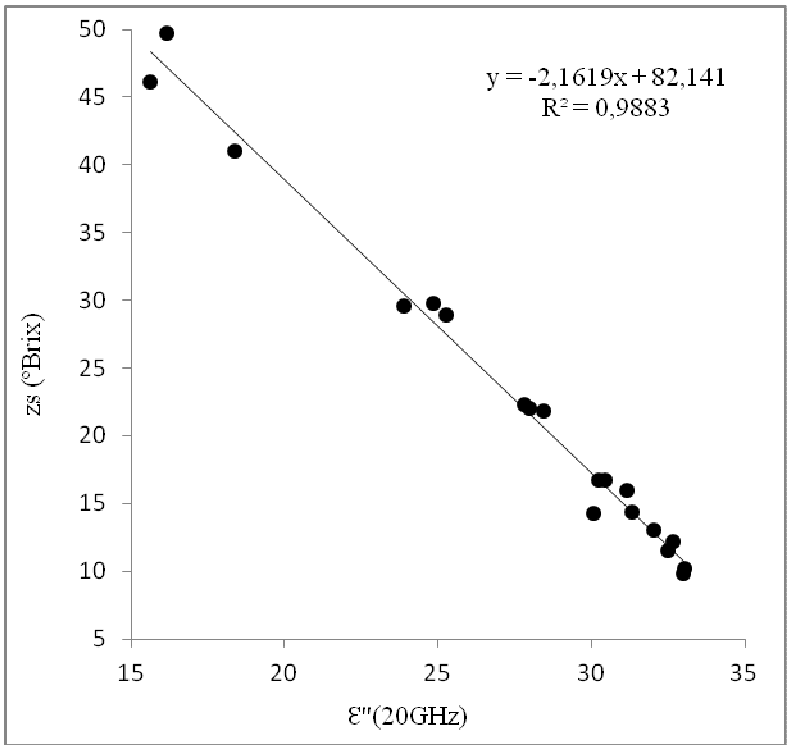

Fig. 16 Correlation between solid soluble content and loss factor at 20 GHz.

Soluble solids content and loss factor at 20 GHz were very good linearly correlated (R^2 0.988) as shown figure 16. As mentioned before a loss factor decreasing is underlined when the soluble solid content raise.

3.3 Conclusion

This results show the possibility to develop a microwave sensor for the industry control. This innovative method based on the dielectric spectroscopy can be applied in the orange juice concentration process. In this way analysis were conducted to simulate as much as possible the real process, so 50°C of temperature were applied to reach 45°brix. A vacuum chamber with temperature and pressure sensor allowed us to work always in the optimum standardized condition and give us the possibility to test the microwave sensor. The physical properties of orange juice were taken into account and preserved to the highest quality product. With this experimental condition the preservation of the aroma was also obtained, particularly in respect to no longer heating conditions persistence. The experimental plan considered the rheological juice behavior by a ratio of ρ/μ that indicates a measure of the orange juice circulation regime type. Good correlation of spectral data point of loss factor at

20 GHz and data of the ratio (ρ/μ) and also between loss factor at 20 GHz and soluble solids content were obtained. These results show the possibility of using dielectric spectroscopy technique to monitor the orange juice evaporation process.

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4. Green and roasted coffee


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Different analytical approaches for the study of water features in green and roasted coffee beans

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The mobility and availability of water in food systems depend on the extent of interactions between the aqueous phase and the biopolymers matrix. In food technology these two parameters and the related interactions are important for microbiological growth or chemical and physical reactions, thus potentially lowering food quality and shelf life (Venturi *et al.*, 2007). In many products with a complex microstructure, water transfer between phases is controlled by physico-chemical and mechanical interactions occurring at the interfaces: capillarity, osmotic effects, surface adsorption, liquid-gas phase change (Ramìrez-Martìnez *et al.*, 2013).

Coffee beans are hygroscopic matrices and can adsorb moisture when exposed to the environmental condition during storage (Pittia *et al.*, 2007). High quality green beans contain 8.5-13% of water, while roasted ground coffee is characterized by about 0.9% of water (Clarke *et al.*, 1985). A raise in moisture content determines undesired phenomena, such as fermentation and mould growth with possibly mycotoxins production in green coffee (Romani et al., 2000), loss of the characteristic brittleness and fragility in roasted coffee beans, and a hardening effect (anti-plasticization) occurring on both green and roasted beans that could increase the energy necessary during grinding.

Moisture content-aw relationship is complex and unique for each material due to the various interactions that can occur between the water and solid components (Slade and Levin, 1991).

A rapid method based on dielectric properties could represent a good alternative to study water content and water activity of food also in reason to the possibility of an on line application. In hygroscopic foods the amount of water is the dominant factor influencing their dielectric properties (Venkatesh *et al.*, 2004).

Castro-Giraldèz *et al.* (2011) shown that bound water decreases the polarization capacity with a reduction of conductivity and an increase of the relaxation time. In this case loss factor could be a good variable to understand the fugacity of water molecules in terms of water activity. Loss factor measures a dissipation of energy, such as gain parameter obtained in a waveguide system. Gain describes the energy loss between received and transmitted signals.

Few works about dielectric properties of coffee are reported in literature, particularly regarding the relation of moisture content and water activity. Moisture content, bulk density and variety of parchment coffee were determined by Berbert *et al.* (2001) measuring dielectric properties in the radiofrequency range. Berbert *et al.* (2007) built mathematical models to determine the moisture content of moving seeds of parchment coffee using dielectric data. Furthermore Berbert et al. (2008) developed dielectric meters to determine moisture content of parchment coffee seeds at the radiofrequency range.

Time Domain Reflectometry was employed to estimate the moisture of coffee grains with a result in terms of correlation coefficient of 0.997 (Toledo *et al.*, 2008). In the patent EP 0 971 227 B1 was explained a non-destructive moisture sensing instrument based on dielectric properties and effective micro-strip permittivity for measuring the moisture content of grains in time domain.

As already reported for different foodstuff (Ragni *et al.*, 2010; Ragni *et al.*, 2012; Cevoli *et al.*, 2012) a waveguide spectroscopy could be applied as a rapid and non-destructive methods in order to predict moisture and water activity of green and roasted coffee.

4.1 Material and methods

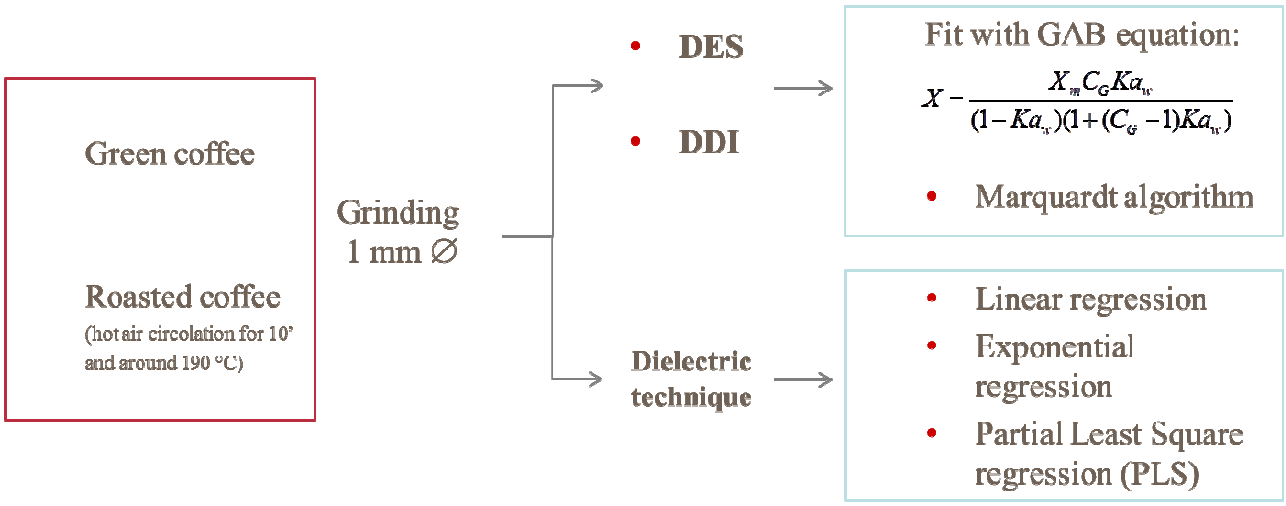

Fig. 17 Experimental plan, DES (Satured salt slurry method) and DDI (Dinamic Dewpoint Isotherm method)

As shown from the experimental plan in figure 17, green and roasted coffee sample blends of Arabica (Coffea Arabica L.) and Robusta (Coffea canephora var. Robusta) were employed for this work section. Green and roasted coffee beans were characterized by 10.12 (±0.06)% and 1.24 (±0.05)% of water content, these values were obtained by the traditional oven method conducted in quintuplicate. The grinding process was performed by using an Officine Vittoria grinder (Bologna, Italy) with conical cutters at 190°C for 10 minutes. Before the subsequent analysis green and roasted coffee beans were sieved to obtain homogeneous particle size of about 1 mm (Mateus et al., 2007; Rocculi et al., 2011).

In order to obtain sorption profile and related data to correlate with dielectric spectral points, the saturated salt slurries method was employed. This is a traditional method that create a sorption profile by placing food material over saturated salt slurry with specific aw values in closed chamber until reach a steady state.

To perform a complete drying, coffee beans were transferred into glass desiccators, containing phosphorus pentoxide (P2O5). Subsequently moisture equilibrium took place in seven sterilized hygrostat by using saturated salt solution in the range of 12–97% relative humidity (aw = 0.12, 0.33, 0.44, 0.57, 0.75, 094 and 0.97). Dried samples of about 1 g were inserted into oven dried bottles half open and placed inside the hygrostat to check the moisture equilibrium. The bottles were weighed until reached a constant weight for 3

consecutive times. Equilibrated sample aw was controlled by a dew-point hygrometer, mod. Aqualab (Decagon Devices Inc., Pullman, WA) and the water content percentages are hereafter expressed on a dry matter bases. The GAB equation was used to fit water sorption isotherms data (Barbosa-Cánovas et al., 2007).

$$x = \frac{X_m C_g K\, a_w}{(1 - K\, a_w)(1 + (C_g - 1) K\, a_w)}$$

where x is the water content (g water/100 g solids or % dry basis), aw is the water activity, Xm is the water content of the monolayer (g water/g solids), Cg is the constant related to monolayer sorption heat, and K is the constant related to multilayer sorption heat.

Waveguide system

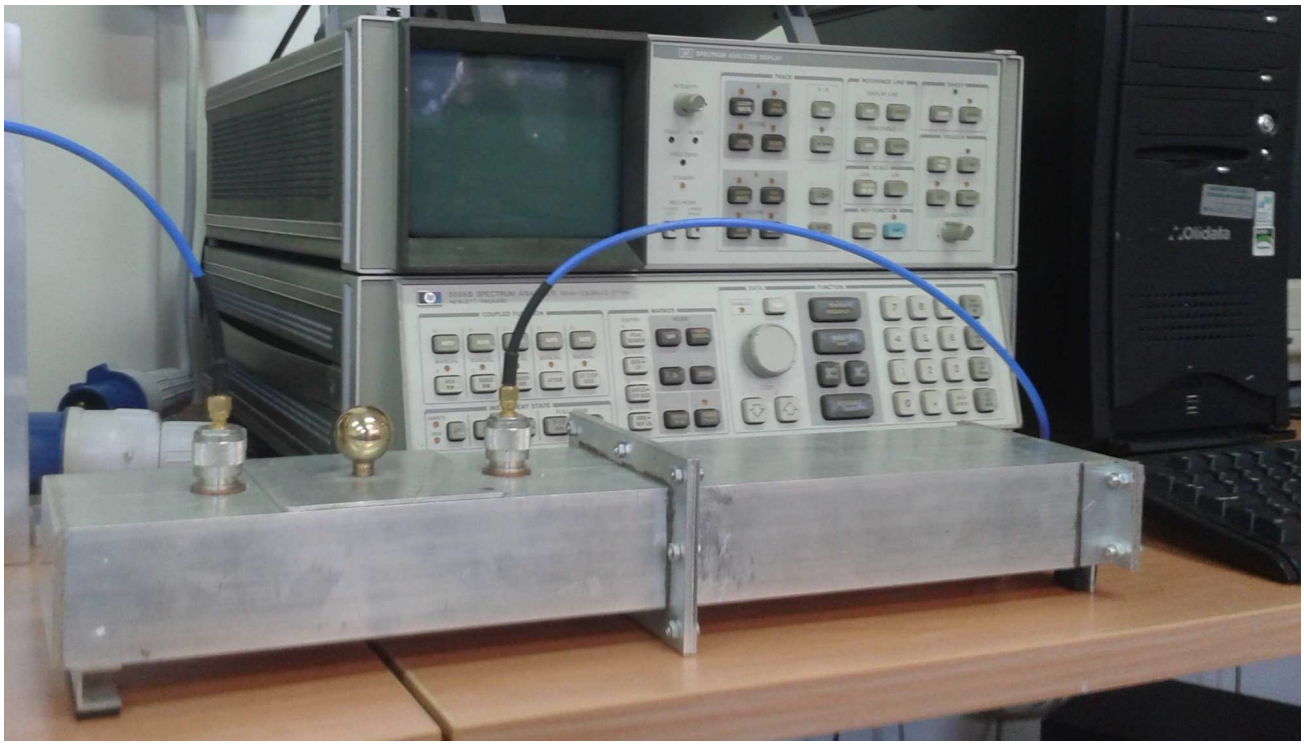

Fig. 18 Layout of the instrumental chain.

A waveguide system was used to conduct the measurements (Fig. 18; Ragni et al., 2010). The instrumental chain was composed by an aluminum rectangular waveguide, a sweeper

(HP 8350B + 8352B) and a spectrum analyser (HP 8566B) interfaced with a personal computer. The waveguide is made with specific dimension: internal dimension of 96x46 mm^2, a length of 245 mm and a thickness of 2 mm. To minimize reflections the device is provided with a termination section 234 mm long. The cut-off frequency was 1.561 GHz.
A square window (70 x 70 mm^2) on the top of the guide allows the introduction of the sample, as shown the figure 19.

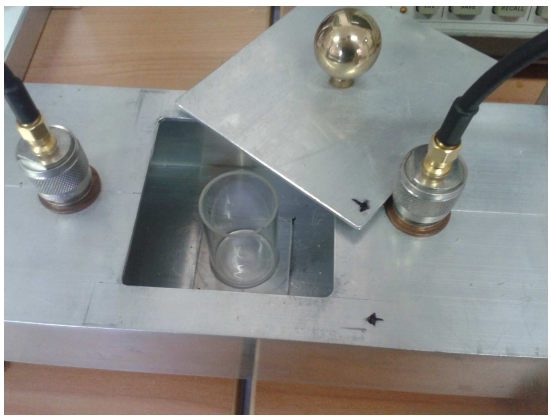

Fig. 19 Square window for sample holder introduction.

The coffee samples were introduced in the guide through a glass cylinder with a diameter of 29 mm, a height of 44.11 mm and thickness of 1.39 mm. The instrument includes two antenna, one for transmitting and one for receiving the signal. The transmitting antenna is connected to the sweeper by a coaxial cable. The received signal was captured by the spectrum analyzer also connected by a coaxial cable to the receiving antenna, and it is interfaced with a personal computer. The sweeper oscillator has a frequency range of 0.01–20 GHz. As reported by Ragni et al. (2012) and Cevoli et al. (2012), the spectral data for 2–3, 5–6, 17–18 GHz frequency ranges results better correlated with water content in foods. In this way, the mentioned frequency ranges were selected. The sweep time was set to 60 s for each 1 GHz range and three replications were carried out for each moisture and a_w value, for green and roasted coffee, respectively. To minimize the possible differences due to environmental parameters as temperature, humidity and instrument warming, the gain (dB) was calculated by subtracting spectral data with and without sample. The obtained 1001 spectra points were subsequently processed by statistical analysis. Linear regression between spectral data points and moisture or a_w values were obtained for green and roasted

coffee as well. Furthermore exponential regression was tested to predict a_w. Partial Least Square Regression was performed to increase linear correlation between spectral data and moisture or a_w, so predictive models were built by using full cross validation: a sample belonging from the data set was removed one by one from the model calibration and used to validate it.

4.2 Results and discussion

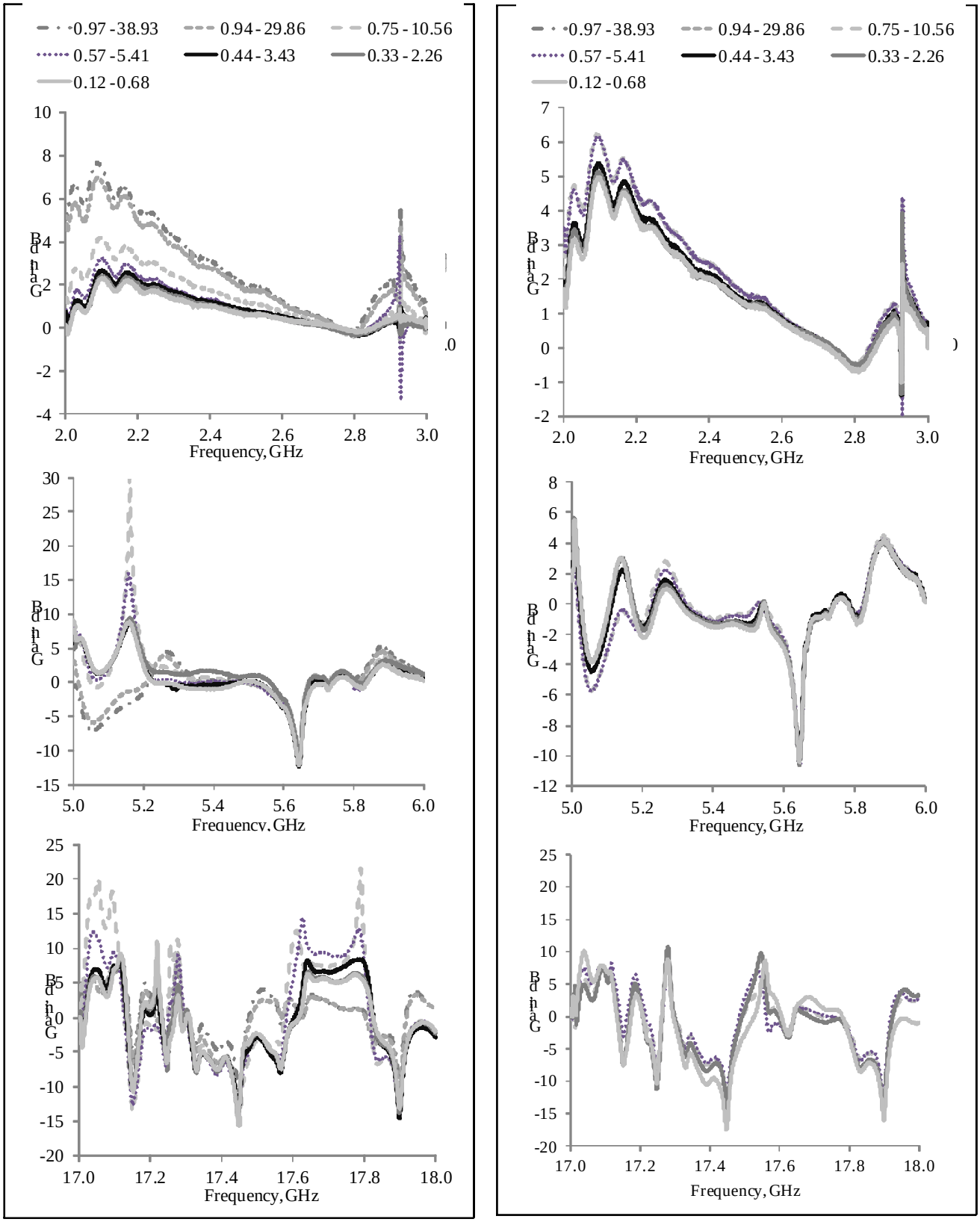

Fig. 20 Acquired spectra for green (on the right) and roasted coffee (on the left) in the frequency range selected for water activity and moisture, 2-3, 5-6 and 17-18 GHz.

Averaged gain signal concerning test on moisture and water activity are shown for both green and roasted coffee in Figure 20. The acquired spectra showed different trend for the selected frequency range 2-3, 5-6, 17-18 GHz.

The coefficient trend, of linear regression for moisture prediction into 2-3 GHz frequency range of roasted coffee, in addition to a gain spectrum was reported (figure 21) to figure out which part of the signal contains most information.

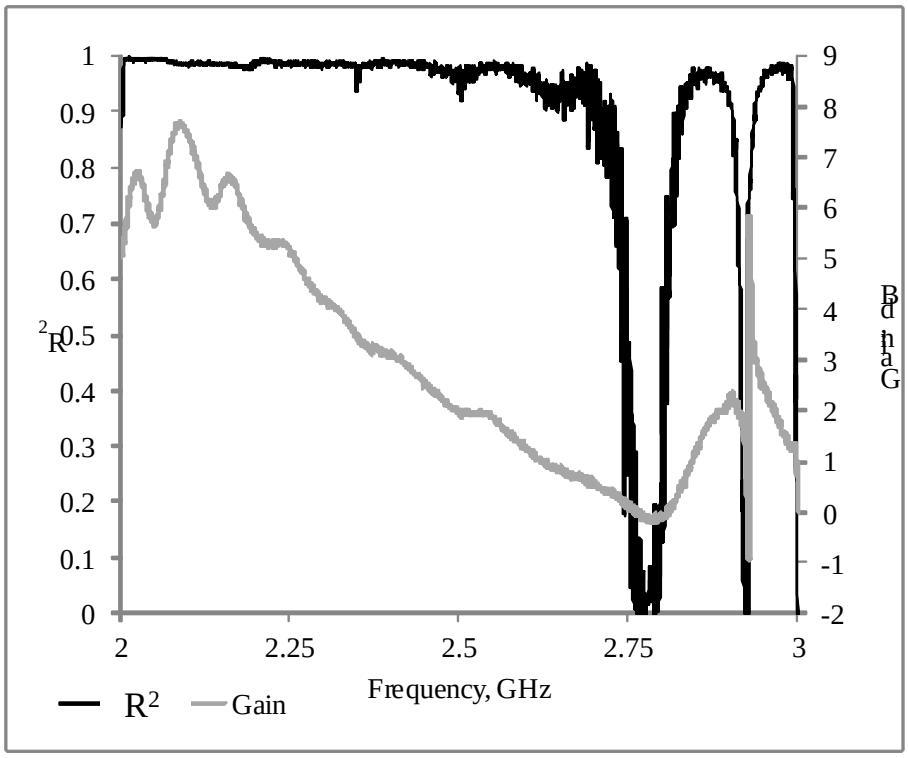

Fig. 21 Determination coefficient trend and spectrum of 2-3 GHz.

The higher R^2 values were found can be reached from 2 to 2.6 GHz with values up to 0.94. The higher coefficient of determination for moisture content prediction are shown in tables 4 and 5 and the R^2 values of the linear correlation of spectrum data of all the range considered.

Sample	Frequency	Linear regression	Partial least square regression			
			Calibration	RMSEC	Cross validation	RMSECV
roasted coffee	2-3GHz	0.995	0.991	1.314	0.990	1.440
	5-6 GHz	0.993	0.991	1.306	0.989	1.531
	17-18 GHz	0.978	0.999	0.344	0.999	0.526
green coffee	2-3GHz	0.960	0.998	0.156	0.973	0.597
	5-6 GHz	0.981	0.999	0.051	0.998	0.158
	17-18 GHz	0.943	0.996	0.207	0.995	0.261

Table 4 Statistical analysis for the correlations between gain and moisture for roasted and green coffee.

Sample	Frequency	Linear regression	EXP	Partial least square regression			
				Calibration	RMSEC	Cross validation	RMSECV
roasted coffee	2-3GHz	0.874	0.976	0.990	0.029	0.983	0.04
	5-6 GHz	0.859	0.908	0.996	0.017	0.984	0.036
	17-18 GHz	0.888	**NC**	0.993	0.024	0.988	0.032
green coffee	2-3GHz	0.924	0.95	0.997	0.009	0.979	0.033
	5-6 GHz	0.989	0.989	0.993	0.017	0.988	0.025
	17-18 GHz	0.983	0.977	0.997	0.011	0.996	0.014

Table 5 Statistical analysis for the correlations between gain and aw for roasted and green coffee.

For the linear regression, the best prediction concerning the test for moisture was obtained in the 2-3 GHz for roasted coffee with R^2 up to 0.995 while for green coffee in the 5-6 GHz

with an R^2 of 0.981. Considering water activity evaluation the best results is 0.989 and could be found in 5-6 GHz frequency range for green coffee. For roasted coffee is obtained in 17-18 GHz with a R^2 of 0.888. As reported in table 5 roasted coffee does not have a good linear correlation for the water activity prediction, so an exponential regression was also performed (for the green coffee too). In table 5 is also reported the results of the exponential regression and the best result in terms of R^2 of 0.989 was observed in 5-6 GHz frequency range. Exponential regression often shows better results compared to the linear one probably due to the existence of an exponential relation between moisture and aw. Moreover green and roasted coffee showed different behavior as a probably consequence of very different structure of matrix. In this way it could be assumed that the prediction of aw is related to an indirectly water content assessment. This event is absent in 17-18 GHz frequency range where no exponential correlation can be applied but only linear correlation founds application, so it may be hypothesize a direct estimation of water activity.

Furthermore PLS regression analysis was conducted to estimate water content and water activity and results are summarized in tables 4 and 5. For water content assessment the best results in terms of R^2 in full cross validation were obtained at 17-18 GHz frequency range for roasted coffee (R^2 0.999) while for green coffee at 5-6 GHz (R^2 0.998). Regarding the test for water activity prediction R^2 of 0.988 was observed for roasted coffee and R^2 of 0.996 for green coffee both in 17-18 GHz frequency range.

4.3 Conclusion

In the light of these results the estimation of water content seems more accurate at low frequencies while the dielectric signal obtained at high frequencies seems more related to water solid matrix interaction useful for water behavior understanding.

4.4 References

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5. Parmigiano Reggiano cheese

The main content of this topic were published on Journal of Food Engineering as shown below.


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Estimation of the main compositional features of grated Parmigiano Reggiano cheese by a simple capacitive technique

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Parmigiano Reggiano cheese is an additive free hard cheese made in Italy by partly skimmed, and un-pasteurized milk (Malacarne et al., 2008). Parmigiano Reggiano cheese can be sold as entire or portion of wheel, but also grated and packaged as ready to use products. The grated Parmigiano Reggiano cheese must be manufactured exclusively from whole cheese wheels according to the production standard imposed by Parmigiano-Reggiano Cheese Consortium. The grated cheese must be characterized by moisture no less than 25% and no more than 35%, typical amino-acid composition of the cheese matured for a period of at least 12 months and rind not over 18%, (D.P.C.M. 4/11/1991). So, the assurance of the authenticity and the respect of the high quality parameters imposed by D.P.C.M. are the primary goal of the production process. Moreover the grated cheese production chain give a huge importance to marks and brand identification, because embossed on the rind are lost.

Recently Cevoli et al. (2012) predicted the rind percentage, ripening and moisture content of the grated Parmigiano Reggiano cheese by using waveguide spectroscopy. In addition differences between true Parmigiano Reggiano cheese and competitors were determined.

Monitoring grated Parmigiano Reggiano cheese is an arduous challenge due to the variability of the product caused by different reasons.

The first variability to take into account for quality evaluation regards the cheese making technology and the dimension of the wheel (22–24 cm high, 40–45 cm diameter) of this long-ripened cheese. Both these parameters during ripening lead to differential of chemical/physical parameters development between the inner and the outer zones (Malacarne et al., 2009; Tosi et al., 2008; Panari et al., 2003; Careri et al., 1996; Pecorari et al., 1995). Moreover the packages of grated cheese are filled with product belonging from different places of the wheel. For these consideration several parameters had to take into account to determine a quality assessment such as rind percentage, months of ripening, moisture content and protein content. By using only few of these values the product evaluation became difficult because these parameters involve similar effects, mainly due to the moisture content, that decreases during the ripening and with rind content (Cevoli et al., 2012). On the other hand, moisture and protein content slightly or do not significantly vary with orographic zone and production season (Careri et al., 1996; Malacarne et al., 2009); on the contrary, they significantly change during ripening, in a complementary manner (Tosi et. Al., 2008; Malacarne et al., 2009).

The dielectric measurement techniques have been used principally in the analysis of cheese composition and maturity. By using different probes and frequency ranges, researches showed that dielectric properties depend on the chemical composition of the cheese, such as the moisture, inorganic salt (Everard et al., 2006; Fagan et al., 2005), and fat contents (Herve et al., 1998; Green, 1997).

In this way a technique for the non-destructive assessment of the rind percentage, ripening time and chemical composition (moisture, protein and fat content) of mixtures of grated Parmigiano Reggiano cheese by means of a capacitance measurement in the range of 100 Hz-10 kHz is proposed. This dielectric method could aid in the development of a rapid tool for on-line and off-line quality control of the grated cheese production.

5.1 Material and methods

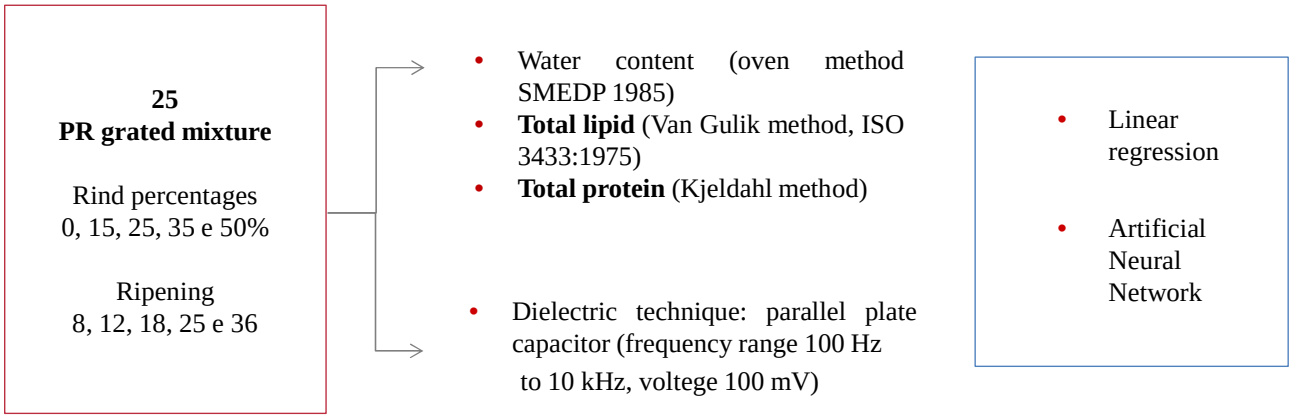

Fig. 22 Experimental plan

The Parmigiano-Reggiano cheese Consortium (CFPR) provided samples of about 2 kg deriving from 5 whole cheese wheels, produced in different seasons and ripened for 8, 12, 18, 25, 36 months, respectively. The experimental plan above explain all the measure conducted (figure 22).

The rind parts of the portions from all wheels, characterized by different ripening time, were separated from the samples and grated together, according to the procedure adopted by diary CFPR factories. The remaining parts of cheese were also grated. The particle size ranged between 0.5 and 1.5 mm.

For each ripening time, five mixtures characterized by 0%, 15%, 25%, 35% and 50% of rind, were prepared. In total twenty-five mixtures were obtained. Mixtures were stored at 4°C in plastic-sealed bags, in order to avoid changes in moisture.

The chemical composition of the Parmigiano Reggiano mixture was assessed by determining moisture, fat and protein. For each mixture, moisture was obtained in triplicate by drying at 105±2°C for 16-18 hours according to the standard method for the examination of dairy products (SMEDP, 1985).

Determination of fat was conducted on about 3 g of grated sample according to Van Gulik method described in ISO 3433:1975.

Total nitrogen content was obtained on about 300 mg of each grated sample as described in International Dairy Federation Standard (IDF) 20B:1993.

Then, the protein content of the cheese samples was determined by Kjeldahl, as N × 6.38. Moisture, rind, protein, and fat content were expressed and used in the regression model as percentage.

Parallel plate capacitor system

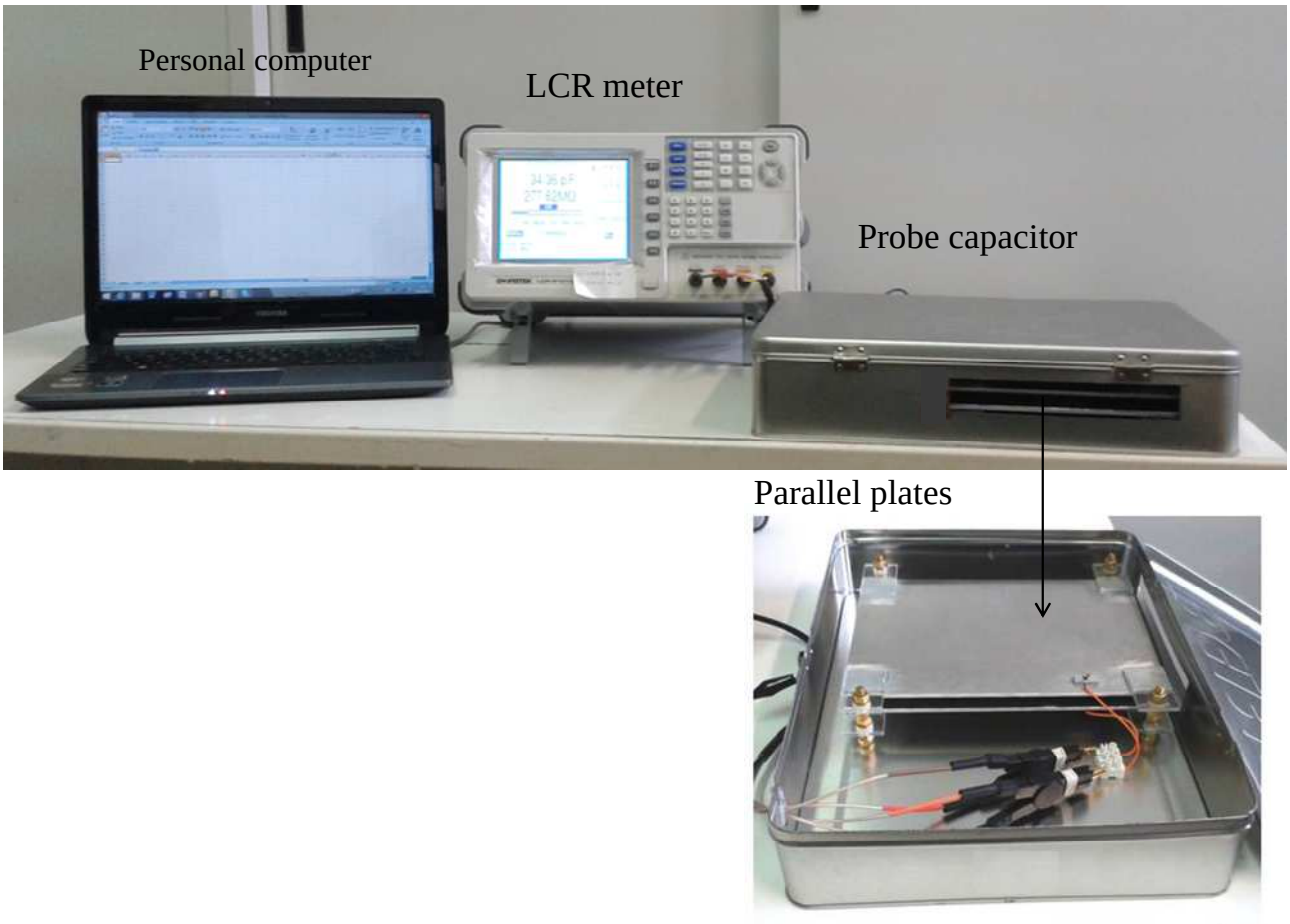

Fig. 23 Instrumental chain

Figure 23 shows the instrumental chain set up. The electrical measurements were performed with a capacitor probe and a LCR meter (LCR-8101G, GW-Instek, Good Will Instrument Co. Ltd, Taiwan) connected to a personal computer.

The capacitor probe was made by two parallel plates made of aluminum (thickness 3 mm) with a rated capacitance of 34.41 pF in air and it was allocated in a metal box in order to avoid electromagnetic interference during the analysis. The dimension of the parallel plates should be proportional with respect to the sample measured to provide a sensing area which

rends the measuring methods independent of local irregularities in moisture distribution in the material (Vlachos et al., 2000). In this way, the parallel plates were larger than the sample container as concerning the most common probe used in electric moisture measurement (Henderson et al., 1997). A criteria for the selection of surface area of the electrodes was based on the average volume of modelling porous media (Carbonell and Whitaker, 1984), allowing a higher sensibility and preventing error.

The dimensions of plates are the following: length of 230 mm, width of 160 mm and distance between plates of 9.60 mm. The direct contact of mixture with plates can influence capacitive measurements in terms of conductive phenomena. To avoid this error at least one plate has to be insulated from the mixture itself and an open container made of PET was suitable for this purpose. The sample container was characterized by the following dimensions: length of 154 mm (flared of 22 mm), width of 104 mm (flared of 22 mm), height of 8.50 mm, thickness of plastic material of 1.50 mm.

Fig. 24 Sample container.

The grated mixture sample (30±0.1 g) was placed inside the container and a uniformity of the sampling was obtained through a light compression provided by a slight leveling which brought all samples to the same volume. This good practice was conducted to obtain the same distribution of dielectrics materials between the capacitor plates which plays a crucial role in the determination of the total capacitance.

When the container with the cheese is inserted between the plates, the resulting system can be considered as a combination of parallel and series capacitors.

The insertion of the container between the plates, with regard to its spatial positioning on the horizontally point of view, is not critical because the generated different capacitances work in parallel. On the contrary, a change of few tenths of a millimeter in the air thickness along the series capacitances involves a dramatic variation of the total capacitance. This rigorous sample preparation maintains the uniformity in geometrical parameters and avoid errors.

Despite this, the repeatability of data confirmed that the small changes occurring in the mass, volume and in the way in which the grated cheese is added to the container and leveled did not affected the resulting signal.

The frequency range selected for the capacitance measurements was from 100 Hz to 10 kHz, with a step of 202 Hz (50 frequencies) and voltage of 100 mV. Measurement were conducted at 20 ±1°C in triplicate and averaged (5 subsequent measurements). Linear regressions were performed to correlate the obtained 50 spectral points and the corresponding reference values (months of ripening, rind percentage moisture, protein and fat percentages). Furthermore the spectral data were used as input to develop an Artificial Neural Network (ANN) to predict moisture, protein, rind content and ripening time.

The software used for the investigation was STATISTICA Neural Networks 4.0 (StatSoft Inc., Tulsa, OK, USA). Looking for the best prediction different node numbers in the hidden layer were tested. The dataset was divided into training set (70%) and validation set (30%). A back propagation was used as function transfer to minimize the influence of the initial weight value.

5.2 Results and discussion

Table 6 showed below reports the chemical parameters of Parmigiano Reggiano cheese mixture. Mean values and standard deviation describe variable trend in function of ripening time and rind content. The manufacture of Parmigiano Reggiano include artisan procedure which influence the quality parameters in terms of natural creaming for fat (Panari et al.,

2003) or moisture and protein change during ripening, as reported in literature (Panari et. Al, 2003; Malacarne et al., 2009; Tosi et al., 2008; Pecorari et al., 2007).

Ripening time (months)	Rind content (%)	Moisture content (%)	Protein content (%)	Fat content (%)
8	0	29.71 (0.17)	31.90 (0.38)	28.96 (0.69)
8	15	28.22 (0.06)	33.53 (0.01)	30.91 (0.08)
8	25	26.14 (0.07)	34.48 (0.26)	31.08 (0.88)
8	35	25.63 (0.09)	35.61 (0.33)	32.27 (0.27)
8	50	23.19 (0.06)	36.68 (0.15)	31.29 (0.45)
12	0	28.07 (0.18)	31.67 (0.13)	30.70 (1.05)
12	15	27.78 (0.07)	32.60 (0.06)	32.39 (0.34)
12	25	25.33 (0.08)	34.32 (0.91)	32.38 (0.67)
12	35	24.45 (0.05)	35.72 (0.81)	31.99 (0.02)
12	50	22.07 (0.17)	36.89 (0.53)	33.49 (0.21)
18	0	27.65 (0.03)	32.41 (0.77)	29.11 (0.23)
18	15	27.20 (0.07)	33.77 (0.51)	29.64 (0.32)
18	25	25.34 (0.08)	35.19 (0.28)	30.13 (0.42)
18	35	23.89 (0.16)	36.61 (0.57)	30.14 (0.32)
18	50	21.98 (0.20)	37.85 (0.23)	30.34 (0.91)
25	0	26.20 (0.11)	32.87 (0.38)	32.39 (0.09)
25	15	25.99 (0.09)	33.20 (0.54)	31.76 (0.72)
25	25	25.21 (0.09)	35.16 (0.87)	30.81 (0.46)
25	35	23.67 (0.05)	37.30 (0.53)	30.64 (0.29)
25	50	21.26 (0.16)	38.12 (0.76)	33.10 (0.19)
36	0	27.00 (0.07)	32.65 (0.03)	27.69 (0.19)
36	15	25.90 (0.15)	34.40 (0.02)	32.10 (0.20)
36	25	24.30 (0.21)	35.87 (0.06)	30.03 (0.07)
36	35	23.21 (0.09)	36.97 (0.11)	29.60 (0.19)
36	50	20.85 (0.09)	38.15 (0.48)	30.53 (0.27)
-	100	14.95 (0.18)	42.49 (0.02)	35.00 (0.23)

Table 6. Main compositional parameters of Parmigiano Reggiano cheese as function of rind content and ripening tiome (standard deviations values are in brackets).

Figure 25 reports the correlation between protein and moisture with a good result in terms of coefficient of determination (R^2=0.895).

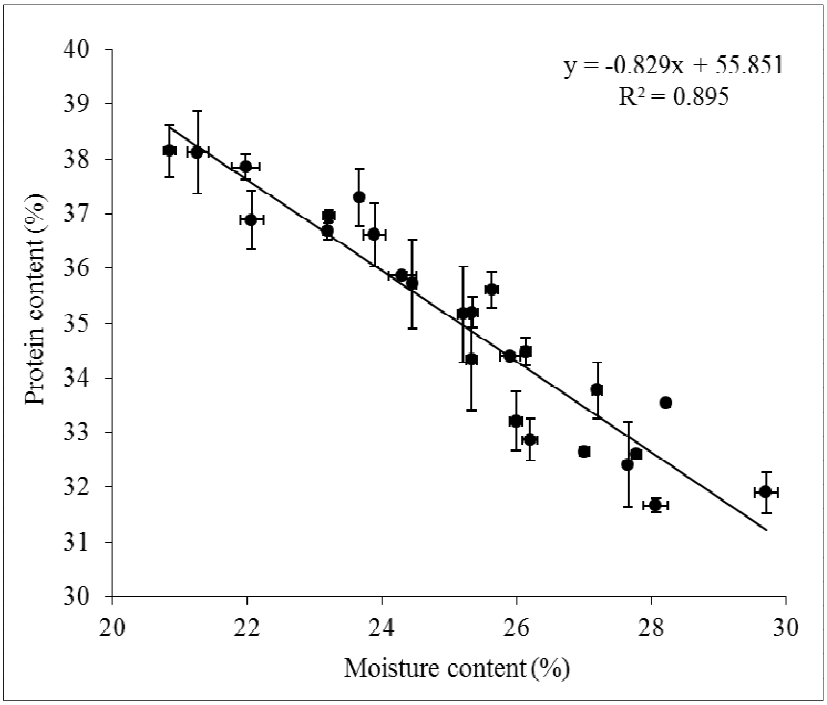

Fig. 25 Correlation between moisture and protein content (the bars show standard deviations).

As reported by Tosi et al. (2008) and showed by figures 25 and 26 by considering all ripening time and from 0 to 50% of rind, moisture decreases and protein rises. For moisture and protein good correlations were observed in terms of coefficients of determination 0.819 and 0.897, respectively.

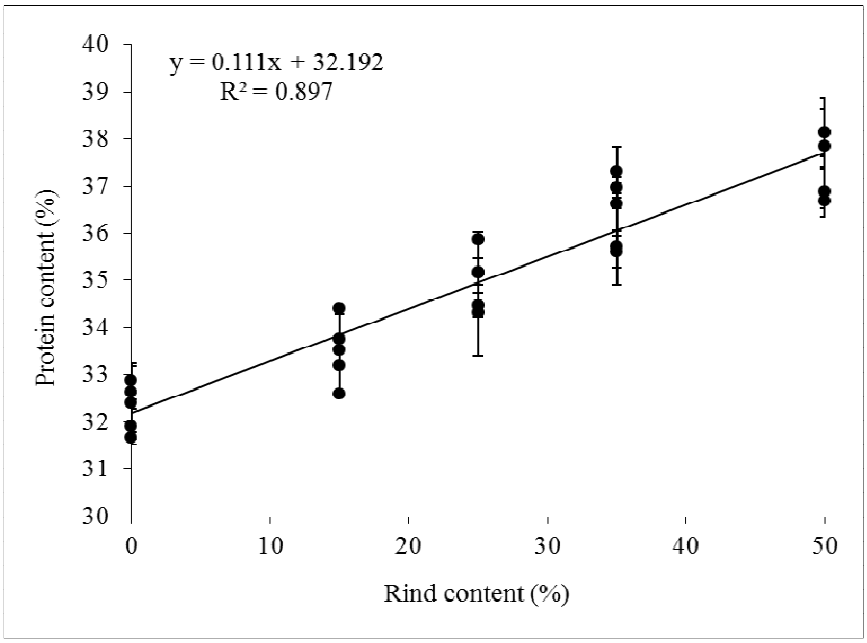

Fig. 25 Correlation between rind and protein content (the bars show standard deviations).

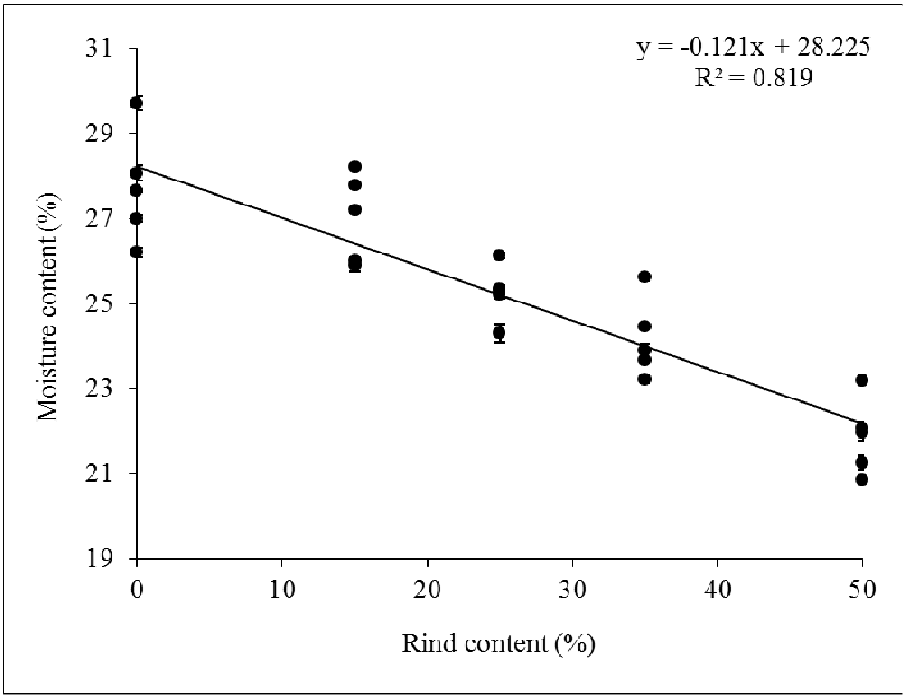

Fig. 26 Correlation between rind and moisture content (the bars show standard deviations).

As regarding protein, a similar behavior was underlined by Cattaneo et al., (2008) where the presence of specific peptides was associated to a very slow proteolysis process during ripening. Otherwise no good correlation can be observed concerning fat (R^2 0.237).

Figure 26 showed average signal spectra of all sample analyzed by considering all mixture for different ripening time and rind percentages. The capacitance spectra are the response of the interaction between the electromagnetic field and the main compositional parameters of foodstuff (as protein, fat and moisture).

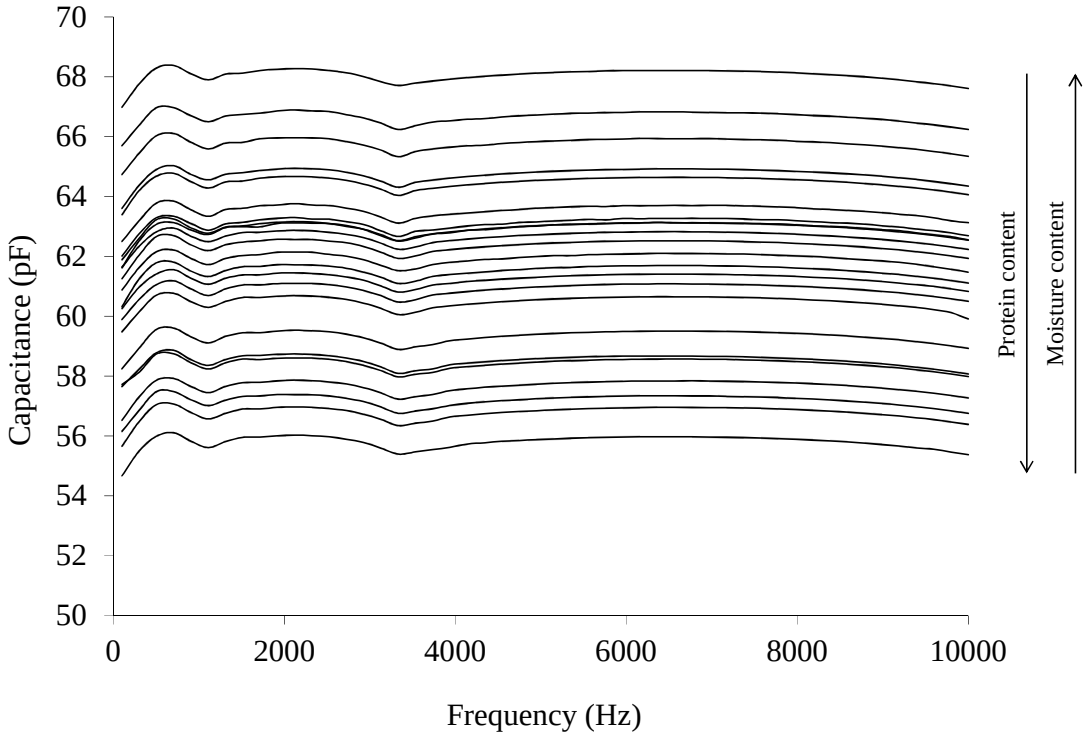

Fig. 27 Average capacitance spectral signals of all the analysed mixtures.

As reported in literature (Venkatesh et al., 2004) water is the main constituents of cheese, but also of food, that influence the capacitance determination as a consequence to a high polarization capacity and consequently an high dielectric constant. In this way the moisture rise is complementary to a protein decrease.

The frequency range explored passed from 100 Hz to 10 kHz and the maximum capacitance change was 2.6%.

Table 7 and 8 show the results belonging from the linear correlation between spectral point, months of ripening, rind, moisture and protein percentage in terms of maximum, mean and standard deviation values. Particularly table 7 summarized the results as function of ripening time by varying the rind percentage and table 8 represent samples prepared maintaining constant the rind percentage with a the ripening time variation.

Ripening time (months)	R^2								
	Moisture			Protein			Rind content		
	Max	Mean	SD	Max	Mean	SD	Max	Mean	SD
8	0.890	0.887	0.002	0.988	0.988	0.001	0.914	0.913	0.001
12	0.772	0.765	0.003	0.876	0.869	0.002	0.937	0.933	0.002
18	0.912	0.906	0.007	0.972	0.969	0.003	0.987	0.985	0.003
25	0.926	0.918	0.002	0.980	0.969	0.001	0.978	0.975	0.001
36	0.897	0.889	0.004	0.994	0.984	0.003	0.967	0.962	0.004
All	0.812	0.808	0.001	0.811	0.807	0.002	0.649	0.639	0.001

Table 7 Linear regression between dielectric data and compositional parameters in function of ripening time (SD = standard deviation).

Rind content (%)	R^2								
	Moisture			Protein			Ripening time		
	Max	Mean	SD	Max	Mean	SD	Max	Mean	SD
0	0.752	0.734	0.007	0.567	0.544	0.007	0.994	0.987	0.002
15	0.621	0.618	0.003	0.513	0.478	0.008	0.884	0.883	0.002
25	0.737	0.725	0.004	0.618	0.598	0.011	0.872	0.870	0.002
35	0.666	0.647	0.007	0.806	0.798	0.004	0.955	0.950	0.002
50	0.843	0.826	0.003	0.907	0.902	0.004	0.963	0.951	0.002
All	0.812	0.808	0.001	0.811	0.807	0.002	0.399	0.396	0.002

Table 8 Linear regression between dielectric data and compositional parameters in function of rind content (SD = standard deviation).

As expected, no good correlation between fat and rind during all ripening time was obtained. All ripening time and rind were considered to predict moisture and protein with very similar results (R^2 Max=0.812 and R^2 Max=0.811 respectively). Quite low determination coefficients were obtained to predict rind (R^2 Max=0.649) and ripening time (R^2 Max=0.399).

In table 7 where the ripening time is constant, the best result in terms of coefficient of determination was reported for protein parameter (R^2 Max=0.994). The highest values of the

averaged coefficient of determination for all ripening time was for protein (0.962), instead the lower one was for moisture (0.879). All samples together give a worst prediction than that of values for rind are reported.

Maintaining constant the rind values (as showed in table 8), the best result was obtained for the ripening time ($R^{2=}$0.994). Furthermore as mentioned before R^2 values for ripening time are higher than values considering all samples together.

This concept was not surprising, as previously reported by Cevoli et al. (2013), considering all ripening time and rind percentages together by using infrared spectroscopy the prediction is very difficult and low coefficients of determination are expression of this.

The sample mixture composition change in a complementary way. In particular, sample characterized by long ripening time and low rind content can have a dielectric behavior very similar to sample with short ripening time and high rind percentage. This opposite condition can led to a misinterpretation of data and a difficult discussion of the results.

Figure 28 is showed the trend of the linear correlation between spectral data, moisture and protein, to well describes that the prediction is possible for a long frequency range.

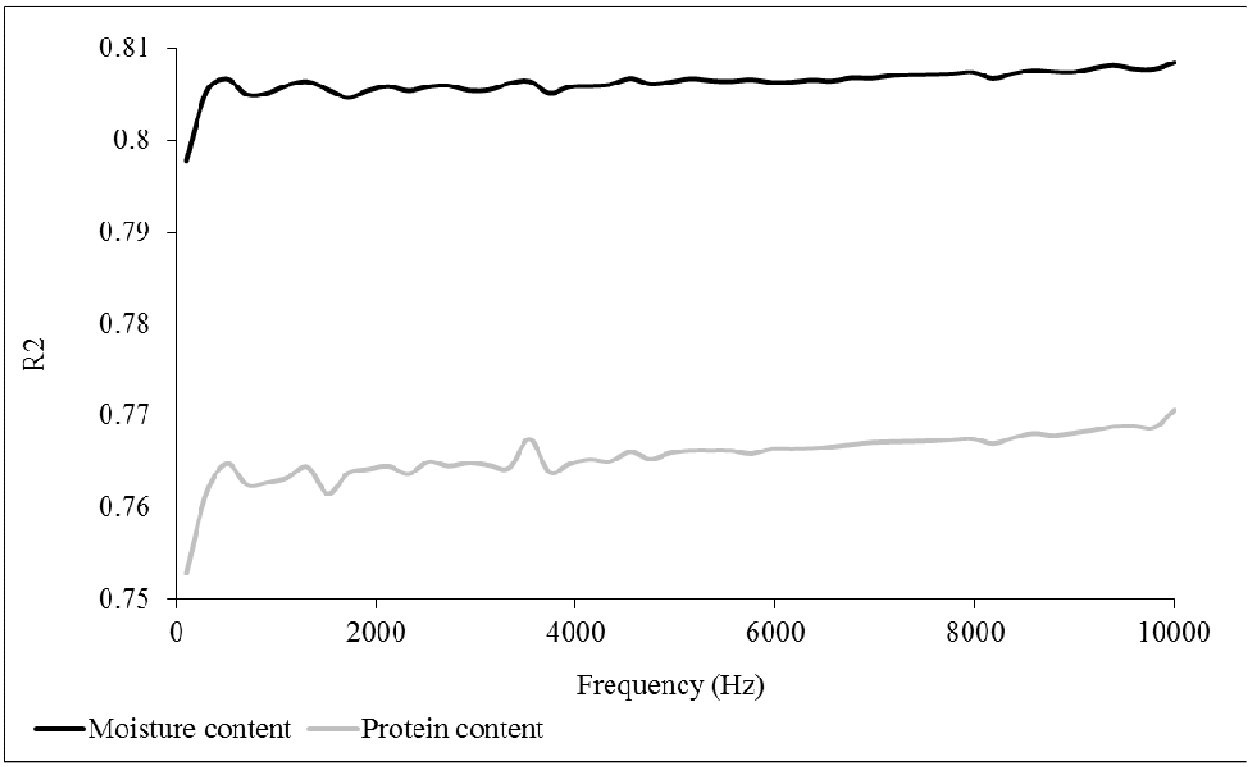

Fig. 28 Trend of the linear correlation between spectral data, protein and moisture.

As function of rind content, in figure 29, the trend of the determination coefficient for all ripening times (from 8 to 36 months) was reported. Maintaining constant the ripening time of a similar behavior was also found for the rind content.

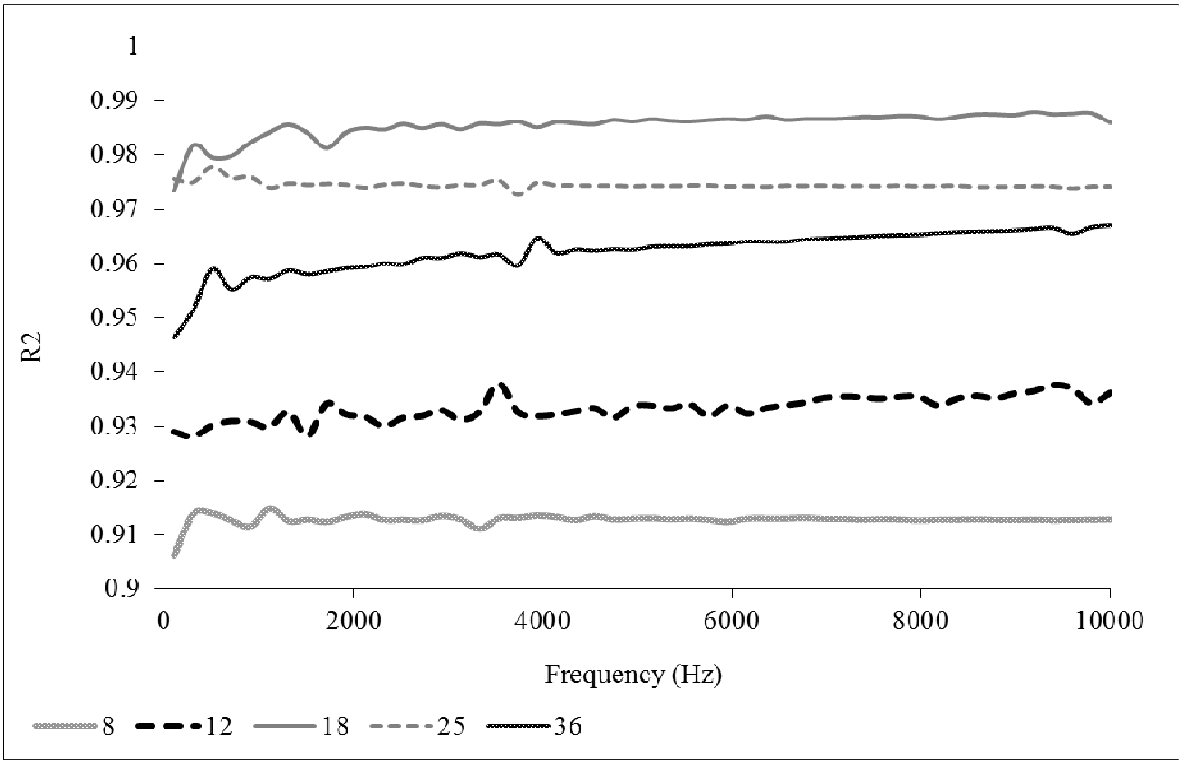

Fig. 29 Trend of the determination coefficient for all ripening times.

Dielectric properties are function of frequency, as well known and this can be observed looking at the rise of R^2 increasing this parameter. At the lowest frequency (up to 0.5 kHz) the correlation was more poor than the other part of the spectrum, where the coefficient of determination showed a light increasing trend with frequency. Despite this, according to the values of mean and standard deviation reported in table 7 and 8, the variation of the coefficient of determination in function of frequency is very small (0.008 and 0.003 are the highest and the average values of standard deviation observed, respectively).

Moisture, protein, rind content and ripening time were also predicted by using Artificial Neural Network (ANN). The results in terms of R^2 for both training and cross validation are summarized in table 9. The best prediction results were obtained with a three layer network, having only 2 nodes in the hidden layer, a learning rate of 0.01 and a momentum of 0.8. The best results were obtained for protein prediction with an R^2 of 0.834 and a similar coefficient

of determination was revealed for moisture content (R^2 of 0.822). Rind content and ripening time estimation showed low determination coefficient, 0.658 and 0.482 respectively.

	R^2 Training	R^2 Cross Validation
Moisture	0.852	0.822
Protein	0.842	0.834
Rind content	0.677	0.658
Ripening time	0.501	0.482

Table 9. Results of the Artificial Neural Network

5.3 Conclusion

Finally the simple capacitance instrumental chain was able to estimate some main constituents of grated Parmigiano Reggiano cheese. The correlation with moisture and protein were stronger if one of the variable parameters, ripening time and rind, is maintained constant, so the determination of a constituent can be achieved indirectly by the other one.

5.4 References

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6. Brief practical applications

6.1 Geographical origin discrimination by using a waveguide system

One of the most consumed dry fruit in the world is pistachio *Pistacia vera* L. (Tsantilli et al., 2010). The main aspect involved in the trade of the pistachio is the verification of the authenticity of the product intended as product characteristics and geographical origin.

Pistachio nuts sold fresh or subjected to process treatments may also lose the peculiar characteristics, making more difficult the control and classification.

Recently, in order to assess the geographical origin of the pistachio different techniques destructive and not were used, including the evaluation of the lipid fraction and the use of NIR spectroscopy (Arena et al., 2006; Silaghi, 2011).

Several researche studies have been conducted by studying the interaction between electromagnetic fields and the product by using waveguide system as previously reported (Ragni *et al.*, 2010; Ragni *et al.*, 2012; Cevoli *et al.*, 2012; Iaccheri et al., 2015). In this way, the present experiments has the objective to discriminate samples of pistachio as a function of the origin by using waveguide spectroscopy and "cluster analysis".

The research was conducted by analyzing Iranian, Californian and Sicilian pistachios without shell, collected at full maturity, stored at -18 °C for about six months and subsequently ground at different particle sizes after a further storage at room temperature (20-22°C).

For each zone of origin about 200 g of pistachios were milled with a commercial mill (Moulinex, D56) (for about 30-60 s) in order to obtain three different particle size: the “a, unrefined”, " b, intermediate" and "c, fine" as shown in figure 30.

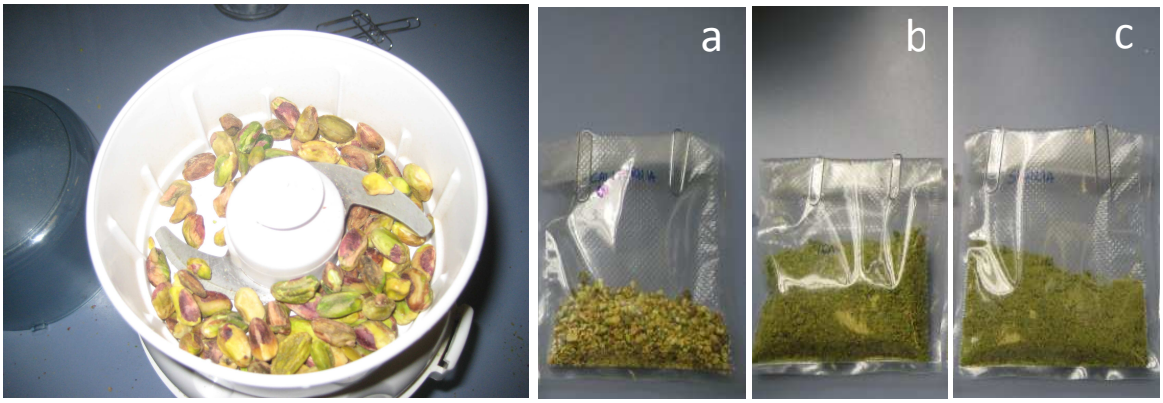

Fig. 30 Different Pistachio granulometry: a, unrefined, b, intermediate e c, fine.

The used instrumental chain for spectral acquisition consisted of an integrated tool under patenting process (scalar analyzer for the acquisition of gain, db, and vector for the Phase, °) based on waveguide spectroscopy in the frequency range 1.6 - 2.7 GHz interfaced to a PC via USB. The spectra obtained in terms of gain (dB) and Phase (°) were analyzed with "hierarchical cluster analysis".

In figure 32 were reported all gain spectra in the selected frequency range 1.6-2.7 GHz subsequently analyzed by using the cluster analysis.

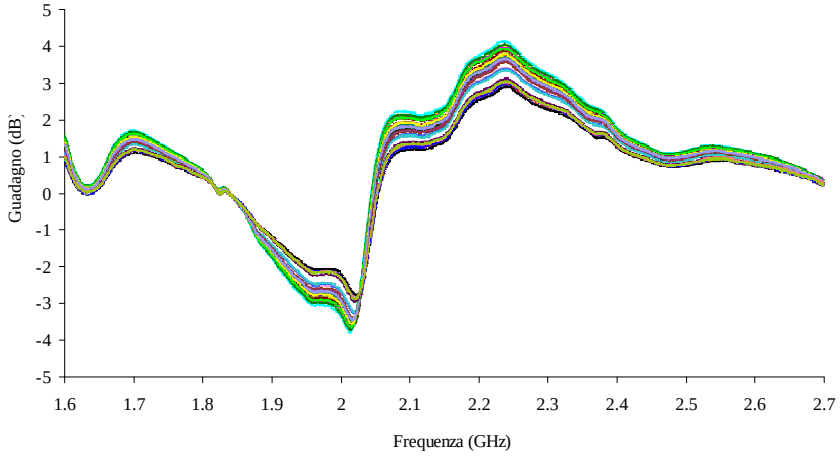

Fig. 32 Gain spectra (Gain, dB) in the analyzed frequency range.

Cluster analysis results showed a classification for the different origin area, maintaining constant the particle size dimension. In figure 33 the very good classification of the most fine particle size (c) is shown.

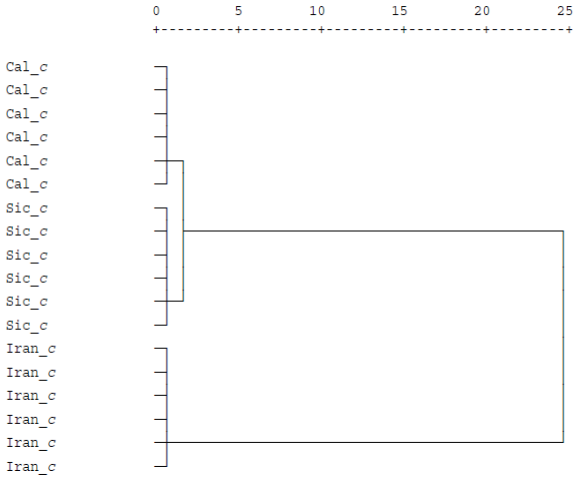

Fig. 33 (Rescaled distance - method Ward) Iranian, Californian and Sicilian samples (fine, c).

The results of the "cluster analysis" carried out, for phase spectra (figure 34), in order to discriminate between the different origins of pistachio are shown in figure 35, and showed a good classification (fine particle size, c) as reported previously by gain.

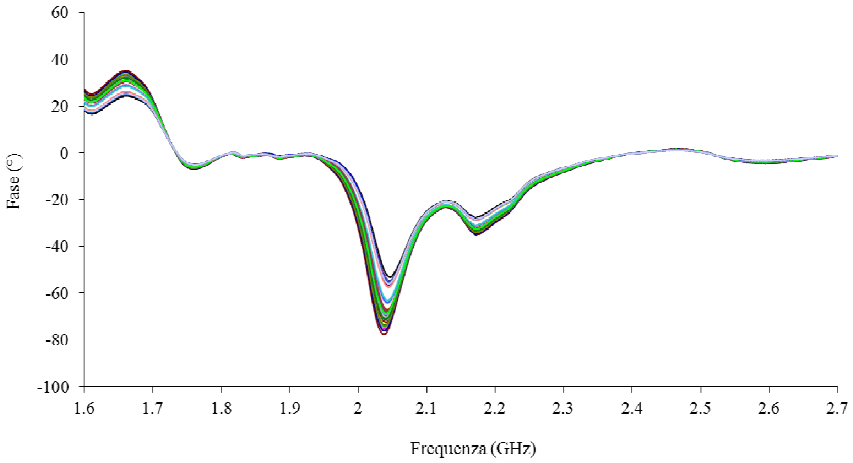

Fig. 34 Phase spectra (°).

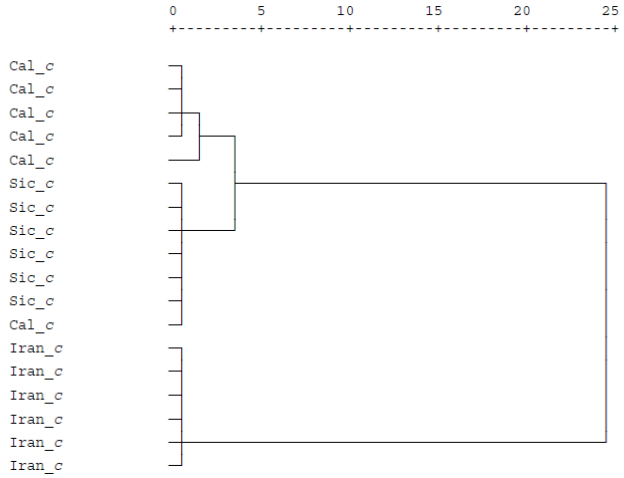

Fig. 35 (Rescaled distance - method Complete linkage) Iranian, Californian and Sicilian samples (fine, c)

Conclusion

For both the gain and phase the "cluster analysis" has revealed that the acquired spectra contain information able to discriminate between the different origins (for the same grain size) due to the different composition. The results obtained in this first validation encourage new tests aimed to faster and more accurate estimate physic-chemical parameters, related to origin and related to the authenticity of the products. Moreover the waveguide system is cheaper and easier to use compared to traditional spectroscopic instruments.

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6.2 A capacitive technique to monitoring a freezing process of “milkshake” product

A capacitive technique was developed to control the freezing process of a like milkshake product (MS), a drink that contains ice crystals and air. Ice crystals and air cells play an important role in terms of sensorial attributes (Hartel, 1996; Trgo et al., 1999). According to Thomas (1981), an increase in air cell dispersion can limit the size of the ice crystals. To ensure the desired final quality a monitoring of the dimension of ice crystals and content of air bubbles is required.

Accordingly to literature (Grossi et al., 2011; Beer et al., 2013) impedance spectroscopy can provide useful information about the physical state of ice cream during freezing. In this way a capacitive device consisting of two juxtaposed and sealed supports (88 mm × 45 mm × 5 mm) made of synthetic glass on whose inner surfaces the lines for inflow and outflow of the MS was developed. The inflow and outflow lines were filleted with PET pipes for injection of the MS to simulate an on-line application. The capacitive element, placed in a central position, was made from PCB with copper as a conductor sheet and epoxy composite material as an insulator. The insulator layer was thinned to leave a thickness of about 350 µm. To avoid the impregnation of liquid due to contact with the MS, the insulating surface, suitably polished, was coated with acrylic paint. The surface of the plates of the capacitor measured 20 mm × 35 mm, and the distance between them was 2 mm. The capacitor with air had a capacitance of 7.16 pF. Three frequency ranges were explored: from 500 Hz to 5 kHz, from 5kHz to 50 kHz and from 50 kHz to 1 MHz.

The freezing process during time evidenced an increase of the dimension of the ice crystals together with the increase of the air bubbles, as shown from the figure 36.

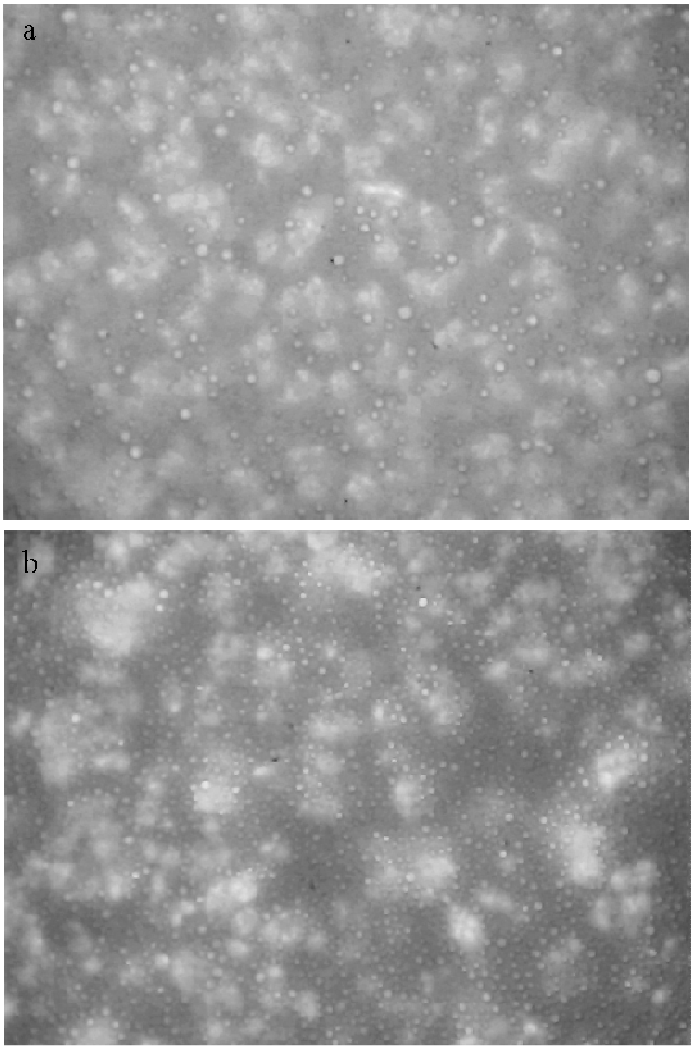

Fig. 36 "Milk shake" images after (a) 3 h and (b) 24h from the beginning of the freezing process.

The values of the capacitance obtained with the capacitive device were reported, for the frequencies from 50 kHz to 1 MHz during the freezing time, in Table 10.

Frequency (kHz)	Capacitance (pF) Time (h)							R^{2*}
	1.33	3	5	7	9	24	29	
50	42.86 (0.12)	42.71 (0.10)	42.26 (0.19)	42.37 (0.08)	42.28 (0.12)	41.71 (0.38)	41.75 (0.16)	0.945
156	42.54 (0.11)	42.55 (0.05)	41.40 (0.12)	41.36 (0.03)	41.43 (0.05)	40.83 (0.16)	40.89 (0.12)	0.856
261	41.41 (0.10)	41.35 (0.06)	41.03 (0.11)	40.95 (0.04)	41.06 (0.04)	40.53 (0.02)	40.51 (0.12)	0.931
367	41.06 (0.09)	41.02 (0.06)	40.74 (0.11)	40.69 (0.02)	40.75 (0.02)	40.29 (0.03)	40.22 (0.10)	0.933
472	40.78 (0.08)	40.76 (0.06)	40.47 (0.09)	40.40 (0.02)	40.51 (0.02)	40.05 (0.03)	39.98 (0.08)	0.915
578	40.68 (0.08)	40.66 (0.06)	40.39 (0.09)	40.33 (0.02)	40.42 (0.02)	39.97 (0.02)	39.93 (0.09)	0.915
683	40.57 (0.08)	40.55 (0.06)	40.30 (0.08)	40.22 (0.02)	40.33 (0.01)	39.87 (0.02)	39.85 (0.08)	0.909
789	40.48 (0.08)	40.47 (0.06)	40.23 (0.08)	40.16 (0.03)	40.29 (0.01)	39.84 (0.02)	39.80 (0.05)	0.889
894	40.43 (0.08)	40.43 (0.07)	40.20 (0.07)	40.14 (0.03)	40.26 (0.01)	39.81 (0.02)	39.78 (0.02)	0.879
1000	40.41 (0.07)	40.42 (0.06)	40.20 (0.07)	40.13 (0.03)	40.26 (0.01)	39.82 (0.02)	39.81 (0.02)	0.870

Table 10. Capacitance values measured at different frequencies during the freezing process.

Freezing parameters, such as the area of crystals and total area and number of air bubbles followed a logarithmic trend, increasing with time. The lower ranges, such as under 50 kHz, showed a high instability of measurements and give very poor correlation. Instead, measures at 50 kHz and 367 kHz given the best correlations with time. The coefficient of logarithmic correlation for all frequencies was reported in table 11.

Parameter	Equation	R^2
Ice crystal area (mm^2)	0.3979ln(t)+0.1859	0.957
Number of air bubbles	344.22ln(t)-174.21	0.974
Total area of air bubbles (mm^2)	3.5072ln(t)-0.8498	0.956
Average area of air bubbles (mm^2)	-0.0095ln(t)+0.037	0.614
Voltage (mV)	305.24ln(t)+518.84	0.964
Capacitance* (pF)	-0.3876ln(t)+43.033	0.945

Table 11 . Equations and determination coefficient of the functions for the different parameters during the freezing time.

Differences in capacitance due to the freezing time appeared low and ranging from a minimum of 0.60 pF (1 MHz) to a maximum of 1.66 pF (at 156 kHz).

The correlations between the capacitive devices and the parameters describing the state of the milkshake product during freezing process ranged from a minimum R^2 values of 0.881 for the total number of bubbles and a maximum R^2 values of 0.961 for the area of crystals (as reported in figure 37).

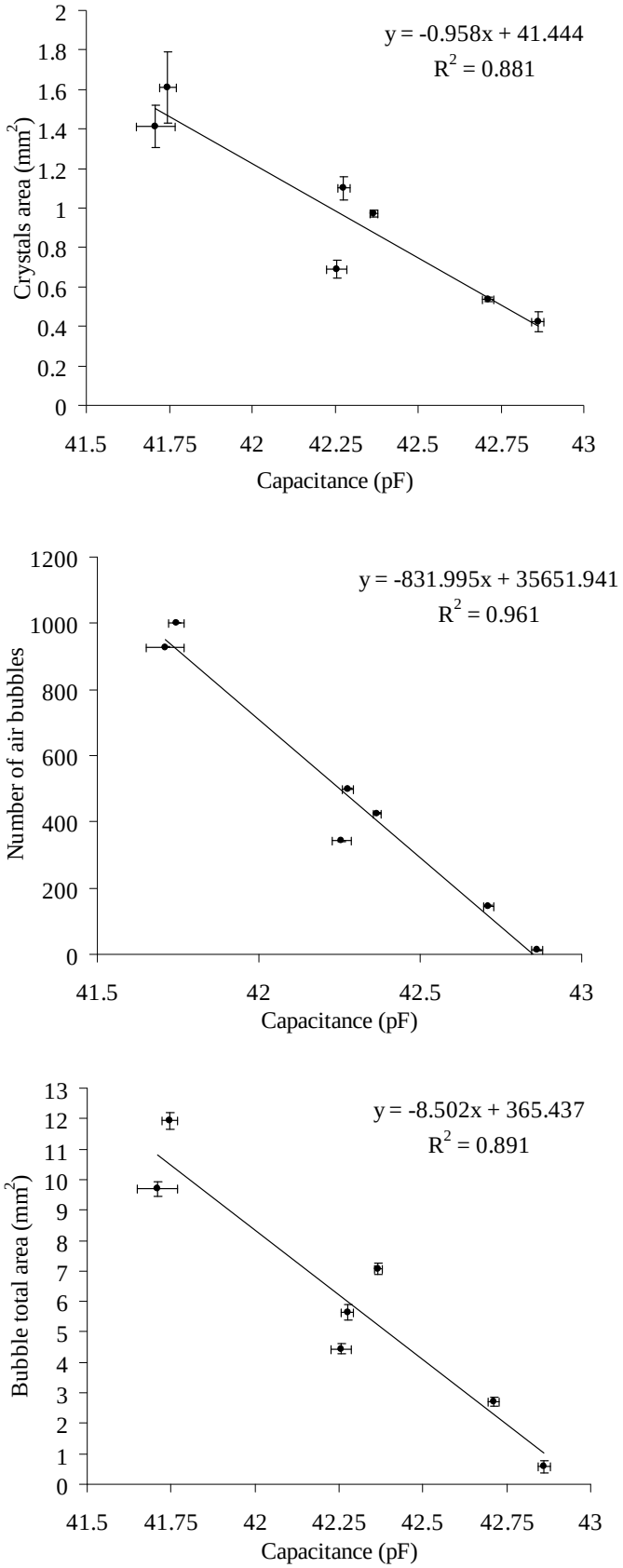

Fig. 37 Correlations between the capacitance and freezing process parameters (with standard error bars).

Conclusion

Beyond the results presented herein, it should be considered that the capacitive measurements are based on very small changes in capacity, which requires stable operating conditions and good instrumental measurements. However, this fragility maybe overcome by increasing the intrinsic capacity of the capacitor with a multi-plate structure.
Thus, this technique might advantageously used to monitor the freezing process, especially when processing a product characterized by a constant composition.

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6.3 Time Domain Reflectometry as screening for EVOO quality parameters assessment

The study of measurement systems for the assessment of basic qualitative and compositional parameters, based on the interaction of electromagnetic fields with oil products

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The assessment of quality and chemical parameters of EVOO is performed with different spectroscopic technique such as Near Infrared (Armenta et al., 2010; Jimenez et al., 2000; Muik et al., 2004; Bendini ety al., 2007) Infrared (Vlachos et al., 2006; Cerretani et al., 2010) and NMR spectroscopy (Hatzakis and Dais, 2008) in addition with statistical tools.

Recently, presence of water and adulteration detection have been conducted by using dielectric properties, by means of several technique such as parallel plate capacitor, open ended coaxial probes, transmission lines and resonant cavities (Icier and Baysal, 2004).

Dielectric properties of edible oils were explored and used for the prediction of water content (Lizhi et al. 2008 and 2010). Moreover Ragni et al. (2013) tested the effect of moisture content and fatty acid composition of different EVOO samples explored by using a parallel plate capacitor.

In this way the interaction between electromagnetic field and EVOO would be observed by using time domain reflectometry (TDR) measurements and multivariate statistical method. Relationship between the reflectometric signals and fatty acids alkyl esters content is the goal of the research.

Two olive cultivars characterized by different contents of fatty alkyl esters were employed for the analysis. The differences in terms of fatty alkyl ester acid content are due to different storage time conditions of olives. In order to produce two samples characterized by low and high levels of fatty acid alkyl esters, three olive storage times were defined: immediately after the harvesting for both cultivars, after seven days for Correggiolo and after for fifteen days of storage at atmospheric condition for “Canino”.

The instrumental chain was characterized by two silver plated copper wires covered by glass (to avoid electrostatic discharge) connected to a sampling head with TDR function fitted in an oscilloscope (Tektronix, 11801B) by a coaxial cable. Three ml translucent PE cuvette (Sigma, Milan, Italy) filled with 2.6 ml of oil sample was inserted in the probe. The reflections in the time domain were acquired (resolution 0.01 ps and 5120 stored data) by using a software written in Labview 8.2 (National Instruments, NI, USA). The instrumental chain was switched on 3 h before the beginning of the experiment to reach the thermal and electrical equilibrium. Five replications for each sample were carried out. The TDR signal obtained from each sample was subtracted from the signal acquired only with air.

The determination of fatty acid methyl esters (FAMEs) and fatty acids ethyl esters (FAEEs) were carried out according to the official method (IOC/T.20DOC., 2010; EC Commission Regulation EEC 2568/91, 2011).

A Principal component analysis (PCA) was applied to well understand the relations between the alkylester content and the time domain reflection signals.

Table 12 summarizes the mean values of the fatty acid alkyl esters of the EVOO samples used for TDR measurements. In terms of sum of FAME and FAEE mean values ranged from 66.6 to 701.8 mg/kg oil for “Correggiolo” (COR) and from 22 to 219, 6 mg/kg oil for “Canino” (CAN). A mixture between the two “Canino” samples (equal volumes) was also produced for TDR measurements.

Fatty acids Alkyl Esters (mg/kg oil)	COR 0	COR 15	CAN 0	CAN 7
FAME	26.4 (0.2)	191.6 (1)	22 (3.3)	184.9 (5)
FAEE	40.2 (5.9)	510.2 (2.8)	0 (0)	34.7 (2.5)
FAME+ FAEE	66.6 (6.1)	701.8 (1.9)	22 (3.3)	219.6 (7.6)
FAEE/FAME	1.5 (0.2)	2.7 (0)	0 (0)	0.19 (0)

Table 12 Fatty acids alkyl esters (Values between brackets are standard deviations).

Examples of the acquired waveforms (amplitude, V) in the time domain for the measurements conducted in oil and air are shown in figure 41.

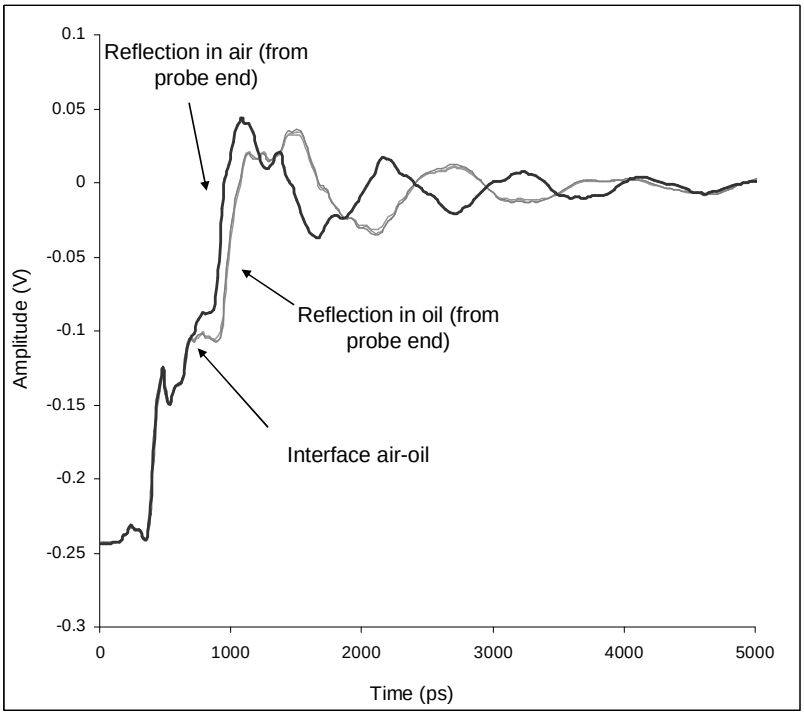

Figure 38. Amplitude (V) of the TDR acquisitions in air and oil.

TDR signals were analyzed by using a multivariate analysis approach to underlined the differences between EVOO composition. The principal component analysis conducted on the entire signal explained differences between sum of FAME and FAEE by the first principal component (PC1, figure 39) showing high loading values in the first rise step of the signal (Figure 40).

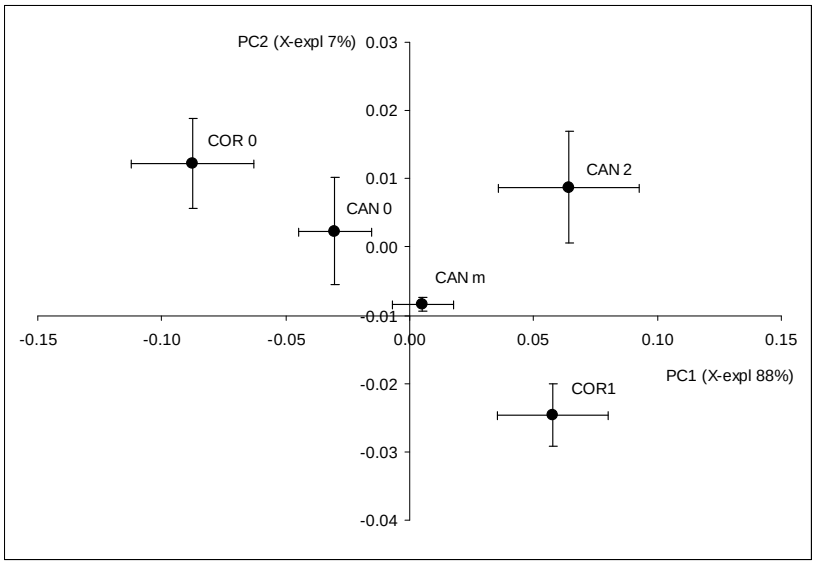

Figure 39 Scores plot (mean values) for the first two principal components of the TDR acquisitions Horizontal and vertical bars are standard deviations respectively for PC1 and PC2.

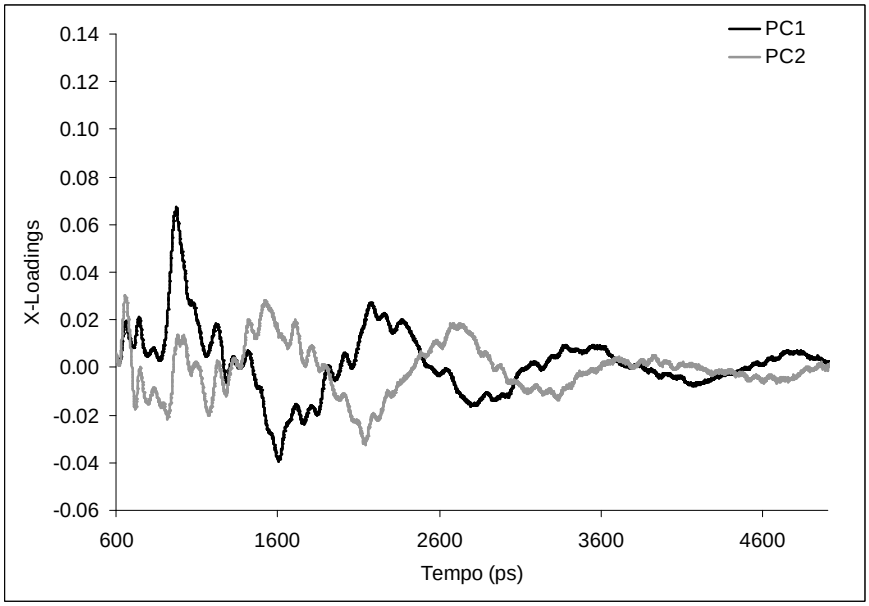

Figure 40 X-loadings for the entire TDR signal.

The single FAME and FAEE behaviours were not clearly distinguished probably due to the different cultivars and storage times.

Conclusion

Even if preliminary, these results show that TDR measurements and PCA could be useful for a rapid screening of important compositional EVOO quality components, such as alkyl esters fatty acids.

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6.2 Capacitive system for the estimation of wafer biscuit cooking process

Capacitive measurements were undertaken to wafers with the aim of estimating the degree of cooking during the production process. The wafer sheet of high quality level are characterized by low humidity. Furthermore, the quality of this baked products is also determined mainly by the flour, mixing process, the time and the cooking temperature. The baking process of the wafer takes place in stainless steel plates (shown in figure 41), at temperature of 160-190 °C and for a time between 1.5 and 2.5 minutes. Therefore, to ensure the high quality of the final product is important to monitor and maintain the ideal degree of cooking. The measures have been carried out after 5 minutes from the discharge of the cooking process, for 5 different degrees of cooking.

Fig. 41 Cooking machine for wafer sheet.

The instrumental chain was developed by using a capacitive system with a parallel plate capacitor as probe (Figure 42) made of stainless-steel with rough dimension of a wafer (260

x 440 mm). The distance between the plates was varied with the intention to measure the capacity of a single or more wafers overlapping.

Fig. 42 Parallel plate capacitor

At the end of the capacitive measures were undertaken compression tests on laboratory for the determination of the breaking strength (Figure 43).

Fig. 43 Compression device with cell of charge of 1 kg.

The moisture content was determined according to the oven method (105°C for 16h). For all the cooking degree the water content of the wafers was very low, always less than 1 % (figure 44).

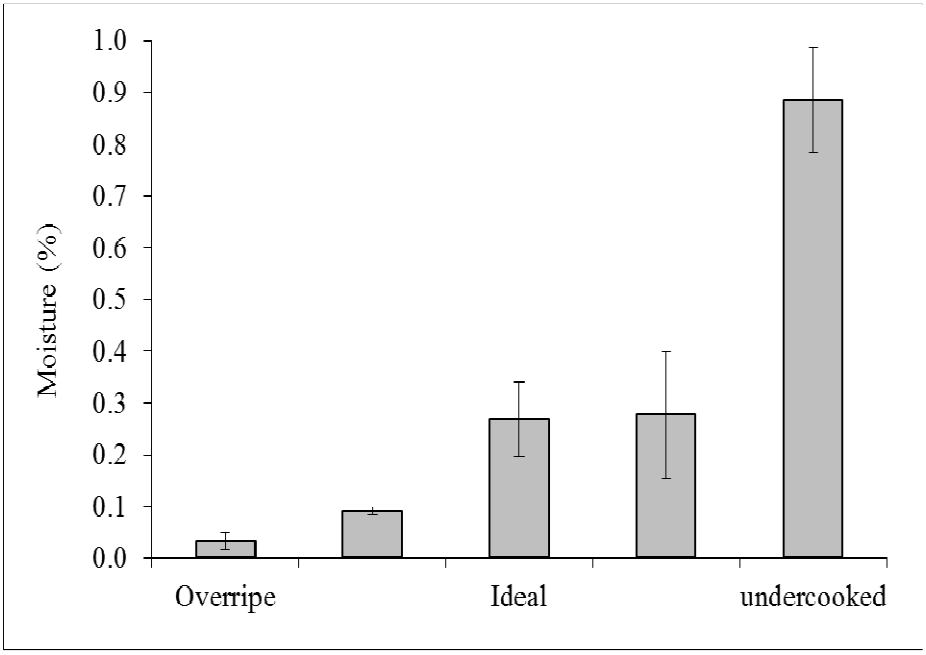

Fig. 44 Moisture content in function of the coking level.

As expected the force of rupture decrease with the level of cooking (Figure 45). The force of rupture of samples overripe declined to increase the level of cooking.

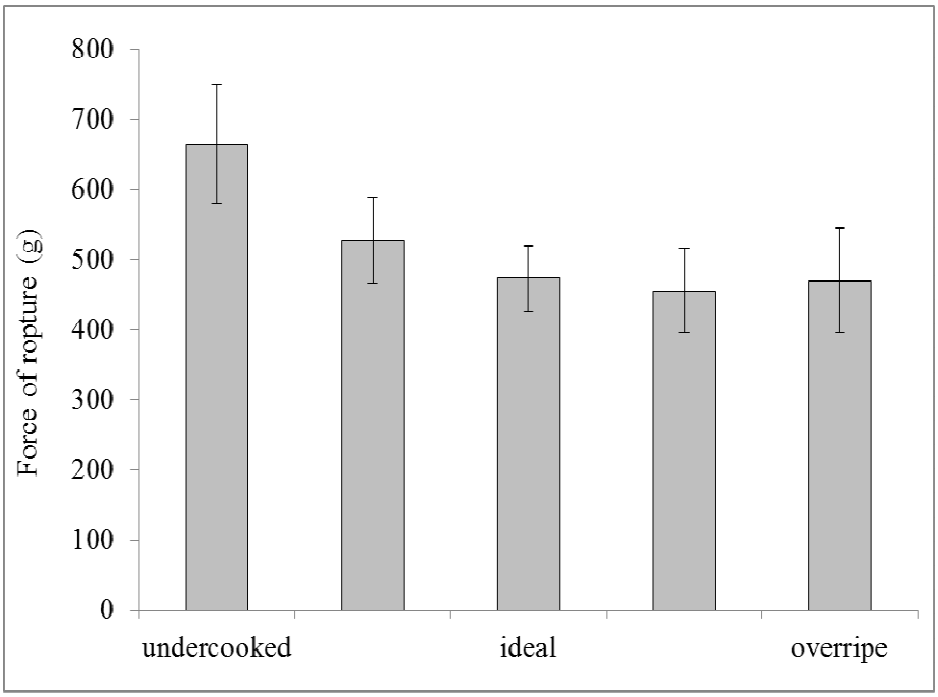

Fig. 45 Force of rupture trend in function of the cooking level.

For each measure was determined the value of the capacitance with the probe empty to subtract from the measurement made on the wafer.

Figure 46 shows the trend of the capacitance values measured and the level of cooking of one wafer sheet. Considering only one sheet have not been observed strong differences between the level of cooking. This result can be probably due to the intrinsic variability of the wafer sheet.

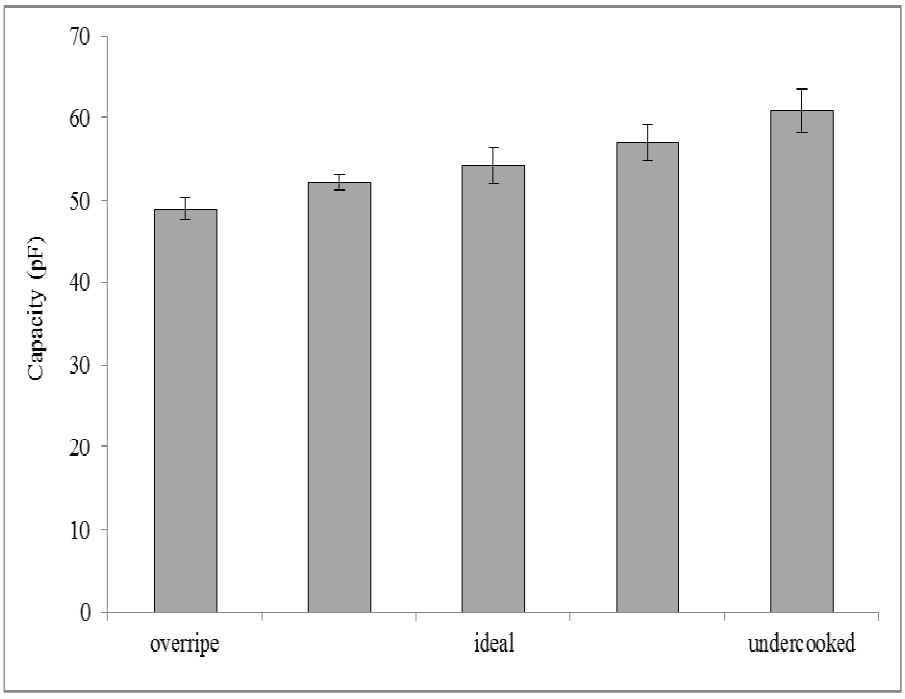

Fig. 46 Capacitance values of one wafer sheet in function of the cooking level.

In this way five wafer sheets overlapped were submitted to test. All samples with different levels of cooking have proved to be significantly different. The analysis of five wafer sheet was found to be more efficient, since it allows to limit the error due to the inherent variability of the product.

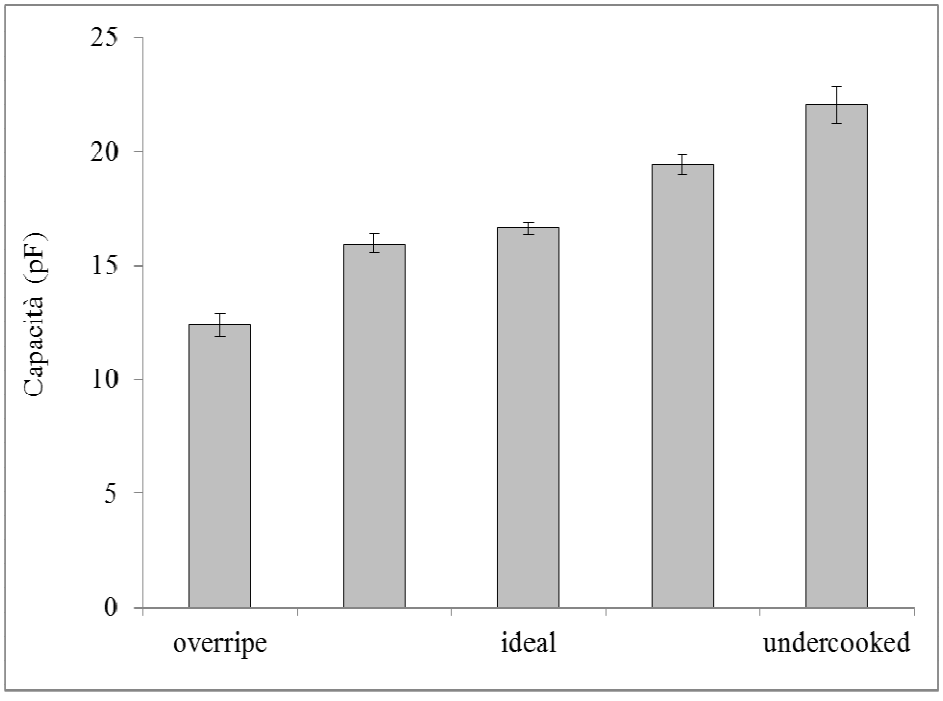

Fig. 47 Capacitance values of five wafer sheets in function of the coking level.

Conclusion

The method based on the use of mechanical press was not able to discriminate the wafer sheet as function of the degree of cooking.

On the contrary, the capacitive measures resulted in instance to discriminate wafer in function of the five degrees of cooking identified. The method of more wafers at the same time has proved to be more accurate, and has allowed us to limit the error due to the inherent variability of the wafer.

In conclusion, the proposed method can be easily applied in-line process control and it does not require any particular preparation of the operator.

7. Conclusion

The interest in the measurement of the dielectric properties is not an end goal into itself, but should be an intermediate vehicle for explaining certain physic-chemical behavior of food.

This thesis showed how based on dielectric properties sensors, devices and technique can identify small quantities of chemical species, probe the mobility of food molecules and look inside them with minimal intrusion, in real time for evaluation of almost of the food property. The assessment by these electronics devices provide fast data useful to made possible efficient process control.

Advancement can be done to realize the technological transfer to introduce effective application of novel apparatus for potential modern control system in food industry.