Dielectric spectroscopy in agrophysics

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Abstract. The paper presents scientific foundation and some examples of agrophysical applications of dielectric spectroscopy techniques. The aim of agrophysics is to apply physical methods and techniques for studies of materials and processes which occur in agriculture. Dielectric spectroscopy, which describes the dielectric properties of a sample as a function of frequency, may be successfully used for examinations of properties of various materials. Possible test materials may include agrophysical objects such as soil, fruit, vegetables, intermediate and final products of the food industry, grain, oils, etc. Dielectric spectroscopy techniques enable non-destructive and non-invasive measurements of the agricultural materials, therefore providing tools for rapid evaluation of their water content and quality. There is a limited number of research in the field of dielectric spectroscopy of agricultural objects, which is caused by the relatively high cost of the respective measurement equipment. With the fast development of modern technology, especially in high frequency applications, dielectric spectroscopy has great potential of expansion in agrophysics, both in cognitive and utilitarian aspects.

Keywords: agrophysics, dielectric spectroscopy, food quality

Introduction

Agrophysics is a specialized scientific field derived from the branch of the agricultural sciences (Michalek, 2006). Its aim is to apply physical methods for studies of properties of materials and processes occurring in production and processing of crops and food of agricultural origin. Dielectric properties of all materials existing in Nature are dependent on their molecular structure. Specifically, they depend on the distribution of electric charges, which are either constantly embedded within the molecules or become temporarily induced on their surfaces. It is also known that the molecular structure of objects determine their physical and chemical properties. Therefore, one may suppose that the dielectric properties of mixtures of various molecules constituting a given material will uniquely identify it. It means that dielectric properties can successfully diversify physical and chemical properties of a tested material. This idea is presented in Fig. 1. The crucial point of the application of the dielectric spectroscopy measurement techniques in agrophysics is the utilization of their advantages for rapid and non-destructive assessment of the quality of the agricultural objects. It may be done by searching for dependencies between the dielectric properties and other physical and chemical properties of tested materials of agricultural origin.

Behaviour of any material in the electric field is unique, because of the unique molecular structure of each material. On the other hand, physical and chemical properties of materials determine their quality, which in the case of food products is closely related to their commercial and nutritional value. Therefore, it is reasonable to assume that the dielectric properties, uniquely describing each complex material (consisting of various substances mixed in different proportions), may provide information about its quality. This hypothesis has been verified in various scientific studies dealing with diversification of the quality parameters based on electric, especially dielectric properties of tested objects (Hlaváčová, 2005; Nelson and Datta, 2001; Nesvadba et al., 2004; Ryyänen, 1995; Venkatesh and Raghavan, 2004). More detailed research results are described below. However, practical implementations of the materials characterization in a broad frequency range by dielectric spectroscopy is still rare. According to Kaatze (2008), this can be done by accuracy enhancement of dielectric measurements and development of sensors as well as measurement systems.

Let us analyze a simple example: we want a good yoghurt. Despite subjectivity of the ‘good yoghurt’ expression, it is possible to analyze chemically and physically a sample of

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yoghurt and in effect receive a set of numbers uniquely describing the physical and chemical parameters of the sample. The examined properties include density, viscosity, the content of protein, fat, water, carbon, nitrogen and other elements, the amount and type of bacteria, etc. The more data has been gathered, the more we know about the material under test. Therefore, it may be possible to replicate the yoghurt sample while conserving its ‘goodness’. However, some of the necessary examinations are time consuming and require an expensive laboratory equipment. In most cases, we are interested whether a given batch of yoghurt is the same as the previous one, which has already been thoroughly examined and has been commercially successful. Because of that, one needs to find a fast and reliable indicator, which would contain comprehensive information about parameters of a ‘good yoghurt’. It is expected to find such an indicator among the dielectric parameters of yoghurt.

There exists the need for a quality index which would unambiguously describe the uniqueness of a tested material, while being easily and rapidly measurable. Also, it would be desirable for such measurements to be non-destructive or even non-invasive. Dielectric spectroscopy of agrophysical objects gives promising tools for achieving this objective and the text below presents the state of the art in this field with some introduction about its physical fundamentals.

**Physical fundamentals of dielectric spectroscopy**

Dielectric spectroscopy provides tools for examining the interactions between the electric field and tested materials. It is necessary to consider various dielectric mechanisms and polarization effects, which comprise the dielectric permittivity of the object. The electric charges become polarized in order to compensate for the applied electric field, so that the positive and negative charges move in opposite directions. Each of the polarization mechanisms: ionic, dipolar, atomic and electronic (Fig. 2) possesses its own limiting frequency.

![Fig. 1. Quality parameters of heterogeneous materials of agricultural origin described by physical and chemical parameters as well as the dielectric ones.](image)

![Fig. 2. Frequency dependence of the dielectric polarization mechanisms and corresponding ranges of the electric field frequency for a salt and water solution: MW – microwave, IR – infrared, V – visible, UV – ultraviolet (Agilent, 2006).](image)

When the frequency rises above the specific limiting value, the slower mechanism, previously determining the real part of the complex permittivity, gives way to the faster effect. For practical applications in agrophysics, the applied frequencies usually do not exceed 20 GHz. It is the consequence of the special role of water, relaxation frequency of which is approximately equal to 19 GHz (Kaatze, 2005). Therefore, our considerations will focus on two dielectric mechanisms: ionic and dipolar.

Dielectric permittivity $\varepsilon^*$ (F m$^{-1}$) of a material is a complex physical quantity, which is usually given as a relative value with respect to vacuum permittivity $\varepsilon_0 = 8.85 \times 10^{-12}$ (F m$^{-1}$). The real part of the dielectric permittivity, $\varepsilon_\rho$, indicates the amount of energy stored in a dielectric material as a result of the applied external electric field. For a pure dielectric in a constant electric field, this quantity is known as the dielectric constant. The imaginary part of the dielectric permittivity, $\varepsilon''$, represents energy loss of the external electric field when
applied to the tested material and is called the loss factor. At low frequencies, an electric dipole of a water molecule rotates freely following the direction of the electric field. This type of polarization is a form of energy storage. Simultaneously, positive and negative ions of dissolved salts move in accordance with the electric field. Such electric current is then responsible for energy loss. When rising the frequency, water molecules will not be able to keep up with the changes of the direction of the electric field, because of their inertia that is described by relaxation time, \( \tau \). This is the reason for a decrease in the electric field energy storage and an increase in the rotation energy losses. The frequency for which this phenomena occurs is called the relaxation frequency, \( (2\pi\tau)^{-1} \) of a given polarization mechanism. At even higher frequencies, water molecules do not respond to the electric field.

Two basic agrophysical applications of the dielectric spectroscopy include measurements of water content in liquids, solids and multiphase mixtures, and microwave heating, are closely connected with the unique structure of water molecules. These molecules possess an intrinsic dipole moment, which is the reason for a relatively high value of the real part, \( \varepsilon'_r \), of the relative complex dielectric permittivity, \( \varepsilon^*_r \) (approximately equal to 80 at room temperature). For solids and non-polar liquids this value does not exceed 5, and for air it is equal to 1. Salinity is another parameter which significantly modifies the quality of the agrophysical objects. Salinity affects their dielectric conductivity \( \sigma \) \((\text{S m}^{-1})\) and simultaneously it is one of the constituents of the imaginary part, \( \varepsilon'_i \), of the complex dielectric permittivity of agrophysical materials, which can be described by the relation (Chełkowski, 1993):

\[
\varepsilon^*_r = \varepsilon'_r - j\varepsilon'_i = \varepsilon'_r - j(\varepsilon'_D + \varepsilon'_G),
\]

where: the energy losses of the applied electric field are caused by the inertia of the dipole molecules in high frequencies and by the ionic conductivity, which are described correspondingly by \( \varepsilon'_D \) and \( \varepsilon'_G \), \( j = \sqrt{-1} \). The second component results from the dissolution of salts and is given by the expression \( \varepsilon''_r = \frac{\sigma}{2\pi f \varepsilon_0} \), where \( \sigma \) \((\text{S m}^{-1})\) is a low-frequency ionic conductivity, \( f \) is the frequency and \( \varepsilon_0 = 8.85 \times 10^{-12} \text{ (F m}^{-1}) \) is the vacuum permittivity. Other mathematical model of the complex dielectric permittivity, \( \varepsilon^*_r \), of polar liquids developed by Debye (1929) is given by the formula:

\[
\varepsilon^*_r = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + j\omega\tau},
\]

where: \( \varepsilon_\infty \) and \( \varepsilon_S \) are the values of the real part of the dielectric permittivity of polar molecules at very high and very low frequencies, respectively, \( \omega = 2\pi f \) and \( \tau \) is the molecules relaxation time. Figure 3 presents the frequency dispersion of the real and imaginary parts of \( \varepsilon^*_r \) for the NaCl water solution. It shows that for low frequencies the energy loss is caused mainly by the ionic conductivity, \( \sigma \), while for high frequencies it is due to the inertia of the electric dipoles \( \varepsilon'_D \).

For most substances, the dielectric permittivity and electrical conductivity are constant only in a limited frequency range. With the rise in frequency, the dielectric permittivity decreases while the conductivity abruptly increases. These abrupt changes are called dispersions, and each of them represents a given polarization mechanism (Fig. 5). Agrophysical materials are mainly biological in nature and they are characterised by high dispersions, especially the one in low frequencies, which is caused by an interfacial polarization on surfaces between the constituents of a tested material (Markx and Davey, 1999).

The theoretical studies concerning the dielectric models of multiphase materials and verification of such models are already being conducted for many years (Asami, 2002). Nowadays, the dielectric spectroscopy measuring techniques undergo rapid development, thanks to the widespread use of computer controlled measuring devices and the availability of specialized high-frequency electronic components as the result of rapid increase of the data transfer rate through the omnipresent cellular networks. Therefore, having now necessary measuring tools in microwave frequency range,

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**Fig. 3.** The real part (a) and the absolute value of the imaginary part (b) of spectra of the complex dielectric permittivity of water (inverted triangles) and 0.5 mol l\(^{-1}\) NaCl water solution (points, circles, semisolid circles). For the salt solution, total losses were presented, including the effect of the ionic conductivity and the dielectric losses (Kaatze, 2007).
validation of the developed dielectric models of agrophysical objects is now possible. This technological development is especially prominent in the high-frequency reflectometric frequency-domain (FDR) and time-domain (TDR) techniques (Chen et al., 2010; Piuzzi et al., 2009; Skierucha, 2009; Skierucha and Malicki, 2004). The gigahertz frequency range is essential, due to the relaxation time of free water of about $8.3 \times 10^{-12}$ s (Kaatze, 2007). The aforementioned technological development has increased the measurement capabilities in the microwave range, thus enlarging the importance of the dielectric spectroscopy techniques in studies of materials, the properties of which change along with the water content.

Among the techniques of the high-frequency domain, one may distinguish the reflectometric and transmission methods for analysing the response of a tested material to a given electric signal (Fig. 4).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig4}
\caption{Measuring techniques of dielectric spectroscopy analysing reflected and transmitted signals (Agilent, 2000).}
\end{figure}

In contrast to the transmission techniques, the reflectometric ones applied in the dielectric spectroscopy allow for construction of portable sensors and meters for assessing dielectric properties of materials. Because of that, the dielectric spectroscopy is a very promising method eg for industrial quality control of materials and products of the agricultural origin (Venkateshand Raghavan, 2004) and biomass (Kiviharju et al., 2008). With these techniques, it is possible to control the quality of the aforementioned materials even in real time during their processing. Also, they may be especially useful for determining the quality of the materials and products of agricultural origin (Nelson and Datta, 2001).

\section*{Examples of applications}

The practical interest in the dielectric properties of agricultural materials and food products of the agricultural origin is mainly due to the need for optimization of microwave drying and heating processes (Rynänen, 1995), as well as the development of reliable techniques for rapid measurements of the water content (Nelson and Trabelsi, 2009). The dielectric behaviour of single-phase materials eg water, methanol is comprehensively described in literature (Hasted, 1973). However, the agrophysical objects are usually multiphase materials, like soil. The analytical description of the complex dielectric permittivity of such objects is complicated. These difficulties are caused by physical and chemical effects occurring on phase boundaries. The observed dielectric phenomena show temperature dependence, dispersion and existence of many characteristic points on the graph, providing great research opportunities (Nelson, 2010). Particularly, it is possible to diversify these materials with respect to their dielectric properties and correlate those properties with the tested objects quality parameters, commonly determined by their physical and chemical properties.

\subsection*{Microwave aquametry of porous materials}

The unique properties of water in a natural manner direct applications of the dielectric spectroscopy in agrophysics towards determinations of water content in porous materials. Moisture and salinity are essential for quality assessment of agricultural porous media, which include soil and granular as well as powder materials of agricultural origin. Grain stored in silos cannot be too moist, because, being a biological material, it is susceptible to degradation in the presence of water. The excessive moisture of grain often causes significant financial losses (Nelson et al., 1999). The content of water and organic salts in materials and products of agricultural origin are main factors affecting their quality, which in turn translates into their commercial value (Lewicki, 2004). Most of the structural defects of biological materials are caused by improper storage, transportation or manufacturing process. These defects affect the volumetric proportions and concentrations of aqueous solutions present in the objects. The widespread use of the dielectric permittivity sensors and meters would allow for rapid, non-destructive, reliable and definite assessment of the quality parameters of the porous bodies.

The application of the microwave techniques enabled the development of the non-destructive methods of porous media water content control in production, trade, processing and storage of these materials. The new-born field of metrology is called microwave aquametry (Agilent, 2006; Kraszewski, 2001). As a result of particular properties of the microwave radiation (of frequencies between 1 and 100 GHz), the microwave techniques for moisture assessment proved to be more advantageous than other methods, including the use of radio frequencies (of the order of 1 MHz), infrared or ionizing radiation. The obvious advantages of application of microwaves, determined by existing studies, are listed below:

\begin{itemize}
  \item in contrast to the low frequencies, the influence of electrical conductivity on the measurement selectivity is negligible,
  \item the penetration depth is much greater than for the infrared radiation techniques, which allows for examination of the greater volumes of material transported on conveyor belts or through pipelines,
  \item the physical contact between a measuring device and a tested object is not necessary, which enables continuous remote monitoring,
\end{itemize}
– in contrast to the infrared radiation, microwave techniques are relatively insensitive to environmental factors, therefore dust and water vapour occurring in industrial conditions do not influence the measurement,

– liquid water reacts in a specific manner in selected frequencies of the microwave range (the relaxation effect), thus enabling detection of even small amounts of water,

– in contrast to chemical methods eg Karl Fischer titration, microwave techniques do not pollute the tested material, therefore provide the means for non-destructive measurements.

**Hydrological modelling and weather forecasting**

Protection of natural environment that constitutes the habitat of human beings, is another field of the research interest of agrophysics. Collection, archiving and processing of relevant environmental data are necessary for successful conservation efforts. Monitoring of soil moisture, snow and flood banks may help to prevent catastrophic results of floods, avalanches and mudslides. The knowledge about the water balance in the soil will improve management of this deficit natural resource. It will also optimize food production, improve weather forecasts and support decision making about strategic investments (Seneviratne et al., 2010).

Dielectric moisture measurement techniques (especially the TDR technique), giving the possibilities of automatic measurements, allow for the construction of inexpensive soil moisture monitoring stations. This in turn enables verification of hydrological models and assess soil water balance at point, field, catchment, state and even continental scales. Data from these stations are necessary for calibration, interpretation and validation of the Earth satellite images (Kerr, 2006). Computer processing of the huge amount of available data requires access of a large number of scientists. With this in mind, the International Soil Moisture Measurement Network (Dorigo et al., 2011) is an example of an open access research network. Scientific collaboration enables distribution of data from various ground stations that monitor soil water content. For example, soil moisture data from six ground monitoring stations located in the Polesie National Park are made available by the Institute of Agrophysics PAS in Lublin (Skierucha et al., 2010) within the aforementioned network.

**Dielectric properties of granular materials of agricultural origin**

Dielectric properties of grains and seeds in a wide range of frequency and moisture have been described in various studies (Nelson, 2010; Nelson et al., 1999). Also, theoretical models describing the dielectric permittivity of cereal grains as a function of frequency, moisture and density have been developed (Kraszewski and Nelson, 1989; Nelson, 1987). The values of the dielectric permittivity of one variety of wheat for the frequencies from 10 to 1 800 MHz and temperatures from 25 to 95°C have also been examined (Nelson and Trabelsi, 2006). The conducted studies provide the basis for the calibration of the moisture meters for grain stored in silos and for developing adequate temperature corrections.

Furthermore, the research on the dielectric properties of grains and oilseeds in the microwave frequency range has proved that the density of grain or seeds mixtures with air may be determined independently of moisture, which is especially important for on-line monitoring of materials transported on conveyor belts or through pipelines (Trabelsi et al., 1998a, b).

The influence of drying processes on the quality of rape-seeds (Kachel-Jakubowska and Szpyrgiel, 2008) and the effect of contaminations on their storage (Tys et al., 2003), are exemplary problems, which may be solved with application of the dielectric techniques. It is evident that the dielectric spectroscopy shows a great research potential in this field.

**Dielectric properties of liquid materials of agricultural origin**

Various groups of liquid foods and agricultural materials were examined. For example, dielectric properties of vegetable oils and fatty acids in low frequencies (0.1-1 MHz) were studied by Lizhi et al. (2008). It occurred that, for the applied frequencies, one may distinguish various oils and fatty acids by analysing their frequency spectra of the dielectric permittivity. On the basis of this research it is therefore possible to detect whether olive oil has been adulterated with cheaper vegetable oil (Lizhi et al., 2010).

Aqueous solutions were also tested. For example, Garcia et al. (2004) examined the complex dielectric permittivity of a grape juice and wine for frequencies from 0.2 to 3 GHz using a coaxial open-ended probe. It was found that the dielectric properties of those liquids allow for their identification. Next, solutions of the acetic acid and vinegar were studied by Bohigas and Tejada (2009) in the frequency range 1-20 GHz, while examinations of the dielectric properties of various fruit juices (apple, pear, orange, grape and pineapple) for frequencies 20-4 500 MHz at temperatures 15-95°C were conducted by Zhu et al. (2012). It was observed that the real part of the dielectric permittivity decreases linearly with the increase in temperature. Furthermore, various juices are selectively differentiated by the values of both parts of the complex dielectric permittivity.

Because of their complicated chemical composition, dairy products are another interesting agrophysical objects for dielectric studies. For example, Nunes et al. (2006) examined the complex dielectric permittivity of UHT milk in a frequency range 1-20 GHz. Their research included analysis of the influence of spoilage and organic compounds content on the dielectric parameters of milk. The expected effect has been observed. However, obtained spectra were too smooth to allow distinguishing between chemical species in milk. Also, dielectric properties of natural and sweetened yoghurt has been studied in frequencies 1-20 GHz.

**Protection of natural environment**

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(Bohigas et al., 2008). The conclusion was that the dielectric spectroscopy measuring techniques are sensitive enough to detect sugar concentration in yoghurt samples.

**Dielectric properties of fruit**

Cultivation of orchards, especially production of drupes, is the main agricultural activity in many regions of Poland. Rapid, reliable and non-destructive assessment of quality parameters of fruit eg firmness, soluble solids content, pH, moisture, electrical conductivity, is helpful in production, harvesting, storage and processing. So far, research utilizing the measurement potential of the dielectric spectroscopy techniques for examinations of quality of fruit and products made from fruit has not been conducted in Poland. Such studies are underway in other countries, however their scope is limited to laboratory examinations.

The differences between the dielectric permittivity value of peel and pulp of apples and melons have been presented in several papers (Guo et al., 2007b, 2011b; c; Nelson et al., 2006). The values of permittivity of fresh fruit and vegetables are measured in various frequency ranges in order to identify mechanisms of the electric polarization occurring in the tested materials. Those frequencies include ranges 10-1 800 MHz (Wang, 2003) and 0.2-20 GHz (Nelson et al., 1994). Moreover, the dielectric properties were studied for the purpose of determining the postharvest changes in the fruit pulps in various storage conditions. It has been found that the dielectric constant and loss factor depend linearly on the soluble solids content, mainly glucose and fructose, in the melon pulp (Guo et al., 2007a; Nelson et al., 2006), as well as for watermelons and apples (Guo et al., 2007b). However, the obtained results could not been used for prediction of glucose and fructose content both in watermelons and apples. The causes for changes in the dielectric permittivity of fruit during storage are analyzed by comparing the dielectric properties of tested objects with their other physical and chemical properties. A good correlation has been found between the apple maturity index (Thiault Index) and newly defined dielectric maturity index (Castro-Giráldez et al., 2010). The dielectric maturity index has been based on measurements of the loss factor determined for two frequencies: 0.5 GHz and the dipolar relaxation frequency, which depends on a tested material. The studies were conducted with the use of a type 87070 Agilent open-coax probe (Agilent, 2008a), which is an accessory to a vector network analyzer (VNA). So far, this is the only commercially available sensor used for broadband measurements of the dielectric properties of liquid and solid materials. Unfortunately, this measuring system is too expensive for industrial applications.

**Microwave heating**

It is possible to selectively destroy pests feeding on grains eg grain weevils, by subjecting a grain batch to microwave (MW) or radio frequency (RF) heating. Cereal grains are susceptible to heating at a much higher frequency of the applied electric field than the biological tissues of pests. Nelson (1996) proved that the loss factor for wheat weevil achieves the maximum value at the RF frequency range 10-100 MHz.

Heating by an alternating electric field may be used for development of effective pasteurization techniques. In order to eliminate harmful microorganisms, pasteurization processes are usually applied before packaging of the final product. Thermal conditioning is also used to dissolve sugar crystals, delay the crystallization processes and maximally preserve the commercial properties of food products. However, because of small thermal conductivity, conventional thermal treatments are time-consuming and require high temperatures. In turn, this may negatively influence the treated products (Guo et al., 2011a) eg by destroying the vitamins and nutritional substances. Dielectric heating, with regard to the RF and MW frequencies, through direct transfer of electromagnetic energy into the interior of the material, enables fast heating of a selected volume (Wang et al., 2007). The high rate of the RF and MW heating, energy efficiency and bulk influence on a sample preserve the product quality and increase the effectiveness of the pasteurization processes. However, the optimal selection of frequency and the penetration depth are necessary conditions for achieving high efficiency of RF and MW heating for a given material undergoing the thermal treatment (Wang, 2003). Additionally, the individual properties of a thermally treated material, such as viscosity, water content and chemical composition, influence its dielectric properties and therefore have an impact on RF and MW heating efficiency (Piyasena et al., 2003).

**Measuring equipment**

Dielectric permittivity measuring equipment as well as selection and construction of test fixtures depend on an examined dielectric material (liquids, solids or mixtures), its texture, measurement volume, frequency range, accuracy required, availability of equipment and other necessary measures, including financial resources (İçeri and Baysal, 2004; Venkatesh and Raghavan, 2005). Vector network analyzers (VNA) (Agilent, 2000) are expensive, but very versatile and useful for broadband frequency examinations, including research on dipolar polarization mechanisms of a test material (γ dispersion in Fig. 5). Scalar network analyzers and impedance analyzers (Agilent, 2008b) are cheaper. However, their applicability is limited to the frequency range of the α and β dispersions.

An open-coax probe type 85070 from Agilent Technologies (Agilent, 2008a) working in the frequency range 0.2-50 GHz is a commonly used instrument for measurements of the complex dielectric permittivity spectrum of liquids, biological materials and multiphase mixtures. The probe with specialized software is an accessory of VNA and
it measures the S11 reflection parameter from the contact surface of the probe with the tested material (Fig. 6a). S11 stands for the ratio of the magnitude change and the phase shift of the reflected signal from the probe to the incident signal generated by VNA. Using models incorporated in the supplied software the user acquires real and imaginary parts of the dielectric permittivity of the material. In more economical solutions, instead of the expensive 85070E probe, modified type N or SMA coaxial connectors are used. They perform correctly up to the frequencies of several GHz (Skierucha et al., 2004; Zajíček et al., 2008). By using microwave waveguides or coaxial transmission lines, it is possible to measure the S21 transmission parameter (the ratio of transmitted signal through the tested material to the incident one) in addition to S11. The interpretation of the S21 parameter allows for determination of not only the complex dielectric permittivity (Fig. 6b), but also the magnetic permeability of a sample (Shang et al., 1999).

In the reflective mode of work the VNA generates a sine wave signal in a broad frequency range eg 20 kHz – 8 GHz in the case of the Rhode and Schwarz VNA of the ZVCE type, which reflects from the probe and is received by the VNA, where the separation of the incident and the reflected signals occurs (Agilent, 2006). The phase and the amplitude of the signal reflected from the probe depend on the dielectric properties of the tested material. The frequency spectra of $\varepsilon'(f)$ and $\varepsilon''(f)$ are calculated on the basis of theoretical models describing the probe in a dielectric medium. Development of an appropriate broadband model, which relates the VNA response to the complex dielectric permittivity of a material, requires numerical calculations as well as calibration measurements of objects, usually liquids, of known $\varepsilon*$(f) characteristics (Skierucha and Wilczek, 2010). It needs to be stressed out that the application of high frequency fields is necessitated by the measurement selectivity of the real part $\varepsilon'$ of $\varepsilon*$. Furthermore, it is required to treat the elements of the measuring system as a distributed parameter system (Wilczek et al., 2011).

At low measurements frequencies, where the dielectric permittivity sensor may be regarded as a lumped parameter system, it is possible to apply techniques and equipment used in the impedance spectroscopy (Agilent, 2008b). FDR (frequency-domain reflectometry) meters for soil moisture measurements use sensors, which are described by a capacitor that changes its capacity depending on the soil water content. Such instruments are widely commercially available for soil moisture measurements (Bogena et al., 2007). They perform usually at a constant frequency below 100 MHz. However, they require individual calibrations and give significant measurement errors due to salinity of the soil (Skierucha and Wilczek, 2010).

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**Fig. 5.** An idealized spectrum of the dielectric properties of biological materials. The abrupt changes of the dielectric permittivity are called the dielectric dispersions and are caused by the losses from several polarization mechanisms, which correspond to given frequency ranges. The $\alpha$ dispersion is caused by a parallel flow of ions through the cell walls. The $\beta$ dispersion is due to the accumulation of the electric charge on the cell membranes, a phenomenon described by the Maxwell-Wagner effect. Next, the $\delta$ dispersion is caused by the influence of the bound water, whereas the $\gamma$ dispersion is due to the intrinsic electric dipoles of small molecules, particularly water (Markx and Davey, 1999).

**Fig. 6.** Dielectric sensors for porous materials, solids, multiphase mixtures and liquids: a – open-coax type reflection probe, b – transmission probes in a waveguide and a coaxial cable (Agilent, 2000, 2008a).
Time-domain reflectometry (TDR)

The frequency spectrum of complex dielectric permittivity of a material may also be obtained from the Fourier transform of a relectogram of the sensor response to the forcing pulse. In this case, a section of a parallel waveguide consisting of two or three stainless steel rods placed in a tested material acts as a dielectric permittivity sensor. The input data of this transform is obtained by a TDR technique, which was adopted from the telecommunication technology by agrophysics as a method for evaluating soil moisture (Malicki and Skierucha, 1989, 2002; Malicki et al., 1992; Skierucha, 2000; Topp et al., 1980) and soil salinity (Malicki and Walczak, 1999; Friedman, 2005).

An electric pulse on an input of a waveguide of length, \( l \), travels along the waveguide, reflects from its end and returns. Identification in time of the reflections of the pulse inside the waveguide allows to calculate the travel time, \( t_p \), on distance, \( 2l \), with the use of Eq. (3) and the following relation. It gives (Kupfer and Trinks, 2005):

\[
  t_p = \frac{2l}{v} = \frac{2l}{c} \sqrt{\varepsilon_r - \frac{1}{2} \sqrt{1 + \tan^2 \delta_e + 1}},
\]

where: \( \delta_e = \varepsilon'_e / \varepsilon''_e \) is defined as a loss tangent or dissipation factor, \( v \) is the speed of the pulse in the material and \( c \) is the speed of light in the vacuum. In the case of a non-saline material when its conductance is negligible, it is possible to assume that \( \tan^2 \delta_e \approx 0 \). Therefore, formula (3) will simplify to:

\[
  t_p \approx \frac{2l}{c} \sqrt{\varepsilon_r}.
\]

The real part of the complex dielectric permittivity of a material calculated from TDR reflections does not have defined the measurement frequency range, which depends on the rise time of the pulse, the material frequency dispersion, its salinity and the length of the parallel waveguide. Also, sometimes the measured material is not homogeneous like soil in natural conditions. Therefore, it is accepted to give to the TDR-calculated real value of dielectric permittivity the name of the apparent or bulk dielectric permittivity. It represents a mean value of \( \varepsilon'_e \) of the tested material in the volume of a cylinder with the TDR sensor parallel waveguide inside in the middle. One of the advantages of the TDR technique in determination of water content of porous materials is that the resulting value of the dielectric permittivity is approximated over the sample volume determined by the length of the waveguide rods. It is important especially for inhomogeneous distribution of water inside the volume of a material such as soil.

The popularity of the TDR techniques comes from the availability of the equipment, feasibility of automatic and non-destructive measurements, ease of calibrations and its universal form for the determination of moisture of various groups of materials. Therefore, it is possible to apply this technique to other studies, including analysis of spatial variability of soil moisture (Janik, 2008), determination of soil density (Durham, 2003), water conductivity and water capacity of construction materials (Pavlik et al., 2006; 2008), determination of quality of biomass and biofuels (Paz et al., 2010), level assessment of liquid petrochemical materials in industrial applications (Pizziet al., 2009), quality evaluation of vegetable oils (Cataldo et al., 2010). The Institute of Agrophysics PAS in Lublin has significant scientific achievements and practical implementations in this area (Malicki and Skierucha, 1989; Malicki and Walczak, 1999; Malicki et al., 1996; Skierucha, 2009; Skierucha et al., 2008a, b). TDR meters of soil moisture, salinity and temperature developed by the Institute of Agrophysics PAS in Lublin are used in many laboratories worldwide.

Two of the devices are presented below: an eight-channel meter type TDR/MUX/mpts with a GPRS modem MIDL-2 type and a field meter FOM/mts with a field probe type FP/mts (Figs 7 and 8). They are exemplary implementations of the dielectric spectroscopy developed by the Institute of Agrophysics PAS in Lublin in the recent years. The meters are able to determine three quantities: moisture, temperature and salinity of soil at the same time and from the same sample volume. The accuracy of the soil moisture measurement is ±2% of the measured value. The eight-channel TDR/MUX/mpts meter is equipped with an integrated data logger, serial USB port for communication with user PC and a serial RS485 port allowing connection of multiple devices and controlling their measurements by a single PC.

A handheld meter for soil moisture, temperature and salinity of the FOM/mts type, presented together with an FP/mts probe in Fig. 8, is dedicated to mobile measurements of the soil surface layer. The characteristic properties of the device include: power supply from an internal battery, low power consumption, internal memory for storage of about 1 000 measurement results, an LCD display for initial assessment of the measurements taken, USB port for communication with the user PC, a GPS localization module (optional).

Fig. 7. Constituents of a telemetric soil moisture, salinity and temperature monitoring station: an eight-channel TDR meter of the TDR/MUX/mpts type together with a GPRS modem MIDL-2 type.
With the telemetric system of the soil moisture, temperature and salinity (Fig. 7), the users gain secure access to their data stored on a WEB server located in IA PAS in Lublin. Using a WEB browser, the user may load onto their PC the data collected by the probes and meters installed in any location within the mobile phone network range. It is also possible to modify the order and the time distance between measurements. This system is continuously running for several years in Polesie National Park (Skierucha et al., 2010) and also in Spain, China, Ukraine and many Polish scientific institutions. It is successfully used in six measurement stations for the SMOS images validation program (Skierucha et al., 2006; Usowicz et al., 2009). The functionality and low power consumption of the measurement system from the Institute of Agrophysics PAS make it especially useful for a long-term research on flood banks, places endangered by mudslides or for soil water balance determinations.

SUMMARY

The developments in electronics and modelling techniques in high frequency domain increase an interest in research on polarization mechanisms of heterogenic materials, as well as in relations between the dielectric properties of such materials and their quality indices, determined so far by laborious and time-consuming physical and chemical laboratory analyses. It applies especially to materials and products of agricultural origin, necessary for human existence. Techniques and instruments of the dielectric spectroscopy offer non-destructive and rapid measurements, the possibility of automation and accuracies often close to the analytic laboratory methods. The dielectric measurement techniques not only broaden our knowledge, but also increase the standard of life through the control and quality preservation of food. Research on polarization mechanisms and development of sensors and measurement techniques of the dielectric spectroscopy in application to agrophysical objects, especially in the microwave frequency range, are scientific objectives of the newly created Laboratory of Dielectric Spectroscopy in the Institute of Agrophysics PAS in Lublin.

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