TD-NMR to understand water-binding food properties

Elvira Rodriguez-Alonso¹ | Frank J. Vergeldt² | Atze Jan van der Goot¹

¹Food Process Engineering Laboratory, Wageningen University & Research, Wageningen, The Netherlands
²Laboratory of Biophysics and MAGNe tic resonance research FacilitY (MAGNEFY), Wageningen University & Research, Wageningen, The Netherlands

Correspondence
Elvira Rodriguez-Alonso, Food Process Engineering Laboratory, Wageningen University & Research, Bornse Weilanden 9, 6708 WG Wageningen, The Netherlands.
Email: elvira.rodriguez.alonso@gmail.com

1 | INTRODUCTION

Nuclear magnetic resonance (NMR) is a versatile technique that allows assessing the composition and structure of food samples. It provides information on molecular properties, which can be used for quantification of concentration and interactions of components within the food samples. Due to the fact that many foods are proton-rich (with protons originating from water, fat, carbohydrates, and proteins) and carbon-rich (originating from fat, carbohydrates, and proteins), ¹H and ¹³C NMR have become the most common type of NMR in food analysis.[¹–³]

NMR is used in a wide range of applications, included in the fields of food microbiology, food chemistry, food engineering and food packaging (see Table 1)[⁴–²³].

Table 1 shows the multiple applications of NMR in food science. Analysis of food components is nowadays one of the main interests of authors. Water, proteins, and fat have been studied qualitatively, and in some cases, also quantitatively. Other aspects, such as processing, conformational analysis of certain molecules, and packaging, are also among the targets. In case of quality control, NMR is valued to certificate the quality of highly appreciated food products for consumers, for instance, olive oil.

Within the field of food process engineering, two water-in-food issues widely studied with NMR techniques are the translation and location of water in food samples, as well as water-biopolymers interactions.[²⁴–²⁷] Within all types of NMR, time domain nuclear magnetic resonance (TD-NMR) turns out to be a fast and accessible tool to study water populations present in food. Most of the TD-NMR studies on food samples use relaxometry methods. Spectral information seems to provide less information for water-related issues because water present in various physical environments does not give chemical differences (e.g., chemical shifts). The reason is that water is found in various physical environments, but chemical differences barely exist.[²⁶] The relaxometry analyses are based on differences in transverse relaxation times (the so-called T₂, or its inverse R₂ = 1/T₂) of components. T₂ values for water in food depend on the concentration of water in the food matrix, and usually range from microseconds to seconds. These T₂ values can therefore be related to different populations of protons (¹H) with various rotational mobilities, which can then be assigned to different groups of proton-bearing water populations contained in a proteinaceous sample.[⁴,²⁶]

The objective of this perspectives paper is, first, to collect studies on water binding to proteins and their interactions within proteinaceous food samples. Then, perspectives of future work on this topic are presented.

2 | TD-NMR WATER-BINDING ANALYSIS

In order to study water population within samples, Dekkers et al. (2016) associated transverse relaxation times on the TD-NMR spectrum to proton-bearing...
components. As shown in Figure 1, the transverse decay curves were analysed with the Levenberge-Marquardt non-linear least squares algorithm. This algorithm fits a sum of exponential curves—the so-called components—to the decay, resulting in an amplitude $A$ and transverse relaxation time $T_2$ for each component. The longest relaxation time of the sample in the spectrum, which is shorter than that of pure water, would correspond to some relatively mobile water within interstices in the protein matrix. The fact that this relaxation time is lower than that of free water, in their conclusion, may be due to pore confinement and by fast proton exchange with dissolved components. When the concentration of soy protein isolate (SPI) rises, this water population disappears, which suggests stronger water-binding capacity of SPI at this concentration. The relaxation time of the averaged middle two components represented more than 90% of the signal intensity. This signal was assigned to absorbed water. The $T_2$ of this water population decreases as a function of protein concentration, reflecting the decreasing mobility of this fraction. Finally, the component with the shortest relaxation time probably represents protein-bound protons. The intensity of this signal rises with concentration, which leads to think that it could represent the protein-bound proton population. The slight dispersion of relaxation rates of the middle fraction—which corresponds to second and third water populations, averaged on this spectrum—may be due to the heterogeneity within the individual phases.

Another example of information that can be extracted from TD-NMR studies on water is the compared study of water-binding capacity (WBC) of different materials. Figure 2 shows the comparative study of four plant-based materials carried out by Peters et al.\[6\]. It can be observed that vital wheat gluten calibration curve increased more gradually than was found for SPI, pea protein isolate, and lupin protein concentrate. This behaviour might be explained as being related to isolectric point of the proteins. The isolectric point of gluten is around 7.5—whereas the value for the other proteins is around 4.5—

### FIGURE 1  
Time domain nuclear magnetic resonance spectrum of soy protein isolate dispersion with 20% of dry matter content\[4\]
which would lead gluten to less interact with water in these samples.\[28\]

Dekkers et al.\[5\] focused on the WBC of phases in a blend of plant-based materials in order to better understand the rheological behaviour of that blend. The blend consisted of a phase-separated blend of an aqueous SPI phase and aqueous Wheat Gluten (WG) phase. The exact distribution of water over both phases determines the blend rheological properties. In past studies on rheology of biopolymer blends, the water distribution was often taken as a fit parameter. Now, NMR was used to determine the water distribution quantitatively, and the outcomes of NMR turned out to be fully in line with water distributions as predicted by rheology. The authors calculated a theoretical $R_2$ value of water distributions in SPI-WG blends, then compared these values with experimental $R_2$ values of the blends. They observed that experimental $R_2$ values were lower than the calculated $R_2$ values, which would mean that water was more mobile than expected. This could be explained by the fact that water was not evenly distributed among the SPI and WG phases.

Peters et al.\[8\] studied a dairy material for its WBC as well. They compared measurements of WBC on whey protein pellets by weighing the pellet obtained after centrifuging a dispersion with TD-NMR measurements. Previously, it was assumed that the interstitial water (water between particles) can be neglected, implying that all water was absorbed by dry matter in the pellet. However, this assumption turns out to be inaccurate to measure WBC. As a matter of fact, TD-NMR did allow differentiation between water inside and between the particles, which leads to a more accurate assessment of different populations of water inside the food sample. Figure 3 shows how TD-NMR can be potentially useful to study WBC in food samples.

3 | PERSPECTIVES

As stated in the introduction, a need exists for developing a new category of product, being dense protein food products. Partly as healthy foods,\[29\] partly as products...
that can replace products from animal origin. A key element of interest is to better understand the sensory properties of those products. High-protein foods are often associated with hard and dry texture. Furthermore, plant-based products are often less juicy than the animal-based ones.

TD-NMR is an attractive tool to investigate water binding in dense protein products. It allows to differentiate the different water populations in a product as well as to quantify them. Thus, a simple but versatile tool is available to compare differences in water binding of various products.

We can therefore imagine that future research will focus TD-NMR studies on a broad range of samples, including plant-based food samples. For this purpose, both classic ingredients (soybean, lupin, wheat gluten) as well as novel plant-based ingredients (rapeseed, sunflower, pea, faba bean) will be studied.

The first objective will be to identify water populations within the samples and their dependence with certain parameters, such as dry matter content, pH, or amount of added salt. Certain stages of processing, such as heating or shearing, can be included as well. A further step would be to compare the relative TD-NMR signals to carry out semi-quantification. Finally, we will aim to quantify these water populations in absolute units.

The second objective will be the study of the biopolymers, which constitute the food matrix, these include fat, proteins, and carbohydrates as well as the interactions amongst them. Fat content determination is nowadays labour-intensive and invasive, thus a faster and non-invasive alternative is highly desirable. Both identification and quantification of these biopolymers will be aimed.

ORCID

Elvira Rodríguez-Alonso https://orcid.org/0000-0002-7647-8989

REFERENCES

[1] J. P. M. van Duynhoven, A. Voda, M. Witek, H. van As, Annu. Reports NMR Spectrosc. 2010, 69, 145.
[2] A. Spyros, P. Dais, P. S. Belton, R. Wood, NMR Spectroscopy in Food Analysis. (The Royal Society of Chemistry, 2012). https://doi.org/10.1039/9781849735339
[3] M. F. Marcone, S. Wang, W. Alibabish, S. Nie, D. Sommarnain, A. Hill, Food Res. Int. 2013, 51, 729.
[4] B. L. Dekkers, D. W. de Kort, K. J. Grabowska, B. Tian, H. van As, A. J. van der Goot, Food Hydrocoll. 2016, 60, 525.
[5] B. L. Dekkers, M. A. Emin, R. M. Boom, A. J. van der Goot, Food Hydrocoll. 2018, 79, 273.
[6] J. P. C. M. Peters, F. J. Vergeldt, R. M. Boom, A. J. van der Goot, Food Hydrocoll. 2017, 65, 144.
[7] F. L. Chen, Y. M. Wei, B. Zhang, J. Food Eng. 2010, 100, 522.
[8] J. P. C. M. Peters, F. J. Vergeldt, H. van As, H. Luyten, R. M. Boom, A. J. van der Goot, Food Hydrocoll. 2016, 54, 170.
[9] J. P. C. M. Peters, F. J. Vergeldt, H. van As, H. Luyten, R. M. Boom, A. J. van der Goot, Food Hydrocoll. 2017, 63, 533.
[10] H. T. Pedersen, L. Munck, S. B. Engelsen, J. Am. Oil Chem. Soc. 2000, 77, 1069.
[11] J. T. Keeton, B. S. Haflcy, S. M. Eddy, C. R. Moser, B. J. McManus, T. P. Leffler, J. AOAC Int. 2003, 86, 1193.
[12] L. Ballerini, A. Hogberg, G. Borgefors, A. C. Bylund, A. Lindgard, K. Lundstrom, O. Rakotonirainy, B. Soussi, IEEE Trans. Nucl. Sci. 2002, 49, 195.
[13] F. Hu, K. Furihata, Y. Kato, M. Tanokura, J. Agric. Food Chem. 2007, 55, 4307.
[14] G. Nestor, J. Bankefors, C. Schlechtrem, E. Brännäs, J. Pickova, C. Sandström, J. Agric. Food Chem. 2010, 58, 10799.
[15] P. S. Belton, I. Delgadillo, E. Holmes, A. Nichols, J. K. Nicholson, M. Spraul, J. Agric. Food Chem. 1996, 44, 1483.
[16] J. A. Lopes-da-Silva, †, Dora M. J. Santos, †, Andrea Freitas, §, Carla Brites, # and Ana M. Gil*, §, J. Agric. Food Chem. (2007). https://doi.org/10.1021/JF070379+.
[17] M. Gudjonsdottir, V. N. Gunnaugsson, G. A. Finnbogadottir, K. Sveinsdottir, H. Magnunsson, S. Arason, T. Rustad, J. Food Sci. 2010, 75, E527.
[18] E. M. Vilén, L. C. E. Lundqvist, D. Jouanneau, W. Helbert, C. N. M. R. Sandström, Biomacromolecules 2010, 11, 3487.
[19] A. Caligiani, G. Palla, A. Maitelli, M. Cirrini, V. Brandolini, Nutrients 2010, 2, 280.
[20] J.-E. Lee, B. J. Lee, J. O. Chung, J. A. Hwang, S. J. Lee, C. H. Lee, Y. S. Hong, J. Agric. Food Chem. 2010, 58, 10582.
[21] M. Pentimalli, D. Capitani, A. Ferrando, D. Ferri, P. Ragni, A. L. Segre, Polymer (Gulf). 2000, 41, 2871.
[22] R. M. Alonso-Salles, J. M. Moreno-Rojas, M. V. Holland, F. Reniero, C. Guillou, K. Héberger, J. Agric. Food Chem. 2010, 58, 5586.
[23] C. V. Di Anibal, M. P. Callao, I. Ruisánchez, Talanta 2011, 84, 829.
[24] E. Alberti, P. Belton, A. Gil, Annu. Reports NMR Spectrosc. 2002, 47, 109.
[25] Water activity in foods: Fundamentals and applications, Wiley-Blackwell 2007.
[26] P. Belton, Food Rev. Int. 2011, 27, 170.
[27] P. S. Belton, Magn. Reson. Chem. 2012, 49, S127.
[28] A. Gennadios, C. Weller, F. Testin, Cereal Chem. 1993, 70.
[29] N. Purwanti, J. P. C. M. Peters, A. J. van der Goot, Food Funct. 2013, 4, 277.

How to cite this article: Rodríguez-Alonso E, Vergeldt FJ, van der Goot AJ. TD-NMR to understand water-binding food properties. Magn Reson Chem. 2019;57:603–606. https://doi.org/10.1002/mrc.4815