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High-resolution magic angle spinning nuclear magnetic resonance in foodstuff analysis

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ABSTRACT

The development and the application of analytical methods in food science has grown in order to meet the increase in consumer demand. Spectroscopic techniques played a distinctive role among the tools used in food analysis [e.g., nuclear magnetic resonance (NMR) spectroscopy]. High-resolution magic angle spinning (HR-MAS) is an important NMR tool that combines advantages of solid and liquid NMR techniques, offering opportunity to measure intact tissues. The small number of papers in the literature shows that the application of HR-MAS NMR in food analysis is still underexplored. Few kinds of matrix have been analyzed – mainly meat, cheese, grains, spices, fruit and vegetables – to identify compounds, to assign metabolic profiles and to elucidate physical features of macromolecular aggregation. This review presents a comprehensive survey of several HR-MAS NMR applications in foodstuff analysis, highlighting the main methodological aspects.

Contents

1. Introduction 11
2. Methodological aspects of HR-MAS NMR 12
3. Applications of HR-MAS NMR to foodstuff 12
    3.1. Fish, lamb and beef 12
    3.2. Cheese 14
    3.3. Grains 15
    3.4. Spices 15
    3.5. Fruits and vegetables 16
4. Concluding remarks 17
Acknowledgements 17
References 17

Abbreviations: ASA, Assigned Signal Analysis; BGMV, Bean golden mosaic virus; COSY, Correlation spectroscopy; CPMAS, Cross-polarization magic angle spinning; CPMG, Carr-Purcel-Meiboom-Gill; CSA, Chemical shift anisotropy; D_2O, Deuterium oxide; DA, Discriminant Analysis; DAF, Days after flowering; DHA, Docosahexaenoic acid; EPA, Eicosapentaenoic acid; FA, Fatty acid; GABA, Gamma-aminobutyric acid; GC, Gas chromatography; HCA, Hierarchical Clustering Analysis; HMBC, Heteronuclear Multiple-Bond Correlation; HMW, High molecular weight; HPIC, High-performance ion chromatography; HR-MAS NMR, High-resolution magic angle spinning nuclear magnetic resonance spectroscopy; HSQC, Heteronuclear single-quantum coherence; ICP-AES, Inductively-coupled plasma atomic emission spectroscopy; IRMS, Isotope-ratio mass spectrometry; LMW, Low molecular weight; MBC, Mozzarella di Bufala Campana; MRI, Magnetic resonance imaging; MS, Mass spectrometry; NMR, Nuclear magnetic resonance; NOESY, Nuclear Overhauser effect spectroscopy; PCA, Principal Components Analysis; PGI, Protected Geographical Indication; PLS, Partial Least Squares; PLS-DA, Partial Least Squares Discriminant Analysis; SNIF-NMR, Site-specific natural isotope fractionation by nuclear magnetic resonance; SPME-GC-MS, Solid-phase microextraction-gas chromatography-mass spectrometry; TOCSY, Total correlation spectroscopy; TMA, Trimethylamine.

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1. Introduction

Increasing awareness about food quality has attracted general public interest in the properties of foods, such as nutritional value, authenticity, quality and security. These characteristics are, in turn, directly linked to the context in which the food is produced, stored and consumed [1–3]. The effect of food products on human health has been demonstrated through epidemiological studies that relate eating habits and disease risks. Together with the nutritional value of foods, significant attention has also been given to disease prevention [4].

Food science evolved according to the needs and the requirements of the human population, and ensuring the benefits of food for people requires detailed knowledge about its chemical composition. Attempts to identify and to quantify the largest possible number of metabolites in cells, organs and organisms are performed using metabolomics (also called metabonomics) [3,5]. For Villa-Bôas [6], the term "metabolomics" has not yet been well defined and has been misused, being confused with "metabolic profiling" many times. Many authors have considered these terms as synonyms [7,8]. However, according to Villas-Bôas, the essence of studies in metabolomics is to establish the link between the characterization of metabolic phenotypes and their corresponding genotypes. The simple establishment of chemical composition using specific analytical techniques should be defined as metabolic profiling [6].

Recently, the application of "omics" technologies to food and nutrition was defined as "foodomics" [1,9,10], which comprises a broad view on the biochemistry of foodstuffs and a better understanding of the metabolic pathways involved in different processes. Such knowledge gives access to the molecular bases of the organoleptic and nutritional characteristics of foods [3,7,11].

The monitoring of variations in the chemical composition of foods is hard work due to the amount of compounds that can be present and the biochemical changes inherent in each matrix. In general, the change in concentration of a compound directly affects the production of others, causing alterations in taste, texture, flavor, functionality, bioactivity, shelf life and safety of food [3]. The characterization and the quantification of these transformations require suitable tools that may go further than the simple analysis of specific compounds or classes of substances. In such a context, there is a need to improve techniques and methodologies to enable access to the best possible qualitative and quantitative information over a wide range with increased sensitivity, accuracy, specificity and speed of analysis [10].

Food analysis is an important sub-area of analytical chemistry, in which a large number of methods are commonly employed, including spectroscopic, biological, separation, electrochemical and coupled techniques [10]. According to García-Cañas et al., spectroscopic techniques are outstanding in this field, with twice as many papers in 2001–2011 when compared to 1990–2000 [10]. This increase can be justified by both instrumental developments and the use of multivariate analysis that make possible better interpretation of data and extraction of information from complex matrices.

Among the spectroscopic techniques, nuclear magnetic resonance (NMR) has made an important contribution, surpassed only by mass spectrometry (MS) and fluorescence spectroscopy. In recent decades, the development of new probes, magnet designs and polarization techniques offered important improvements in sensitivity and resolution, contributing to the use of NMR as an analytical technique for foodstuffs [11].

NMR allows the analysis of complex samples, whether liquid, solid or semi-solid (gel-like), without altering the original characteristics of the matrices. Different NMR methodologies have been employed, with success, in food analysis, namely high-resolution [12] and low-resolution [13] liquid-state NMR, solid-state NMR [14], magnetic resonance imaging (MRI) [15] and site-specific natural-isotope fractionation NMR (SNIF-NMR) [16]. Such methods provide a wide range of information and should be selected according to the purpose of the work. For example, high-resolution NMR allows qualitative and quantitative structural analysis of a large variety of compounds. Low-field NMR, also called time-domain NMR, gives information about relaxation times, intramolecular and intermolecular motion, diffusion processes and dynamic, thermodynamic and structural properties of fluids in porous systems. MRI is able to create non-invasive images by measuring relaxation times and diffusion coefficients. Finally, SNIF-NMR, one of the most notable NMR tools in food authentication, is based on the determination of the isotopic ratio of deuterium to hydrogen ($^2H/^1H$) in different moieties of a molecule. The resulting isotopic profile can provide relevant information on the origin and the reliability of the sample [12,17,18].

Among these techniques, high-resolution NMR for liquid and solution samples is the most frequently used. Its main disadvantage is the need for sample extraction, which leads to loss of information about the natural state of the sample. Other drawbacks are the amount of sample required to obtain a good signal/noise ratio and the increased cost and analysis time, the latter linked to the extraction process. However, the investigation of samples without any pretreatment and with high resolution can be carried out by high-resolution magic angle spinning NMR spectroscopy (HR-MAS NMR).

HR-MAS NMR allows for the analysis of heterogeneous or semi-solid samples that are characterized by inhomogeneity and restricted molecular motion. In this situation, the magnetic fields generated by different spins interact, resulting in non-zero dipolar coupling (also known as direct dipolar coupling) as opposed to the behavior observed in fluids. Also in this type of matrix, which includes food samples, the magnetic susceptibility of the medium varies with position, leading to a non-uniform magnetization of the molecules by external fields [19–21]. Such characteristics are responsible for broadening signals, mainly due to the spatial differences on the magnetic susceptibility of the medium and in small proportion to the dipolar coupling of the nuclear spins, and chemical-shift anisotropy (CSA). Considering these three factors, the main interaction averaged out by MAS is the non-uniform distribution of magnetic susceptibilities in the samples [19].

All these factors depend on the angular relationship between the internuclear vector and the direction of the static field. This leads to different local magnetic fields for each spin package, depending on its spatial disposition in the sample, resulting in a wide range of precession frequencies and therefore broadening the signal. Submitting the sample to fast spinning about the so-called "magic angle" (54.74°) eliminates or at least minimizes the effect. In this condition, the contribution of dipolar coupling and of differences in magnetic susceptibility becomes zero and the NMR signals are similar to those observed in liquids [19–21].

HR-MAS NMR has a number of positive characteristics, when compared to liquid-state and solid-state NMR, notably the ability to produce high-resolution spectra from direct analysis of the sample. This is because sample-preparation procedures are kept to a minimum, allowing the analysis of compounds in their natural environment. HR-MAS NMR therefore combines typical advantages of liquid-state and solid-state NMR, besides other positive features, such as short acquisition times for ^1H NMR spectra even from few milligrams of sample [22]. It is a sensitive technique, being able to detect compounds with concentrations below 1 μmol L^{-1} in mixtures [23].

Since the HR-MAS-probe configuration is equipped with magnetic field gradient, conventional two-dimensional experiments (e.g., HSQC, HMBC, COSY, TOCSY, NOESY) can also be acquired with high resolution and good signal/noise ratio with the same pulse sequences employed in solution-NMR studies. The spectral quality of 1D and 2D experiments allows the precise identification of compounds, since information, such as multiplicities and homo and