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Magnetic Resonance in Food Science:
Defining Food by Magnetic Resonance

Quantitative NMR

60 MHz ^{1}H NMR Spectroscopy of Triglyceride Mixtures A. Gerdova, M. Defernez, W. Jakes, E. Limer, C. McCallum, K. Nott, T. Parker, N. Rigby, A. Sagidullin, A. D. Watson, D. Williamson, E. K. Kemsley (2015) *in* Magnetic Resonance in Food Science: Defining Food by Magnetic Resonance (eds: F. Capozzi, L. Laghi, P.S. Belton) Royal Society of Chemistry pp17-30

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1 INTRODUCTION

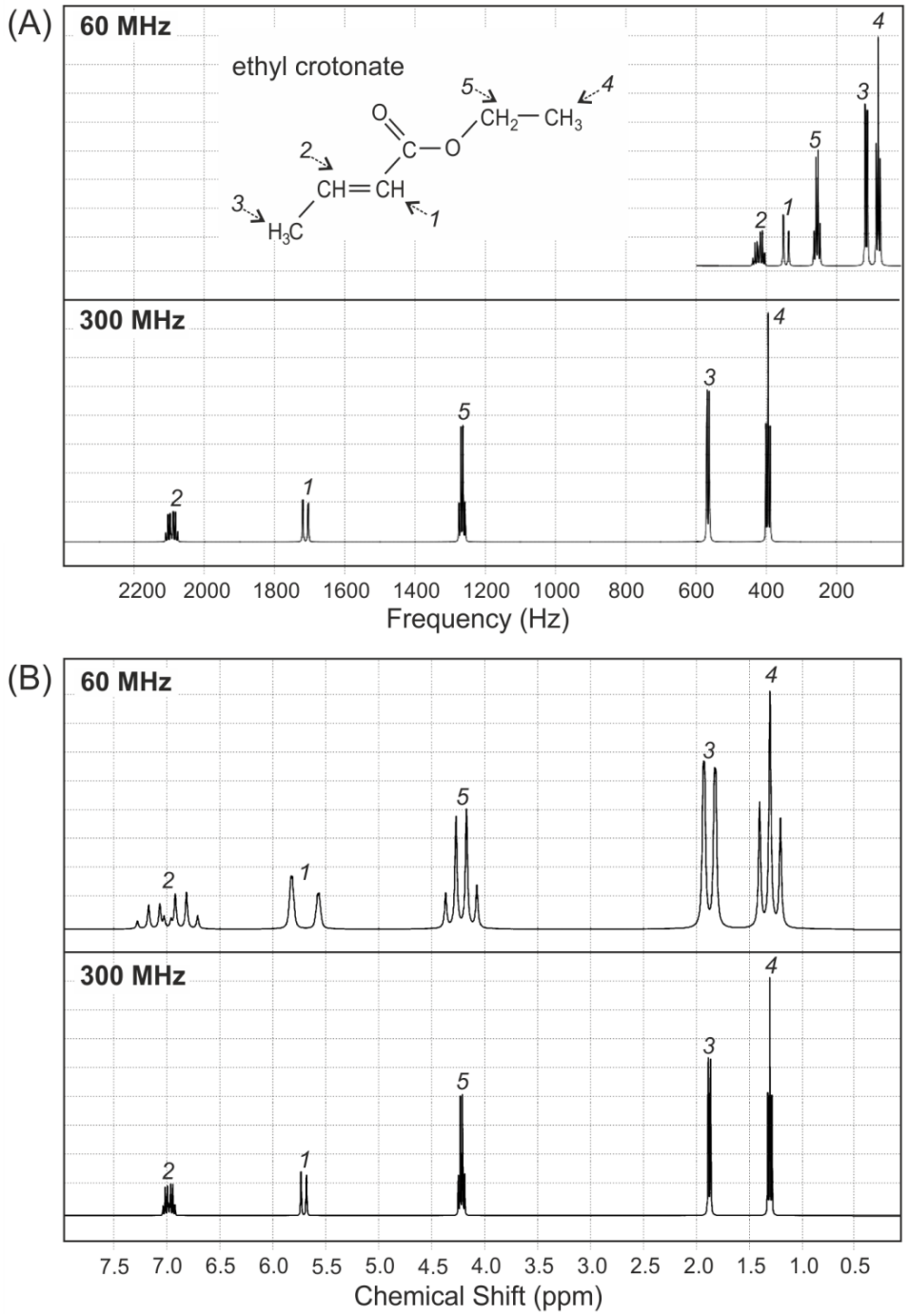
Triglycerides (more properly triacylglycerols, abbreviated to TAGs) are esters of glycerol comprising a glyceride backbone with three fatty acids. Natural chemical diversity is conferred by the fact the three acyl residues need not be the same. Triglycerides are of great economic and nutritional importance: edible oils and fats consist almost entirely of triglycerides.

Food triglycerides have fatty acid chains ranging in length from 4 to 24. These chains may contain 0 (saturated), 1 (mono-unsaturated), 2 or 3 (collectively, poly-unsaturated) carbon-carbon double bonds. The chain length 18 is particularly abundant: for example the average fatty acid composition of olive oil is 75.5% by weight[1] of C18:1 (referring to the chain length of the fatty acid component with a single double bond) and 7.5% by weight C18:2 (two double bonds). The chain length C16 is also relatively common, with olive oil at 11.5%w/w C16:0.

Despite the fact that certain chain lengths are dominant, different edible oils and fats have markedly different triglyceride compositions. Any technique capable of analysing triglyceride mixtures is therefore able to establish key compositional properties of pure oils and fats. In addition, such techniques may potentially be able to detect the addition of one oil to another, as occurs when a high-value oil such as olive oil is fraudulently adulterated with a cheaper substitute.

There are numerous ways of analysing the TAG content of oils and fats, in particular HPLC[2] and GC[3]. However the presence of many hydrogens in the different environments resulting from various double bond configurations implies a role for proton NMR. Indeed high-field ^{1}H NMR has been used extensively to study TAGs, edible oils,[4-7] and mixtures of edible oils.[8]

Here, we outline recent results on triglyceride mixtures obtained using a new, *low-field* ^{1}H NMR spectrometer called Pulsar. Developed at Oxford Instruments (Oxford Instruments, Tubney Woods, Oxford, UK), the Pulsar is based on permanent magnets rather than the superconducting magnets standard in modern high-field instruments. It has a field strength of 1.4 T, corresponding to a ^{1}H Larmor frequency of approximately 60 MHz, is cryogen-free and has a bench-top footprint. Compared to early NMR instruments of similar field strengths the Pulsar gains from improved hardware, electronics, and numerically-intensive chemometrics-based software.



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Figure 1 *Simulated 1H NMR data for ethyl crotonate for 60 and 300 MHz. Expressed in Hz, panel A, the scale for 60 MHz data is relatively compressed. Expressed in ppm, panel B, the more usual representation of NMR data, the same simulation shows broader peaks for 60 than 300 MHz over a common ppm axis*

Operating at such a low-field has implications for the resulting spectra. Figure 1 shows simulated spectra for ethyl crotonate at 60 and 300 MHz. In the upper panel (Figure 1A) the spectra are displayed on a frequency (Hz) scale. This emphasizes how the 60 MHz spectrum appears compressed compared to the 300 MHz spectrum; linewidths here are the same. For real rather than simulated spectra, the Pulsar line width (FWHM) is better than 1 Hz, comparable with ~0.4 to 0.8 Hz for high-field spectrometers.

To aid comparison between data obtained from spectrometers operating at different field strengths it is usual practice to display spectra on the field-independent chemical shift scale,

expressed as parts per million (ppm). Displayed on such a scale (Figure 1B), the 60 MHz peaks appear broadened compared to high-field spectra. Typically, the peaks in low-field spectra are more overlapped, which means that resolving individual resonances can be more challenging. Inter-peak spacings may also change in ways that might seem surprising at first sight. Comparisons with existing libraries of high-field data, useful for identifying peaks,[9] must therefore be done with care.

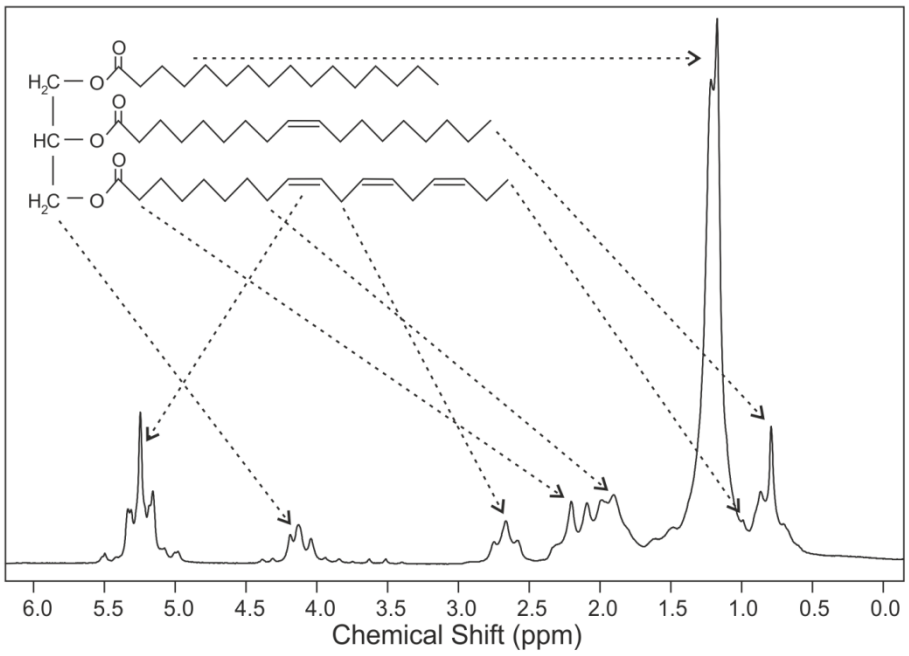


Figure 2 *60 MHz ^{1}H NMR spectrum of linola, a type of linseed oil having low alpha-linolenic content. The inset shows an illustrative triglyceride having 3 distinct acyl residues, C18:0 (saturated), C18:1 (mono-unsaturated) and C18:3 (tri-unsaturated). Arrows link spectral and associated structural features. This Pulsar spectrum has been subject to reference deconvolution*

The 60 MHz ^{1}H NMR spectrum (Figure 2) of an exemplar seed oil, edible linseed oil (linola), shows a number of characteristic peaks. The glyceride backbone contributes a peak at ~4.1 ppm due to hydrogens attached to the two end carbons on the backbone. This peak is present for all triglycerides. A double bond –CH=CH– in the acyl chain contributes an 'olefinic' peak at ~5.2 ppm. Note that the central carbon from the glyceride backbone also contributes to this peak. Towards the lower ppm range is the bis-allylic peak at ~2.7 ppm, arising from protons attached to a carbon sandwiched between two double bonds, =CH–CH_2–CH=. This peak is an important flag for poly-unsaturated TAGs. The zone around 2.0 ppm contains contributions from the carboxyl end of the chain, –OCO–CH_2–, and double bond allylic groups –CH_2–CH=. The dominant peak at ~1.3 ppm is from methylene bridges, –CH_2–, remote from carbon double bonds. Finally, the terminal –CH_3 methyl group contributes a peak at ~0.9 ppm. The position of this peak is sensitive to the proximity of a nearby C=C double bond, which to a good approximation in edible oils and fats occurs in linolenic acid (actually, the α-linolenic isomer) which has three double bonds.[10] Therefore, the terminal methyl peak assumes great significance as a marker of triply-unsaturated fatty acid chains.

In ^{1}H NMR, the area of a peak is proportional to the number of contributing protons, offering a direct route to quantitative analysis. This is a distinct advantage over the competing technique of infrared spectroscopy in which quantitation generally requires a calibration step.

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Furthermore, since the glyceride peak appears for every TAG molecule, it provides an in-built normalization. Quantification of triglycerides using peak areas has a long history.[6, 8, 11] Despite the attractions, peak area quantitation faces several challenges. Reliable peak areas can be difficult to extract due to overlapping peaks, baseline distortion and poor phase correction. An alternative is to follow the infrared example and use chemometric methods that analyse entire spectral profiles.[12, 13] These methods are particularly suited to the classification of a dataset into groups, even when to the eye the underlying spectra are quite hard to tell apart. Authentication questions are naturally of this type: 'is a set of supplied edible oils of the same type as an existing set?', for instance. The outcome is then a decision ('authentic' or 'non-authentic') rather than a composition table, which is the more natural outcome of peak area estimation.

In this work we will demonstrate examples of both peak area estimation and chemometric methods applied to 60 MHz ^{1}H NMR data acquired from triglyceride systems. In addition, sample preparation and data acquisition protocols are kept as simple and cheap as possible, simulating high-throughput regimes consistent with the use of low-field NMR in a screening or quality control capacity. We now describe three 'case studies' that reflect this philosophy.

2 METHODS AND RESULTS

2.1 Composition of Edible Oils and Complex Foods

Twenty four edible oils (18 different types, including some mixtures) from local supermarkets were each combined with approximately equal amounts of non-deuterated chloroform to give 50:50 mixtures in standard 5 mm disposable NMR tubes. The chloroform is useful in this context both to reduce sample viscosity, giving reduced line width, and to provide a reference ppm value. Data was acquired on the Pulsar with a sample temperature of 37 °C using 16 scans with an acquisition time of 30 seconds per scan, giving an overall data acquisition time of ~10 min and a trivial sample preparation step.

The resulting spectra were processed using peak area estimation coded in-house in Matlab (The Mathworks, Cambridge, UK). The relationships between the different peaks mean that they must be calculated in sequence, beginning with the terminal methyl group peak linked to tri-unsaturated acyl chains, so-called omega-3, followed by the bis-allylic peak, followed by the olefinic peak. At each stage the estimate depends on the stage before, meaning that errors tend to accumulate and render estimations of saturated content least robust of all.

Figure 3 shows the results of peak area estimation for poly-unsaturated, mono-unsaturated, omega-3 and saturated fatty acid contents. These results are plotted against GC-FID data acquired in the conventional way following a methyl esterification of the test oils, and ~1 hour GC-FID run per oil sample. The highest omega-3 content is found to be in hemp oil, followed by walnut then rapeseed. The highest poly-unsaturated content is, in descending order, hemp, walnut then grapeseed. The highest unsaturated level is rice bran oil. The key point, however, is that the NMR results tally very well with the GC-FID data, validating the low-field NMR method and the peak area data analysis. The apparently greater scatter in the saturated data points is due in part to the chain of calculation mentioned above, but is also an artefact of the different plot scales. Developments are already in progress that will improve the agreement between the two approaches.

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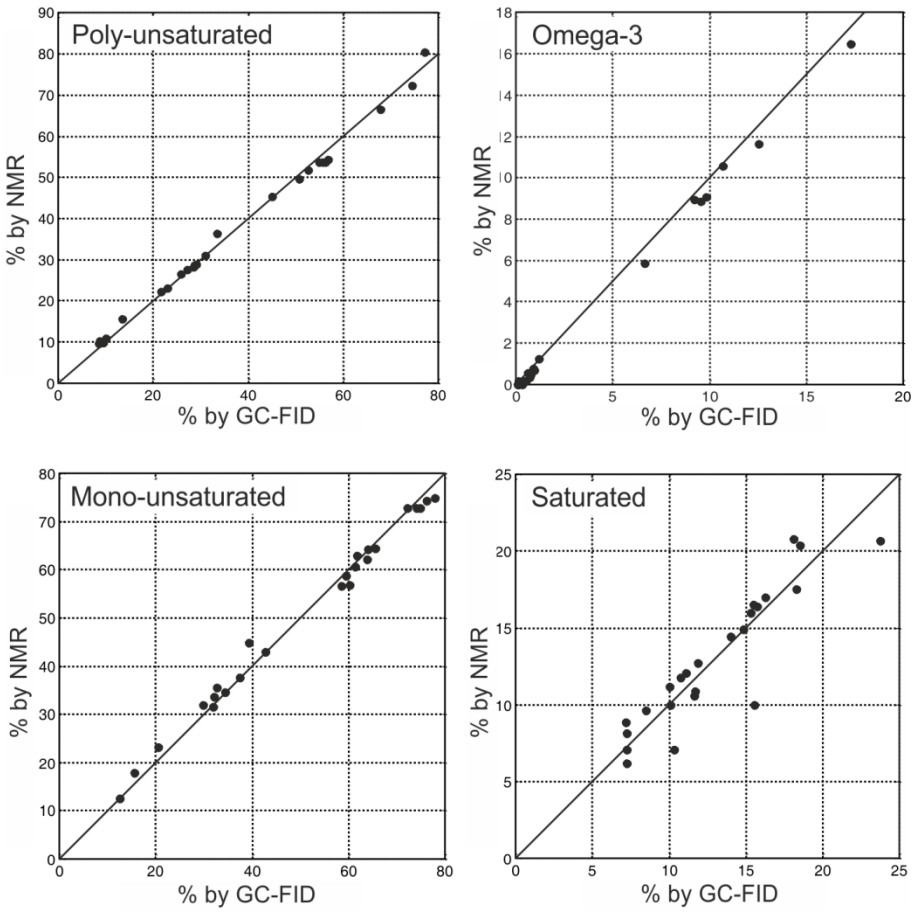


Figure 3 *Comparison of 24 edible oils analysed by GC-FID (horizontal axis) and 60 MHz ^{1}H NMR. The NMR values rely on peak area estimation. Note the different scales*

The 'simple sample preparation' paradigm was pushed to the extreme in an attempt to extend the approach to much more complex foods. Here, 'complex foods' means multi-component food products, rather than simple homogeneous ingredients. For this study, we took a complex food, such as a pork pie, homogenised it in a blender, and mixed the resulting paste with chloroform for a few minutes. The resultant mixture was filtered to remove particulate material and the filtrate analysed by low-field NMR using the same parameters as for the edible oils. Once again the data was processed using peak area measurement.

The results for the saturated fat content of 13 disparate products are shown in Figure 4 plotted against the so-called 'typical' values as stated on the product label. What is striking from these results is the acceptable level of agreement. The choice of foods was uncompromising: apart from pork pies, the analysis included: crisps, which are hard and brittle; salami, which contains macroscopic pieces of fat; and cakes topped with flakes of almond. The TAG extraction protocol was deliberately crude. The results show scatter when compared to label values, but this is likely to reflect sampling effects given the highly heterogeneous nature of the food products. Clearly, the broad level of agreement indicates this to be a valid avenue for further study, and the next step will be to compare label and NMR values with those from GC-FID.

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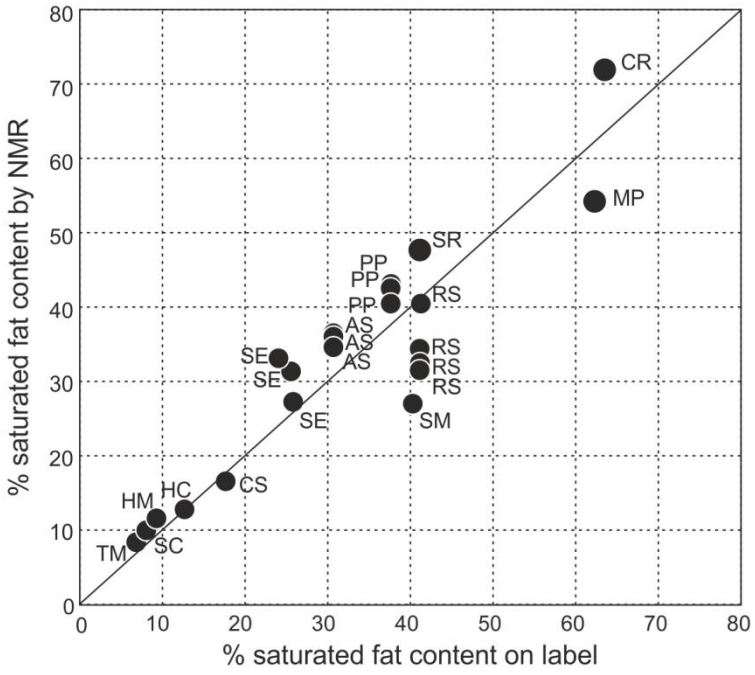


Figure 4 *Saturated fat content as determined by 60 MHz ^{1}H NMR versus the label saturated fat value for a variety of complex foods. RS = raspberry slice (4); CR=croissant; MP=sweet mince pie; SR=sausage roll; PP=pork pie (3); AS=almond slice (4); SE=scotch egg (3); HC=hand-cooked crisps; SC=standard crisps; TM=taramasalata; HM=hummous; SM=salami; CS=chicken samosa. The number in brackets is the number of replicates*

2.2 Authentication of Edible Oils

Another interesting avenue for future exploration is the potential for detecting adulteration of edible oils with lard, an issue of concern to certain faith groups. Lard, derived from pigs, is relatively cheap, making it a candidate adulterant for padding more expensive oils. Lard contains large high levels of unsaturated and mono-unsaturated fatty acids: the average fatty acid composition is 24% 16:0, 14% 18:0, 43% 18:1 and 9% 18:2 (plus other small contributions).[1] Adulteration of commonly used oils such as sunflower (high in 18:2), olive (high in 18:1) and rapeseed (high in 18:1 and 18:3) should be relatively easy to detect.

Figure 5A shows a region of the spectra of lard and sunflower oil. The spectra are normalised to give the same maximum height for the glyceride peak at ~4.2 ppm. The higher levels of poly-unsaturated fatty acid in sunflower oil are presaged by the larger olefinic peak at a chemical shift of ~5.2 ppm and apparent from the larger bis-allylic peak at ~2.7 ppm. We subsequently analysed a set of lard:sunflower oil mixtures by combining them with (deuterated) chloroform and submitting them to low-field NMR using the same settings as above. Even the simple strategy of integrating just the bis-allylic peak is sufficient to show that low-field ^{1}H NMR is a viable candidate for detection of lard adulteration of important edible oils (Figure 5B).

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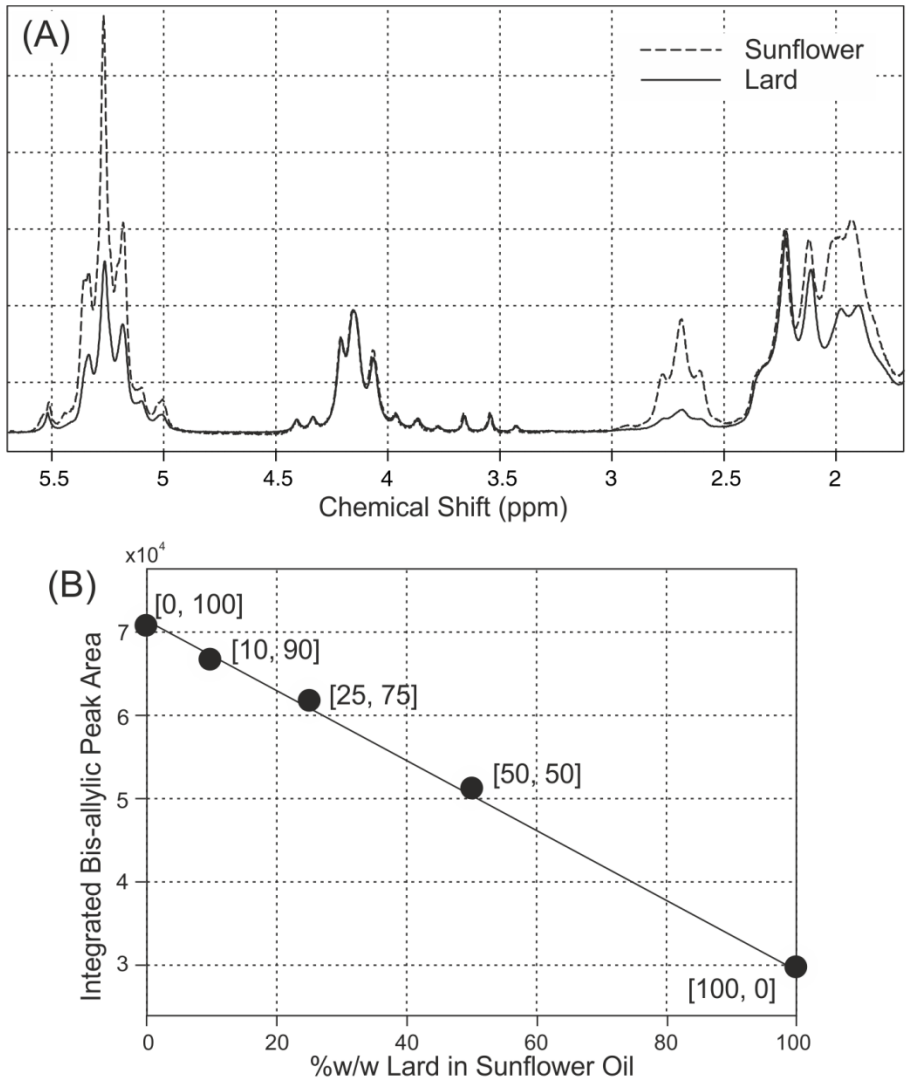


Figure 5 *Lard:sunflower oil mixtures. Panel A shows the 60 MHz ^{1}H NMR spectra for pure lard and pure sunflower oil, on a common scale, for the region 1.7 – 5.7 ppm. The bis-allylic peak at ~ 2.7 ppm is a useful discriminator. Panel B shows the integrated bis-allylic peak area as a function of lard: sunflower oil composition (%w/w). These spectra have been subject to reference deconvolution*

More challenging is the detection of the adulteration of relatively expensive olive oil with hazelnut oil. This is a consequence of the fact that the compositions of these two oils are very similar, even though hazelnut oil is typically listed as containing higher levels of poly-unsaturated fatty acids.[2] Twenty extra virgin olive oils and ten hazelnut oils were purchased from local supermarkets, mixed with chloroform and analysed by low-field NMR broadly as described above. For each pure oil, the mono-unsaturated fraction is plotted against the poly-unsaturated fraction as calculated by peak area estimation (Figure 6). For both oil types, the range of poly-unsaturated values spans ~10% w/w and that of mono-unsaturated ~18% w/w, in keeping with the considerable spread shown in literature values. Despite the variation in levels, however, combining these two simple peak area measurements is enough to divide the oils into two disjoint groups.

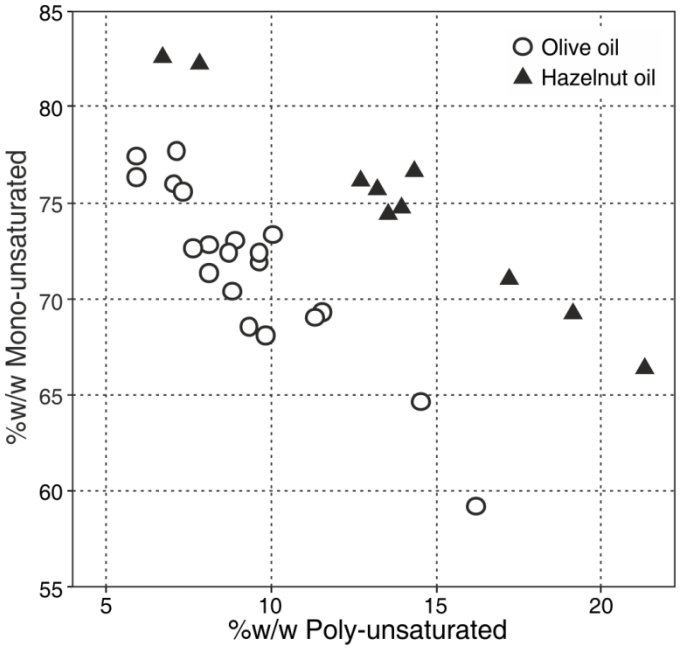


Figure 6 *Mono-unsaturated versus poly-unsaturated levels for hazelnut and olive oils from 60 MHz ^{1}H NMR spectra, calculated using peak areas. The two oils are seen to form two distinct groups on the basis of this simple measurement*

Even the simple ratio of the integrated olefinic to glyceride peak areas is sufficient to distinguish hazelnut oil (ratio > 1.6) from olive oil (ratio < 1.6), and shows systematic differences with mixtures of the two oils. But peak areas alone fail to capture the full complexity of the spectra, for example the small but systematic changes in the dominant methylene peak at ~1.3 ppm with changes in the mixture composition. To capture this additional level of detail, chemometric methods are required that utilise information from across the entire spectrum. We have studied the adulteration of olive oil with hazelnut oil using low-field NMR,[14] developing a PLS regression model of the %w/w of olive oil present in mixtures of hazelnut and olive oils. Using this approach, we were able to establish a limit of detection of 11.2% w/w hazelnut oil in olive oil using low-field NMR data.[14] This outcome compares well with results from high-field studies[8, 15, 16] and with infrared.[14]

A larger range of 10 different edible oils has also been examined. Four or five independent samples of each oil type were analysed, preparing each by mixing with deuterated chloroform (50:50 proportions) and acquiring spectra under the conditions quoted above. PCA was used to visualise the differences between the spectra obtained (Figure 7). For the most part, the different oils are clearly differentiated using only the first two principal components, illustrating the discriminatory power of chemometric methods applied to low-field NMR data. The plot also offers some guidance on the likely success (or to some extent, the limit of detection) of spotting one oil mixed with another. For example, it would probably be relatively difficult to detect low levels of sunflower oil in corn oil. That may not be much of a fraud concern, but detecting sunflower oil in olive oil should be more successful as well as being more of a real-world interest.

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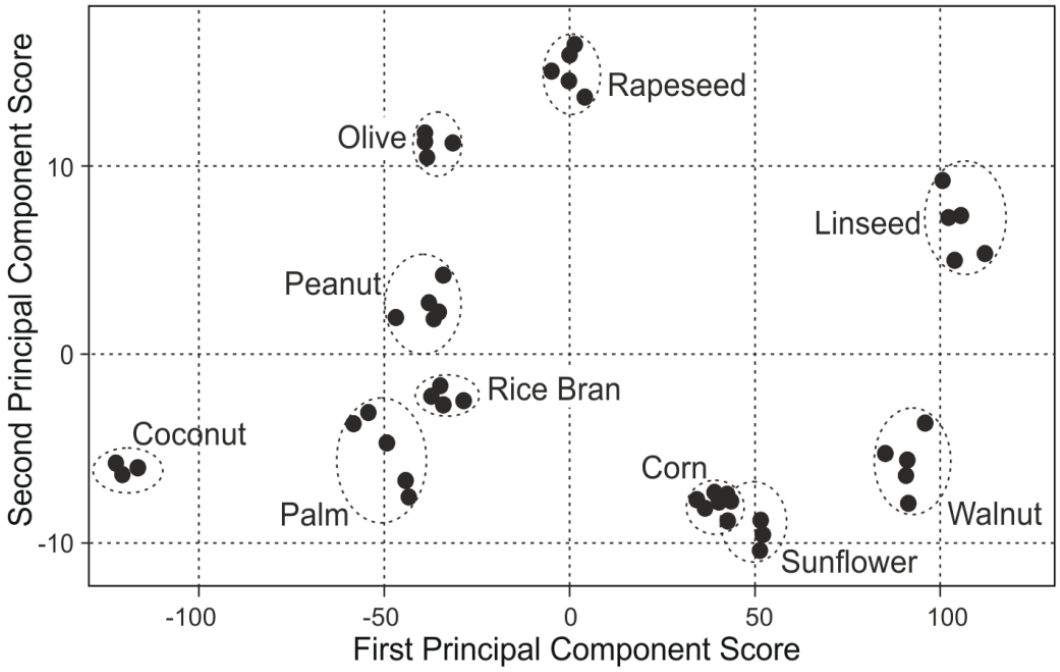


Figure 7 *PCA plot derived from the NMR spectra of 10 edible oils, comprising olive, palm, coconut, walnut, rice bran, rapeseed (canola), linseed, corn (maize), sunflower and peanut (ground nut). Each dot is an independent oil sample. The ellipses are simply to identify members of an oil group and have no statistical significance*

2.3 Authentication of Meat

Low-field NMR is sensitive to different triglycerides and can discriminate between naturally occurring mixtures of triglycerides in the form of edible oils. Since edible animal fat is composed mainly of TAGs, it is natural to speculate that low-field NMR may be able to differentiate between different meats by means of the different TAG make-up of the fat component. This is not a new idea: as long ago as 1938 Paschke used chemical means to investigate mixtures of different meat types based on their TAG content.[17] Much more recently, high-field ^{1}H NMR has already been used to determine the triglyceride composition of different meats.[18, 19] Testing methods for meat species is currently highly topical in the wake of the European horse meat scandal of late 2013, especially methods that might form the basis of a rapid screening protocol.

We purchased fresh beef and fresh pork from local supermarkets and butchers. Horse meat was purchased either from meat suppliers in the UK (frozen only) or from butchers and supermarkets in France and Belgium (fresh and frozen). To extract the triglyceride component, a small piece of meat was homogenised in a blender, then left to steep in chloroform (either deuterated or non-deuterated). The resultant mixture was filtered, and the filtrate introduced to standard 5 mm NMR tubes. A variety of scans and acquisition times were used: data acquisition was performed at two sites on two instruments and the results combined. Comprehensive details covering the horse meat and beef studies will be published elsewhere.[10]

Figure 8 shows a principal components plot from an analysis based around concatenated olefinic, bis-allylic and terminal CH_3 spectral regions only. A training dataset (76 beef extractions from 19 independent samples, 62 horse extractions from 19 samples, data not shown) underpins the ellipse shown in the figure. This ellipse is the line of constant Mahalanobis distance from the beef group centre-of-mass. It delineates an ‘authentic beef’ region ($p=0.001$). Independent test data (91 beef extracts from 31 samples, 16 horse extracts from 6 samples) are displayed in Figure 8. All but one of the beef test data points lie within

the ellipse, meaning that all but one of the beef extracts are correctly classified as authentic. Test data for horse (16 extracts from 6 samples) all lie outside the ellipse and are thus all correctly classified as non-authentic, i.e. not beef. Figure 8 in addition includes data from pork (104 extractions from 28 samples) which also lie entirely outside the ellipse and are therefore also correctly classified as non-authentic. We observe there is most spread in the horse data, which is likely due to the disparate sources of horse meat.

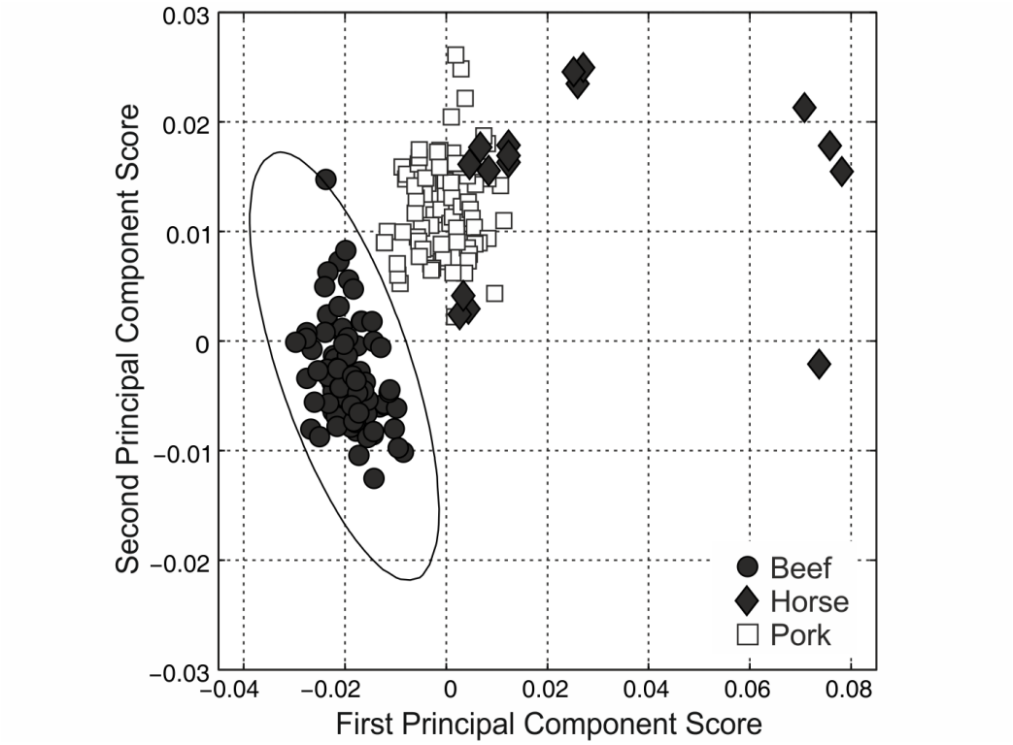


Figure 8 *First versus second principal component plot for test data comprising beef (91 extractions from 31 different samples, ●), horse (16 extractions from 6 different samples, ♦) and pork (104 extractions from 28 different samples, □). The ellipse delineates the beef group according to separate training data*

This analysis was framed to have a 'beef' versus 'not beef' outcome, that is, to function as an authentication protocol for raw beef. However, preliminary work has also been conducted to develop a methodology with a wider-ranging identification outcome ('beef', 'pork', 'horse', etc.) and we conclude with Figure 9, which shows the additional promise of the ^{1}H NMR approach to also distinguish lamb from the other major red meat types.

3 CONCLUSION

Low-field 60 MHz ^{1}H NMR spectroscopy, as opposed to more widely known relaxometry, is able to extract TAG spectra with linewidths in the Hz domain that are comparable to those from much more expensive high-field instruments. Low-field spectra exhibit higher levels of peak overlap than high-field, but with care peak area estimations can still be used to extract useful information from TAG spectra, for example on the saturated fat content of complex foods or to differentiate one edible oil from another. To make the most of the spectral information requires chemometric methods, which are less sensitive to peak overlap. Using these approaches, low-field ^{1}H NMR offers a viable method for testing the authenticity of meat and the detecting the adulteration of edible oils with one another. The case studies presented here rely on sample protocols that are deliberately rapid and inexpensive. Sample

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preparation methods of this type, combined with bench-top NMR, therefore provide a rapid screening technology relevant to triglyceride-rich mixtures such as edible oils and fats.

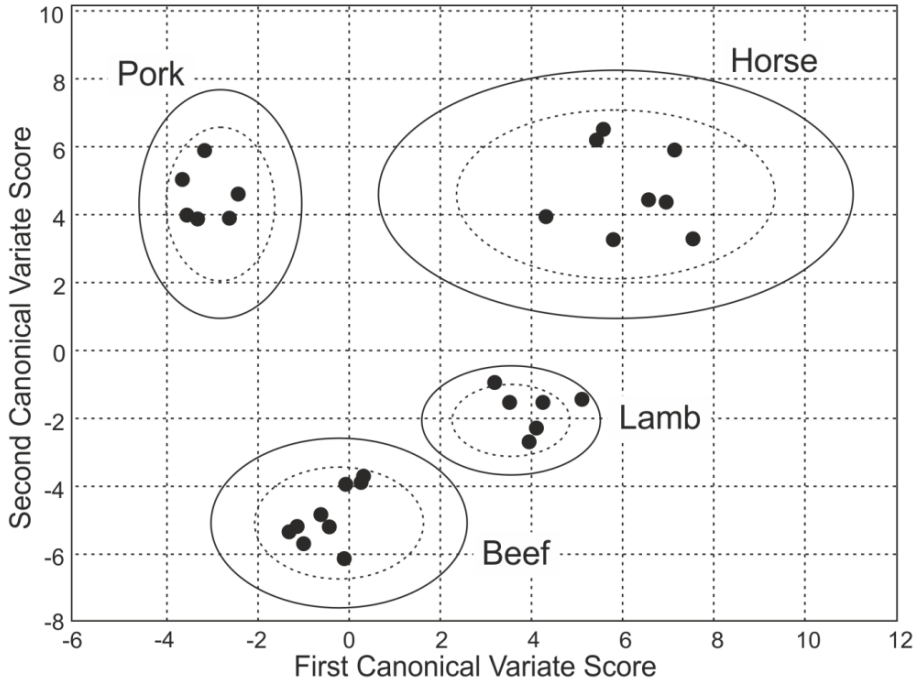


Figure 9 *Preliminary results on classification of meat samples into beef, lamb, horse and pork based on canonical variates modelling using PLS scores*

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