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Influence of metal ions and phospholipids on electrical properties: A case study on pumpkin seed oil

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ABSTRACT

Dielectric spectroscopy at low frequencies was applied to analyze vegetable oils, in particular roasted pumpkin seed oils (RPO). Large differences were observed for electrical conductivity not previously applied as a tool in the analysis of crude vegetable oils. RPO have two orders of magnitude higher conductivity than refined sunflower oils and extra virgin olive oils. Differences in dielectric constant were small and influenced by fatty acid composition and presence of minor components. The conductivity of pumpkin seed oils is highly correlated to phospholipid and metal contents. Phospholipids, magnesium, potassium and sodium are present at mmol/kg concentrations as determined by ICP-MS. We have shown that measurement of electrical conductivity can be used as a cost efficient method to detect adulteration of RPO with refined oils, even for those with similar fatty acid composition. Low background conductivity of triacylglycerols allows that even trace amounts of metals and phospholipids are detected in vegetable oils.

1. Introduction

Dielectric parameters reflect the ability of matter to store and dissipate electrical energy (Datta, Sumnu, & Gaghavan, 2005). Dielectric constant (ε'), a measure of dipole moment in matter, can be calculated from capacitance (C) measurements at low frequencies. Dissipation of the charge stored in the material is closely related to the content of ionic species that move parallel to the direction of an alternating electrical field at low frequencies and have a major influence on the electrical conductivity (κ). This can be obtained from measurements of electrical resistance (R).

Nonpolar triacylglcerols are major constituents of vegetable oils. The dielectric constants of these oils are low (Elshami, Selim, Elanwar, & Elmallah, 1992; Lizhi, Toyoda, & Ihara, 2008, 2010) and refined vegetable oils have even been tested as insulating oils in transformers (Abdelmalik, Fothergill, & Dodd, 2012). Changes in fatty acid composition or chemical modification, such as hydrolysis or oxidation, result in small but measurable increases in ε' (Marmesat, Rodrigues, Velasco, & Dobarganes, 2007). Measurement of capacitance has been applied for analyzing oil type (Lizhi et al., 2008) and determining adulteration (Lizhi, Toyoda, & Ihara, 2010) and as a parameter that is highly correlated to the quality of frying oil (Bou, Navas, Tres, Codony, & Guardiola, 2012; Innawong, Mallikarjunan, & Marcy, 2004). The algorithm of the food oil sensor used in the analysis of frying oil quality is based on the change of dielectric constant of oil during processing (Marmesat et al., 2007).

Electrical conductivity measurements are currently not applied for the analysis of vegetable oils. Typical refined vegetable oils contain very low concentrations of charge carriers, and conductivity can be below the limit of detection (Abdelmalik et al., 2012). Only recently some data about electrical conductivity of vegetable oils were published (Kumar, Singh, & Tarsikka, 2013; Pecovska-Gjorgjevich, Andonovski, & Velevska, 2012). A nonpolar matrix that is practically an insulator, can become conductive in the presence of ionic impurities. Conductivity measurements of crude oils (petroleum) that contain metal ions were, for example, applied to discriminate petroleum from different origins (Vralstad, Spets, Lesaint, Lundgaard, & Sjoblom, 2009). Direct conductivity measurements are nevertheless not used in the analysis and differentiation of crude vegetable oils. This is surprising, since phospholipids, that are potential charge carriers, (Szydlowska-Czerniak & Szlyk, 2003; Vujasinović, Radočaj, & Dimić, 2012) and metal ions (Cindric, Zeiner, & Steffan, 2007; Joebstl, Bandoniene,

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Meisel, & Chatzistathis, 2010; Uluata & Ozdemir, 2012) have also been identified in unrefined vegetable oils extracted from seeds. Styrian pumpkin seed oil prepared by pressing roasted or intact (cold pressed) hull-less *Cucubrita pepo* seeds (Fruhwirth & Hermetter, 2007) is an example of an oil that is a rich source of phospholipids (Vujasinović et al., 2012), metal ions (Cindric et al., 2007) and chlorophyll derivatives (Schoefs, 2002) that could all increase the conductivity. Much lower concentrations of ions were determined in refined oils and in unrefined oils extracted from olives (Cindric et al., 2007).

Its specific sensory properties and health promoting effects (Fruhwirth & Hermetter, 2007; Siegmund & Murkovic, 2004) ensure a high market price for pumpkin seed oil. Various approaches have been proposed as tools to identify its geographical origin or quality (Joebstl et al., 2010; Lankmayr et al., 2004; Wenzl, Prettner, Schweiger, & Wagner, 2002).

In the present study we have sought to determine whether capacitance and resistance measurements can be applied to differentiate between roasted pumpkin seed oils (RPO), cold pressed pumpkin seed oils (CPO), extra virgin olive oils (EVOO) and refined sunflower oils (SO). In addition, we have determined the concentration of ionic species in RPO and CPO and sought for correlations with dielectric constant and electrical conductivity. Low frequency dielectric spectroscopy was also tested as a tool for assessing adulteration of RPO with refined vegetable oils.

2. Experimental

2.1. Chemicals

(±)-α-Tocopherol (T3251), oleuropein (O8889), water (95305, *Trace*SELECT®), hydrogen peroxide (95321, *Trace*SELECT®), nitric acid (84385, *Trace*SELECT®), Na_2MoO_4 (331058) and K_2HPO_4 (P3786) were all from Sigma–Aldrich (Steinheim, Germany). Propan-2-ol (1.09634), propan-1-ol (1.00997), acetone (1.00014), sulfuric acid (1.00731), hydrazinium sulfate (1.04603), KCl (1.04938) and ICP multi-element standard solution IV (1113550) were from Merck (Darmstadt, Germany). 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (850355; DPPC) was from Avanti Polar Lipids, Inc (USA). EVOO, SO, pumpkin seeds and lecithin (Upina) were purchased on the Slovenian market.

RPO and CPO were bought in local stores in the Štajerska and Prekmurje region of Slovenia or purchased locally at the pumpkin seed oil processing facilities. Pumpkin seed oils were produced from a pumpkin variety *Cucurbita pepo* subsp. *pepo* var. *Styriaca*. The technology of oil production in Slovenia is practically identical to that in nearby Austria (Fruhwirth & Hermetter, 2007), which is the world leading producer of pumpkin seed oil. "Štajersko Prekmursko bučno olje" is a product with protected geographical indication within the European Union.

2.2. Dielectric spectroscopy

Dielectric properties of oils were determined by the capacitive method, using a Precision Liquid Test Fixture 16452 A and a precision LCR meter E4980A (both Agilent Technologies). Parameters C (pF) and R (Ω) were measured at 70 frequencies between 100 Hz and 2 MHz at 25.0 °C ± 0.1 °C. Temperature was controlled by a high precision water bath 7320 (Fluke) and external thermometer system 5627A/1502A (Fluke).

The dielectric constant was determined over the whole frequency range, as described in the Agilent instruction manual and assuming the dielectric constant of vacuum (ε_0) can be calculated approximately from the capacitance of air (empty cell under the same conditions) (Lizhi et al., 2008). For correlation analysis, ε' at 10 kHz was collected for each sample (Appendix A). Electrical conductivity was determined using a standard solution of KCl ($0.100 \cdot 10^{-3}$ mol/kg) in a mixture of 30% propan-1-ol and water for trace analysis, according to Wu and Berezansky (1995). Resistance (R) was plotted as a function of frequency^{-1} and the extrapolated value of R at frequency$^{-1} = 0$ used to calculate κ (Bešter-Rogač & Habe, 2006).

2.3. Mineral content

The mineral content of selected vegetable oils was analyzed by ICP-MS following microwave digestion. 0.5 g of oil samples, 8 mL of HNO_3 and 1 mL of H_2O_2 were mixed in the digestion vessel. Microwave digestion was performed in 2 steps; heating up to 180 °C in 10 min, followed by 10 min at 180 °C. After cooling, digestion liquors were transferred quantitatively into plastic containers and diluted to 20 mL with water for trace analysis. Blank samples without oil were heated and diluted to the same volume. All samples and reagent blanks, including those for microwave digestion, were prepared in triplicate.

Calibration curves were prepared by standard solution IV in 3.6 mol/L HNO_3 up to 4 ppm of each metal.

Measurements were performed on an Agilent 7500 Series ICP-MS. Carrier gas flow was 0.9 L/min, makeup gas flow was 0.25 L/min and He gas flow was set at 5 mL/min. The nebulizer and sample pump speeds were 0.07 rpm. The measurement integration time was 0.1000 s. Each result was the average of three measurements. Signals of blanks were subtracted from those for samples.

2.4. Phosphate content – molybdenum blue method

The phosphate content of oil samples was determined according to the spectrophotometric method of (Szydlowska-Czerniak & Szlyk, 2003). 100 mg of each sample was weighed into an HPLC vial and placed in a cold furnace and dry ashing at 600 °C for 5 h was performed. The cooled ash was dissolved in 0.5 mL of 0.5 mol/L sulfuric acid, mixed thoroughly and latter used in the assay. The effectiveness of the digestion was verified by spiking oil samples and reagent blanks with DPPC and K_2HPO_4 prior to digestion. Recoveries were between 96 and 98%.

Results are expressed as mmol of phosphate per kg of oil. The phospholipid content was estimated according to the method of Vujasinović et al. (2012), applying a molar mass ratio between phospholipids and P of 25.

2.5. Fluorescence and absorbance spectrometry

Samples of pumpkin seed oils were weighed into 2 mL microcentrifuge tubes and dissolved in propan-2-ol. The final dilution of oil samples was 200-fold (V/V). Spectra of chlorophyll fluorescence were recorded in 10 mm quartz cuvettes with excitation at 450 nm using a Cary Eclipse fluorescence spectrometer (Varian, Australia) at 25 °C (excitation and emission slits were 5 nm). Absorbance spectra of oil samples at the same dilutions were measured at 25 °C with a Cary 100 UV–Vis spectrophotometer.

2.6. Sensory analysis

Sensory analysis of all RPO and CPO was carried out by a panel of 4 trained panelists. Testing was carried out in individual sensory booths in the Food Sensory Laboratory at the University of Ljubljana, Slovenia.

The panelists were required to test four attributes in the following order: opacity/clarity (3 points), color (3 points), odor (6 points) and taste (8 points).