

Chapter 2

Application of NMR Spectroscopy for Foods and Lipids

Nuclear magnetic resonance (NMR) spectroscopy is one of the most powerful analytical tools to identify organic and bio-organic substances and to elucidate their chemical structures. It is recognized as one of most reliable methods, and it is convenient, fast, and non-destructive. While the proton NMR (^1H NMR) is the most frequently used method, it becomes a more powerful tool for analysis of organic compounds when it is used with the carbon NMR (^{13}C NMR) and two dimensional (2D) NMR techniques such as correlation spectroscopy (COSY), nuclear Overhauser effect spectroscopy (NOESY), J-spectroscopy, exchange spectroscopy (EXSY), heteronuclear single quantum coherence spectroscopy (HSQC), and heteronuclear multiple-bond correlation spectroscopy (HMBC).

The NMR spectroscopy has widely been used for analyses of foods such as beer, wine, soy sauce, vinegar, coffee, tea, fruit juice, mandarin oranges, kiwifruit, mangoes, black raspberries, melons, watermelon, tomatoes, lettuce, *Brassica rapa*, potatoes, carrots, maize, wheat, milk, cheese, butter, margarine, honey, fish, and meat (Guillén and Ruiz 2001; Mannina et al. 2012; Marcone et al. 2013; Siddiqui et al. 2017). Compared to chromatographic methods such as GC/MS, LC/UV, and LC/MS, the NMR method has the disadvantage of lower sensitivity. However, the advantages of the NMR method, such as simpler preparation steps, the possibility of obtaining broad information in one measurement, and the high reproducibility, often make it very useful for analyzing food ingredients (Cazor et al. 2006). The NMR method can provide simultaneous access to both qualitative and quantitative information and are being used for purity assessment of organic compounds and identification of potential impurities (Simmler et al. 2014).

Due to such a great versatility of the NMR method, it has been widely used to analyze the quality, structure, composition, characteristics, and ingredients in foods. Moisture in food is often determined by time-domain nuclear magnetic resonance (TD-NMR) or low resolution NMR for the purpose of quality control and quality

assurance in food industries (Todt et al. 2006). Solid fat contents, the characterization of the ice in frozen food, amounts of biopolymers such as proteins and starch also can be determined using NMR relaxation at low fields (Mariette 2009). The NMR spectroscopy, especially ^1H NMR, has been applied to determine the characteristics of oil and fat. For example, Guillén and Ruiz (2003a) determined the amounts of linolenic, linoleic, oleic, and saturated acyl groups in oil using the area of five discrete proton signals of the ^1H NMR spectrum. The results were in agreement with the actual amounts of these acyl groups. The NMR method was recognized as a very useful tool for fatty acid composition analysis of oils with additional advantages of shorter time, better convenience, and no chemical modification over traditional analytical methods. Similarly, Castejón et al. (2014) also applied the ^1H NMR methodology to the analysis of three different vegetable oils: sunflower, olive, and linseed oils. In this method, it was possible to determine the fatty acid composition in less than 1 min. Furthermore, the accuracy was the same as the traditional method, GC-FID, while the reproducibility was even better. In an attempt to drive forward the automated analysis of the fatty acid composition of edible oils, Castejón et al. (2016) later developed an NMR-based screening method using a 300 MHz NMR instrument, in which the NMR spectra were automatically analyzed and interpreted. This study demonstrated that the complete process from the sample preparation to printing the report takes only 3–4 min.

The amount of free fatty acids in oil can be determined from the areas of the carboxylic group proton (COOH) signal appeared at 11–12 ppm and the methylene proton signal directly adjacent to the carboxyl group resonating at 2.2–2.4 ppm in the ^1H NMR spectrum obtained from oil dissolved in a mixture of CDCl_3 and $\text{DMSO}-d_6$ (5:1, v/v) (Skiera et al. 2012b, 2014). In the test with a total of 305 oil and fat samples, the NMR method showed a very strong correlation with the conventional method except for hard fat that showed somewhat significant deviations, the data obtained by the two methods were in good agreement. The ^1H NMR method also can be used for. The ^1H NMR spectroscopy is also used for analysis of free fatty acids in waxes and oleyloleat, many unsaponifiable materials in oil such as alcohol, sterol, hydrocarbon, and tocopherols. This enables this method to reveal the geographical origin of olive oils and the adulteration of commodity oils (Alonso-Salces et al. 2010). Another important application of the ^1H NMR spectroscopy is found in the quality assessment and authenticity of olive oil, which is a frequent target for adulteration and is often diluted with less expensive oils and labeled as pure olive oil (Dais and Hatzakis 2013).

In addition to the common NMR spectroscopy, in which the sample is dissolved in a deuterated solvent, solid-state NMR techniques, which are performed directly on very small sample pieces (typically, a few milligrams) without any chemical or physical manipulation, are also used to examine food structures, chemical compositions, molecular organization, molecular dynamic behavior, and physical properties such as texture and water content (Ribó et al. 2004; Iulianelli and Tavares 2016). For example, the solid-state NMR was used to evaluate the changes in the chemical structure and molecular dynamic, as a response of time storage (Bathista et al. 2012). One of the solid-state NMR techniques, the HRMAS-NMR (high resolution

magic angle spinning-nuclear magnetic resonance), was used to assess the metabolic profile of sweet pepper (Ritota et al. 2010). In this study, several compounds, including fatty acids, organic acids, amino acids, and other minor compounds such as trigonelline, C4-substituted pyridine, choline, and cinnamic derivatives in sweet pepper, could be identified.

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