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Comparison of homemade TD-NMR device and commercial devices for detection of oil adulteration

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Abstract The analysis of edible oils, which have an important place in human health, is very significant. One of the most widely used edible oil is olive oil, which unfortunately is very frequently adulterated by adding a different, cheaper oil to reduce its cost. Therefore, a useful and economical method or device is needed to detect counterfeiting and adulteration of oils. In this study, a low-cost, easy-to-use, lightweight, and practical time-domain nuclear magnetic resonance (TD-NMR) device was developed for quality control and food safety applications, including testing edible oils. For this purpose, a measurement system, consisting of an O-shaped magnet with NdFeB permanent disc magnets, a radio frequency (RF) detection probe and a temperature stabilization/control system, was designed. Using this homemade device, the spin–lattice (T_1) and spin–spin (T_2) relaxation times of seven different olive oils were measured. The received results were compared with those obtained by two different commercial low-field NMR (LF-NMR) devices. It was established a good agreement between the experimental results obtained on the homemade system and the commercial LF-NMR devices. Detection of various grades of olive oil, as well as oil adulteration, was demonstrated for a set of different olive oils and a mixture of olive and sunflower oils using the developed homemade TD-NMR device.

1 Introduction

Edible oils are excellent source of energy; between 25 and 40% of a daily calorie needs are met from the oils [1]. They also play very significant role in the human body due to their role in providing the vitamins (A, D, E, K), body growth [2], wound healing and cell regeneration [3, 4] etc. The olive oil taken in daily nutrition is a very healthy source of energy, especially for the cardiovascular system and brain [5–7]. However, there is a growing problem of food adulteration, especially for olive oils, due to the intent of some producers to reduce production costs and make more profits. Olive oils are among the most commonly adulterated products, often mixed with other less expensive vegetable oils. It is a very important task to develop technical methods for the detection of the adulteration of oils and quality control of their production.

In principle, there are a number of instrumental methods [8], such as gas chromatography (GC) [9], headspace mass spectrometry [10], high-performance liquid chromatography (HPLC) [11], differential scanning calorimetry (DSC) [12], Fourier transform infrared spectroscopy (FTIR) [13, 14], synchronous fluorescence [15], nuclear magnet resonance (NMR) [16], dielectric spectroscopy [17], to investigate the chemical or physical properties of oils and fats and to evaluate the adulteration of oils and fats. However, many of these methods are not easy to handle, invasive, time-consuming, high-priced, needs in very accurate calibration and high proficiency of operator [18]. Some of additional techniques to detect adulteration in edible oils (especially in olive oil) have been proposed in the mini-review, e.g. voltametric electronic tongues, fiber optic sensing and a DNA-based technique [19], but screening using low-field NMR has not been mentioned. A plethora of various methods to detect adulteration in extra virgin olive oils (EVOO), comparing the advantages and disadvantages of each method, have been given in the excellent review [20]. These are FTIR, MIR, NIR, Raman, NMR, UV–vis, mass, fluorescence, dielectric and other spectroscopies; UV-ion mobility spectrometry, chromatographic techniques, differential scanning calorimetry, thermogravimetry, electronic nose/tongue, digital imaging, voltametric analysis and DNA analysis.

Recently, applications of ^{1}H and ^{13}C NMR spectroscopy have been demonstrated to be an extremely powerful, versatile, non-invasive method for investigating olive oil [18, 21]. However, high-field NMR (HF-NMR) spectrometers are very expensive to purchase, require liquid helium and nitrogen, have high maintenance and repair costs, and require professional staff to operate. In

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the review [20], the NMR spectroscopy has been mentioned as a large and costly instrument not suitable for in-field operations, while low-field unilateral NMR (in fact, time-domain NMR [TD-NMR]) has been stated as having the potential for operation 'in the field' without preprocessing and without a need to take a sample out of their original packing. Therefore, their use is not suitable for many small and medium-sized enterprises or in the case of mobile quality control by relevant agencies [22]. Thus, there is a growing interest in the application of low field (LF) and time domain (TD) NMR devices, which are more compact, user-friendly, light-weighting and inexpensive solutions.

TD-NMR has long been used in the food industry for the determination of oil–water ratio distribution in oily samples, food quality control and analysis of foods [18, 21–24]. TD-NMR generally relies on the detection of decreasing signal amplitude over time to investigate spin–lattice (T_1) and spin–spin (T_2) relaxation times. Depending on the RF probe and magnet configurations, the diffusion constant (D) can be also measured [25]. T_1, T_2 and D constants are rather specific characteristics of a probed material, which depend on its chemical structure, bonding, density, molecular dynamics, and viscosity [26–28]. Each material has its own relaxation times, allowing samples to be analyzed using the TD-NMR. For instance, the multi-parametric time-domain NMR relaxometry combined with machine learning analysis has been used to demonstrate rapid identification and classification of olive oils from various countries in label-free manner [29, 30]. It has been also revealed that machine learning can be applied more efficiently to TD-NMR data rather than to those provided by NIR and UV–vis spectroscopies [30].

In principle, a special version of TD-NMR device, called as unilateral nuclear magnetic resonance (UNMR), can be used as a non-invasive method for evaluation of edible oils [29, 30]. Although use of the UNMR for these purposes looks very attractive because of its small footprint and cost, inherent feature of the UNMR measurements is a low SNR of detected signals, which makes the discrimination of adulterated oils by the UNMR as difficult or very time-consuming procedure [31, 32]. Therefore, an approach proposed in based on use of large bore magnet for non-invasive examination of a whole bottle looks more feasible. Recently, Gradisek et al. [33] have made a detailed study on relaxometry (TD-NMR) measurements of EVOO by NMR in a broad range of frequencies (i.e., at various magnetic field strengths). They have confirmed that TD-NMR at low field combined with inverse Laplace transform (ILT) analysis of relaxation time distribution is a valuable option for the detection of adulteration of EVOOs. Another rather detailed study [34] has applied LF-NMR to measure olive oil samples adulterated with an edible oil (canola, flax, grape seed, peanut, soybean, and sunflower seed oils) and revealed that both bi-exponential fitting to T_2 curves plays and ILT analysis can be applied for the detection of olive oil adulteration.

Thus, recent studies reveal a high potential of the TD-NMR as low-cost, low footprint and fast technique for characterization and identification of olive oils. In this study, an inexpensive and practical TD-NMR setup has been developed to control oil quality and adulteration by probing the relaxation parameters of edible vegetable oils. To compare the home-made setup with commercial devices, relaxation times parameters obtained by two different commercial LF-NMR devices (20 MHz *Bruker Minispec MQ20* and 42.5 MHz *Magritek Spinsolve*) have been measured and compared.

2 Experimental methods and materials

2.1 Experimental setup

The homemade device setup consists of magnetic system, radio frequency (RF) detection probe, temperature stabilization/control system and *Magritek KEA2* NMR console, respectively. In Fig. 1, an image of the homemade device and a block diagram are shown.

2.1.1 Magnetic system

In Fig. 2, the magnet system geometry and magnetic field distribution calculated by finite element method (FEM) simulations are shown.

Before manufacturing the magnets of homemade setup, its basic parameters such as homogeneity and intensity of magnetic field were calculated by *Comsol Multiphysics* 5.6 program AC/DC module [35]. The region with sphere radius of 5 mm with the maximum magnetic field homogeneity, in which the sample is placed, was defined as the region of interest (ROI). The magnetic field uniformity and average magnetic field for the ROI were calculated as 278 ppm with the following equation:

$$\delta = \frac{B_{\text{max}} - B_{\text{min}}}{B_{\text{ave}}} \text{ppm} \tag{1}$$

The calculated results and experimental results for three coordinates (x, y, z) in the ROI are given in the Fig. 3.

For the construction of the magnetic system, nickel-coated NdFeB disc magnets of N33H grade were purchased from *Shanghai Jinmagnets Co. Ltd*. They have a diameter of 100 mm, a thickness of 18 mm, and a permanent magnetic flux density (Br) of 1.13 T. For better magnetic field uniformity, the pole caps made of soft iron with a diameter of 100 mm and a thickness of 10 mm were manufactured and fixed on the permanent magnets. The permanent magnets with the pole caps attached them were surrounded by magnetic field concentrator consisting of soft iron plates with thickness of 35 mm, length of 200 mm and wide of 120 mm. As a result, an O-shaped magnet system with an air gap of 34 mm providing a magnetic field of 0.371 T was constructed.

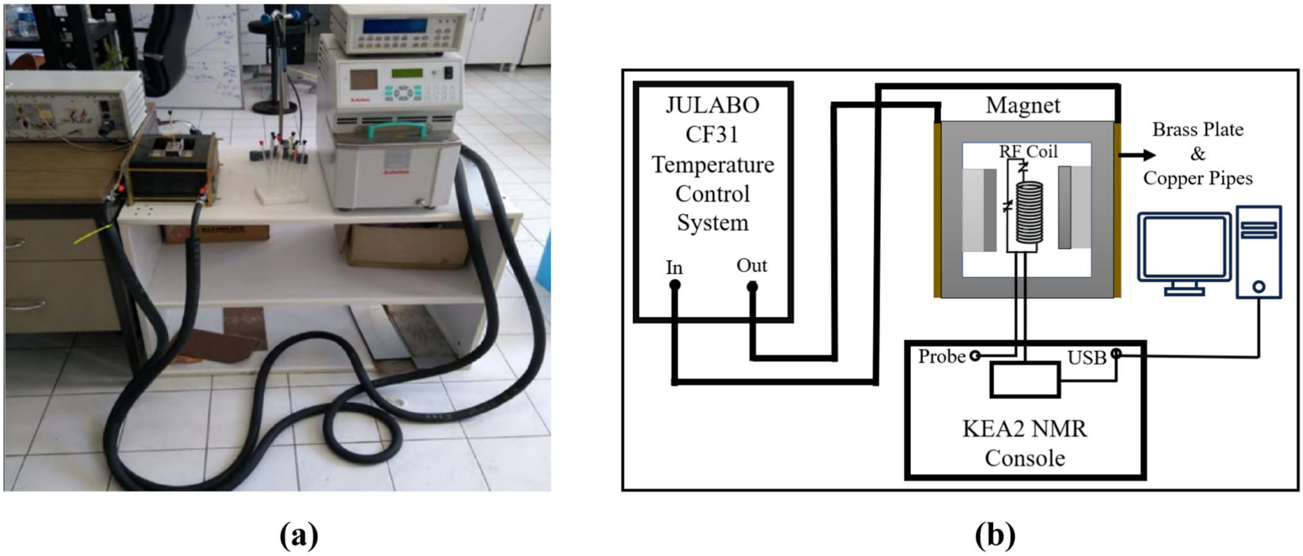
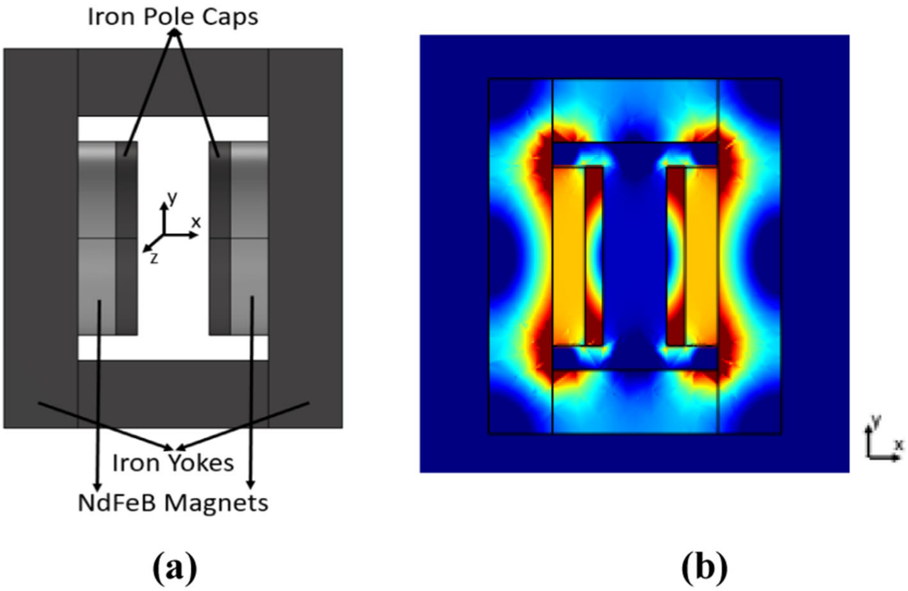


Fig. 1 **a** Photograph of the homemade setup consisting of magnetic system, RF detection probe, temperature stabilization/control system and *Magritek KEA2* NMR console setup, **b** the block diagram of the setup

Fig. 2 **a** The magnet geometry, **b** magnetic field distribution in *x*–*y* plane of magnet



2.1.2 Radio frequency (RF) detection probe

Before manufacturing of the RF detection probe, finite element method (FEM) modeling with *Comsol Multiphysics* 5.6 program (AC/DC module) and circuit calculations were performed. The Larmor frequency of the hydrogen atom at 0.371 T is 15.75 MHz. The modeling of the RF probe consisting of a solenoidal coil for the 15.75 MHz resonance frequency was made. In the simulations, the geometrical parameters suitable for the samples to be measured and providing the 15.75 MHz resonance frequency were determined. In accordance with the model used in FEM calculations an experimental RF probe was manufactured. A 36 mm long and 15 mm diameter solenoidal coil, which is obtained by winding a 0.5 mm diameter copper wire on a 14 mm diameter Teflon cylinder, was used (Fig. 4). The experimental parameters of solenoidal coil made were measured. Finally, these results were compared with the theoretical results.

Variable capacitors (*Voltronics Co.*) were connected in series with a solenoidal coil to form a resonance LC circuit with tunable resonance frequency. The probe circuit was matched to 50 Ohm for maximum power transfer with aid of parallel and series connected SMD capacitors (Fig. 5a). The return loss of the RF probe was calculated with *Advanced Design System (ADS)* program and measured as shown in Fig. 5b.

Fig. 3 Experimental and theoretical distribution of magnetic field inhomogeneity in the *x*, *y* and *z* coordinates in the ROI

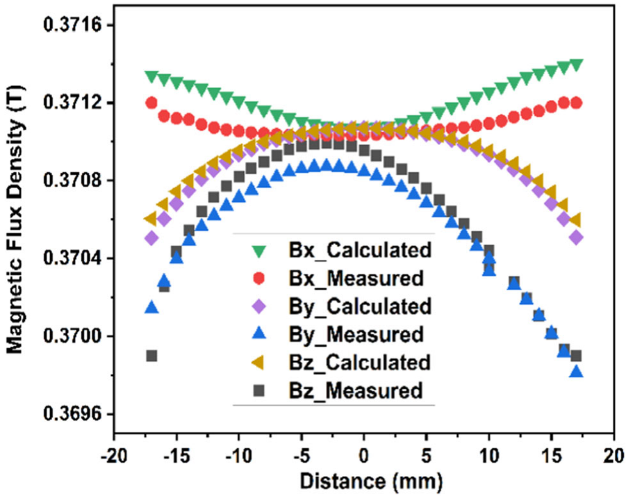
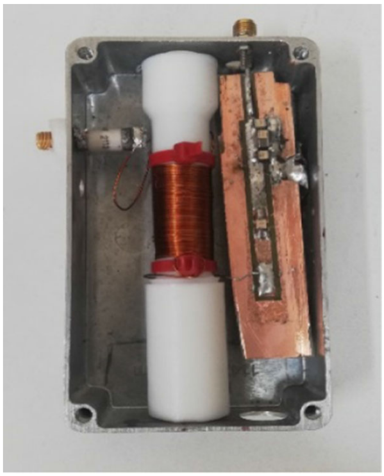
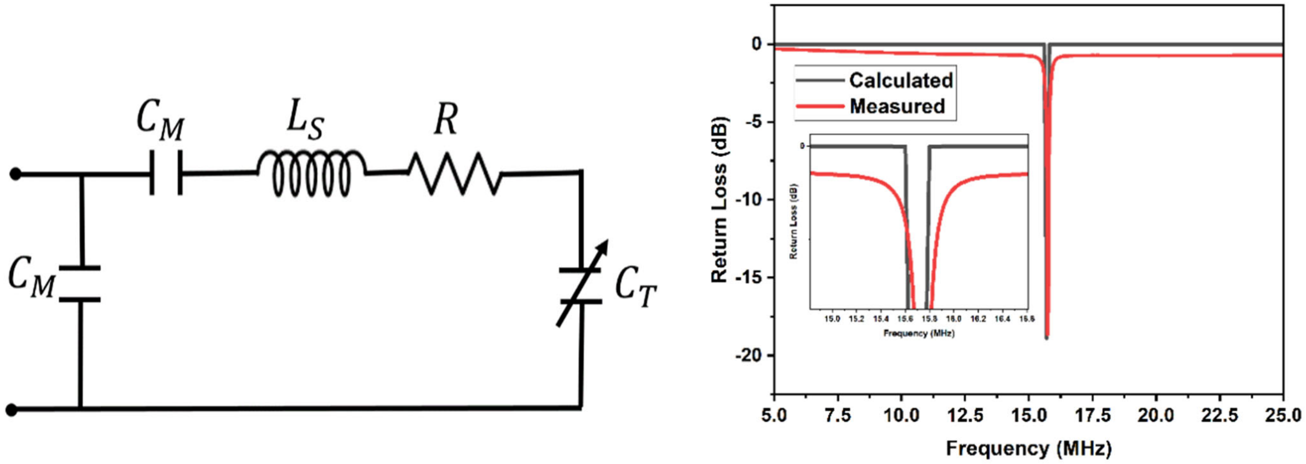


Fig. 4 A view of homemade RF detection probe inside a shielding box





(a) **(b)**

Fig. 5 **a** Lumped model of designed home RF coil, **b** calculated and measured plot of return loss versus resonance frequency of RF probe

Table 1 Calculated and measured parameters of the homemade RF probe for the 15.75 MHz resonance frequency

Parameters	Calculated	Measured
Inductance (L)	24.155 uH	18.565 uH
Magnetic Field (B_1)	2.163 mT	1.758 mT
DC Resistance (R_{DC})	0.276 Ohm	0.26 Ohm
AC Resistance (R_{AC})	17.63 Ohm	19.6 Ohm
Quality Factor (Q)	140	133

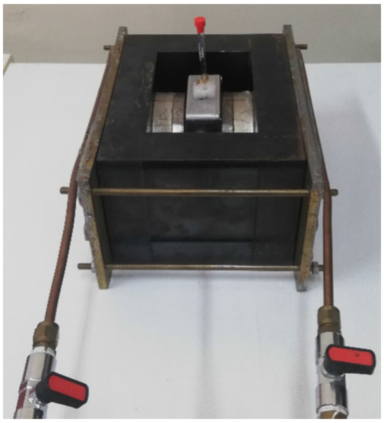


Fig. 6 Temperature stabilization/control radiator

The theoretical quality factor was calculated using the measured series inductance and resistance of the detection probe for the 15.75 MHz resonance frequency using the equation below [36]:

$$Q = \frac{2\pi f L}{R_{AC}} \tag{2}$$

Inductance and AC resistance were measured using *MiniVNA Pro* Vector Network Analyzer. For the DC resistance, B_1 magnetic field (at the center of the coil) and Q-factor measurements, the following equipment was used: *Keysight 34470A* digital multimeter, *Keysight U80324* DC power supply, *Lakeshore* Gaussmeter, *Tektronix TBS1052B* oscilloscope and *Tektronix AFG3101* signal generator. The theoretical and experimental results are given in the Table 1.

2.1.3 Temperature stabilization/control system

Due to strong dependence of the magnet magnetization on the ambient temperature [37], a temporal drift of the magnetic field value and, correspondingly, the Larmor frequency may occur. In this case, inconsistency between the successive measurements may appear. For that reason, the magnet and probe temperature should be stabilized. A temperature stabilization/control system was designed for the homemade device. For the temperature stabilization/control of the system (close to room temperature), the *Julabo CF31* compact circulator device was used to cycle water through a radiator attached to the magnet system. The radiator was made by soldering bent copper pipes with an outer diameter of 6 mm to two brass plates with a thickness of 8 mm on the sides and 120 × 160 mm. The two plates were fixed on both sides of the magnet via 4 brass rods. The temperature stabilization/control radiator is shown in Fig. 6.

2.2 Measurements

In this study, the Inversion Recovery (IR) and Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences were used for T_1 and T_2 measurements, respectively [38]. Experimental parameters of the CPMG and IR measurements for all three compared devices are given Tables 2 and 3, respectively.

In Fig. 7, the "one-pulse" spectrum and T_1 (IR) and T_2 (CPMG) decay curves of TVO(SA) sample are given as a representative result of operation of the homemade device.

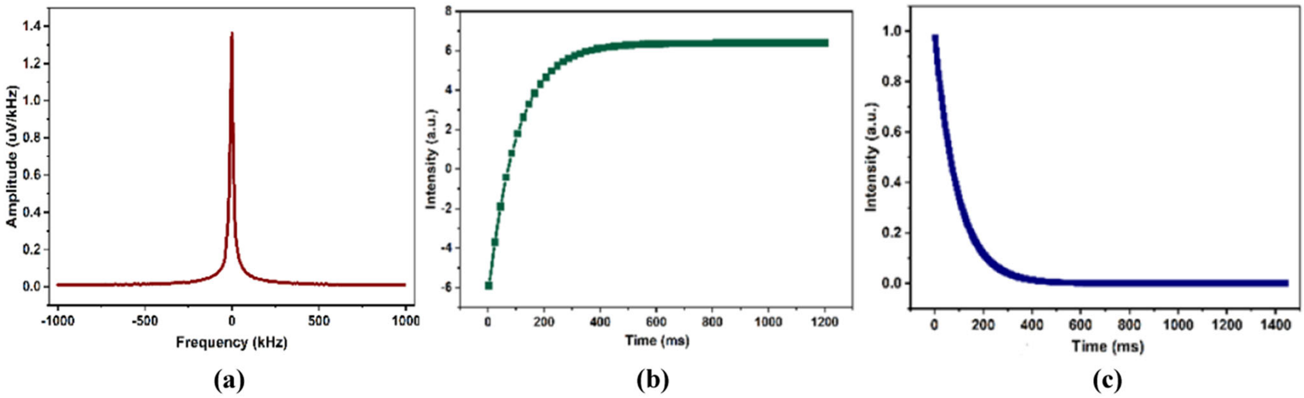
These parameters were calculated by exponential fittings $\left(A = A_0 e^{-t/T_2}\right)$, $A = A_0\left(1 - 2e^{-t/T_1}\right)$ and bi-exponential fittings $\left(A = A_1 e^{-t/T_{21}} + A_2 e^{-t/T_{22}}\right)$, $A = A_1\left(1 - 2e^{-t/T_{11}}\right) + A_2\left(1 - 2e^{-t/T_{12}}\right)$ for T_2 and T_1 respectively.

Table 2 The CPMG parameters

Parameters for CPMG	Homemade	Bruker minispec	Magritek spinsolve
B_1 frequency	15.775 MHz	19.95 MHz	43.5 MHz
B_1 field	0.9 mT	1.76 mT	0.523 mT
Echo time	1200 us	500 us	1000 us
Number of echoes	600	1500	100
Repetition time	2000 ms	2000 ms	2000 ms
90° pulse length	6.5 us	3.32 us	11.2 us
180° pulse length	13 us	6.4 us	22.4 us
Receiver gain	40 dB	64 dB	25 dB
Number of scans	4	4	4

Table 3 The IR parameters

Parameters for IR	Homemade	Bruker minispec	Magritek spinsolve
B1 frequency	15.775 MHz	19.95 MHz	43.5 MHz
B_1 field	0.9 mT	1.76 mT	0.523 mT
Max delay	1200 ms	1500 ms	1000 ms
Number of steps	60	50	41
Repetition time	2000 ms	2000 ms	2000 ms
90° pulse length	6.5 us	3.32 us	11.2 us
180° pulse length	13 us	6.4 us	22.4 us
Receiver gain	28 dB	64 dB	28 dB
Number of scans	1	2	2



(a) (b) (c)

Fig. 7 Measurements of an oil sample with constructed homemade device, **a** frequency spectrum, **b** T_2 decay curve, **c** T_1 decay curve

2.3 Samples

In this study, it was aimed to develop a portable, easy-to-use, and inexpensive homemade TD-NMR device to detect adulteration of edible vegetable oils and to compare the measurements made on this device with measurements obtained with two commercial devices. For this purpose, olive oil of seven different brands was used for investigation. All samples commercially purchased from a local market in Istanbul, Turkey. These selected oils are shown in the Table 4.

Volumetric mixtures of Yudum sunflower oil (YS) and Tarış extra virgin olive oil (South Aegean) (TVO (SA)) were used in the tests on detection of the edible oil adulteration. These oil mixtures and their percentages are represented in Table 5.

All samples were transferred to individual tubes and stored at room temperature. 8 mm diameter fused silica tubes were used for measurements with the *Bruker Minispec* MQ20 device and the homemade device, while standard 5 mm diameter NMR fused silica tubes were used for the measurements with the *Magritek Spinsolve* device.

Table 4 The studied oil samples

Sample code	Sample name
KRO	Komili Riviera Olive Oil
TRO	Tarış Riviera Olive Oil
YRO	Yudum Riviera Olive Oil
YVO	Yudum Virgin Olive Oil
TVO (NA)	Tarış Virgin Olive Oil (North Aegean)
TVO (SA)	Tarış Virgin Olive Oil (South Aegean)
KVO	Komili Virgin Olive Oil
YS	Yudum Sunflower Oil

Table 5 The oil mixtures and their percentages (olive oil is TVO (SA) and sunflower oil is YS, respectively)

Sample code	Percentages of Oil Ingredients
0	%0 Olive Oil and %100 Sunflower Oil
10	%10 Olive Oil and %90 Sunflower Oil
20	%20 Olive Oil and %80 Sunflower Oil
30	%30 Olive Oil and %70 Sunflower Oil
40	%40 Olive Oil and %60 Sunflower Oil
50	%50 Olive Oil and %50 Sunflower Oil
60	%60 Olive Oil and %40 Sunflower Oil
70	%70 Olive Oil and %30 Sunflower Oil
80	%80 Olive Oil and %20 Sunflower Oil
90	%90 Olive Oil and %10 Sunflower Oil
100	%100 Olive Oil and %0 Sunflower Oil

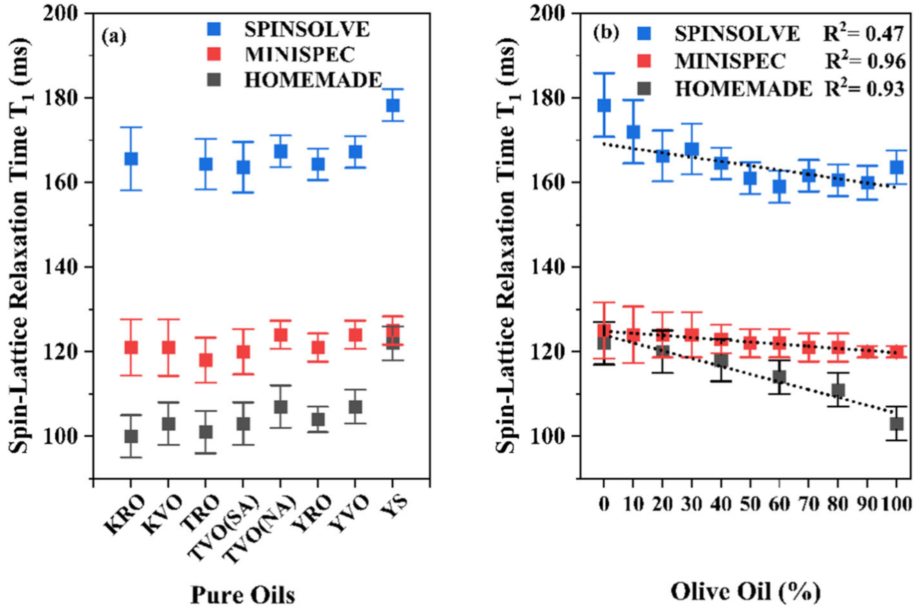


Fig. 8 T_1 measurements for three different device; **a** pure oils, **b** mixture of sunflower oil and Tarış virgin (SA) olive oil

3 Results and discussion

In Figs. 8 and 9, T_1 and T_2 measurements of pure oils and mixture of sunflower oil with Tarış extra virgin (SA) olive oil for three different devices are given. As seen in the figures, the trends obtained from commercial devices were the same for both pure oils and adulterated samples in the homemade device. In particular, it was observed that the trends of T_1 and T_2 measurements taken from adulterated samples were the same in all three devices. The error bars in these Figures indicated that T_1 and T_2 relaxation times could be measured with deviations ranging from 2 to 5.4% at most.

The general trends observed in Figs. 8 and 9 showed that (1) the T_1 and T_2 relaxation times of pure olive oil were shorter compared to sunflower oil, and (2) distribution of T_1 and T_2 relaxation times is better described by three relaxation time peaks

Fig. 9 T_2 measurements for three different device **a** pure oils, **b** mixture of sunflower oil and Tarış virgin (SA) olive oil

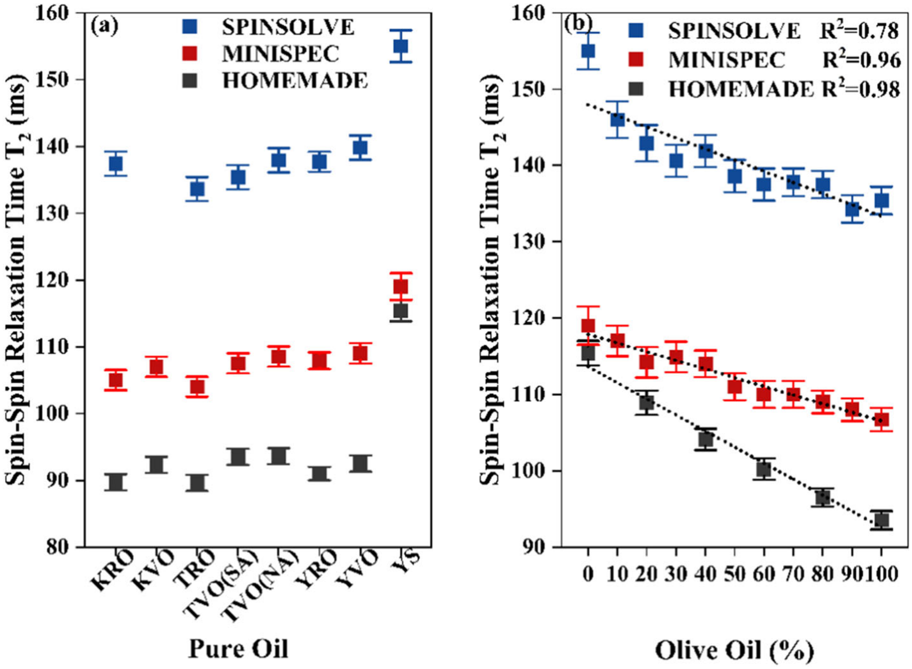


Table 6 Fatty acid % composition of olive oils and sunflower oils obtained using gas chromatography

Oil type	Olive oil			Sunflower oil	
Fatty acids	Ref [31]	Ref [39]	Ref [40]	Ref [39]	Ref [41]
Oleic acid C18:1	79.2	78.1	78.2	19.5	27.49
Linoleic acid C18:2	2.7	7.1	14.4	68.5	59.55
Linolenic acid C18:3	0.6	0.6	1.5	0.1	0.18
Palmitic acid C16:0	12.9	10.2	5.9	5.5	6.5
Steric acid C18:0	3.2	2.5	ND	4.7	4.27

against two relaxation time peaks for olive and sunflower oils, respectively. Furthermore, the effect of sunflower oil in mixture is a nearly linear shift of T_1/T_2 relaxation times to shorter values with increasing of its concentration. In Table 6, typical literature data on fatty acid % composition of olive oils and sunflower oils obtained using gas chromatography are given.

As seen in the results from the relevant references in the Table 6, the main difference between olive oil and sunflower oil in terms of fatty acid is that the percentages of oleic acid and linoleic acid are different in these oils [31, 39–41]. While the percentage of oleic acid was 78.5% for olive oil, it was 23.5% for sunflower oil. On the other hand, while the percentage of linoleic acid was 8% for olive oil, it was 64% for sunflower oil. Other literature studies on vegetable oils and fatty acids revealed similar ratios, confirming higher percentage of oleic acid (and consequently the viscosity) in the olive oil comparing with sunflower oils [42–46].

For comparison with olive oil data, T_1 and T_2 relaxation times of pure oleic acid and linoleic acids were measured using the *Bruker Minispec MQ20* instrument. The relaxation times of oleic acid were measured as 211 ms and 204.4 ms, and the relaxation times of linoleic acid were measured as 285 ms and 287 ms. These results showed that the relaxation times of oleic acid were shorter than the relaxation times of linoleic acid, and the viscosity of oleic acid was higher than that of linoleic acid. As a result of this comparison we came to conclusion that the elongation of the relaxation times is attributed to the decrease in the percentage of oleic acid with the increase in the sunflower oil content in the olive-sunflower oil mixture.

Although relaxation times were showed the same tendency for all devices, there were differences between the relaxation time values. The measured values of T_1 and T_2 for edible oils obtained by homemade device were smaller for 13% comparing with *Bruker Minispec* and for 42% comparing with *Magritek Spinsolve*. One of the possible contributions to these differences is an effect of magnetic field non-uniformity in a sample volume, which is a parameter specific for each TD NMR device. For estimation of an effect of the observed differences in relaxation parameters, T_2 relaxation time parameter of a low-viscous (ethanol) sample was measured using different echo time parameters for each device. The obtained results are given in Fig. 10.

Generally, the T_2 relaxation time of materials under the effect of inhomogeneous magnetic field of the device is defined as following equation [25, 47–49];

$$\frac{1}{T_{2\mathrm{eff}}} = \frac{1}{T_2} + \frac{1}{3}\gamma^2 G^2 D\tau^2 \tag{3}$$

Fig. 10 Measured magnetic field gradient of devices using ethanol as a probe sample

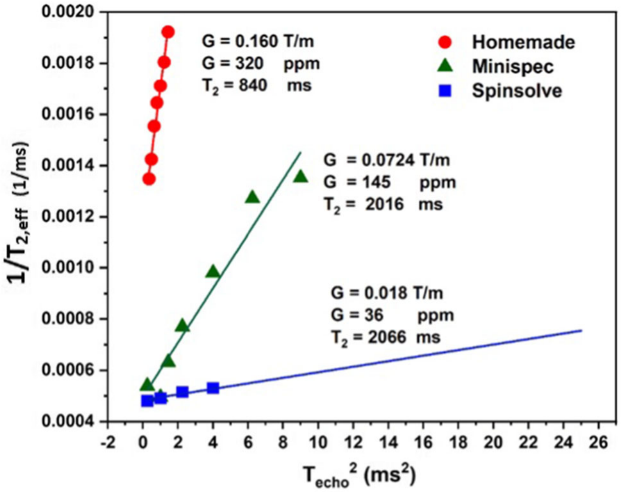
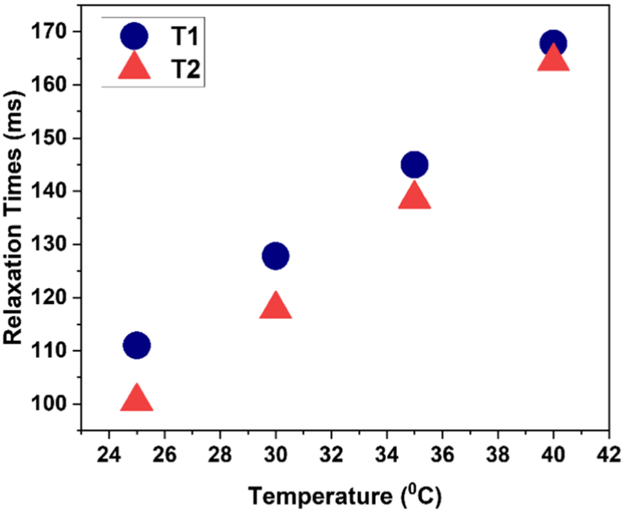


Fig. 11 Dependence of the T_1 and T_2 relaxation times of a TVO (SA) on the temperature measured using the Minispec device



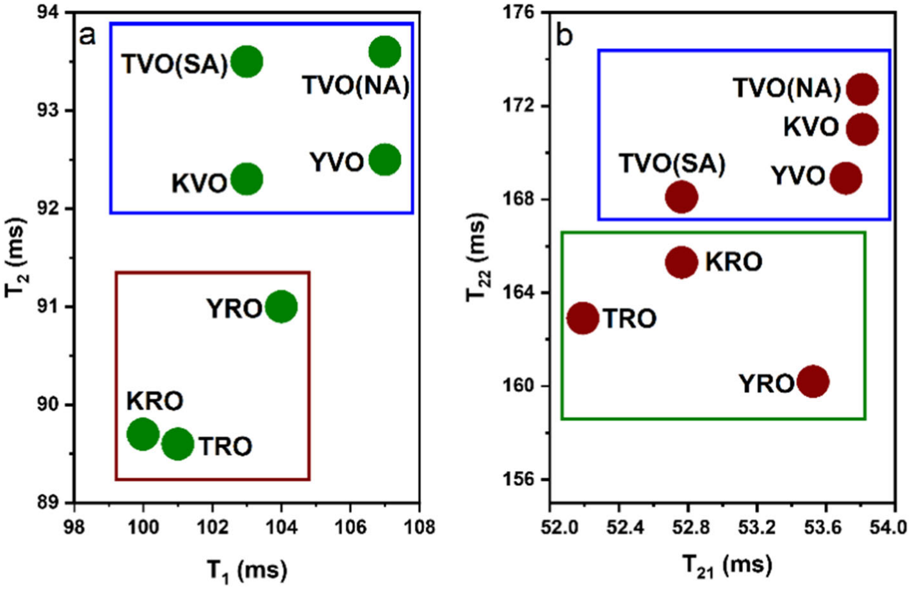
Herein, $T_{2\text{eff}}$ is characteristic spin–spin relaxation time under the CPMG pulse sequence, G is the static magnetic field gradient (i.e., a linear measure of its non-uniformity), D is the diffusion coefficient of a sample, and γ is the gyromagnetic ratio of ^{1}H. From the Eq. 3, the magnetic field gradient values (G) were calculated for homemade and *Bruker Minispec* devices as 0.160 and 0.0724 T/m, respectively. Using these calculated G values, it is easy to estimate that the contribution of the magnetic field non-uniformity in $T_{2\text{eff}}$ value for the olive oil samples studied above is only 5% for the homemade device, and it is negligibly small for *Bruker Minispec*. Therefore, other possible reasons for the observed difference in relaxation times obtained by various devices have to be considered. Another possible explanation is the difference in measurement temperatures of various TD-NMR devices. For qualitative evaluation of this effect, the measurements of both relaxation times of the TVO (SA) as a function of temperature were made using the Minispec device as shown in Fig. 11.

As seen in Figure, a strong dependence of the T_1 and T_2 relaxation times of an olive oil was observed. This result revealed that the higher measurement temperature of the *Spinsolve* device resulted in essentially longer T_1 and T_2 relaxation times comparing with the measurement results received by the *Bruker* and homemade devices. Finally, we cannot exclude a minor contribution of the different magnetic fields (i.e. ^{1}H Larmour frequencies) of the devices used (see, e.g. [33] in the observed difference of the spin–lattice (T_1) relaxation time.

For testing an ability of our home-made setup to discriminate between various grades of olive oils (riviera oil and extra virgin oil), a two-dimensional graphs of T_2–T_1 correlations or T_{21}–T_{22} (two components of T_2) correlations were drawn. It is known that extra virgin olive oil (EVOO) and riviera oil have different amounts of fatty acids depending on the production process. On the other hand, EVOOs of various producers are expected to reveal some differences due to harvest time, geographical region and production line.

For obtaining the Fig. 2a, a mono-exponential fitting to the T_2 decay curve was used for simplicity. For obtaining the Fig. 2b, a bi-exponential fitting to the curves of T_2 relaxation times were used. In these manners, two T_2 components, T_{21} and T_{22}, of spin–spin relaxation times were obtained. It should be noted that ILT analysis provides three relaxation time peaks in both T_1 and T_2

Fig. 12 T_1 and T_2 correlations (**a**), T_{21}–T_{22} correlations (**b**) of various grades of olive oils



distribution. However, taking into account that two components with faster relaxation times have values are close to each other, we preferred to use more robust analysis based on the bi-exponential fit instead that of based on the ILT. From the graphs in Fig. 12a, b, it was seen that extra virgin olive oils and riviera olive oils were formed two clusters separated from each other. This result proves a possibility to use the home-made TD-NMR setup for quality evaluation of olive oils of various vendors, for discrimination between various grades of olive oils as well as to detect their adulteration.

4 Conclusion

In this study, a cost-effective, easy-to-use homemade TD-NMR device was developed to detect adulteration in olive oils. The validation studies were performed with two different commercial devices (*Magritek Spinsolve* and *Bruker Minispec*) to test the accuracy of the device. It was observed that controlling the sample temperature is important for accurate measurements of T_1 and T_2 times and for performing correct comparison with commercial devices, while the magnetic field non-uniformity had only minor effect on the observed relaxation times of olive oils for a typical set of experimental parameters.

The obtained results showed that both olive oil adulteration and the type of olive oil (extra virgin/riviera) could be determined with the developed device. When TD-NMR used in this study was compared to other specific techniques (GC, FTIR, MIR, NIR, Raman, etc.), it was clearly seen that it had some advantages such as fast, simple analysis and more robustness.

During the measurements, it was observed that sample temperature had a direct effect on the prolongation of T_1 and T_2 times, while magnetic field homogeneity had no significant effect. In addition, it was concluded that the homemade TD-NMR device could detect adulteration of olive oil by admixing sunflower oil in the content of 10% and higher (Fig. 9b), while the measurement time is limited to only 1–2 min. Although gas chromatography, frequently used in laboratory analysis of oils, can detect lower adulteration rates (2–5%) [50], TD NMR has advantage of much faster measurement time (~ 1 min in the case of discrimination by T_2 relaxation time against e.g. 35 min in [50, 51]). Comparing the TD-NMR with optical (or, vibrational) spectroscopy techniques (e.g. FTIR, MIR, NIR, Raman; which are much faster than chromatographic ones) we have to note that they are strongly rely on use of advanced analysis approaches, such as chemometry, which are not easy to implement in practical devices. On the other hand, TD NMR technique is simple in analysis; it is low-cost and fast approach. Furthermore, it may be applied in non-invasive manner to screen the container with oil without opening it.

Thus, this study revealed high prospects of the TD-NMR technique in the detection of adulteration of olive oil and for the quality control of various edible oils. Furthermore, the TD NMR has many potential advantages, including a possibility of its implementation as a hand-held device for non-invasive, fast and efficient screening of the highest-grade olive oils (EVOO) to detect possible adulterants at all market and consumer stages.

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Data Availability Statement The data sets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. V. Kostik, S. Memeti, B. Bauer, Fatty acid composition of edible oils and fats. J. Hyg. Eng. Des. **4**, 112–116 (2013)
2. M.B.R. Moreira, M.E. Castell-Perez, *Deep Fat Frying: Fundamentals and Applications* (Aspen Publications, Gaithersburg, Maryland, 1999)
3. D.K. Salunkhe, R.N. Adsule, J.K. Chavan, S.S. Kadam, *World Oilseeds: Chemistry, Technology and Utilization, 1st edn.* (Springer New York, 1992). ISBN978-0-442-00112-4
4. J. Giese, Fats, oils and fat replacers. Food Technol. **50**, 78–84 (1996)
5. P.C. Calder, Functional roles of fatty acids and their effects on human health. J. Parenter. Enter. Nutr. **39**, 18S-32S (2015). https://doi.org/10.1177/0148607115595980
6. F. Pérez-Jiménez, J. Ruano, P. Perez-Martinez, F. Lopez-Segura, J. Lopez-Miranda, The influence of olive oil on human health: not a question of fat alone. Mol. Nutr. Food Res. **51**, 1199–1208 (2007). https://doi.org/10.1002/mnfr.200600273
7. A. Foscolou, E. Critselis, D. Panagiotakos, Olive oil consumption and human health: a narrative review. Maturitas **118**, 60–66 (2018). https://doi.org/10.1016/j.maturitas.2018.10.013
8. Q. Zhang, A.S.M. Saleh, Q. Shen, Discrimination of edible vegetable oil adulteration with used frying oil by low field nuclear magnetic resonance. Food Bioprocess Technol. **6**, 2562–2570 (2013). https://doi.org/10.1007/s11947-012-0826-5
9. M. Hajimahmoodi, Y. Vander Heyden, N. Sadeghi, B. Jannat, M.R. Oveisi, S. Shahbazian, Gas-chromatographic fatty-acid fingerprints and partial least squares modeling as a basis for the simultaneous determination of edible oil mixtures. Talanta **66**, 1108–1116 (2005). https://doi.org/10.1016/j.talanta.2005.01.011
10. I. Marcos Lorenzo, J.L. Pérez Pavón, M.E. Fernández Laespada, C. García Pinto, B. Moreno Cordero, Detection of adulterants in olive oil by headspace-mass spectrometry. J. Chromatogr. A **945**, 221–230 (2002). https://doi.org/10.1016/S0021-9673(01)01502-3
11. S.C. Cunha, M.B.P.P. Oliveira, Discrimination of vegetable oils by triacylglycerols evaluation of profile using HPLC/ELSD. Food Chem. **95**, 518–524 (2006). https://doi.org/10.1016/j.foodchem.2005.03.029
12. E. Chiavaro, M.T. Rodriguez-Estrada, C. Barnaba, E. Vittadini, L. Cerretani, A. Bendini, Differential scanning calorimetry: a potential tool for discrimination of olive oil commercial categories. Anal. Chim. Acta **625**, 215–226 (2008). https://doi.org/10.1016/j.aca.2008.07.031
13. M.J. Lerma-García, G. Ramis-Ramos, J.M. Herrero-Martínez, E.F. Simó-Alfonso, Authentication of extra virgin olive oils by Fourier-transform infrared spectroscopy. Food Chem. **118**, 78–83 (2010). https://doi.org/10.1016/j.foodchem.2009.04.092
14. Q. Zhang, C. Liu, Z. Sun, X. Hu, Q. Shen, J. Wu, Authentication of edible vegetable oils adulterated with used frying oil by Fourier transform infrared spectroscopy. Food Chem. **132**, 1607–1613 (2012). https://doi.org/10.1016/j.foodchem.2011.11.129
15. K.I. Poulli, G.A. Mousdis, C.A. Georgiou, Synchronous fluorescence spectroscopy for quantitative determination of virgin olive oil adulteration with sunflower oil. Anal. Bioanal. Chem. **386**, 1571–1575 (2006). https://doi.org/10.1007/s00216-006-0729-2
16. D. Šmejkalová, A. Piccolo, High-power gradient diffusion NMR spectroscopy for the rapid assessment of extra-virgin olive oil adulteration. Food Chem. **118**, 153–158 (2010). https://doi.org/10.1016/j.foodchem.2009.04.088
17. A. Cataldo, E. Piuzzi, G. Cannazza, E. De Benedetto, L. Tarricone, Quality and anti-adulteration control of vegetable oils through microwave dielectric spectroscopy. Meas. J. Int. Meas. Confed. **43**, 1031–1039 (2010). https://doi.org/10.1016/j.measurement.2010.02.008
18. M.D. Guillén, A. Ruiz, Edible oils: discrimination by 1H nuclear magnetic resonance. J. Sci. Food Agric. **83**, 338–346 (2003). https://doi.org/10.1002/jsfa.1317
19. W.A. Salah, M. Nofal, Review of some adulteration detection techniques of edible oils. J. Sci. Food Agric. **101**, 811–819 (2021). https://doi.org/10.1002/jsfa.10750
20. Xu. Maninder MeenuQianxi CaiBaojun, A critical review on analytical techniques to detect adulteration of extra virgin olive oil. Trends Food Sci. Technol. **91**, 391–408 (2019)
21. G. Guthausen, H. Todt, W. Burk, D. Schmalbein, A. Kamlowski, Time-domain NMR in quality control: more advanced methods. Mod. Magn. Reson. (2008). https://doi.org/10.1007/1-4020-3910-7_195
22. T.A. van Beek, Low-field benchtop NMR spectroscopy: status and prospects in natural product analysis. Phytochem. Anal. **32**, 24–37 (2021). https://doi.org/10.1002/pca.2921
23. H. Todt, G. Guthausen, W. Burk, D. Schmalbein, A. Kamlowski, Water/moisture and fat analysis by time-domain NMR. Food Chem. **96**, 436–440 (2006). https://doi.org/10.1016/j.foodchem.2005.04.032
24. H. Todt, G. Guthausen, W. Burk, D. Schmalbein, A. Kamlowski, Time-domain NMR in quality control: standard applications in food, in *Modern Magnetic Resonance* (Springer, Dordrecht, 2008), pp 1739–1743. https://doi.org/10.1007/1-4020-3910-7_196
25. G.V. Mozzhukhin, G.V. Kupriyanova, S.S. Mamadazizov, A. Maraşlı, B.Z. Rameev, Low-field 14N nuclear magnetic resonance for detection of dangerous liquids. Chem. Phys. **513**, 129–134 (2018). https://doi.org/10.1016/j.chemphys.2018.07.032
26. J.C. Hindman, A. Svirmickas, M. Wood, Relaxation processes in water. A study of the proton spin-lattice relaxation time. J. Chem. Phys. **59**, 1517–1522 (1973). https://doi.org/10.1063/1.1680209

27. Y. Sato, O. Miyawaki, Relationship solutions between proton NMR relaxation time and viscosity of saccharide. Food Sci. Technol. Res. **6**, 136–139 (2000). https://doi.org/10.3136/fstr.6.136
28. J. Bryan, A. Kantzas, C. Bellehumeur, Oil-viscosity predictions from low-field NMR measurements. SPE Reserv. Eval. Eng. **8**, 44–52 (2005). https://doi.org/10.2118/89070-PA
29. X. Hou, G. Wang, X. Wang, X. Ge, Y. Fan, R. Jiang, S. Nie, Rapid screening for hazelnut oil and high-oleic sunflower oil in extra virgin olive oil using low-field nuclear magnetic resonance relaxometry and machine learning. J. Sci. Food Agric. **101**, 2389–2397 (2021). https://doi.org/10.1002/jsfa.10862
30. V.R. dos Santos, V. Goncalves, P. Deng, A.C. Ribeiro, M.M. Teigao, B. Dias, I. Mendes Pinto, J. Gallo, W.K. Peng, Novel time-domain NMR-based traits for rapid, label-free Olive oils profiling. Npj Sci. Food (2022). https://doi.org/10.1038/s41538-022-00173-z
31. P.M. Santos, F.V.C. Kock, M.S. Santos, C.M.S. Lobo, A.S. Carvalho, L.A. Colnago, Non-invasive detection of adulterated olive oil in full bottles using time-domain NMR relaxometry. J. Braz. Chem. Soc. **28**, 385–390 (2017). https://doi.org/10.5935/0103-5053.20160188
32. Z. Xu, R.H. Morris, M. Bencsik, M.I. Newton, Detection of virgin olive oil adulteration using low field unilateral NMR. Sensors **14**, 2028–2035 (2014). https://doi.org/10.3390/s140202028
33. A. Gradišek, M. Cifelli, D. Ancora, A. Sepe, B. Zalar, T. Apih, V. Domenici, Analysis of extra virgin olive oils from two Italian regions by means of proton nuclear magnetic resonance relaxation and relaxometry measurements. J. Agric. Food Chem. **69**, 12073–12080 (2021). https://doi.org/10.1021/acs.jafc.1c00622
34. S. Ok, Detection of olive oil adulteration by low-field NMR relaxometry and UV–Vis spectroscopy upon mixing olive oil with various edible oils. Grasas Aceites **68**, 1–13 (2017). https://doi.org/10.3989/gya.0678161
35. A. Gottvald, Optimal magnet design for NMR. IEEE Trans. Magn. **26**, 399–402 (1990). https://doi.org/10.1109/20.106338
36. M. Gupta, C.P. Safvan, K. Singh, D.K. Lobiyal, P. Yadav, S. Singh, Radio frequency planar coil-based on-chip probe for portable nuclear magnetic resonance. IEEE Sens. J. **19**, 2500–2508 (2019). https://doi.org/10.1109/JSEN.2018.2887274
37. T. Meng, P. Zhang, A review of thermal monitoring techniques for radial permanent magnet machines. Machines (2022). https://doi.org/10.3390/machines10010018
38. H. Malcolm, *Levitt, Spin Dynamics: Basics of Nuclear Magnetic Resonance*, 2nd edn. (Wiley, Chichester, 2008)
39. T. Řezanka, H. Řezanková, Characterization of fatty acids and triacylglycerols in vegetable oils by gas chromatography and statistical analysis. Anal. Chim. Acta **398**, 253–261 (1999). https://doi.org/10.1016/S0003-2670(99)00385-2
40. A. Vávra, M. Hájek, D. Kocián, The influence of vegetable oils composition on separation of transesterification products, especially quality of glycerol. Renew. Energy **176**, 262–268 (2021). https://doi.org/10.1016/j.renene.2021.05.050
41. C. Xing, X. Yuan, X. Wu, X. Shao, J. Yuan, W. Yan, Chemometric classification and quantification of sesame oil adulterated with other vegetable oils based on fatty acids composition by gas chromatography. LWT **108**, 437–445 (2019). https://doi.org/10.1016/j.lwt.2019.03.085
42. H. Yalcın, T.D. Capar, H. Kavuncuoglu, Effects of extra virgin olive and Riviera olive oil addition on the properties of butter: an optimization study based on D-optimal mixture design. Eur. J. Sci. Technol. 546–555 (2019). https://doi.org/10.31590/ejosat.580737
43. M. Davila, X. Liu, Z. Yusufali, X. Du, Using texture analyzer to characterize pecan and olive oil tactile properties, compare to viscometer analysis, and link to fatty acid profile and total polyphenols. J. Texture Stud. (2022). https://doi.org/10.1111/jtxs.12664
44. N. Deng, N. Cao, P. Li, Y. Peng, X. Li, L. Liu, H. Pu, S. Xie, J. Luo, Z. Wu, M. Liu, Microfluidic evaluation of some edible oil quality based on viscosity and interfacial tensions. Int. J. Food Sci. Technol. **53**, 946–953 (2018). https://doi.org/10.1111/ijfs.13667
45. P. Hlaváč, M. Božiková, A. Petrović, Selected physical properties assessment of sunflower and olive oils. Acta Technol. Agric. **22**, 86–91 (2019). https://doi.org/10.2478/ata-2019-0016
46. A.C. Okafor, T.O. Nwoguh, A study of viscosity and thermal conductivity of vegetable oils as base cutting fluids for minimum quantity lubrication machining of difficult-to-cut metals. Int. J. Adv. Manuf. Technol. **106**, 1121–1131 (2020). https://doi.org/10.1007/s00170-019-04611-3
47. H.C. Torrey, Bloch equations with diffusion terms. Phys. Rev. **104**(3), 563–565 (1956)
48. P. Charles, *Slichter, Principles of Magnetic Resonance* (Springer, Berlin, 1990)
49. R. Kimmich, *NMR – Tomography, Diffusometry, Relaxometry, 1st edn.* (Springer, Berlin, 1997). e-ISBN-13: 978-3-642-60582-6
50. N.K. Andrikopoulos, I.G. Giannakis, V. Tzamtzis, Analysis of olive oil and seed oil triglycerides by capillary gas chromatography as a tool for the detection of the adulteration of olive oil. J. Chromatogr. Sci. **39**, 137–145 (2001). https://doi.org/10.1093/chromsci/39.4.137
51. H. Jabeur, A. Zribi, J. Makni, A. RebaiI, R. Abdelhedi, M. Bouaziz, Detection of chemlali extra-virgin olive oil adulteration mixed with soybean oil, corn oil, and sunflower oil by using GC and HPLC. J. Agric. Food Chem. **62**, 4893–4904 (2014)