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ON THE USE OF DIELECTRIC SPECTROSCOPY FOR QUALITY CONTROL OF VEGETABLE OILS

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Abstract – Quality control of vegetable oils is becoming more stringent, and related laws are being enforced, especially for avoiding adulteration. As a result, there is a substantial need for methods of analysis that could provide real-time in-situ monitoring, especially for quality control purposes during production process. In this regard, the present paper investigates the possibility of monitoring qualitative characteristics of vegetable oils through microwave dielectric spectroscopy, which is a highly versatile investigative approach. In particular, the Cole & Cole frequency-domain dielectric parameters are known to be strongly related to the compositional characteristics of various substances. This way, starting from traditional Time Domain Reflectometry measurements performed on oils, the corresponding frequency domain information is retrieved. Successively, through a minimization routine, the Cole & Cole parameters of each considered oil are extrapolated. Results show that different dielectric characteristics can be associated with different oils. It is important to point out that the characteristics of the proposed procedure can be automated and, therefore, it may represent a promising solution for practical monitoring applications.

Keywords: Dielectric spectroscopy, Quality control, Microwave Reflectometry

1. INTRODUCTION AND MOTIVATION OF THIS WORK

Vegetable oil production and related industry play a dominant economic impact in the Mediterranean areas. Particularly, extra virgin olive oil production is an important agribusiness sector. The quality of olive oil ranges from the high quality extra virgin olive oil to the low-quality olive-pomace oil (or raw residue oil). The most significant parameter that commonly identifies the qualitative status of different olive oils is the acidity. In fact, the acidity content depends on the overall quantity of free fatty acids, and it is taken as a useful indicator of the product quality and of the respective commercial value.

Extra virgin olive oil, which is the oil with best quality whose acidity (according to EU regulations) must not exceed 0.8%, is produced by mechanical press and without application of additional refining processes. Extra virgin olive oil has a high market-value; therefore, it is sometimes adulterated with cheaper oils. The most common adulterants used for virgin olive oil are refined olive oil, seed oils (such as sunflower, soy, corn, and rapeseed oils) [1], and nut oils (such as hazelnut and peanut oils) [2].

It goes without saying it that the close relation between "actual" quality and final market value of the product requires frequent, time-consuming laboratory analysis. Indeed, more rapid methodologies are commonly available for routine acidity analysis, such as those based on chemical titrations: standard test kits consist of portable instruments or simple colour reaction sticks. Nevertheless, all these methods are affected by some limitation: they are not performed in real time and they are very laborious. Additionally, traditional methods of analysis require skilled operators, and, most importantly, they cannot provide any information about the possible presence of adulterants.

On the other hand, highly sophisticated methods for the analysis of the authenticity of olive oil have been developed, such as gas chromatography [3] and liquid chromatography [4], but, obviously, they are not easily applicable for routine or continuous controls. More recently, Fourier transform infrared (FTIR) [5], Raman spectroscopy [1], and nuclear magnetic resonance (NMR) [6] spectroscopy have been considered as potential methods for discriminating between extra virgin olive and seed oils. Unfortunately, the complexity and the high costs related to these techniques make these methods unsuitable for the quality control of oil processing industries: often, neither SMEs, nor individual producers can afford the necessary equipment.

On the basis of all the above-discussed aspects, it comes as no surprise that the possible implementation of a reliable, real-time, and in-situ quality control procedure is a key-issue, whose feasibility strongly motivates research efforts.

As largely reported in related literature, microwave and millimeter wave-based techniques, such as time or frequency domain reflectometry, which do not suffer from any particular application limitations, have become effective methods for various industrial monitoring applications [7].

In such a context, microwave dielectric spectroscopy of liquids has proven an attractive approach for qualitative characterization of liquids. As an example, in the industrial liquid processing, several properties such as density, viscosity, size distribution of the molecules, and the amount of polar components, can be correlated to the dielectric parameters [7].

Additionally, microwave reflectometry can be successfully applied also for characterizing food and/or for

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monitoring the product process. As a matter of fact, microwave and millimeter wave-based methods of dielectric spectroscopy can provide useful information on the quality status of various substances: they provide fast, on-line data about production processes [8]-[10].

Indeed, no current work has so far considered the possibility of applying reflectometry-based techniques for vegetable oil quality control purposes. On such bases, the present paper is intended as an ongoing study attempting to fill this gap. The approach proposed herein is based on the investigation of the frequency-dependent dielectric properties of different vegetable oils associated to the corresponding reflection scattering parameter ($S_{11}(f)$) measurement. As will be detailed in the next sections, these data are extracted from time domain reflectometry (TDR) measurements, in conjunction with a robust minimization procedure [11].

This combined approach ensures, in turn, the adoption of relatively inexpensive and portable TDR devices suitable for in-situ monitoring applications, without compromising measurement accuracy and reliability.

Experimental measurements have been performed on seven different vegetable oil samples: results show that different oils exhibit different dielectric characteristics.

The ultimate goal of the proposed method is to assess the feasibility of TDR-based spectroscopy as a real-time, less-expensive measuring tool for estimating the adulteration of extra virgin olive oil with other vegetable oils such as corn, sunflower, or olive residue oils.

2. EXPERIMENTAL SETUP AND PROPOSED PROCEDURE

2.1. Experimental setup

The TDR measurements were performed through a Tektronix DSA8200, equipped with the TDR 80E04 module. This instrument generates a step-like voltage signal that provides a useful frequency range of analysis up to approximately 15 GHz.

A custom made coaxial probe was used for the TDR measurements. The probe was designed and realized in order to ensure a stable 50 Ω-impedance matching along its length. In particular, to guarantee the desired characteristic impedance Z the following equation was considered [7]:

$$Z = \frac{60}{\sqrt{\varepsilon_r}} \ln\left(\frac{b}{a}\right) \qquad (1)$$

where a is the external diameter of the inner conductor, b is the inner diameter of the outer conductor, and ε_r is the relative permittivity of the material filling the probe. For the considered probe the dimensions of the conductors are a = 2 mm and b = 4.4 mm. In particular, b was chosen to match the outer conductor dimensions of standard SMA 3.5 mm connectors, whereas a was consequently chosen to yield a resulting characteristic impedance of the probe in air ($\varepsilon_r \cong 1$) equal to 50 Ω, so as to ensure an impedance matching with the TDR instrument coaxial connector. The probe, whose length is 66 mm, is filled with the liquid under test. The probe is short-circuited on the distal end and has an SMA 3.5 mm male connector on the other side. This is a great advantage of the used probe, since the SMA connection allows performing a short-open-load (SOL) calibration at the probe port, thus compensating for systematic errors contributions. Figure 1 shows a schematization of the designed probe.

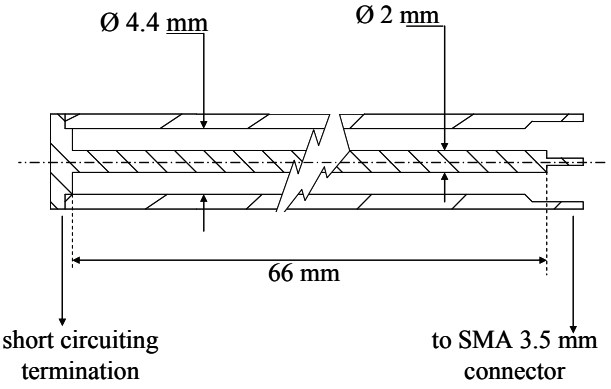


Fig. 1. Schematic configuration of the used coaxial probe.

Experimental measurements were performed on seven different vegetable oil samples: peanut oil, corn oil, sunflower oil, soybean oil, various seed oil, and two different olive oils. The two olive oils have an acidity of 1.2% and 4.0%, respectively: these values were measured through a titration procedure, with a maximum uncertainty of 0.1%.

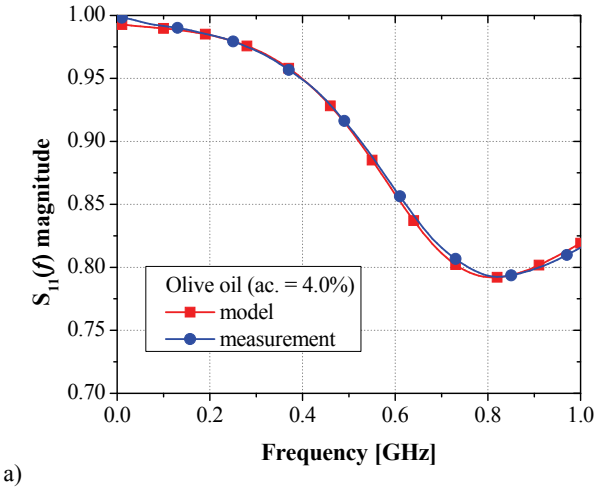
2.2. Proposed approach

For each of the considered oils the following procedure has been followed.

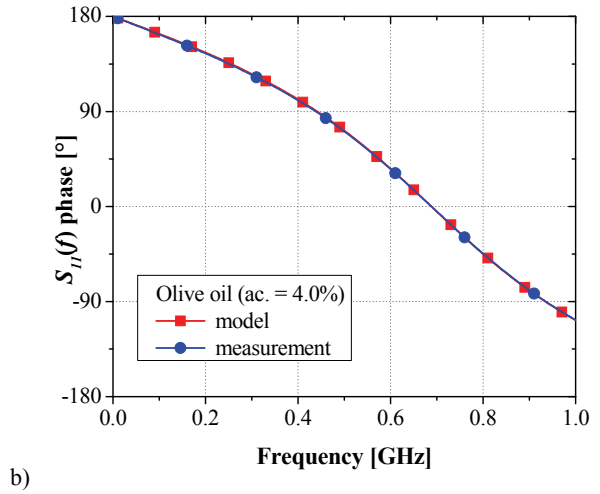
1) The TDR waveform of the oil was acquired along with the SOL calibration standards (measurement average = 4,096 waveforms);
2) The collected time domain data were processed through an FFT-based algorithm (implemented in MATLAB) that allows retrieving the desired information in frequency domain: in particular, the calibrated $S_{11}(f)$ was evaluated. The used algorithm is described in detail in previous works of the Authors' [7], [11]; however, it is worth mentioning that the used algorithm takes into account several signal processing techniques (such as Nicolson algorithm and padding) that enhance the accuracy of results;
3) The transmission line model of the system (experimental setup, probe, and filling liquid) was implemented through a commercial software (Microwave Office). This model includes a length of short-circuited coaxial probe filled with a material characterized through its relative complex permittivity. The frequency-dependent dielectric permittivities of liquid samples are described by the Cole & Cole model, which includes five parameters: ε_s (static permittivity), ε_∞ (permittivity at extremely high frequencies), f_r

(relaxation frequency), β (dispersion parameter), σ_s (static conductivity). The appropriateness of such a model was verified through preliminary measurements on well-referenced materials (i.e., air, bi-distilled water, and acetone) [7], [11];

4) Through an optimization procedure based on the simplex algorithm (performed in Microwave Office), differences between the measured $S_{11}(f)$ and the modelled $S_{11\text{-}MOD}(f)$ were minimized, thus estimating the optimal Cole & Cole parameters for each oil sample [7], [11]. As an example, Fig. 2 shows the comparison between the measured $S_{11}(f)$ and the modelled $S_{11\text{-}MOD}(f)$ (after the minimization procedure) for the olive oil sample with acidity 4.0%. For all the considered samples, a good overall agreement is noticed, due to the highly accurate modelling and to the appropriateness of the minimization procedure.



a)



b)

Fig. 2. Comparison between the modelled scattering parameter and the measured $S_{11}(f)$, for olive oil with acidity 4.0%: a) magnitude, b) phase.

3. RESULTS AND DISCUSSION

The procedure described in the previous section was used for estimating the Cole & Cole parameters of seven different vegetable oils. Table 1 summarizes the results (each set of parameters has been calculated as the average of ten repetitions); the corresponding standard deviations (σ) are summarized in Table 2. The electrical conductivity was neglected, since its value for vegetable oils is usually in the order of some pS/m. It is worth mentioning that the values of the static permittivity have been verified through low-frequency measurements performed through an LCR meter.

Table 1. Cole & Cole parameters for the seven types of oil.

Type of oil	ε_s	ε_∞	f_r **[MHz]**	β
Olive (ac. = 1.2%)	3.14	2.38	288	0.36
Olive (ac. = 4.0%)	3.19	2.34	249	0.42
Peanut	3.05	2.40	334	0.28
Sunflower	3.12	2.40	292	0.31
Corn	3.11	2.41	309	0.29
Soybean	3.09	2.41	390	0.30
Various seed	3.10	2.43	371	0.27

Table 2. Standard deviations for the results reported in Table 1.

Type of oil	$\sigma_{\varepsilon s}$	$\sigma_{\varepsilon\infty}$	σ_{fr} **[MHz]**	σ_β
Olive (ac. = 1.2%)	0.01	0.01	9	0.02
Olive (ac. = 4.0%)	0.03	0.02	5	0.02
Peanut	0.01	0.01	5	0.01
Sunflower	0.04	0.01	5	0.01
Corn	0.02	0.01	6	0.02
Soybean	0.01	0.02	7	0.02
Various seed	0.02	0.01	5	0.01

The obtained results are in good agreement with the few data available in the literature [12]-[14]. It is interesting to note that, as can be seen from Table 1, f_r is the parameter that exhibits the most considerable variations among the considered oils. To better evidence this trend, for each considered oil, Fig. 3 shows the expanded uncertainty range $\pm 2.26\sigma$; where σ is the standard deviation corresponding to the Gaussian probability distribution (which, in turn, has been verified through the χ-square test). The expanded uncertainty has been evaluated considering the *t*-distribution of Student, and 2.26 is the t-score that corresponds to a confidence level of 95% and to 9 degrees of freedom [15].

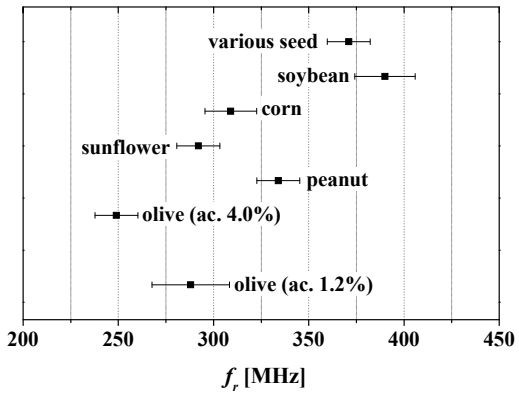


Fig. 3. Summarized comparative results of the averaged values of f_r for the considered oils. Related expanded uncertainty bars (with confidence level of 95 %) are also reported.

The extracted Cole & Cole parameters were used to plot the relative dielectric permittivity, thus providing a dielectric spectral "signature" for each different type of oil.

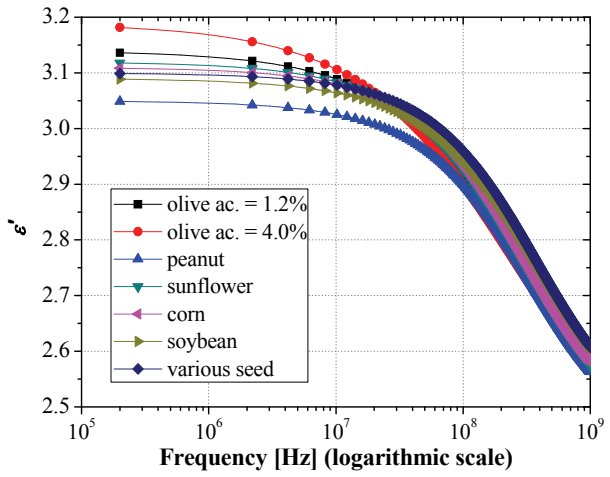


Fig. 4. Real part of the relative permittivity for the seven types of oil.

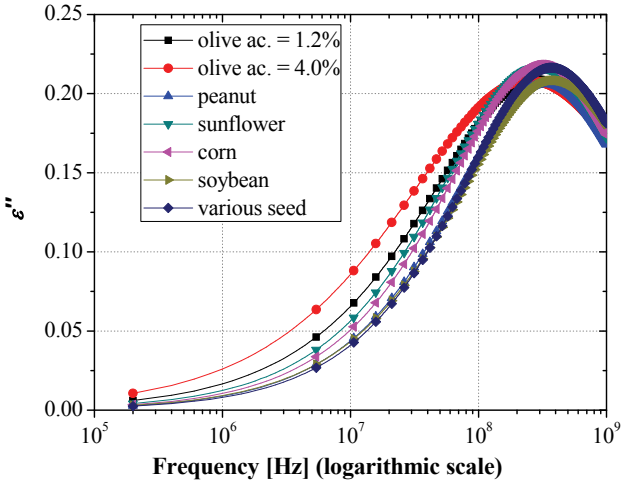


Fig. 5. Imaginary part of the relative permittivity for the seven types of oil.

Fig. 4 and Fig. 5 show the real part (ε') and the imaginary part (ε'') of the relative dielectric permittivity, respectively. As can be seen from Figs. 4 and 5, there are specific frequency ranges in which the permittivities of the different oils can be discriminated. In particular, the vegetable oils show the most distinct behaviour in the 0.2-100 MHz frequency range. Additionally, the permittivity curves of olive oils appear to be above the curves related to the other oils. This might be attributable to the different amount of monounsaturated fatty acid present in the olive oils (amount that, typically, is higher than in other kinds of oil). Altogether, it can be concluded that by jointly using information about static permittivity and relaxation frequency it is possible to distinguish among different oils.

4. CONCLUSIONS

In this work, an alternative method for monitoring characteristics of oils was investigated. The proposed approach relies on the evaluation of the Cole & Cole parameters for oils as a quality indicator of the characteristics of vegetable oils. The Cole & Cole parameters are calculated through the combination of TDR measurements, frequency domain processing, and an enhanced minimization routine. This approach preserves low costs (thanks to the use of instrumentation operating in time domain) and, additionally, anticipates the possibility of in-situ real-time monitoring (thanks to the possibility of using portable TDR instruments). Results showed that different oils can be discriminated in terms of dielectric parameters; in particular, the significant changes in the relaxation frequency can be attributed to the differences among oils. The next step is to further investigate the possibility of relating the permittivities of oils to the corresponding qualitative characteristics.

REFERENCES

[1] F. Guimet, J. Ferre and R. Boque, "Rapid detection of olive-pomace oil adulteration in extra virgin olive oils from the protecteddenomination of origin Siurana using excitation–emission fluorescence spectroscopy and three-way methods of analysis", *Analytica Chimica Acta*, vol. 544, n.° 1-2, pp. 143-152, 2005.

[2] G. P. Blanch, M. del Mar Caja, M. L. Ruiz del Castillo and M. Herraiz, "Comparison of different methods for the evaluation of the authenticity of olive oil and hazelnut oil", *Journal of Agricultural and Food Chemistry*, vol. 46, n.° 8, pp. 3153-3157, 1998.

[3] G. Morchio, A. DiBello, C. Mariani and E. Fedeli, "Detection of refined oils in virgin olive oil", *Rivista Italiana Sostanze Grasse*, vol. 66, n.° 5, pp. 251-257, 1989.

[4] A. H. El-Hamdy and N. K. El-Fizga, "Detection of olive oil adulteration by measuring its authenticity factor using reversed-phase high-peformance liquid chromatography", *Journal of Chromatography*, vol. 708, n.° 2, pp. 351-355, Aug. 1995.

[5] A. Tay, R. K. Singh, S. S. Krishnan and J. P. Gore, "Authentication of olive oil adulterated with vegetable oils using Fourier transform infrared spectroscopy", *Lebensmittel-Wissenschaft und-Technologie*, vol. 35, n.° 2, pp. 99-103, Feb. 2002.

[6] R. Sachhi, F. Adeo and L. Polillo,"^{1}H and ^{13}C NMR of virgin olive oil. An overview" *Magnetic Resonance in Chemistry*, vol. 35, n.° 13, pp. 133-145, 1997.

[7] E. Piuzzi, A. Cataldo, L. Catarinucci, "Enhanced reflectometry measurements of permittivities and levels in layered petrochemical liquids using an 'in-situ' coaxial probe", *Measurement*, vol. 49, n.° 5, June 2009.

[8] M. S. Venkatesh1 and G. S. V. Raghavan, "An overview of microwave processing and dielectric properties of agri-food materials", *Biosystems Engineering*, vol. 88, n.° 1, pp. 1-18, 2004.

[9] N. Miura, S. Yaghihara and S. Mashimo, "Microwave dielectric properties of solid and liquid foods investigated by time-domain reflectometry", *Journal of Food Science*, vol. 68, n.° 4, pp. 1396-1403, 2003.

[10] S. O. Nelson and P. G. Bartley Jr., "Measuring frequency- and temperature-dependent permittivities of food materials", *IEEE Transactions on Instrumentation and Measurement*, vol. 51, n.° 4, Aug. 2002.

[11] A. Cataldo, L. Catarinucci, L. Tarricone, F. Attivissimo and E. Piuzzi, "A combined TD-FD method for enhanced reflectometry measurements in liquid quality monitoring", *IEEE Transactions on Instrumentation and Measurement*, in press.

[12] K. Fenske and D. Misra, "Dielectric materials at microwave frequencies", Applied Microwave & Wireless, vol. 12, n.° 12, pp. 92-100, 2000.

[13] H. Lizhi, K. Toyoda and I. Ihara, "Dielectric properties of edible oils and fatty acids as a function of frequency, temperature, moisture and composition", *Journal of Food Engineering*, vol. 88, n.° 2, pp. 151-158, Sept. 2008.

[14] T. S. Ramu, "On the high frequency dielectric behavior of castor oil", *IEEE Transactions on Electrical Insulation*, vol. 14, n.° 3, pp. 136-141, June 1979.

[15] Guide to the Expression of Uncertainty in Measurement, ISO/IEC Guide 98:1995, 1995.