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Portable NMR in food analysis

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Abstract

Low-field ^{1}H NMR relaxometry is an important tool used to investigate on the most abundant components of intact foodstuffs based on relaxation parameters and amplitude of the NMR signals. In particular, information on water compartments, diffusion and movement can be obtained by detecting proton signals prevalently ascribable to H_2O contained in foodstuffs. The main advantage of this technique is that it does not require any pretreatment of the sample and once developed, standard protocols based on rapid measurements can be easily transferred to quality control applications. An actual breakthrough for the low-field NMR application to food science has certainly been the development of unilateral NMR sensors. These devices present an attractive option for non-invasive assessment of compositional and microstructure of food materials. They are portable and allow easy sample access, which makes them attractive for quality control in industrial environments and directly on sealed packaged foods. A price to pay is the inhomogeneity of the magnetic field, which compromises the sensitivity of these devices. However, recent developments in unilateral magnets design offer larger sensitive volume, higher sensitivity and shorter dead times. In this brief review, we highlight the different uses of unilateral NMR devices in food analysis.

Keywords: Portable NMR, Food science, Relaxation times, Water mobility, Self-diffusion coefficient, Quality control process

Background

Pulsed low-resolution NMR is an appreciated and powerful technique in food science and technology. NMR instruments operating in the time domain (TD) at low field are widely used for investigating on relationships between food properties and its composition and structure. In fact foodstuffs are structurally and chemically heterogeneous systems whose constituents, due to the different molecular mobility, show different relaxation and diffusive properties. Pulsed low-resolution NMR technique is suitable to study the dynamic properties of matter like self-diffusion, flow and relaxation. The two major NMR relaxation phenomena are longitudinal relaxation characterized by a relaxation time T_1, and transverse relaxation, characterized by T_2.

Hahn echo decay experiment can be used to measure the transverse relaxation time. The amplitude of the echo is recorded for different spacings of the two pulses. Echo amplitude is influenced by molecular diffusion (Brownian motion) because of the fluctuations of the local magnetic field. Thus, the amplitude of the echo at the time t is related to the transverse relaxation T_2, gradient G, self-diffusion coefficient D, gyromagnetic ratio γ, and the half echo spacing τ through the following equation:

$$M_t = \exp\left(-\frac{1}{T_2} - \frac{\gamma^2 G^2 D \tau^2 t}{3}\right) \qquad (1)$$

In the case of most conventional NMR magnets, the field inhomogeneity is sufficiently small that at short τ values the second term of the equation becomes negligible even for faster diffusing molecules such as water. Instead, in the case of a strong inhomogeneous magnetic field the second term of Eq. (1) cannot be neglected.

The pulsed field gradient NMR method is one of the main NMR methods for obtaining dynamic information, such as the self-diffusion coefficient. Self-diffusion data provide detailed information about molecular organization and phase structure. Self-diffusion rates are quite sensitive to structural changes and to binding and association phenomena. Experimental self-diffusion values are directly related to molecular displacement.

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Many analytical protocols have been established for rapid and precise measurements of compositional properties [1–4]. These protocols are particularly appreciated in the food supply chain for quality and process control. In many applications, differences in self-diffusion coefficient and relaxation times have been exploited to differentiate different phases in food matrices [1–3]. For example, ^{1}H pulsed low-resolution NMR has been applied to study the effect of different physiological conditions on kiwifruit [5, 6], apple [7–10], carrot [11] and strawberry [3, 12].

The effect induced by ripening, drying, freezing, high-pressure processing, bruising, browning, aging and osmotic drying has been studied [1, 2, 13–15].

The relationships between ^{1}H NMR relaxation data and some technological parameters of meat have been investigated [16–18].

NMR is a well-accepted analytical tool for evaluation of oil and moisture content in food [1, 19]. The presence of non-freezable water, water mobility as well as the phase compositional and hydration phenomena have been investigated in many food matrices [1].

A breakthrough in the application of TD NMR to food science has been represented by the conceiving of compact and portable NMR sensors which enable the analysis of intact food matrices in a non-destructive, non-invasive way in situ. Sensors based on permanent magnets have been developed during the last years covering applications involving relaxometry, imaging and even spectroscopy with hand-held systems [20–23]. These devices require low maintenance costs and allow easy sample access, which makes them attractive for quality and process control in industrial environments.

Portable single-sided NMR sensors with open geometry

In conventional NMR instruments, the geometry of the magnet is referred to as closed geometry and the sample under study is placed in a homogeneous magnetic field. While this facilitates high signal-to-noise, geometrically correct, spatially resolved magnetic resonance imaging (MRI), it limits the range of samples that can be examined. In recent years, this limitation has been addressed by development of portable or unilateral NMR [22–24]. The geometry of portable NMR sensors, in which the object is exposed to the stray field of the magnet, is referred to as open geometry. In this case, the magnet may be placed to one side of the object fully preserving the integrity and the dimension of the sample under investigation and also allowing the measurement to whole packed products.

Nowadays, the unilateral NMR sensors available can be categorized into two classes. The first group operates in a strong magnetic field gradient [24], whereas the second one operates in region under more or less homogeneous

magnetic field [22, 23]. Both approaches have their strengths and weaknesses.

Unilateral NMR developed by Blumich et al. [25] is characterized by a high magnetic field strength operating in the proton frequency range of 13–18 MHz with a strong magnetic field gradient. This sensor requires very short (in the range of the microseconds) and very powerful RF pulses to achieve the desired frequency bandwidth. An example of such a sensor is sketched in Fig. 1a. Two antiparallel magnets are mounted on an iron yoke and the radio-frequency coil is positioned in the gap between the two magnets. The magnet may be designed either parallel or perpendicular to the sensor surface. Using this sensor, the depth of measurement into the investigated object may be varied by changing the RF coil [26]. The signal-to-noise ratio decreases by increasing the depth of measurement due to the B_1 stray field.

Another class of unilateral NMR instrument has been developed by Marble et al. [22, 27]. In these sensors, the unilateral magnet array consisted of three block magnets all magnetized along the same directions, see Fig. 1b. The sensitive spot (c) is located ~1 cm above the face of the magnet. The magnet spacings are optimized to produce a locally homogeneous field in this region creating a relatively large MR sensitive volume above the surface RF coil (b). The resonance frequency of the NMR system is 4.68 MHz and all pulse lengths are about of 8 μs with 6 dB attenuation for the 90° pulse and no attenuation for the 180° pulse [22, 28].

Another portable NMR sensor with a novel one-sided access magnet design, termed NMR-MOLE (mobile lateral explorer), has been developed by Manz et al. [23]. This sensor is very efficient in terms of sensitivity and penetration depth. The magnet array is based on a barrel magnet operating at 3.3 MHz with a central magnet positioned to provide a homogeneous region from 4 to 16 mm away from the probe, with maximum sensitivity at a depth of 10 mm. Because of the lower diffusion attenuation in homogeneous field sensors, they are better suited for studying liquid samples such as aqueous solutions and biological tissue where unilateral or portable access is required.

A recent evolution of NMR sensors with an open geometry is the profile NMR MOUSE [29]. The magnet geometry consists of four permanent magnet blocks positioned on an iron yoke, see Fig. 1c. Two magnets are polarized along y and two along $-y$. Magnets with the same polarization are separated by a small gap d_S whereas magnets with opposite polarization are separated by a gap d_B. The sensor is placed on a lift which moves the sensitive volume constituted of a thin slice at a well-defined position through the object by varying the distance between the sensor and the object see Fig. 1d. The slice thickness depends on the experimental conditions and typically ranges between a few micrometers and 100 μm. The

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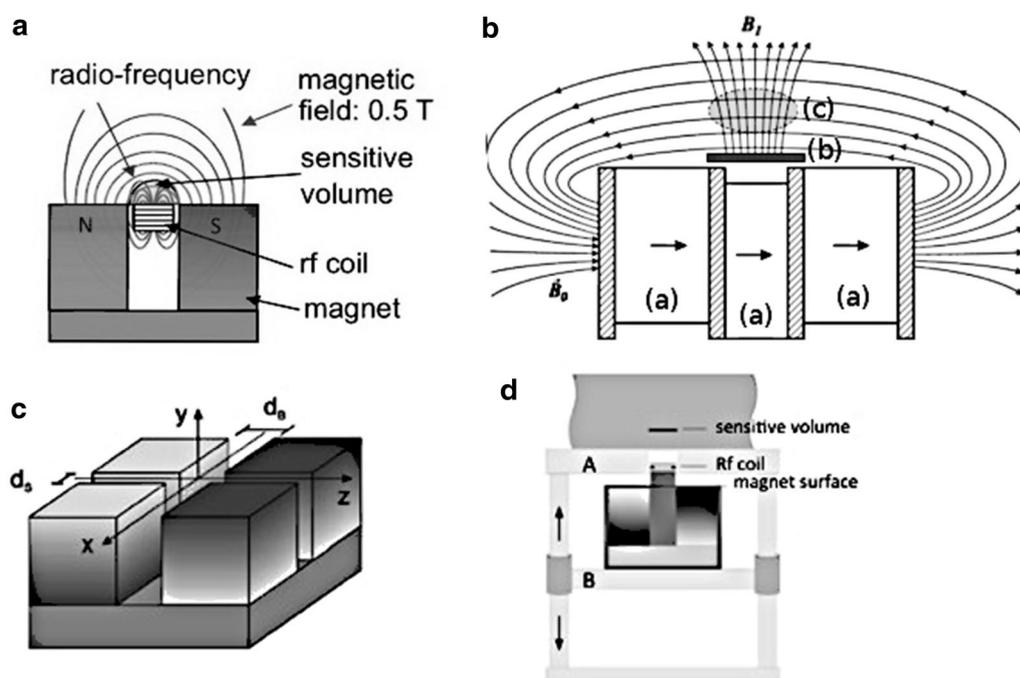
Fig. 1 **a** Skecth of a single-sided NMR sensor with open geometry (reproduced with permission from [25]). **b** Sketch of a single-sided magnet array with a sweet-spot (reproduced with permission from [41]). **c** Sketch of the geometry of the magnet of the profiler NMR MOUSE. **d** Sketch of the lift used to reposition the sensitive slice across the sample with a micrometric precision. The object is placed on *top* of the *plate A*, which is parallel to the movable *plate B* where the magnet is mounted (reproduced with permission from [28])

magnetic field varies linearly with the space generating a constant magnetic field gradient of about 20 T/m [29].

The amplitude values recorded by a modulated displacing of the sensor may provide a profile of proton spin densities as a function of the depth into the sample. However, not only the signal amplitude but also other parameters (i.e. relaxation times) can be reported against the depth scanned. Presently, a penetration depth up to 2.5 cm may be achieved with these sensors.

Due to strongly inhomogeneous magnetic field, the applications of portable NMR are limited as compared to those performed by benchtop instrumentation. FID cannot be detected, because NMR signal decays very quickly and must be recovered as an echo. The measurement of transverse relaxation time suffers for artifacts resulting from molecular diffusion in the strong magnetic field gradient. These artifacts are more pronounced in the case of small molecules that diffuse rapidly. In the presence of diffusion process, the transverse relaxation time values are shortened with respect to those measured in homogeneous field. Furthermore, the decay of the observed transverse magnetization in inhomogeneous field is a mixture of T_1 and T_2 and the early echoes oscillate in amplitude thus leading to an affective echo train decay time $T_{2\text{eff}}$ instead only T_2 [30–32]. As well known, it is possible to reduce the effect of molecular diffusion on the

NMR signal collected in the magnetic field gradient by generating a series of spin echoes making the interpulse delay τ between $\pi/2$ and π pulses as short as possible.

Another limit in working with permanent magnets is represented by the temperature sensitivity. The NMR MOUSE is not temperature stabilized due to the high gradient of the sensor; a temperature change of the magnet causes a slight shift of the position of the sensitive volume [33]. Consequently, when working at room temperature, the applications are limited as compared to those performed by benchtop instrumentation and are mainly focused on the development of protocols applied in online inspections and for monitoring processes such as ripening, growth rate of fruits, drying process, and so on. Since T_2 tightly depends on temperature, in case of applications in an outdoor environment characterized by a temperature close to that of room temperature, a system to control the temperature during the measurements is strongly recommended to guarantee a good reproducibility. Anferova et al. [34] described two different types of mobile temperature control units operating with the NMR-MOUSE. They reported that in the case of elastomers, by the temperature stabilization the relative error of T_2 decreased by a factor of four on the short time scale. Without temperature stabilization, it may reach 30% in the long time range because of temperature changes in the laboratory.

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Application of single-sided NMR sensors to food matrices

Interesting applications of portable single-sided NMR sensors to food matrices have been reported in literature [24, 35]. Despite the inhomogeneous field generated by these open geometry sensors, their potentiality for food analysis and control has been explored. An overview of food examined by unilateral devices is reported in Table 1. The advantage of this methodology is the possibility to analyze foods just placing the sensor on the food surface without needing to cut the sample into pieces suitable to fit into an NMR tube.

The determination of solid fat content (SFC) in food based on pulsed low-resolution NMR is an internationally accepted procedure [1]. Basically, the difference in transverse relaxation properties of solid and liquid fats was exploited to determine the solid and liquid contents. Although this technique is widely used even in industrial processes it cannot be applied on line.

Guthausen et al. investigated the applicability of a single-sided NMR sensor to measure the fat content in packaged food products [36, 37]. At this aim, two methods [35] were applied. One is based on differences in relaxation times which depend on molecular mobility and, consequently on the molecular structure (relaxation weighted method), whereas the other one exploits the fact that the diffusion coefficients of water and fat differ by more than an order of magnitude (diffusion-weighted method). A pulse sequence was purposely developed for measuring fat and water content in packaged coffee creams. The packing material does not influence significantly the measure because it is relatively thin and the polymer material exhibits a short $T_{2\text{eff}}$ relaxation t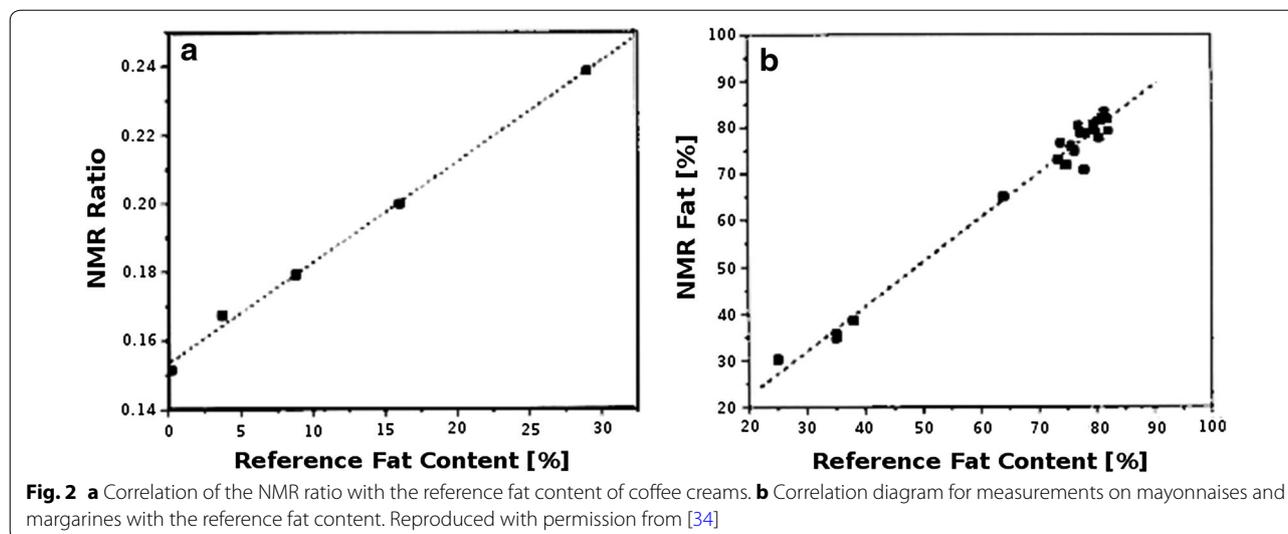ime. The measurement time was about 1 min using the surface resonance frequency, whereas measurements at 3 mm depth resulted in considerable longer acquisition times (about 5 min). The ratio of the final echoes and the first few echoes was the relevant NMR parameter, named NMR ratio. The NMR ratio exhibits a linear dependence with fat content (linear regression with a correlation coefficient of 0.996) thus indicating that a reasonable determination of the fat content is possible, see Fig. 2a.

The relaxation method was used for calibrating the fat content in packaged mayonnaises and margarines. In fact, the relaxation time differences of fat and water protons may be exploited to generate a contrast by allowing a more accurate content determination. Again, a linear correlation was found between the fat percentage measured by NMR and the reference fat content, see Fig. 2b. In this case, data were analyzed by a chemometric approach obtaining a correlation coefficient of 0.991. Such a linear correlation confirms the reliability of single-sided NMR for fat measurements even in packaged food. The chemometric approach was applied to the NMR signal which can be analyzed using supervised or unsupervised pattern recognition methods [38, 39]. These methods may be applied in food analysis for both quantitative and qualitative assessments. The knowledge of reference values allows for the calibration of the NMR response.

In another paper, Martini et al. [40] compared SFC determination obtained using conventional offline NMR instrument with determination obtained by single-sided NMR sensor. Authors explored the use of single-sided NMR to measure variation of SFC online during the crystallization of a fat product. Interesterified hydrogenated palm oil was added to canola oil in different proportions to obtain blends with different SFC values. Two different experiments were carried out to study whether the

Table 1 Reviews of portable NMR technologies and their applications in food science

Reference	Food	Focus	Year
Guthausen et al. [36]	Margarine; mayonnaise	Measurements of fat content	2004
Guthausen et al. [37]	Coffee cream	Water moisture and fat analysis in packaged products	2006
Martini et al. [40]	Vegetable oils	Solid fat content determination	2005
Pedersen et al. [41]	Vegetable oils	Measurements of fat content	2003
Haiduc et al. [42]	Fat emulsions	Microstructural quality of packaged food emulsion	2007
Stork et al. [44]	Bottled beverages	Determination of dissolved oxygen in unopened table waters	2001
Xu et al. [46]	Adulterated virgin olive oil	Detection of the adulteration of virgin olive oil in sealed bottles	2014
Pinter et al. [48]	Tomato paste	Monitoring of spoilage in tomato paste processing industry	2014
Veliyulin et al. [43]	Salmon	Fat content in live fish	2005
Veliyulin et al. [28]	Dairy products	Measurements of fat content in packaged dairy products	2008
Capitani et al. [49]	Kiwifruit	Water status as a function of season	2010
Capitani et al. [50]	Kiwifruit	Monitoring of development and ripening	2013
Capitani et al. [51]	Blueberry	Monitoring of shelf life	2014
Adiletta et al. [52]	Pear	Monitoring of drying process	2015

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Fig. 2 a Correlation of the NMR ratio with the reference fat content of coffee creams. **b** Correlation diagram for measurements on mayonnaises and margarines with the reference fat content. Reproduced with permission from [34]
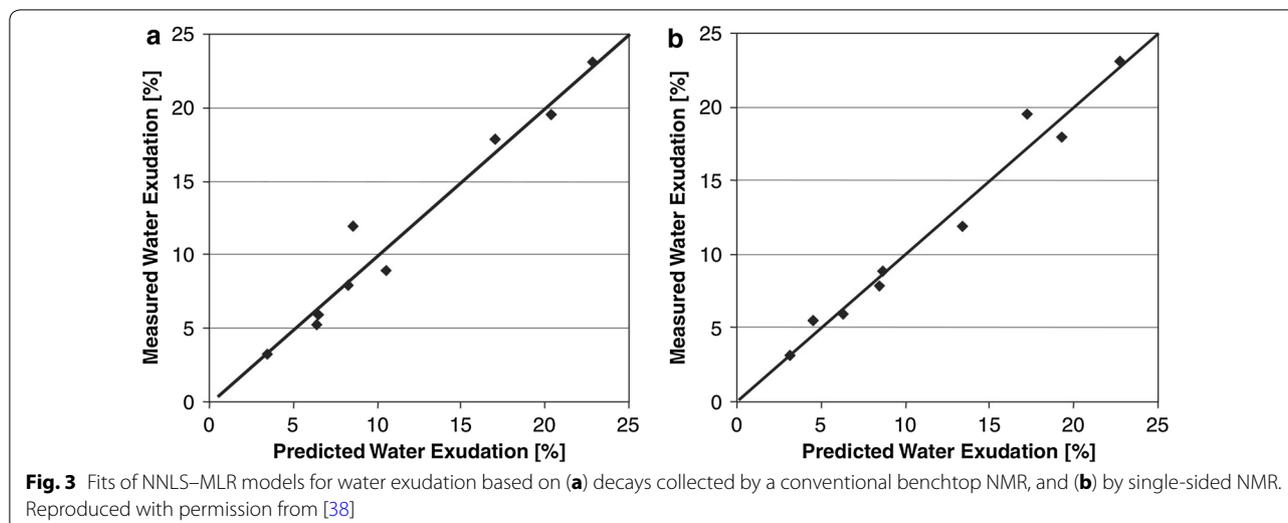
motion during the crystallization affected the measurements. In one experiment, agitation was stopped during the measurement and then restarted to let the crystallization continue until the next measurement. In the other experiments, measurements were carried out under agitation. To eliminate the temperature effect on measurements carried out by single-sided sensor, a proper correction was applied to the collected data. In the former case, the corrected data were close to those collected by a conventional offline NMR instrument particularly at intermediate SFC values, whereas in the latter case data were found to be significantly different from those determined by the off-line instrument.

The performance of conventional benchtop NMR and single-sided NMR applied to the study of sunflower oil-in-water emulsions was investigated by Pedersen et al. [41]. With conventional NMR, the decay rate of pure water obtained after applying a CPMG sequence is much longer than that of oil, which means that the relaxation behavior of the two components is very different. With single-sided NMR, the presence of a strong magnetic field gradient heavily modifies the decay of magnetization; in fact, the decay rate of water is much faster than that of oil because water is much more affected by diffusion than oil. Nevertheless, this effect makes it possible to unequivocally distinguish the signal of water from oil. The trend in relaxation behavior with increasing oil content measured by single-sided NMR was found to be the reverse of that obtained by conventional benchtop NMR. The reverse of the trend in the decay rates with decreasing the oil content is also foreseeable as a result of the strong magnetic field gradient which affects the apparent transverse relaxation time of water due to its rapid diffusion rate. Authors demonstrated that NMR decays

obtained by both conventional benchtop NMR and single-sided NMR can be readily deconvoluted in two components in the case of oil-in-water emulsions with oil content ranging from 10 to 67%.

Hiaduc et al. [42] reported a feasibility study on the use of single-sided NMR for the non-invasive 'through-package' assessment of the microstructural quality of food material. Authors investigated model systems consisting of oil-in-water emulsion gels stabilized by proteins. These systems form complex structures made of fat droplets and a protein aggregate network where water is dispersed in pores with different size. An important quality parameter of such systems is the water exudation (WE). In a classical approach, WE is determined by measuring the amount of water lost from the system when subject to gravitational forces. Multivariate calibration techniques were applied to establish a relation between signals obtained by single-sided NMR and WE. Specifically, to obtain a calibration model allowing for a physical interpretation, an approach based on multilinear regression (MLR) was applied to decays collected with a benchtop instrument and with a single-sided sensor as well. Decays were transformed from the continuous domain to the discrete domain of $T_{2\text{eff}}$ distributions and amplitudes using the non-negative least squares (NNLS) algorithm. The decays were averaged and the obtained data fitted without any initial guess on the number of components or $T_{2\text{eff}}$ values. To summarize, the MLR model was built using the NNLS amplitudes as responses, and the functional parameters as predictors. The goodness of fits of NNLS_MLR model based on conventional benchtop NMR decays (a) and decays measured with single-sided NMR (b) is observable in Fig. 3. The quality of MLR model applied to both set of data is comparable, thus indicating that single-sided NMR
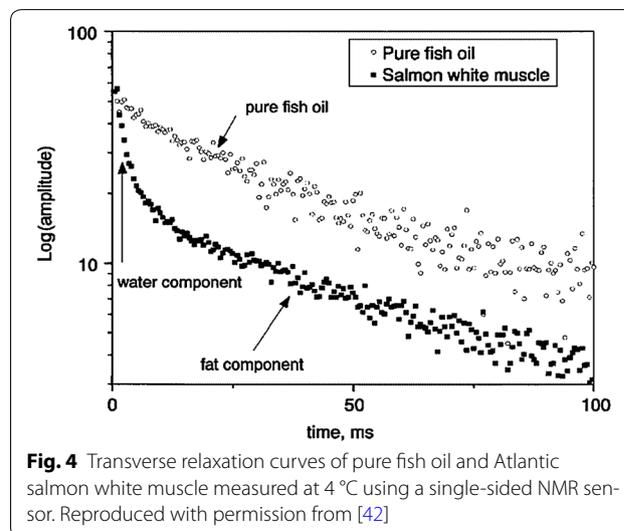
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Fig. 3 Fits of NNLS–MLR models for water exudation based on (**a**) decays collected by a conventional benchtop NMR, and (**b**) by single-sided NMR. Reproduced with permission from [38]

may also allow for the assessment of WE in a through package mode. It must be taken into account that due to slow T_1-relaxation, the delay between the individual averages was set to 4 s, which yields an experimental time of 8 min for one MOUSE measurement.

A new procedure for rapid and non-destructive determination of the fat content in dairy products has been proposed by Veliyulin et al. [28]. In this work, a novel design of unilateral NMR instrument with larger measurement volume and higher signal to noise ratio [22, 27] has allowed to reduce the time measurement of the fat content in packaged dairy products about up to few seconds. Two methods were tested: a diffusion-edited CPMG technique and a strongly T_1-weighted conventional CPMG method requiring total measurement times of about 39 and 7 s, respectively. The latter technique has a potential for being implemented for industrial monitoring of the fat content in both packaged products and larger batches of dairy products. Linear relationship between the transverse relaxation time of the fat component and the inverse fat content was observed.

The same unilateral NMR device was tested by Veliyulin et al. [43] to set up rapid non-destructive measurement of the fat content in live or slaughtered Atlantic salmon. The total analysis time per fish was about 20 s. The distribution of transverse relaxation times when measured with a conventional benchtop NMR instrument shows three peaks. The shortest component is usually ascribed to water closely associated with macromolecules, the intermediate one to intracellular water or water within the myofibrillar structure, whereas the longest one accounts for both lipids and water. The overlapping of the fat signal with that of extra-myofibrillar water (both contributing to the longest component) makes very difficult to differentiate fat and water content based on the quantitative $T_{2\text{eff}}$

measurements. When measurements are performed by a single-sided sensor, the effective transverse relaxation time is affected by strong field gradient generated by the sensor which influences the self-diffusion coefficient. Because the average self-diffusion coefficient of water in fish muscle is considerably faster than that of fat, this difference may be exploited to make accurate quantification of the fat component from the transverse relaxation response. Figure 4 compares the transverse relaxation curves of pure fish oil and Atlantic salmon white muscle obtained applying a CPMG sequence optimized to ensure the best separation between water and fat components. Prior to perform measurements, the instrument was calibrated using samples with known fat content (mixtures of fish oil and agarose) and characterized by NMR relaxation properties similar to those of fish fat. A significant correlation was

Fig. 4 Transverse relaxation curves of pure fish oil and Atlantic salmon white muscle measured at 4 °C using a single-sided NMR sensor. Reproduced with permission from [42]

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found between the fat content measured by single-sided NMR and that measured by chemical analysis. Furthermore, the mobile single-sided sensor was used to map the fat distribution over the whole fish surface. The NMR signal measured on about 50 regions was processed to obtain a post-mortem fat distribution image in the white muscle, red muscle and belly flap of Atlantic salmon.
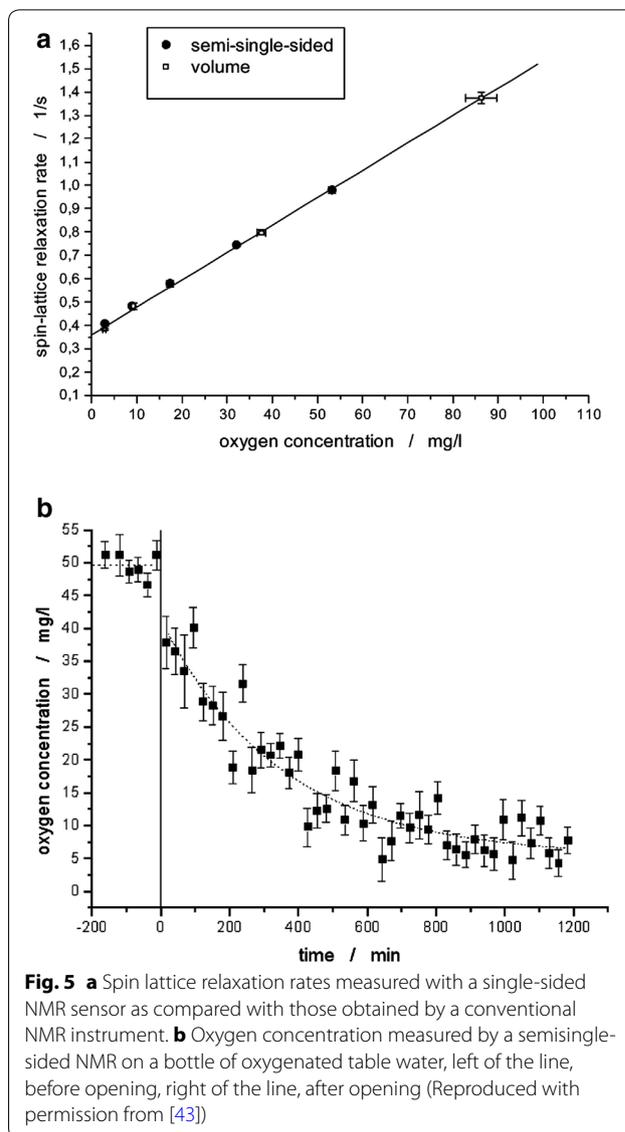
It is well known that the application of conventional single-sided NMR to highly mobile, watery phases in foods and beverages is hampered by the strong magnetic field. In their paper, Stork et al. used both a single-sided NMR sensor with a reduced magnetic field gradient and another ("semisingle-sided") sensor design with an open sample bay for determining the oxygen content in unopened bottles with superoxygenated table water, and compared the obtained results with those from conventional NMR [44]. In the semisingle-sided sensor, the distance between the two arrays of magnet bricks was chosen in a way that 1.5-L bottles fit in the gap of the magnet system. The latter design allows much better sensitivity without sacrificing the necessary open access needed for measurements on entire food packages such as bottle. For the NMR determination of dissolved oxygen in table waters, the longitudinal relaxation time of the water was measured. It was related to the oxygen concentration C_{Ox} according to the following relationship:

$$\frac{1}{T_1} = \frac{1}{T_{1o}} + r_{1,ox}C_{ox} \tag{2}$$

where T_{1o} denoting the relaxation time of the oxygen-free water.

As the relaxivity $r_{1,ox}$ of oxygen in water is field dependent [45] and no sufficiently precise relaxation data at a proton resonance frequencies of 5–6 MHz are available in the literature, authors performed calibration measurements against samples with a known (supersaturated) oxygen concentration.

Figure 5a shows the comparison between the spin–lattice relaxation rate measured with a single-sided NMR sensor and that measured by conventional NMR. The two sets of data were found to be in a very good agreement. The semisingle-sided sensor was also used for determining the oxygen concentration in a commercial bottle before and after opening the bottle by measuring the water relaxation time; data are reported in Fig. 5b. The sensor was capable of monitoring the oxygen concentration that was constant before opening, and progressively decreased after opening the bottle, thus indicating the possible use of this sensor for online application after a suitable calibration procedure. To achieve a better signal/noise ratio, the measuring times for each relaxation time in these curves were several hours per data point in the single-sided setup and about 40 min in

Fig. 5 a Spin lattice relaxation rates measured with a single-sided NMR sensor as compared with those obtained by a conventional NMR instrument. **b** Oxygen concentration measured by a semisingle-sided NMR on a bottle of oxygenated table water, left of the line, before opening, right of the line, after opening (Reproduced with permission from [43])

the semisingle-sided setup. Therefore, single-sided setup imposes a measuring time about four times longer than that for semisingle-sided.

Another paper reports a method based on the use of the profile NMR MOUSE [29] to detect adulteration of virgin olive oil through sealed bottles [46]. With this method, the transverse relaxation time and the self-diffusion coefficient of virgin olive oils adulterated with different percentages of sunflower oil and red palm oil were investigated. Authors developed a two-dimensional Laplace inversion according to the algorithm by Venkataramanan [47] to reconstruct the two-dimensional probability density distribution of the transverse relaxation time and self-diffusion coefficient. The two-dimensional D–T_2 distributions were projected to the D axis and T_2 axis, as shown in Fig. 6a, b.

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In Fig. 6a, from right to left, there are four peaks representing the pure red palm oil, 10% red palm and 90% olive mixed oil, 20% red palm and 80% olive mixed oil and the pure extra virgin olive oil. The self-diffusion coefficient increases as the percentage of red palm oil increases. While in Fig. 6b, the T_2 decreases as the percentage of red palm oil increases, giving 67.5, 64.1, 60.8 and 54.9 ms, respectively. Comparing with the pure extra virgin olive oil, the red palm mixed oil has a larger self-diffusion coefficient but smaller T_2. These data indicate that the adulteration of extra virgin olive oils with sunflower oil may be readily detected from the self-diffusion coefficient behavior, whereas the adulteration with red palm oil can be detected from both diffusion and transverse relaxation behavior.

The tomato paste processing industry is very interested in developing methods to detect tomato spoilage in 1000-L non-ferrous, metal-lined containers without violating the seal. An early spoilage detection would eliminate shipping costs and disposal costs when spoiled tomato paste arrives at destination. Pinter et al. [48] explored the relaxation

properties of sterile and unsterile tomato paste samples as a function of time at both low and room temperature. As long as the storage temperature was maintained below 5 °C, T_1 and T_2 values remain constant over the course of at least 1 month, suggesting that the low temperature significantly slows the bacteria-mediated tomato paste spoilage. At room temperature where tomato processing, packaging and storage occur, the relaxation times for sterile and unsterile samples were different. Although the room temperature T_2 value was constant as a function of time for these samples, the corresponding T_1 value increased exponentially in the first days and tended to a limit value, indicated as T_1^∞, for long time of observations. Specifically, the steady-state limit value of spin lattice relaxation time T_1^∞ obtained by the regression of T_1 values measured as a function of time was the parameter chosen by authors to differentiate between spoiled and unspoiled tomato paste. This result prompted them to extend the study to 1000-L non-ferrous, metal-lined totes using single-sided NMR. To perform measurements directly on the metal container,
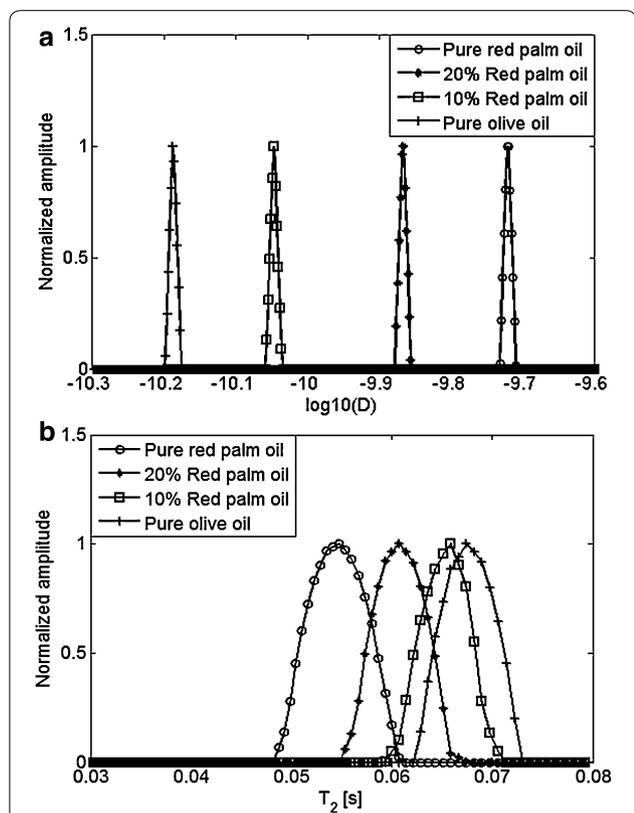

Fig. 6 *D-T_2* distribution maps of oils. From the top to the bottom (**a**) pure extra virgin olive oil, extra virgin olive oil adulterated with 10 and 20% of sunflower oil, pure sunflower. **b** Pure red palm oil, extra virgin olive oil adulterated with 10 and 20% of red palm oil, and pure extra virgin olive oil (Reproduced with permission from [45])
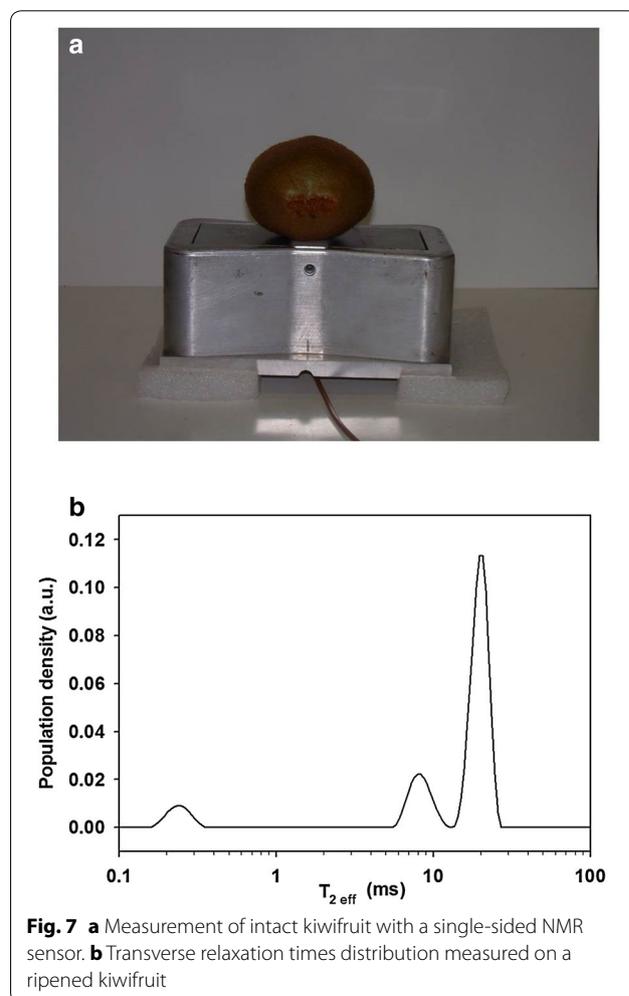
Fig. 7 a Measurement of intact kiwifruit with a single-sided NMR sensor. **b** Transverse relaxation times distribution measured on a ripened kiwifruit

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its effect on the circuit tuning and impedance matching properties was properly compensated. A modified saturation recovery sequence was used to measure the longitudinal relaxation with single-sided NMR. The NMR signal and T_1 values obtained from the large format container with the single-sided sensor suggested that this device can be used to study tomato paste spoilage in factory process environments.

Capitani et al. monitored the water status of kiwifruits as a function of season using a single-sided NMR sensor [49, 50]. Using this sensor, it was possible to measure the entire fruit at a depth of about 0.5 cm from the peel surface without cutting it, see Fig. 7a. The $T_{2\mathrm{eff}}$ distribution of a mature kiwifruit measured by single-sided NMR shows three peaks, see Fig. 7b. According to the literature, the longest $T_{2\mathrm{eff}}$ component was assigned to
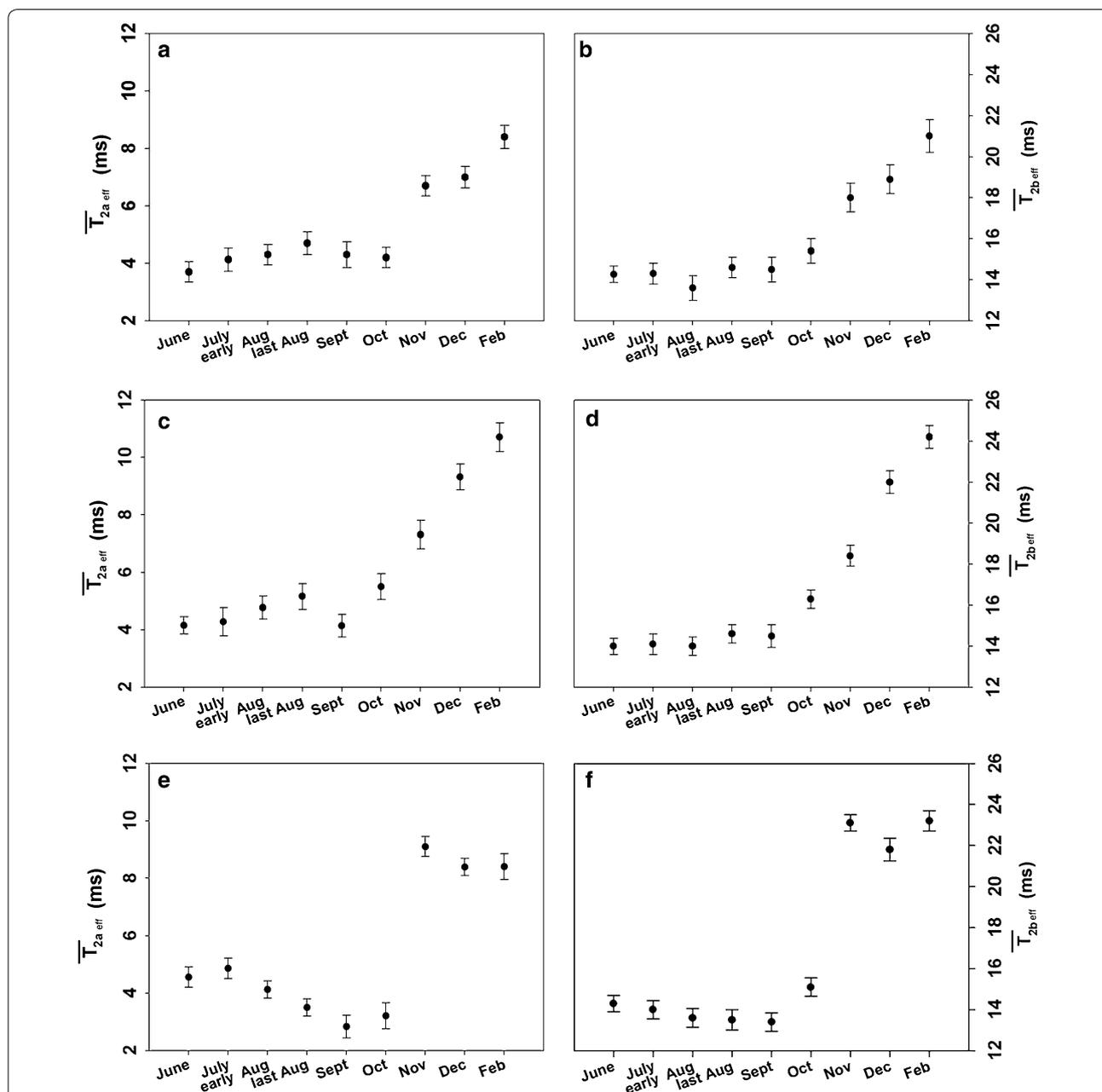
Fig. 8 Average T_2 values for the intermediate ($\bar{T}_{2a}$) and the longest ($\bar{T}_{2b}$) components measured on Hayward (**a**, **b**), CI.GI (**c**, **d**), and Zespri (**e**, **f**) kiwifruits as a function of their developmental stage (Reproduced with permission from [49])

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protons in vacuole, the intermediate one to proton in cytoplasm and extra-cellular space, and the shortest one to proton in cell walls. It must be noted that the presence of the strong magnetic field gradient of the single-sided sensor heavily shortens $T_{2\text{eff}}$ values. In fact in the case of ripened kiwifruit measured in homogeneous fields, literature data report average $T_{2\text{eff}}$ values of 800–1000 ms for the longest component, 200–400 ms for the intermediate component, and 20–80 ms for the shortest one. With single-sided NMR, the longest component is as short as 20 ms. Nevertheless, single-sided NMR was suitable to monitor the growth of kiwifruit. Because the shortest component was very poorly affected by the season, only the intermediate and longest components were taken into account. Figure 8 reports the average values of the intermediate component ($\bar{T}_{2a\text{eff}}$) and the longest component ($\bar{T}_{2b\text{eff}}$) measured on nine kiwifruits of three cultivar,

namely Hayward (a, b), CI.GI (c, d), and Zespri (e, f) at different stages of development. In all cultivars, $T_{2\text{eff}}$ values were found to be rather constant until October, thereafter they increased. The tendency toward longer $T_{2\text{eff}}$ relaxation times later in the season is consistent with a change in the fruit texture occurring during fruit development. However, whereas in Hayward and CI.GI a gradual lengthening of $T_{2\text{eff}}$ was observed, in Zespri, a net and sharp lengthening of both components occurred between October and November, indicating the earlier maturation of Zespri.

The ripening of kiwifruits was also monitored in field on fruits attached to the plant during three campaigns of measurement carried out in October, November and December, see Fig. 9. Figure 10 shows the transverse relaxation decays measured in field. A preliminary optimization of conditions was necessary to achieve a good signal to noise ratio and minimize the measuring times (within 8 min). In all cultivars, a lengthening of the decays with the season was observed; however, the process was complete already in November for Zespri as shown by the perfect overlapping of decays measured in November and December. In agreement with data collected in laboratory on intact kiwifruits, these data confirmed the earlier maturation of Zespri.
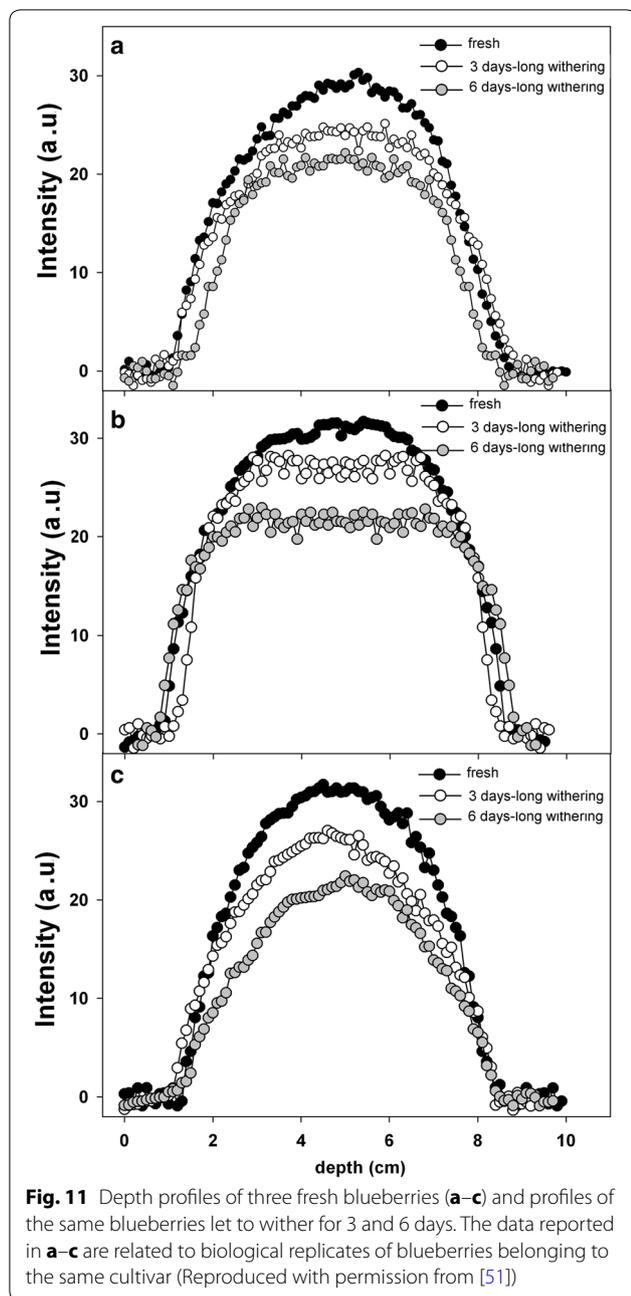
The profile NMR MOUSE was used to get preliminary results on three fresh intact blueberries (belonging to the same cultivar) and evaluate the effects of withering outside the fridge for 3 and 6 days [51], see Fig. 11. With this sensor NMR depth profiles were collected, these profiles encode the amplitude of the ^{1}H NMR signal as a function of the depth scanned. The amplitude of profiles measured on withered blueberries was found to be

Fig. 9 NMR measurements in field on entire kiwifruits attached to the plant (Reproduced with permission from [49])
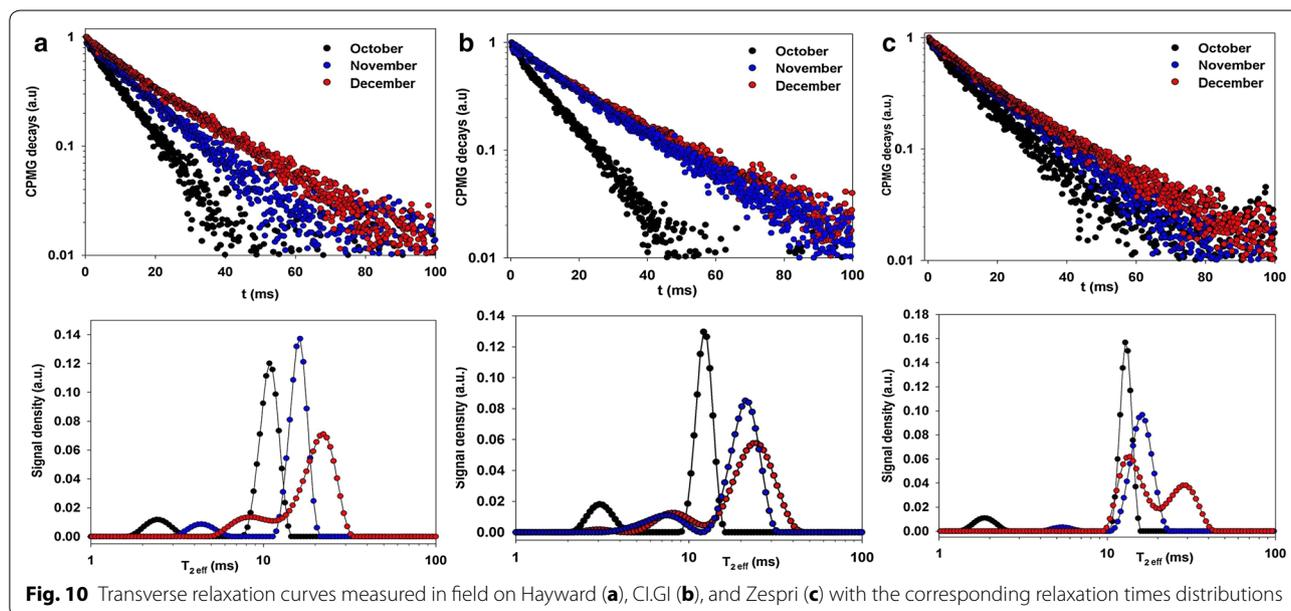
Fig. 10 Transverse relaxation curves measured in field on Hayward (**a**), CI.GI (**b**), and Zespri (**c**) with the corresponding relaxation times distributions
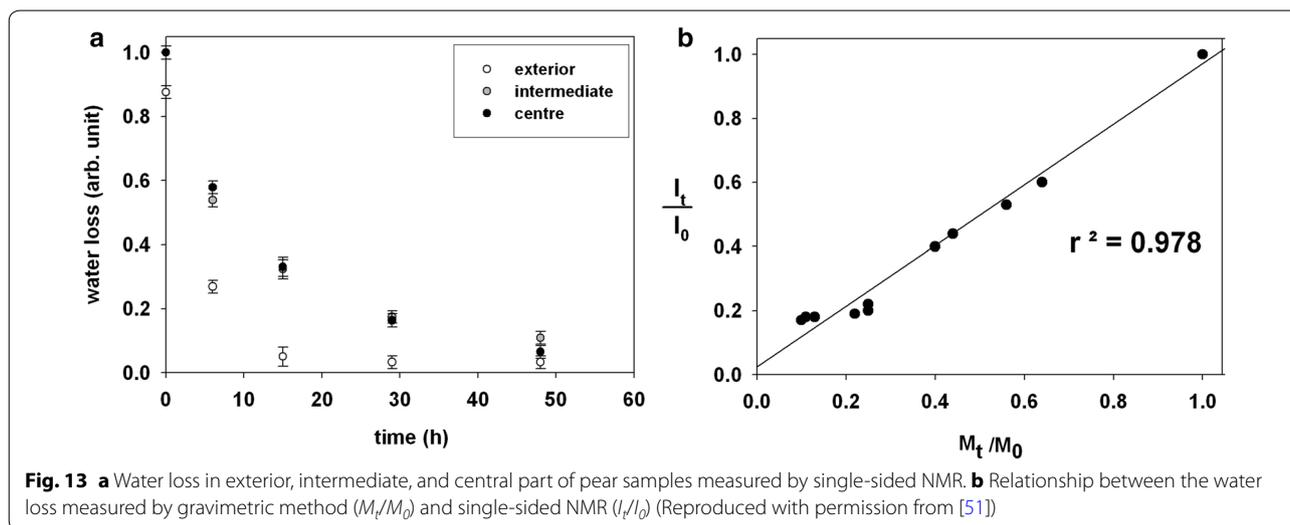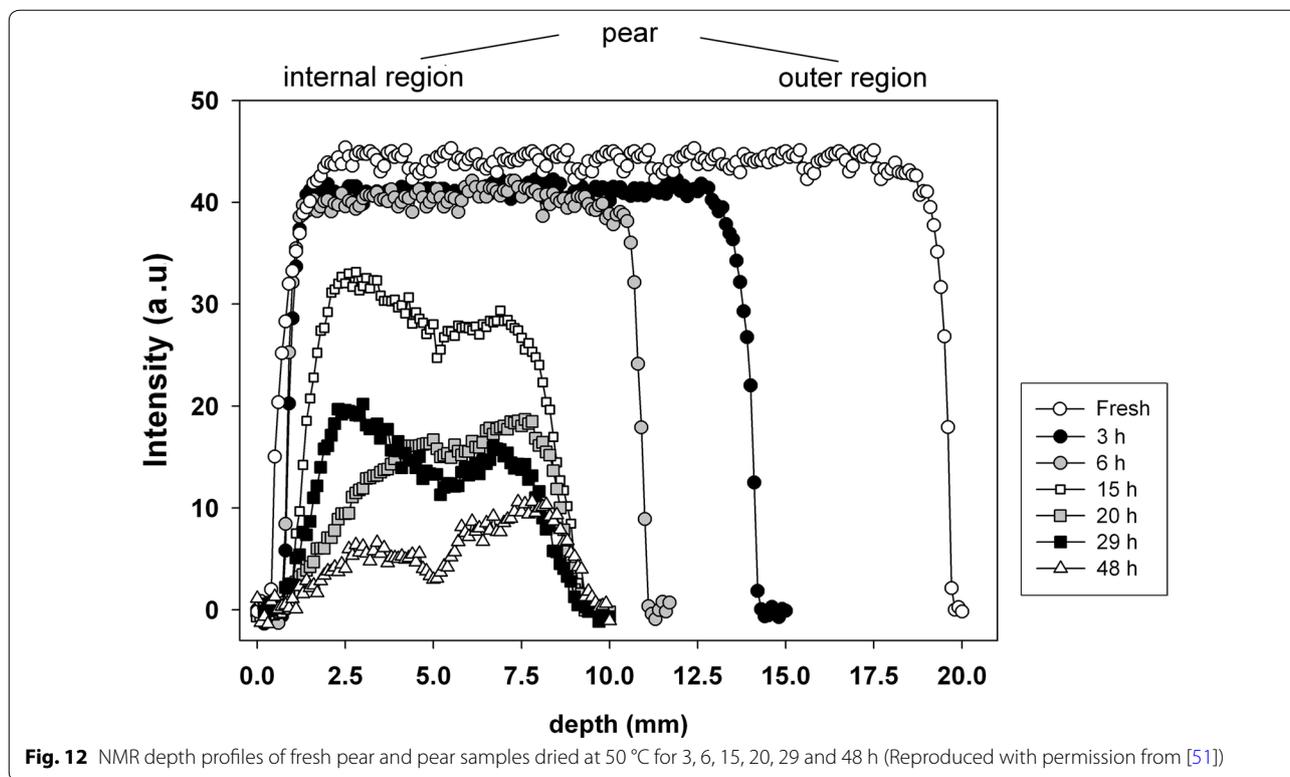
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Fig. 11 Depth profiles of three fresh blueberries (**a**–**c**) and profiles of the same blueberries let to wither for 3 and 6 days. The data reported in **a**–**c** are related to biological replicates of blueberries belonging to the same cultivar (Reproduced with permission from [51])

lower than that measured on fresh blueberries, indicating a loss of water that was quantified by integrating the profiles. After 3 days of withering, a loss of water of 13% (a), 11% (b), and 16% (c) was measured, whereas after 6 days the loss of water was found to be 30% (a), 20% (b), and 34% (c). Therefore, the integral of the profile is a suitable index of water loss. The same index may be used to monitor changes in foodstuff texture due to maturation, ripening, water and osmotic stress, for monitoring the effect of different types of processing on food matrices, and the effect of storage.

Adiletta et al. used the profile NMR MOUSE to investigate the drying process on pears [52]. Drying is an important process for conservation and marketing of fruits due to their high water activity which makes them perishable. Therefore, the knowledge and optimization of drying process are very important to minimize thermal damage and quality loss. Information on drying kinetics was obtained by measuring the intensity of ^1H NMR signal as a function of the thickness of the sample. Figure 12 shows the comparison among profiles of fresh pear and pears dried for 3, 6, 15, 20, 29, and 48 h. The amplitude of profiles measured in dried samples progressively lowered and also the thickness of the profiles progressively decreased, thus indicating a loss of water with increasing of drying time which was accompanied by shrinkage. An evaluation of the loss of water in the outer, intermediate and central regions of pears samples was obtained simply by integrating the profiles in three corresponding regions (without cutting the samples); the results obtained are reported in Fig. 13a. As expected, the water content of the outer region decreases more quickly than that of the intermediate and central ones. Such differences become less pronounced at relatively long drying times. Figure 13b shows the good agreement between values of moisture content (M_t/M_0), obtained by gravimetric method and values of hydrogen content (I_t/I_0) obtained by integrating NMR depth profiles, with a regression coefficient of 0.978.

Concluding remarks

Research applications described above illustrate that unilateral NMR sensors present an attractive option for non-invasive assessment of compositional and microstructure of food materials. The first applications of the unilateral NMR devices in foods were aimed at measuring the water/oil contents in food emulsions and to determine solid fat content. Successively their use has been extended to other foodstuffs as well as at packaged foods. Several applications focused on assessment of food quality and monitoring processes such as ripening, growth rate of fruits, drying process, and so on. The fact that single-sided NMR devices allow easy sample access and portability makes them attractive for quality and process control in the food industry. A main handicap of these devices is magnet field inhomogeneity, which significantly compromises sensitivity and robustness under practical circumstances. The use of echo techniques is typically necessary since FIDs obtained by such devices are also compromised by very short $T_{2\text{eff}}$ values. Other unilateral magnets have been developed with more homogeneous magnetic field, larger sensitive volume and higher sensitivity. These sensors allowed to shorten

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Fig. 12 NMR depth profiles of fresh pear and pear samples dried at 50 °C for 3, 6, 15, 20, 29 and 48 h (Reproduced with permission from [51])

Fig. 13 a Water loss in exterior, intermediate, and central part of pear samples measured by single-sided NMR. **b** Relationship between the water loss measured by gravimetric method (M_t/M_0) and single-sided NMR (I_t/I_0) (Reproduced with permission from [51])

measurement times thus paving the way to their future employment in a quality control context.

Nevertheless, use of unilateral NMR devices is still limited. Further studies are needed to expand their utilization to other food matrices and develop protocols to be applied in online inspections for monitoring quality and food processes.

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