Evaluation of food-grade vegetable oils using ultrasonic velocity measurement and fatty acid composition

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I. INTRODUCTION

Extra virgin olive oil (EVOO) is extracted from olives using mechanical cold pressing techniques, and thus has high nutritional quality and value. Lower grade olive oils such as refined olive oil (ROO) use heat, steam and chemical treatments to control odor, flavor and color. Pomace olive oil (POO) consists of the oil remaining in the olive pulp from EVOO pressing, typically extracted using solvents and then further refined [1]. The adulteration of EVOO using lower grade olive oils or cheaper seed or nut oils such as rapeseed oil (RSO), sunflower oil (SFO) and peanut oil (PNO) give ample opportunities for food fraud. The use of ultrasound as a nondestructive method of evaluating different food-grade oils may be an additional valuable tool to verify the authenticity and type of oil.

Previous work in the use of ultrasound for investigating edible oils typically uses measurements of ultrasonic velocity [2] and frequency content via ultrasonic spectroscopy [3], as good correlation with the density [4] and rheological properties [5] of the oils has been shown. More recent work has investigated ultrasonic techniques for detecting adulteration of olive oil with soya oil [6, 7] and developing appropriate models for attenuation of edible oil mixtures [8].

The purpose of this study was to investigate the potential use of ultrasonic velocity measurement techniques, in conjunction with independent measurements of density, dynamic viscosity, and fatty acid (FA) composition of different food grade oils as a possible non-destructive method of discrimination between the different oil types, with an emphasis on EVOO in comparison to other oils commonly used in its adulteration.

II. APPARATUS AND EXPERIMENT

A. Ultrasonic velocity measurement

The apparatus for measuring the ultrasonic velocity in the different oils was constructed as shown in Fig. 1. An adjustable volume sample test cell was made using a transparent polycarbonate tube and a stainless steel cylinder, such that the cylinder could be moved vertically to define a different test cell

Abstract— Extra virgin olive oil (EVOO) is a high-value food commodity and is often a target for food fraud, in which the EVOO is adulterated with lower grade oils such as refined olive oil (ROO), pomace olive oil (POO) and other vegetable oils of nut or seed origin such as rapeseed or canola oil (RSO), peanut oil (PNO) and sunflower oil (SFO). The objective of this study is to investigate ultrasonic techniques to distinguish between different food-grade oils based on their fatty acid (FA) composition. An ultrasonic pulse-echo system was used to measure the propagation delay and hence the velocity of ultrasonic waves at 5 MHz in three different types of olive oil (EVOO, POO and ROO) and three other vegetable oils of nut or seed origin (PNO, RSO and SFO). The ultrasonic system was temperature controlled in a heated water bath at 23.5°C±0.05°C. The ultrasonic velocity was determined using the differential propagation delay from four 2.00 mm increments in the propagation path, determined using a micrometer to ±0.005 mm to eliminate any uncertainty in the initial propagation path. The FA content of each oil was determined using an ISO 12966-2 (2017) automatic BF3 transmethylation procedure followed by gas chromatography according to ISO 12966-4 (2015) using an Agilent HP7890A Gas Chromatograph. 80 different samples were tested, using extra virgin olive oil (n=30), refined olive oil (n=15), pomace olive oil (n=15), rapeseed/canola oil (n=10), sunflower oil (n=5), and peanut oil (n=5). The FA composition and ultrasonic velocity of each sample were measured. A statistically significant correlation between polyunsaturated fatty acid (PUFA) content and ultrasonic velocity, and a statistically significant negative correlation between monounsaturated and saturated fatty acid (MUFA and SFA) content and ultrasonic velocity, were noted. The ultrasonic velocity may thus be used to help distinguish between different food-grade vegetable oils that have a high PUFA content, such as sunflower oil and rapeseed/canola oil, and those with a high MUFA content such as olive oil and peanut oil. The FA composition appears to influence the density and compressibility of the oil, which determine the ultrasound velocity.

Keywords—ultrasonic velocity, extra virgin olive oil, fatty acid methyl ester (FAME) test, oil viscosity, density

J. Yan would like to acknowledge PhD financial support from the China Scholarship Council (201506910048).



Fig. 1. The oil sample test cell apparatus.

volume. O-rings were used to maintain a leak-proof seal between the cylinder and tube. An ultrasonic immersion transducer holder was attached to the movable slider of a micrometer translation stage, which was fixed to a vertical bracket with a base plate such that the center of the immersion transducer was coincident with the center of the sample cell and the motion of the movable slider was perpendicular to the top surface of the cylinder. Hence, the distance between the front face of the transducer and the top surface of the stainless steel cylinder could be adjusted with $\pm 5 \,\mu m$ precision.

An overall schematic of the system is shown in Fig. 2. A Krautkramer 0.5" diameter 'Alpha' series 5 MHz immersion transducer was fixed into the holder and connected to a Panametrics NDT 5800PR pulser/receiver unit. The ultrasonic signals received were digitized using a Tektronix TDS200 series digital oscilloscope and then transferred via a GPIB interface into a PC via MATLAB for storage and analysis.

The oil sample test cell apparatus was placed in a heated water bath maintained at a temperature of 23.5 ± 0.05 °C. The oil samples were poured into the sample holder and left to reach a temperature of 23.5 °C, which was monitored using a Digitron 2000T thermometer fitted with a K-type thermocouple, placed directly in the oil sample.



Fig. 2. Schematic diagram of the test system.

The ultrasonic velocity c, in ms⁻¹, in each oil sample was measured by recording the propagation delay t, in seconds, of an ultrasonic pulse in the oil over four different path lengths x, in meters. The initial path length was set at 10.00±0.005 mm. The measured propagation delay included unknown delays in the pulser-receiver electronics, transducer and possible initial positioning offsets. Hence, a differential measurement was used in which the propagation path length was increased in 2.00±0.005 mm steps and the propagation time recorded. The difference in propagation times would then eliminate the unknown timing errors, which were assumed constant, and the slope of a linear least-squares regression line through the points on a plot of distance vs time would give an appropriate value of the ultrasonic velocity (c = dx/dt).

B. Dynamic viscosity measurement

The dynamic viscosity of each oil sample was measured using a HAAKE RotoVisco 1 rotational rheometer fitted with a Z41 rotor and a Z43 cup. 10 ml of each oil was placed in the rheometer and left for 1 minute to reach equilibrium at 20°C. The shear rate was ramped up from 0 s⁻¹ to 200 s⁻¹ over 120 seconds and held at 200 s⁻¹ for another 120 seconds during which time the average viscosity was measured. The shear rate was then ramped down from 200 s⁻¹ to 0 s⁻¹ over 120 seconds. Multiple measurements of each oil sample were taken and averaged. The sample temperature was maintained at 20.0±0.05°C using a digital water bath.

C. Density measurement

The density of each oil sample was determined by recording the combined initial mass m_i , in grams, of an empty flask and an empty 25 ml pipette using electronic scales with a precision of ±0.0005 g. A volume v of 25 ml of oil was then pipetted into the flask and the combined final mass m_f of the flask, oil and pipette was recorded, in grams, using the same electronic scales. The density ρ of the oil was determined using:

$$\rho = 1000(m_f - m_i)/v$$
 (1)

in kgm⁻³, and the density measurements were repeated and averaged for each oil.



Fig. 3. Ultrasonic signals recorded in a typical EVOO sample at 5 MHz over different propagation path lengths in the oil.



Fig. 4. Plot of incremental propagation distance and time in a typical EVOO sample, used to determine the ultrasonic velocity in the oil samples.

D. Fatty acid methyl ester (FAME) analysis

A fatty acid methyl ester (FAME) analysis was performed to determine the fatty acid composition of the different oils. The FAME analysis was carried out using an Agilent HP7890A Gas Chromatograph fitted with a 100 m x 0.25 mm fused silica capillary column with a 0.2 μ m film thickness, and a flame ionization detector. The samples were prepared using a standard ISO 12966-2 automatic BF3 transmethylation procedure [9] and analyzed according to the standard ISO 12966-4 procedure [10].

III. RESULTS AND DISCUSSION

80 different food-grade vegetable oil samples were collected and tested. These comprised 30 extra virgin olive oils (EVOO), 15 refined olive oils (ROO), 15 pomace olive oils (POO), 10 rapeseed or canola oils (RSO), 5 sunflower oils (SFO) and 5 peanut oils (PNO). A series of typical ultrasonic signals obtained for a sample of EVOO are shown in Fig. 3. The initial path length was set at 10.00 ± 0.005 mm. The position of the maximum amplitude in each pulse was determined and the corresponding differences in propagation time and distance between each signal acquisition were used to determine the ultrasonic velocity in each sample of oil, as shown in Fig. 4 for



Fig. 5. Plot of mean ultrasonic velocity vs. mean PUFA content in the oil samples.



Fig. 6. Plot of mean ultrasonic velocity vs. mean MUFA content of the different oil types.

a representative sample of EVOO with an estimated speed of sound of 1451.4 m/s.

A plot of the measured ultrasonic velocity in the oils and the measured proportion of polyunsaturated fatty acids (PUFA) in the oils, comprising C18:2n6 and C18:3n3 fatty acids, is shown in Fig. 5. There was a strong positive correlation (r = 0.74, p < 0.01) between the measured ultrasonic velocity and the PUFA content. A strong negative correlation (r = -0.66, p < 0.01) was also observed between the measured ultrasonic velocity and the mono-unsaturated fatty acid (MUFA) content and saturated fatty acid (SFA) content of the oils, as shown in Fig. 6. and Fig. 7, respectively. These correlations are related to the intermolecular activity as it has been shown previously that the oil density increases with the degree of unsaturation [11, 12]. This can be seen in Fig. 8, where the mean density of the oils increases with the proportion of PUFA.

It should be noted that there is a distinct separation in the ultrasonic velocity between the olive oils and the oils of different botanical origin, although the standard deviation error bars show some overlap between PNO and POO. It is difficult to distinguish between the different types of olive oil (EVOO,



Fig. 7. Plot of mean ultrasonic velocity vs. mean SFA content of the different oils in the study.



Fig. 8. Plot of mean density vs mean PUFA content in the different oils.

ROO and POO) as they all have similar fatty acid profiles of approximately 10% PUFA, 75% MUFA and 15% SFA. PNO tends to have a higher proportion of SFA and a lower proportion of PUFA in comparison to the other non-olive oils, meaning that its ultrasonic velocity overlaps significantly with that of POO. The ROO and EVOO also have very similar density and velocity profiles. The ultrasonic velocity c, in ms⁻¹ and the measured density ρ , in kgm⁻³, are linked by the well-known Newton-Laplace equation

$$c = \sqrt{(K/\rho)}, \qquad (2)$$

where K is the bulk modulus, in Pa. Hence, the similar relationships between PUFA content and ultrasonic velocity (Fig. 5) and density (Fig. 8) are expected.

The measured dynamic viscosity of the different oils is shown against the average PUFA content in Fig. 9, where the average viscosity decreases as the proportion of PUFA in the oil increases. This is in keeping with previous work [12] in which a higher degree of unsaturation resulted in a lower viscosity oil. A more complete set of ultrasonic velocity, density, viscosity and fatty acid compositional data for each of the 80 individual oil samples tested may be found in [13].

IV. CONCLUSIONS

A series of measurements of ultrasonic velocity were made in 80 different food-grade vegetable oil samples of EVOO, ROO, POO, PNO, RSO and SFO. A sample cell for the oils was constructed in which a 5 MHz ultrasonic immersion transducer could be positioned with a precision of ± 0.005 mm. Independent measurements of oil density and dynamic viscosity were also made to try and distinguish between the different oil types. The fatty acid composition of the oils was also measured using FAME analysis via gas chromatography. A strong correlation was observed between the degree of unsaturation of the oils and their ultrasonic properties. The technique was able to distinguish between olive oils and vegetable oils with a high PUFA content, but not between oils with very similar fatty acid profiles. Future work will include an analysis of ultrasonic attenuation as an additional non-destructive test for evaluating food-grade vegetable oils.



Fig. 9. Plot of mean viscosity vs mean PUFAcontent in the different oils.

ACKNOWLEDGMENT

The authors wish to thank T. Dennehy and J. A. O'Mahony in UCC for their rheometer technical support.

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