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Dielectric properties of grape marc: Effect of temperature, moisture content and sample preparation method

Katalin Sólyom [a], Stefan Kraus [b], Rafael B. Mato [a,*], Volker Gaukel [b], Heike P. Schuchmann [b], María José Cocero [a]

[a] University of Valladolid, Industrial Engineering School, Department of Chemical Engineering and Environmental Technology, High Pressure Processes Group, C/Dr. Mergelina, s/n, 47011 Valladolid, Spain
[b] Institute of Process Engineering in Life Sciences, Section I: Food Process Engineering, Karlsruhe Institute of Technology, Kaiserstrasse 12, 76131 Karlsruhe, Germany

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ABSTRACT

Microwave assisted extraction enhances antioxidant extraction kinetics in grape marc processing. For an effective microwave process design, the dielectric properties (DPs) of the material must be known under different conditions. This study focused on the DP measurement of grape marc using a resonant cavity measuring device. Grape skin, seeds and their mixtures with three different moisture contents were studied at 28, 39 and 50 °C. At higher moisture content DP showed increasing tendency, while temperature didn't have a definite effect. Good correlation was achieved with the experimental results applying the complex refractive index mixing equation between 0.4 and 0.6 porosity. Also, despite the complexity of natural products properties, the experimental DP values of the real mixture were in agreement with values estimated from DP properties of its individual constituents (grape skin and seeds). Milling was performed to obtain homogeneous material for the measurements, and this effect on the results was also studied.

1. Introduction

There is an increasing interest in antioxidant extraction from industrial by-products such as the grape marc obtained from red wine production (Spigno and De Faveri, 2007). The conventional extraction processes can be enhanced with novel techniques such as the application of microwaves, where the dipole molecules are mostly affected by the oscillation of the dielectric field. Microwave assisted extraction processes may lead to increased extraction yields in short extraction times while using a smaller amount of solvent (Proestos and Komaitis, 2008). However, the efficiency of any microwave process depends on the correct design of the microwave applicator. For this reason, the interaction between the treated material and the applied electric field must be known. In order to describe this interaction, the complex dielectric permittivity (Eqs. 1, 2) of the material should be known (Metaxas and Meredith, 1988).

$$\varepsilon = \varepsilon_0 \varepsilon_r \tag{1}$$

$$\varepsilon_r = \varepsilon_r' + j\varepsilon_r'' \tag{2}$$

In Eq. (1) ε_0 and ε_r refer to the free space permittivity and the complex dielectric constant, respectively. Eq. (2) shows the real part of the complex dielectric constant (ε_r'), which corresponds to the energy stored in the material when an electric field is applied, and the imaginary part (ε_r''), corresponding to the energy which is converted into heat.

During the microwave process, the material undergoes physical and perhaps chemical changes (moisture content, temperature and salt concentration) which would affect its interaction with the dielectric field. These factors must be taken into account when characterizing the dielectric properties of the sample (Venkatesh and Raghavan, 2004).

In former studies the grapes' dielectric constants were measured for microwave drying purposes (Dev et al., 2009; Tulasidas et al., 1995). In those measurements whole grapes or grape skin, excluding seeds, were measured in an open ended coaxial line measurement setup, requiring perfect contact between the probe and the sample. The same method was used for fresh fruit and vegetable slices, where non-monotonic dielectric behavior was reported above 65 °C, corresponding to the cell breakage of plant tissues (Nigmatullin and Nelson, 2006). The dielectric properties of grape juice were studied at different frequencies (García et al., 2001), also with an open-ended coaxial line probe. The conductivity of the sample was also considered, as it strongly affected the measurement results at higher frequencies. When measuring wine

* Corresponding author. Tel.: +34 983423177.
E-mail address: rbmato@iq.uva.es (R.B. Mato).

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(García et al., 2004), it was reportedly difficult to establish perfect contact between the probe and the liquid sample because of the presence of disturbing CO_2 bubbles in the fermented wine. In the afore-mentioned literature all measurements were done with seedless grape berries. The inclusion of grape seeds affects the microscopic and macroscopic content of the raw material, and so dielectric properties may change. The dielectric properties of a mixture of grape seeds and skin had apparently not been measured in former studies.

When complex semi solid material is measured, open ended coaxial line probes present two main problems. On one hand, it is difficult to establish the necessary physical contact between the sample and the probe; on the other hand, the results may rely on the position and distance of the different constituent parts in the inhomogeneous material. For such samples, the resonant cavity method may be more suitable, if measurements are performed at a constant frequency (Nelson, 1991), because this measurement method reflects the overall dielectric constant of the complex sample placed into the cavity.

Otherwise, the global dielectric properties of a multiphase material can also be estimated from the proportions and properties of their individual constituent phases by using mixing equations. Some of the previously reported correlations are derived from Maxwell's equations, while others are semi empirical models (Sheen et al., 2010; Simpkin, 2012; Nelson, 2005; Erle et al., 2000). The wide variety of equations used for different materials confirms that none of them gives the exclusive solution to the estimation of the dielectric properties of a complex mixture, and in any case, the best fit should be chosen depending on the material type, shape and complexity. Sheen et al. (2010) compared exponential and logarithmic models, estimated their theoretical error and correlated them with experimental data. They suggested that the complex refractive model and the random model were the most suitable for a polymer-ceramic mixture at a high volume fraction of the dispersed phase. These models are also widely mentioned in case of agricultural and food products (Venkatesh and Raghavan, 2004). Therefore, the Complex Refractive Index Mixing model (CRIM, Eq. (3)), the Random model (Landau–Lifshitz–Looyenga, Eq. (4)) and a Logarithmic model (Lichtenecker–Rother, Eq. (5)) were used in this study to estimate the material dielectric properties of an air-particle mixture as a function of the sample porosity:

$$\sqrt{\varepsilon_m} = v_1\sqrt{\varepsilon_1} + v_2\sqrt{\varepsilon_2} \tag{3}$$

$$\sqrt[3]{\varepsilon_m} = v_1\sqrt[3]{\varepsilon_1} + v_2\sqrt[3]{\varepsilon_2} \tag{4}$$

$$\ln \varepsilon_m = v_1 \ln \varepsilon_1 + v_2 \ln \varepsilon_2 \tag{5}$$

In Eqs. (3)–(5) ε_m refers to the dielectric property of the mixture, ε_1 and ε_2 correspond to the air and grape marc phases, respectively, and v_1 and v_2 to their volume fractions in the sample.

The object of this study was to describe the behavior of the dielectric properties of grape marc at changing moisture content and temperature, as these are the variables which would change during a microwave pre-treatment, prior to the antioxidant extraction process. During measurement the sample holder contains a mixture of grape marc and air, as it is not possible to separate all the air from grape marc without altering the material. In order to estimate the grape marc properties themselves, it is necessary to have a proper mixing equation too. Good experimental reproducibility was obtained from homogenized material; however, homogenization could vary the measurement results. To evaluate the measured results from the homogenized samples some values obtained using the original unhomogenized material was compared to those from the homogenized grape marc. Finally, the mixing equation was applied in order to predict the dielectric properties of a grape marc mixture from the proportion and properties of their constituents: grape skin and seeds.

2. Materials and methods

2.1. Raw material

Fermented grape marc was provided by the Matarromera winery (Spain) in November 2011. It was a mixture of pressed, partially ruptured grape skin and whole seeds, which contributed to the color development of the red wine during the fermentation process. For industrial reasons the samples had a 0.1 wt% of added potassium metabisulfite.

During the measurement, the initial mixture of skin and seeds was used either in milled form, or was manually separated into skin and seed fractions and measured either in milled or in original form.

Samples were stored in a freezer at −20 °C and thawed for use in experiments at room temperature overnight.

2.2. Analysis of moisture content

Moisture content was determined by an infrared moisture analyzer (Kern®-MLS) at 105 °C until reaching a stable weight. Original moisture content was 59.7% for the milled skin and seeds mixture, which contained 42 wt% seeds and 58 wt% skin. The original seeds and skin had a moisture content of 49.2% and 65.9%, respectively.

2.3. Preparation method

Some of the samples were milled, before thawing, in a Thermomix for 20 s/100 g to obtain <1 mm particles.

Desired moisture content was achieved by drying at 40 °C (VWR® Incu-Line IL23) at atmospheric pressure.

2.4. Density measurement

Sample density was determined for the milled and original samples, and for all moisture contents in a gas pycnometer (Quanta Chrome®), by applying the gas at room temperature. The average value of 5-fold measurements was used in further calculations.

2.5. Measurement of dielectric properties

A Püschner Dielectric Measurement Kit® was used for the measurements, with 1 ml glass vials of 35 mm height and 6.2 mm inner diameter. The device measures the frequency response (2.45 GHz) with the cavity perturbation method, where firstly the empty sample holder was measured, followed by the filled sample holder. From the frequency shift and quality factor difference, the software provided (Microwave Dielectric Kit 3.0.3®) was able to calculate the dielectric constant and dielectric loss.

For every measurement point, six sample holders were prepared and the dielectric properties were measured. The bulk densities (ρ_{bulk}; [g/cm^3]) were determined from the sample weight and the volume in every sample holder. Porosity (ϑ) was calculated from the density of the material ($\rho_{material}$; [g/cm3]), and the prepared bulk density in the sample holder. (Eq. (6)) The average results of the dielectric properties from the 6-fold measurements are presented with the corresponding standard deviation for every measurement point.

$$\vartheta = 1 - \frac{\rho_{bulk}}{\rho_{material}} \tag{6}$$