Food Research International 209 (2025) 116327

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Current applications of benchtop FT-NMR in food science: From quality control to adulteration detection[☆]

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ARTICLE INFO

Keywords:
Benchtop NMR
Food
Low-field NMR
Spectroscopy
Chemometrics
Quality control
Adulteration

ABSTRACT

The introduction of benchtop FT-NMR spectrometers in recent years represents a remarkable innovation in various fields, including the food sector. Modern benchtop FT-NMR spectrometers are low-field instruments, with a magnetic field ranging from 1 T to 2.35 T (^{1}H resonance frequency from 43 MHz to 100 MHz), characterized by compact design, ease of use, and low maintenance costs. As in the case of high-field NMR instruments, benchtop NMR spectra (obtained by Fourier transformation) contain important information useful for compound identification and quantification.

In this review, a description of the fundamental steps useful both to acquire benchtop NMR spectra and to treat the obtained data is reported together with a wide range of applications in the food field. In particular, peculiar aspects of commercial benchtop instruments as well as NMR data acquisition, processing and treatment are reviewed reporting also a practical pipeline and a list of good practices for benchtop NMR applications. Benchtop FT-NMR applications, mainly focused on food adulteration detection and quality control, are discussed here using targeted, metabolomic, and fingerprinting approaches. Finally, the industrial applicability of benchtop NMR methods in either static or continuous mode is reported.

1. Introduction

In recent years, a new scenario emerged in the world of magnetic resonance offered by benchtop FT-NMR instruments. Generally speaking, high-field magnetic resonance is used to determine the structure of compounds and to study mixtures, whereas low-field magnetic resonance provides information on the most abundant components of samples measuring relaxation parameters. Therefore, using high- and low-field NMR experiments, distinct and complementary aspects are instigated as also reported in the food investigations (Capitani et al., 2013). What about benchtop FT-NMR instrument? Benchtop FT-NMR instruments have permanent magnets operating at low-field

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[☆] This article is part of a Special issue entitled: 'Miniaturized Spectroscopy' published in Food Research International.

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https://doi.org/10.1016/j.foodres.2025.116327
Received 30 January 2025; Received in revised form 22 March 2025; Accepted 30 March 2025

strengths, typically from 1 T to 2.35 T corresponding to proton resonance frequencies of 43–100 MHz, but the Fourier transformation procedure enables the acquisition of spectra in the frequency domain (Blümich, 2019). These instruments require no cryogens, are simple to use, and occupy less space, resulting in significantly lower capital and maintenance costs. Moreover, a benchtop spectrometer can operate without deuterated solvents thanks to a built-in external lock system. These innovations have made the powerful diagnostic capabilities of NMR spectroscopy accessible to a much broader range of users. However, benchtop FT NMR spectra have lower resolution, due to a smaller chemical shift dispersion, and lower sensitivity, with a lower signal-to-noise ratio, compared to high-field NMR spectra. The chemical shift dispersion limitation becomes more complex in the presence of many compounds in the samples as is the case of food matrices, leading to high overlapping and strong signal distortion in the spectra. Moreover, the strong solvent signal represents another problematic factor in the already crowded situation (Matviychuk et al., 2019). All these aspects suggest that the choice of the most suitable instrumentation depends strongly on the problem that has to be addressed.

Benchtop NMR applications support, as with high-field NMR spectra, various approaches for data handling: targeted analysis, metabolomic analysis, and metabolite fingerprinting (Mannina et al., 2012; Sobolev et al., 2022). Both targeted and metabolomic analysis require the compounds' identification. In targeted analysis, a single or a few marker compounds are identified and quantified based on prior knowledge of the food being investigated. The selected signals are typically directly linked to the food characteristics or aspects under investigation, with chemometric analysis applied rarely. Hence, in the targeted approach, which is based on a prior hypothesis, all other signals are deliberately excluded except for specific ones (Monakhova et al., 2015; Tanaka et al., 2014). Conversely, the metabolomic approach seeks to identify and quantify as many metabolites as possible, without relying on a predetermined hypothesis, striving for the most comprehensive description of the NMR spectrum while determining the identity of the signals (Di Matteo et al., 2021; Ingallina et al., 2023; Spano et al., 2023). The quantified metabolites are typically used as input for chemometric analysis. Fingerprinting approach does not require metabolite identification (Cagliani et al., 2013; Lee et al., 2010):the full spectra or binned data are then used as input for chemometric analysis. In all these approaches the use of chemometric tools on the collected data demonstrated to enhance the evaluation and interpretation performances of benchtop NMR data (Galvan et al., 2023).,

In the available literature, several review articles provide a comparison of the different available low-field NMR instruments, including benchtop FT-NMR (Blümich, 2019; Dalitz et al., 2012; Meyer et al., 2016; Mitchell et al., 2014). A number of review articles on benchtop FT-NMR deal with the various application fields of this instrument, i.e., forensic chemistry, process control, material chemistry, reaction monitoring, pharmaceuticals, polymer materials, fuels and biofuels, natural products, and biological fluids, including the food science sector (Galvan et al., 2023; Grootveld et al., 2019; Van Beek, 2019; Yu et al., 2021). However, no review articles fully dedicated to exploring benchtop FT-NMR applications specifically in the food field, reporting and correlating all existing studies, are available to date (as analyzed in the **Supplementary table 1**).

In this review, the potentiality of modern benchtop FT-NMR is discussed reporting the literature studies carried out in the last decade in food science. A description of the steps necessary to set up a benchtop NMR analysis and how to treat the obtained data is provided and a practical pipeline for benchtop NMR applications is proposed. Adulteration detection and quality control come out to be the two most promising sectors. The types of approaches to manage the NMR spectrum information namely targeted, metabolomic and fingerprinting are discussed together with the type of chemometrics analysis and the food applications.

2. Comparison of benchtop FT-NMR with the other techniques for food quality and adulteration detection

The most widely applied analytical techniques for food quality assessment and adulteration detection, include chromatographic techniques, such as high-performance liquid chromatography (HPLC) and gas chromatography (GC), vibrational spectroscopy techniques, such as Raman, mid-infrared (MIR), and near-infrared (NIR), and the NMR methodology (Elumalai & Natarajan, 2024; Zhang et al., 2024). None of these is a universal technique; each has its own advantages and limitations (Dunn et al., 2005). The Venn diagram in Fig. 1, based on the information of **Supplementary table 2** and adapted from Dunn et al. paper (Dunn et al., 2005), presents a comparison between NMR methodologies and these others commonly used analytical techniques in food quality and adulteration detection.

Chromatographic techniques are among the most sensitive, particularly when coupled with mass spectrometry (MS) detectors (Quintanilla-Casas et al., 2024; Di Stefano et al., 2012; del Mar Contreras et al., 2019; Esteki et al., 2020; Zhong et al., 2022). However, they require high-cost instrumentation and consumables (including organic solvents), as well as not portable equipment and specific sample preparation. In contrast, vibrational spectroscopy techniques offer a lower-cost alternative, enabling rapid analysis with minimal expense (Grassi & Alamprese, 2018; Sun et al., 2022; Zhang et al., 2024). Sample preparation is typically not required, allowing direct analysis of a liquid food sample in its natural form. Additionally, these techniques can be used for on-line process monitoring. However, their primary application in food analysis is based on fingerprinting methods combined with chemometric data processing. High-field NMR is a stand-alone technique for structural elucidation and supports multiple approaches to food analysis (Sobolev et al., 2019). It can be used based on signal identification (targeted and metabolomics approaches) or as fingerprinting analysis without signal identification. However, it is a costly technique in terms of both acquisition and maintenance, requiring liquid nitrogen and helium refills. Sample preparation is necessary, typically involving the addition of deuterated solvents, and its application is limited to static analysis. Benchtop NMR instruments, on the other hand, provide a more affordable alternative to high-field NMR (Meyer et al., 2016). They can directly analyze liquid samples without prior sample preparation and are suitable for on-line process monitoring. However,

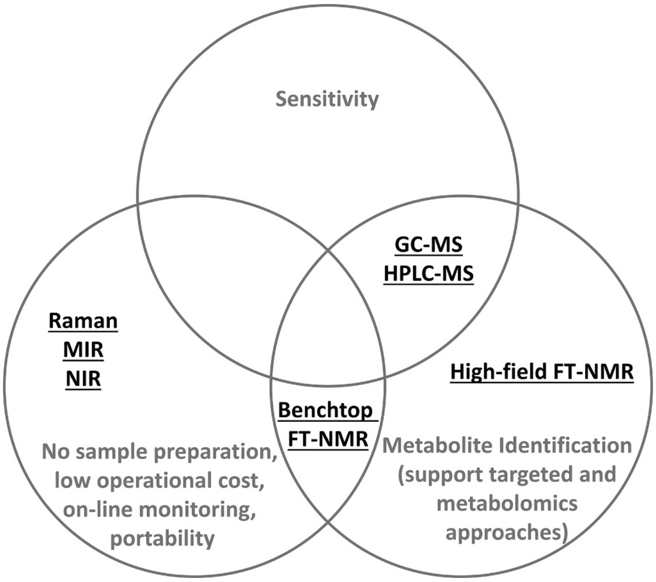

Fig. 1. Venn diagram comparing benchtop FT-NMR with other analytical techniques commonly used for food quality assessment and adulteration detection based on their distinct characteristics.

they are no longer stand-alone tools for structural elucidation. Instead, signal information obtained from high-field NMR can support targeted and metabolomics analyses using benchtop NMR. Additionally, fingerprinting analysis remains feasible, as with the others spectroscopic techniques based on molecular vibrations and rotations (Raman, MIR, NIR) (Grassi et al., 2023).

3. Benchtop FT-NMR for foods: From Spectrum acquisition to data analysis

3.1. The choice of benchtop instrument for NMR analysis

In the selected papers, benchtop NMR instruments ranging from 43 MHz up to 80 MHz of different brands (Bruker, Magritek, Nanalysis, Oxford Instruments) have been used. Each instrument has a different grade of automation and user-friendliness useful to reach also non-NMR experts. Each instrument has pros and cons import to know to best tackle a research stud or quality control before facing. A comparative analysis of the most important characteristics related to commercially available benchtop NMR instruments has been previously reported (Van Beek, 2019). The main characteristics that distinguish the different instruments include weight and portability, field strength, cost, external lock, automation grade, available nuclei, etc. Weight could be a very important parameter in searching for a portable instrument: the addition of an autosampler increases the automation level of the instrument but reduces the portability. Increasing the field strength from 1 to 2.35 T (from 43 MHz to 100 MHz) enhances both sensitivity and resolution, but leads to higher costs. Moreover, different brands and configurations present differences in available nuclei, external lock configuration and automation. It is noteworthy also to consider the expertise level of user and the type of application: industrial applications for non-NMR experts can orient the choice toward a brand with more user-friendly software, whereas research applications may require a brand with more complex software to obtain a wide range of information. Based on the brand and the related software, a different set of experimental parameters can be modified by the users. All the available instruments allow several possible NMR experiments, both mono- and bi-dimensional. In the studies selected in the present review, mainly 1D ^{1}H experiments, with or without the addition of the solvent suppression, have been carried out. In some case, 1D ^{31}P experiment (Gouilleux et al., 2019) and 2D NMR experiments (Gouilleux et al., 2018) are also reported.

3.2. NMR data acquisition

3.2.1. Parameters optimization

To develop a protocol based on benchtop NMR, the first step is to choose the NMR experiment according to the type of sample and the nature of compounds. Then, the optimization of several parameters must be carried out. For 1D ^{1}H experiment, the main parameters to be optimized are the temperature inside the probe, the number of scans, and the relaxation delay. In particular, the number of scans is optimized based on the compound concentration. For a quantitative experiment, the relaxation delay must be optimized by measuring longitudinal relaxation times T_1 of nuclear spins in the sample. The repetition time must be at least 5 times the longest T_1 in the sample (Soyler et al., 2020, 2021; Wu et al., 2021).

3.2.2. Shimming

In the development of a benchtop NMR procedure, it is fundamental also to schedule a routinary shimming protocol to avoid variance in peak heights/areas. The consistency of the line shape, considering an optimum linewidth among 0.6 and 0.9 Hz, could potentially be enhanced through more frequent shimming, albeit at the expense of a longer overall procedure. However, the shim frequency and shim type are rarely reported in the available articles. Some authors reported a standard shim protocol at the start of each day's analysis based on low-order shims (Gunning et al., 2020) or more complete (low-order and some high-order shims), and time-consuming, shims adjustment (Head et al., 2024; Kim et al., 2018; Krause et al., 2018). While others resort to shimming process as needed based on daily checks (Defernez et al., 2017; Gunning et al., 2018, 2020, 2022, Gunning, Davies, & Kemsley, 2023; McDowell et al., 2019), or use a quick shim method of 2–5 s every hour (Kim et al., 2018), or shim before every spectra acquisition (Isaac-lam, 2016; Matviychuk et al., 2021).

3.2.3. Solvent suppression

Benchtop spectrometers allow to work without deuterated solvents; however, the direct analysis of food and biological matrices will lead to a strong signal of residual non-deuterated solvent, especially water. The water residual signal can be a real challenge because tends to obscure other neighbors' signals, due to its consistent broadening at the base (Höpfner et al., 2021; Lam & Simpson, 2008; Pellizzari et al., 2024; Simpson et al., 2006). In this context, Pellizzari and coworkers explored the most commonly utilized water suppression sequences using Redbull™ and highly concentrated sucrose solution as samples (Pellizzari et al., 2024). They have shown that the most common water signal suppression is the radiofrequency pre-saturation sequence (pre-SAT) thanks to its simplicity and robustness (Hoult, 1976; Mo & Raftery, 2008). However, in many low-field NMR analysis, the water signal can be too strong or too broad and the pre-SAT sequence could fail. Many other suppression methods based on more complex sequences could be applied: NOESY-PR, g-NOESY-PR, JRS, W5-WATERGATE, and PURGE sequences. In NOESY-PR and g-NOESY-PR, a 1D-NOESY sequence has been applied to improve solvent suppression. These sequence can reduce the strong water signal using an adjustable delay, called mixing time, to enhance T_1-relaxation before the detection; residual water magnetization can be further controlled by phase cycles and gradients (Mckay, 2011). In and the W5-WATERGATE suppression method, a set of binomial delays is used to control the suppression bandwidththe bandwidth narrows when the delay is lengthened because relaxation occurs. (Brenner et al., 2018; Liu et al., 1998). A total of 36 binomial delays is used, and the most challenging issue is to find the optimal binomial delay length, because a too short delay is not performing for a good water suppression, while too long delay can result into a too much time-consuming experiments (Pellizzari et al., 2024). Lastly, the Pre-saturation Utilizing Relaxation Gradient and Echoes (PURGE) sequence came out to be the best water suppression of all tested sequences, due to the management to recover the full intensity of anomeric signals of all sugars in the studied samples (sucrose solutions and Redbull™), the production of flat baseline, the excellent phase properties, the high selective suppression, and the relative easy setting (few parameters to be settled up) (Pellizzari et al., 2024; Simpson & Brown, 2005). Other information for a proper selection of the solvent suppression sequence was reported in the article of Gouilleux and coworkers (Gouilleux et al., 2017). The authors compare the major solvent suppression methods showing that the WET-180-NOESY experiment, both under static and continuous conditions, revealed an optimal performance. The importance of a proper solvent suppression experiment selection is undoubted, especially for a low-field NMR. However, it should be considered that most of the actual Benchtop NMR instruments on the market are developed with an easy handling policy, so the choice among different solvent suppression experiments is not yet implemented. In the future, implementing additional NMR experiments could play a crucial role in integrating benchtop NMR into industry workflows.

3.3. NMR data processing

Once the low-field NMR data is acquired as raw time-domain data (Free Induction Decay, FID), the data processing is performed with the proper software specific for each NMR instrument as for high-field NMR data. Data processing refers to the FID transformation into the frequency-domain spectrum through Fourier Transformation (FT), and the other manipulations performed before and after on the single NMR data (Jacobsen, 2007). Before FT, manipulation on the FID through Zero Filling or Weighting or Window Functions could be applied. After FT, manipulation of the frequency-domain spectrum with peaks is carried out. The common manipulations are phase correction, baseline correction, and reference setting. When targeted and metabolomic approaches are carried out, commonly the processed spectra are studied through peak picking and selected signals are integrated. To obtain absolute quantification of the compounds, the measured area or signal intensity is typically normalized to the intensity or area of an internal standard with a known concentration. On the other hand, in the relative compounds' quantification, the area or intensity of the signals is normalized to the area or intensity of the sum of total peaks. Lastly the quantities of each metabolite can be directly submitted to statistical analysis.

3.4. Magnitude spectrum

An interesting approach for the characterization of a complex mixture, applicable for both high-field and low-field NMR, is the magnitude spectrum (de Harrington & Wang, 2017; Gouilleux et al., 2018; Gunning et al., 2022; Kemsley, 2024). In fact, magnitude spectra do not separate the real part of the spectrum from the imaginary part, and then there is no need for manual phasing, avoiding many artifacts and operator errors. Magnitude spectra have proven to be a valuable tool in edible oil authentication, as demonstrated by Gunning and coworkers, who applied this method to screen the authenticity of 410 edible oils using a 60 MHz benchtop spectrometer (Gunning et al., 2022). Similarly, magnitude spectra were effectively utilized in Ultrafast 2D NMR approaches on a 43 MHz benchtop NMR system, further emphasizing their utility in this field (Gouilleux et al., 2018). The transformation allowed, in both cases, the exploration and modelling of the data without phase corrections.

3.5. Statistical analysis

Statistical analysis of the NMR data plays a fundamental role in food applications assuring the robustness of the results and, in the cases of the fingerprinting approach, it is an unavoidable step to extract the relevant information from NMR spectra.

3.5.1. Spectra pre-treatment

In the fingerprinting approach, the processed spectra are usually submitted to various pre-treatments to prepare them for inclusion in a dataset for chemometric analysis (Ebrahimi et al., 2017).

The first step is to define the NMR spectra region to consider. Usually, the regions discarded are the empty baseline (before 0 ppm and after 10 ppm) and around the solvent signal. The different spectra of the samples are aligned by linear alignment using a reference peak (Gunning et al., 2022, Gunning, Defernez, & Kemsley, 2023; Krause et al., 2018) or icoshift (interval correlation optimized shifting) (Giebelhaus et al., 2023; Grassi et al., 2024; Head et al., 2024; Tomasi et al., 2011; Truzzi et al., 2023). After dealing with missing data and outliers, a data normalization step is generally performed, prior to finalize with other pre-treatments such as centering, scaling, denoising, and data transformation (Parvaneh Ebrahimi et al., 2017) (**Supplementary table 3**). Moreover, several strategies exist to remove systematic bias from datasets, with most being integrated into the software used for data acquisition or available through freely accessible tools (Worley & Powers, 2014; Zhao et al., 2006). After pre-treatment the data can be submitted to the chosen chemometrics analysis related to the scientific problem to solve. Here below the regression and classification models are discussed.

3.5.2. Regression modelling

Quantitative benchtop NMR-based food product analysis contributes to chemical characterization, quality control and online process monitoring, as well as adulteration and fraud detection. In the targeted approach, specific signals are selected based on a prior hypothesis and these peaks are integrated if they are well-resolved along the horizontal axis. Then the NMR data can be analyzed by univariate or multivariate approaches. Different research activities based on benchtop instruments developed univariate approaches for compound quantification mainly based on linear regression and ternary plot; in only one case a Naïve Bayes classification model was applied (**Supplementary table 3**).

On the other hand, the metabolomic approach, meant to identify as many metabolites as possible, integrate values of the identified peaks, which are then quantified. The approach could lead to the resolution of adulteration by identifying significant differences between authentic and adulterated samples. This is the case of Kim and coworkers (Kim et al., 2018) who discriminated authentic perilla oil samples from samples adulterated with soybean oils - added at concentrations of ≥6 vol% – with a two-tailed Student's *t*-test. This approach has been explored by several other articles (Gunning et al., 2020; Matviychuk et al., 2021; Pajuelo et al., 2023; Soyler et al., 2021). Furthermore, quantitative multivariate strategies could be applied following the fingerprinting approach. In this case, the full spectra, after data pretreatment, are used as input for chemometric algorithms. They are particularly useful for enabling quantitative analysis of more complex spectra obtained by benchtop instruments when the traditional method of peak integration could yield insufficient results. The first application of chemometric analysis to NMR spectra dates back to the early eighties (Johnels et al., 1983). The multivariate approaches generally start from data exploration, often performed by Principal Component Analysis (PCA) (Galvan et al., 2021; Giebelhaus et al., 2023; Gouilleux et al., 2018; Gunning et al., 2022; Head et al., 2024; Ozbay et al., 2024). Results from PCA could be used for detection and removal of outliers, dimensionality reduction and obviously for sample distribution and variable load visualization. Then, when the goal is to predict a quantitative response, supervised methods such as Partial Least Squared Regression (PLSR), are mandatory (Galvan et al., 2023).

PLSR is undoubtedly the most used algorithm and could be considered the benchmark linear model for comparison purposes, however, other regression algorithms could be used, such as Support Vector Machine (SVM) (Galvan et al., 2021) and Artificial Neural Networks (ANN) (Soyler et al., 2021). PLSR, SVM and ANN have been applied in benchtop NMR field to construct regression models to predict the concentration of a specific compound, to predict the percentage of adulteration or to classify products of different origins and different properties (**Supplementary table 3**), indeed due to the intrinsic characteristics of the low-field NMR technique, both linear and non-linear methods could be useful. Model accuracy could be evaluated by different Figures of Merit (FoM), mainly the coefficient of determination (R^2), and Root Mean Squared Error (RMSE) as for univariate linear regression modelling. The coefficient of determination, R^2, is commonly used to assess the regression model's performance, the higher the better, considering its maximum equal to 1. A good practice is to compare R^2 across different model evaluation steps—such as calibration, cross-validation, and prediction—to assess model stability. However, relying solely on R^2 for model evaluation is insufficient, as a regression model can have a high R^2 value yet still exhibit significant errors, such as a high Root Mean Square Error (RMSE). RMSE measures the average magnitude of errors. A low RMSE indicates presumably good model performance; comparing RMSE against a baseline (e.g., mean of the target variable or a simpler model) is a good practice to determine model effectiveness. Therefore, it is recommended to combine the evaluation of R^2 with RMSE, especially when the compound of interest shows a wide range of variability, converging R^2 to 1.00 with low RMSE. Additionally, the reasonableness of the RMSE value should be assessed in relation to potential sources of measurement error, such as reference methods (e.g., standard error of the laboratory), reproducibility error, or the limit of detection. The error evaluation could also be performed referring to the ratio of performance deviation (RPD), the ratio of error range (RER), mean relative error percentage, and the coefficient of variation (CV) (Grassi et al., 2023).

These FoM could give an evaluation of the error independently from the measurement units, however none of the revised works adopted those strategies. The use of RPD, largely applied in the evaluation of multivariate regression models in other spectroscopic fields, allows for comparison across models predicting different compounds with different SI. In any case, the comparison of the FoM among the different modelling phases – calibration, internal validation and prediction - is crucial for assessing the reliability, robustness, and generalizability of the model. A very high R^2 and low RMSE in calibration may not be generalized well beyond the training data. A stable performance across calibration and validation ensures the model is not just modelling the training data but learning generalizable patterns. Finally, the model should guarantee stable performance in prediction, indeed, if the model performs well in calibration and internal validation (or cross-validation) but poorly in prediction, it may suffer from overfitting, data drift, or an insufficiently representative of the training set. For further discussion, readers may read the following works (Engelsen et al., 2013; Galvan et al., 2023; Parvaneh Ebrahimi et al., 2017).

3.5.3. *Classification modelling*

Different multivariate algorithms exist for classification purposes, i.e. for the categorization of data into distinct groups (or classes) based on their chemical properties, enabling the identification and prediction of unknown samples based on their characteristics. In some research activities, PCA has been used as a qualitative method to assess if a sample belongs to “authentic” or “adulterated” class. However, it should be considered that PCA is not a classification approach, so assumptions about class membership cannot be retrieved from a scores plot. Indeed, results from PCA could be used for detection and removal of outliers, dimensionality reduction and obviously for sample distribution and variable load visualization. Sometimes, data processing ends with exploratory analysis (Killeen et al., 2017), and this could be understandable if the goal is a preliminary approach to highly informative data, and any assumption about class belonging is given. In classification applications, two main families of techniques can be distinguished: class modelling methods and discriminant methods. Out of the specific sector, these terms might be confusing. In fact, both assign objects to defined classes. However, they answer different questions. Class modelling algorithms, also known as one-class classifiers, check if a sample is comparable or not with the characteristics of a target class of interest (Oliveri, 2017). In other words, the model defines a region where samples belonging to the target class are more likely to be found (Vitale et al., 2023). Soft Independent Modelling of Class Analogy (SIMCA) and its variants (Vitale et al., 2023) are among the most used methods. On the other hand, discriminant approaches (e.g., Linear Discriminant Analysis, LDA or PLS Discriminant Analysis, PLS-DA) force the assignment of samples to one class among a number of predefined classes, which should be at least two, and all meaningfully defined and representative (Oliveri, 2017). These models are designed to work only with previously defined classes. If a sample from a new and different class is tested, it will still be classified—albeit incorrectly—into one of the existing categories. This is one of the main reasons why, in the context of food authenticity, where the target class to be authenticated is well-defined but not all potential false or non-authentic samples are known, class modelling approaches should be considered the most suitable. The most commonly used supervised methods for classification purposes with benchtop NMR are PLS-DA (Gunning et al., 2022; Head et al., 2024; McDowell et al., 2019) and SIMCA (Gunning et al., 2023; McDowell et al., 2019; Ozbay et al., 2024) (**Supplementary table 3**). The evaluation of a class-modelling method, such as SIMCA, is performed by analyzing the model’s reliability parameters, which are calculated from the confusion matrix. In this matrix, predicted samples are identified as true (TP), false negative (FN), true negative (TN), and false positive (FP). A good classification model should have high TP and TN while keeping FP and FN low (Oliveri, 2017). Maximizing TP and TN means the model correctly identifies class members and correctly excludes non-members. Minimizing FP ensures that non-class samples are not mistakenly classified as belonging to the target class; whereas minimizing FN ensures that true class members are not wrongly rejected. In addition to being assigned to a specific class in the model, samples may also be assigned to multiple classes or to no class at all (Oliveri, 2017). Based on the values in the confusion matrix, a series of FoMs can be calculated, with sensitivity and specificity being the most used (Oliveri, 2017). Sensitivity represents the model’s ability to correctly identify samples belonging to the target class, while specificity measures the model’s ability to correctly reject samples not belonging to the target class. Both values are dimensionless and range from 0 to 1, or they can be expressed as percentage for easier interpretation. A well-balanced model should aim for high sensitivity (approaching 1 or 100 %) and high specificity to provide reliable classifications (approaching 1 or 100 %). Additionally, the results can be visualized through graphical representations, such as Coomans’ plot (Grassi et al., 2023). Unlike class modelling, PLS-DA and other discriminant analysis methods forcefully assign samples to one of the predefined classes. In these cases, it is more appropriate to calculate accuracy from the confusion matrix. Accuracy is defined as the ratio of the number of samples correctly assigned to their respective classes to the total number of samples considered. Thus, high accuracy (close to 1 or 100 %) means the model is making very few classification errors. However, some authors also calculate sensitivity and specificity when building discriminant models. A commonly used graphical tool for assessing the performance of a discriminant model is the Receiver Operating Characteristic (ROC) curve (Oliveri, 2017). In a good classification model, the ROC curve should show a high discrimination ability between classes. In detail, the curve should rise steeply toward the top-left corner, indicating high TP rate (sensitivity) and low FP rate; the area under the curve (AUC-ROC) should be close to 1, and it should be far from the diagonal line, which represents random guessing (with AUC-ROC = 0.5) (Oliveri, 2017). As for regression models, the consistency of the considered FoM in calibration, cross-validation and prediction phases is crucial for assessing the reliability, robustness, and generalizability of the model.

3.5.4. *Validation of statistical models*

To develop a regression or classification chemometric model, a set of samples with known true values for the responses—such as the content of a specific compound or the origin—must be used during the calibration phase and initial validation steps. Robust validation procedures are essential to ensure reliable and reproducible results when developing regression or classification models. It is recommended to test the model using an entirely independent dataset, such as data from a different production batch, supplier, or harvesting season. Balanced and representative calibration and validation sets were used by Jakes and coworkers (Jakes et al., 2015), Head and coworkers (Head et al., 2024), and Galvan and coworkers (Galvan et al., 2021) (**Supplementary table 3**). Another strategy is to use statistic algorithms, such as Kennard-Stone, to divide the collected data into calibration and test set(Galvan et al., 2021; Krause et al., 2018; McDowell et al., 2019). Furthermore, sample independence should be guaranteed between calibration and validation (Daszykowski et al., 2002). This has been considered by Gunning and coworkers (Gunning et al., 2022) who developed a classification method considering inter-laboratory, batch and season variability when collecting their sample set. Finally, different authors (Gunning et al., 2018, 2020; Gunning, Davies, & Kemsley, 2023; Wu et al., 2021) considered testing the developed models for commercial sample prediction, revealing their reliability in detecting adulterated samples or quantifying specific compound concentrations in real cases. However, in some cases (Giebelhaus et al., 2023) the validation ends with a cross-validation step, which is not an independent validation procedure, as it uses the same samples that were used in calibration to iteratively recalculate the model. This approach is, however, appropriate for selecting model dimensionality, such as the number of latent variables (LVs) in Partial Least Squares Regression (PLSR), as reported by Galvan and coworkers (Galvan et al., 2021). When leave-one-out cross-validation (LOOCV) is performed, the occurrence of overfitting is most likely. Whereas the choice of other strategies, such as Venetian blinds (Giebelhaus et al., 2023; Pajuelo et al., 2023) or batch-based cross-validation (Parker et al., 2014) could guarantee more representativeness, even though external validation is the only strategy to independently test the prediction performance.

4. Alternative innovative methods for data processing/ visualization

Some recent research articles have developed alternative visualization/processing methods and databases/webtools to help the low-field NMR spectra interpretation and analysis.

4.1. Spectral reconstruction/deconvolution

Recently, Matviychuk and co-workers developed an interesting quantum mechanical model to reconstruct the total FID of a mixture spectrum by summing up the single FIDs of each present compound (Matviychuk et al., 2019). In this study, a 43 MHz benchtop Magritek spectrometer and 400 MHz Agilent spectrometer were both used to analyze natural fruit juices to demonstrate the applicability of the method, previously tested on the standard solutions of glucose, fructose, and sucrose. A quantification model, based on the mole fraction of each compound, with a synthetic signal as reference was proposed, showing a good accuracy if compared with the high-field qualification. Similar theoretical algorithms have also been developed for the reconstruction of high-resolution spectra. Especially in the field of biofluids in metabolomics, methods like AMARES, QUEST, AQSES, and Global Spectral Deconvolution helped the interpretation and quantification of complex spectra (Poullet et al., 2008; Ratiney et al., 2004; Vanhamme et al., 1997).

4.2. Visualization methods

In the study of Kemsley and coworkers (Kemsley, 2024) hydrophilic and lipophilic coffee extracts were characterized with both high-field and benchtop NMR, with different processing, and statistical algorithms. First, the authors analyzed the coffee extracts by a 600 MHz spectrometer, highlighting that diterpenoids were difficult to study, since the low signal intensities compared to fatty acids and triglycerides signals. The authors successfully overcame this problem by using a combination of logarithmic compression of relative signal intensities, heatmapping and bucketing. Logarithmic compression allowed for the reduction of strong signals that obscured or reduced the intensity of minor components in the mixture. In this case, all strong fatty acid signals were reduced with respect to smaller signals of diterpenoids. Logarithmic compression of NMR data for multivariate analysis was first described by Parson and Purohit as a powerful method to prepare NMR data for different statistical analysis, such as PCA, Linear Discriminant Analysis (LDA), PLS-DA and more (Mehrotra & Mendes, 2006; Parsons et al., 2007). After logarithmic compression, NMR spectra were turned into a heatmap, where a color replaced the intensity of a signal (Gunning et al., 2022; Parsons et al., 2007). All the different intensities were turned into different colors, allowing the authors to transform all the compressed spectra into a colorful matrix, which better underlined some systematic effects that were impossible to visualize using staked spectra (Mehrotra & Mendes, 2006). A potential issue with combining heatmaps into a single large data matrix is the lack of signal alignment, which can be addressed through correlation-optimized alignment (Gunning et al., 2022). This approach could also help in selecting the most suitable bucketing process for a specific dataset, as it is well known that misleading signals can pose significant challenges during the bucketing process (Harrington & Wang, 2017). Bucketing is a well-known method to analyze spectra of complex mixtures. It involves the systematic separation of the spectrum into small, equal bins, followed by the application of statistical analysis tools to identify which signals varies significantly (Harrington & Wang, 2017). It is noteworthy that these methods were applied to each single element of the dataset and not directly to the whole data matrix. Authors almost fully characterized these coffee extracts using a combination of these three methods (logarithmic compression, heatmapping and bucketing) plus some clustering algorithms. This strategy was applied also for the acquired spectra of coffee lipophilic extract by 60 MHz benchtop spectrometer studying the diterpenoids signals and allowing interspecies differentiation, also through the conversion of log-compressed spectra into a heatmap. Hence, the methods were demonstrated to be powerful tools also in benchtop NMR of complex mixtures. Finally, Hara and coworkers developed a new transfer simulation method from high-field NMR to low-field NMR based on Short Time Fourier Transform and T_2* reconstruction for ^{1}H NMR visualization (Hara et al., 2022). They tested this method on different food matrices like tuna, yogurt, and boiled carrots, demonstrating the efficacy of this tool to recover T2 relaxation time from benchtop NMR data and the feasibility of data transfer despite the significant difference in signals dispersion between low-field and high-field NMR.

4.3. Webtools and databases

Chikayama and coworkers developed a free webtool called FoodPro to evaluate correlations and covariance in the NMR spectra of food (Chikayama et al., 2016). FoodPro is a webtool developed in 2016 based on a small database composed by 236 aqueous and 131 hydrophobic extracts obtained with a 60 MHz benchtop spectrometer, roughly classified in two sections: fish and vegetables. FoodPro can analyze those foods considering also types of processing, cooking, fermentation, and storage, linking together these characteristics with tasting and hardness, but also estimating correlation and covariance of spectra. A more general webtool for NMR is InterSpin, developed by Yamada and coworkers in 2019 (Yamada et al., 2019). InterSpin is a pre-processing free webtool that works with many different spectra types, from low- to high-field spectra, different species range, from small to macromolecules, and different samples, like food, solid matter, and environmental samples. Authors put many efforts to improve sensitivity from spectra integration and peaks separation. For the first issue authors developed a new algorithm called SENSI1D, based on the integration of multiple spectra without additional measurement, while for the second issue the PKSP algorithm, a multivariate method for spectral decomposition, was created. Another interesting webtool for metabolomics and complex mixture analysis is called SpinCouple, developed by Kikuchi and coworkers (Kikuchi et al., 2016). SpinCouple has a database fully composed by 2D ^{1}H—^{1}H -JRES spectra from 598 different metabolites, including *J*-couplings and ^{1}H chemical shifts. SpinCouple can be used also for quantification. Authors successfully quantified different amino acids, organic acids, and sugars in different biological mixtures. However, due to the proposed query tolerance of 0.83 Hz for *J*-coupling and 0.018 ppm for chemical shifts, the webtool is reasonably applicable only to high resolution NMR spectra.

5. Benchtop NMR applications

The current review delves into the scientific literature of the last ten years about the use of benchtop FT-NMR spectroscopy applied to the analysis and control of food production. Two major areas of application come out: adulteration detection with eighteen works available (Table 1 and Table 2), and quality control applications in both static or continuous mode with fifteen works available (Table 3 and Table 4).

Table 1
Benchtop FT-NMR in quality control and chemical characterization in static mode.

Food category	Benchtop NMR Instrument and ^{1}H experiment parameters[1]	Approach	Sample preparation[2]			Quantified compounds	Quantification method	Aim	Reference
			US	**DS**	**NDS**				
Fermented beverages	- MHz: 60 MHz - scans: 16 - texp: ~8 min	Metabolomic	X		X	Alcohols, organic acids, sugars	Internal standard	Quantitative compositional analysis of wine and other fermented beverages by Benchtop NMR. Moreover, important physicochemical parameters like total acidity, soluble solids, and alcoholic force of the samples were also determined.	(Matviychuk et al., 2021)
Alcoholic beverages	- MHz: 45 MHz - scans: 16 - T: 25 °C	Targeted			X	Alcohol	Internal standard and standard addition	Quantitative analysis of alcohol content in several alcoholic beverages by benchtop NMR. A comparison among internal standard and standard addition analytical quantification methods was also performed.	(Isaac-lam, 2016)
Milk	- MHz: 43 MHz - scans: 64 - texp: ~7 min - T: 29 °C	Metabolomic	X			Lactose, glycerol, fat	Internal standard	Quantification of lactose, glycerol and fat in milk and discriminative analysis on 36 milk samples of different type, milk source, and geographic origin by Benchtop NMR analysis and Artificial Neural Network (ANN) model	(Soyler et al., 2021)
Ham	- MHz: 80 MHz - scans: 256 - texp: ~60 min - T: 25 °C	Metabolomic		X		MUFA, PUFA, SFA	Relative quantification	Benchtop NMR spectroscopy to analyze the lipid profile of Iberian hams as a determinant of quality. In particular benchtop NMR was successfully used to classify Iberian ham according to the diet of pigs.	(Pajuelo et al., 2023)
Hop	- MHz: 43 MHz - scans: 60 - T: 20 °C	Targeted		X		α:β-acids ratio	Calibration curve	Determination of bitter acid profile of lupulin glands by benchtop NMR analysis as useful method to develop for hops breeders at field stations for hop screening.	(Killeen et al., 2017)
Cinnamon	- MHz: 60 MHz - scans: 2000 - texp: ~2 h - T: 37 °C	Targeted		X		Coumarin, cinnamaldehyde	Internal standard	Quantification of coumarin and cinnamaldehyde in cinnamon by benchtop NMR. For dietary supplements, this approach allowed to identify samples containing a higher quantity of hepatotoxic coumarin and thus presenting a potential risk to the health of consumers.	(Wu et al., 2021)
Edible oils	- MHz: 60 MHz - scans: 32 - texp: ~5 min - T: 35 °C	Metabolomic	X			MUFA, PUFA, SFA	Relative quantification	Determination of MUFA, PUFA and SFA composition of different edible oils through calibration with the reference composition values obtained by GC-FID analysis of FAMEs and applying a multiple linear regression method	(Gunning et al., 2020)
Edible oils	- MHz: 43 MHz, 60 MHz - scans: 4 - texp: ~30s - T: 28.5 °C, 26.5 °C	Fingerprinting	X			MUFA, PUFA, SFA, Iodine Value	/	Determination of MUFA, PUFA, SFA and Iodine Value of various edible oils through regression models based on linear PLSR and nonlinear SVR algorithms calibrated with official GC-FID method. Three NMR instruments performance, 43, 60 and 400 MHz NMR spectroscopy, were compared.	(Galvan et al., 2021)

[1] MHz: proton frequency of the spectrometer; scans: number of collected scans; texp: total acquisition time; T: spectrometer temperature.

[2] US: Untreated sample; NDS: Non deuterated solvent; DS: Deuterated solvent.

Table 2
Benchtop FT-NMR for online processes monitoring.

Topic	Aim	Field strengths	Reference
Real time monitoring of enzymatic hydrolysis	Benchtop NMR was used to monitor both online and offline hydrolysis of fishery and to analyze the obtained products. The NMR measurements were performed for enzymatic hydrolysis reactions on red cod, salmon and shrimp.	43 MHz	(Anderssen & McCarney, 2020)
Online monitoring of sucrose hydrolysis	Online monitoring of sucrose hydrolysis by benchtop NMR has been successfully performed and the kinetic constant was extrapolated by the fractional conversion model.	43 MHz	(Soyler et al., 2020)
Online monitoring of lactose hydrolysis	Online monitoring of lactose hydrolysis in the industrial production of lactose-free milk by benchtop NMR has been successfully performed and the kinetic constant was extrapolated by the fractional conversion model.	43 MHz	(Soyler et al., 2021)
Online monitoring of ethanol during fermentation process	Online monitoring of the fermentation process of a barley malt mash by benchtop NMR through quantification of ethanol by internal standard method with TSP.	60 MHz	(Burkhardtsmaier et al., 2021)
Quantitative ^{31}P NMR analysis	NMR ^{31}P lipidomic has been applied to detect, identify and quantify several types of phospholipids in mixture using benchtop NMR spectroscopy.	43 MHz, 80 MHz	(Gouilleux et al., 2019)
Monitor of lipid accumulation in microalgae	Monitor lipid accumulation in microalgae through the integration of selected lipid peak in a short timeframe.	43 MHz	(Bouillaud et al., 2019)
Monitor of lipid accumulation in microalgae	Benchtop NMR has been connected to a photobioreactor and the real time measure, in a non-invasive way, of the total lipid concentration directly in microalgae cells has been performed.	43 MHz	(Bouillaud et al., 2020)
pKa determination	A new method for pKa determination by benchtop NMR is proposed. The method involves creating a pH gradient directly within the NMR tube and using a device to vertically shift the NMR tube for measurements at various pH values.	43 MHz	(Putko et al., 2024)

5.1. Benchtop NMR in chemical characterization, quality control and online process monitoring

Benchtop NMR has the potential to make a significant contribution to improve quality control. The chemical characterization of foods helps determine its composition and plays a crucial role in quality control. It also helps optimize processing methods and ensure compliance with regulatory standards.

By benchtop NMR the analysis can be performed in both static and continuous mode. Eight works regarding quality control in static mode (Table 1) and eight works in continuous mode (Table 2) are discussed in the paragraphs below.

5.1.1. Chemical characterization and quality control

Benchtop FT-NMR analysis is widely used for the chemical characterization and the identification of key components in beverages, dairy products, meat products, spices, aromatic plants and edible oils. The analysis can serve several purposes from compound quantification to quality control.

5.1.1.1. Aromatic plants. Beer brewing industries have a great interest in developing products with specific aromas and flavors. The peculiarity of the final product is the combination of these two sensorial characteristics. Bitterness is mostly attributed to the β -acids produced by hops whereas aromas are due to volatile sesquiterpenes and monoterpenes. Killeen and coworkers (Killeen et al., 2017) have reported the chemical characterization of hop cultivars carried out using both high-field and benchtop NMR. High-field NMR has allowed the quantification of α-acids using the integrals of humulone, cohumulone and adhumulone signals, and β-acids using the integrals sum of major and minor tautomers of adlupulone, colupulone and lupulone. The metabolites have been quantified by the corresponding calibration curves. The α:β-acids ratio together with the cohumulone content have been used to identify differences among cultivars based on PCA. The same methodology has been followed using benchtop NMR with the same quantification approach. The calculation of the α:β-acids ratios was possible since the signals of the α- and β-acids turned out to be resolved, whereas the resolution of cohumulone and admuhulone signals was not suitable to have signals quantification. Therefore, a preliminary use of benchtop NMR for hops breeders to check the bitter acids profile has been proposed.

5.1.1.2. Dairy products. Another sector of high interest is the milk production. In the Soyler and coworkers investigation, the discrimination of 36 milk samples according to the geographical origin (France or Turkey), the heat treatments (pasteurized or UHT), and the productive processes (organic or conventional) has been carried out using a metabolomic benchtop NMR analysis coupled with ANN (Soyler et al., 2021). The signals of glycerol, lactose and fats have been integrated with respect to imidazole signal, used as an internal standard. Using this approach, the integrals of the three compounds combined with the metadata about production type and processing, succeeded in the classification of the samples according to their origin. Similarly, good prediction resulted for heat treatment classification ($R^2 = 0.85$). However, a few misclassified samples were predicted for production type

Table 3
Benchtop FT-NMR in adulteration detection of edible oil.

Food category	Adulterants	Benchtop NMR Instrument and ^{1}H experiment parameters[1]	Approach	Sample preparation[2]			Chemometrics method	Outcome (% adulteration detection)	Reference
				US	**NDS**	**DS**			
Extra virgin olive oil	Hazelnut oil	- MHz: 60 MHz - scans: 16 - texp: ~10 min - T: 37 °C	Targeted		X		Linear regression	~13 %w/w	(Parker et al., 2014)
			Fingerprinting		X		PLS	~11 %*w*/w	
Extra virgin olive oil	20 different non-olive oils	- MHz: 60 MHz - scans: 16 - texp: 1.6 min - T: 32 °C	Fingerprinting			X	PCA, PLS	~10 %*v*/v	(Giebelhaus et al., 2023)
Extra virgin olive oil	Sunflower and soya oils	- MHz: 60 MHz - scans: 32 - texp: ~5 min	Fingerprinting	X			PCA, PLS-DA, RF, NN-OCC	10 % w/w	(Gunning et al., 2022)
Extra virgin olive oil	Hazelnut oil	Ultrafast 2D COSY experiment	2D experiments		X		PCA, PLS	10 %w/w	(Gouilleux et al., 2018)
Argan oil	Sunflower oil	- MHz: 60 MHz - scans: 32 - texp: ~5 min - T: 35 °C	Targeted	X			Ternary plot	20 % w/w	(Gunning et al., 2020)
			Fingerprinting	X			Nearest neighbor outlier detection method	20 % w/w	
Argan oil	Sunflower and soya oils	- MHz: 60 MHz - scans: 32 - texp: ~5 min	Fingerprinting	X			PCA, PLS-DA, RF, NN-OCC	20 % w/w (for adulteration with soya oil)	(Gunning et al., 2022)
Cold pressed rapeseed oil	Refined rapeseed oil and refined sunflower oil	- MHz: 60 MHz - scans: 16 - texp: ~4 min - T: 25 °C	Fingerprinting		X		PLS-DA, SIMCA, LDA-KNN, LDA-SVM, PLS-R	12.2 % w/w for refined sunflower oil and 74 % w/w for refined rapeseed oil	(McDowell et al., 2019)
Perilla oil	Soybean oil	- MHz: 43 MHz - scans: 32 - texp: ~5 min - T: 25 °C	Metabolomic			X	Two-tailed Student's *t*-test, Pearson's correlation test	6 % *v*/v	(Kim et al., 2018)
Patchouli essential oils	Miscellaneous adulterants	- MHz: 60 MHz - scans: 32 - texp: ~2 min	Fingerprinting	X			Similarity analysis based on Mahalanobis distance	20 % w/w	(Krause et al., 2018)
Edible oils	Other edible oils	- MHz: 43 MHz, 60 MHz - scans: 4 - texp: ~30s - T: 28.5 °C, 26.5 °C	Fingerprinting	X			PCA, PLSR, SVR	15–20 % v/v	(Galvan et al., 2021)

[1] MHz: proton frequency of the spectrometer; scans: number of collected scans; texp: total acquisition time; T: spectrometer temperature.

[2] US: Untreated sample; NDS: Non-deuterated solvent; DS: Deuterated solvent.

classification together with a low R^2 (0.42) in the production type model. The reliability of the developed model is poor, especially related to the sample size ($n = 36$) since machine learning models are highly susceptible to overfitting, and small size datasets may fail to capture the total variability. Moreover, particularly in the case of milk, many other factors can alter the profile of the product including breeding methods, and seasonal variations. The model demonstrated the potential of benchtop NMR spectra for distinguishing between milk samples and offered valuable insights for a more extensive authentication study.

5.1.1.3. Beverages. Ethanol concentration in a variety of beverages has been also investigated using two different quantification methods, The internal standard and standard addition methodologies in benchtop NMR and in a 400 MHz instrument have been compared analyzing alcoholic beverages with a 9.0–49.5 % *v*/v range of ethanol concentration (Isaac-lam, 2016). For benchtop NMR, the internal standard method consisted of the addition of acetic acid or acetonitrile to the spirits in a concentration of 10 % v/v. In contrast, the standard addition method consisted in adding a known amount of ethanol to the spirits meant to correct matrix effects.. The added absolute ethanol varied from 0 % to 50 % of the total volume and the internal standard has been added in a concentration of 5 % v/v. The internal standard method resulted the best method for both instruments due to the highest accuracy. The excellent linearity results (R^2 0.989, 0.995 for the methyl and methylene groups,

Table 4
Benchtop FT-NMR in adulteration detection of various foodstuffs.

Food category	Adulterants	Benchtop NMR Instrument and ^{1}H experiment parameters[1]	Approach	Sample preparation[2]			Chemometrics method	Outcome (% adulteration detection)	Reference
				US	**NDS**	**DS**			
Saffron	*Arnica montana*, *Calendula officinalis*, *Carthamus tinctoris*, *Curcuma longa*, *Capsicum annuum*, *Santalum* genus and tartrazine	- MHz: 60 MHz - Scans: 256 - texp: 36 min - T: ~35 °C	Fingerprinting			X	PCA, DD-SIMCA, NN-OCC and IF	5–30 % w/w	(Gunning et al., 2023)
Honey	Syrups: corn, brown rice, glucose, sugar cane, and wheat	- MHz: 43 MHz - scans: 8 - texp: 8–10 min - T: 25 °C	Targeted			X	Linear regression, Ternary plot	5 % w/w	(Rhee et al., 2023)
Honey	Syrup: glucose, maple and invert sugar	- MHz: 60 MHz - scans: 64 - texp: 10 min - T: 25 °C	Fingerprinting			X	PCA, HCA and SIMCA, PLS-R	0.96 % w/w in monofloral honeys, 1.55 % w/w in polyfloral honey, 1.93 % w/w in honeydew honeys	(Ozbay et al., 2024)
Arabica coffee	Robusta coffee	- MHz: 60 MHz - scans: 256 - texp: 40 min - T: 37 °C	Targeted			X	Linear regression, Matched filtering test statistic	10 %–20 % w/w	(Defernez et al., 2017)
Arabica coffee	Robusta coffee	- MHz: 60 MHz - scans: 256 - texp: 40 min - T: 37 °C	Targeted			X	Linear regression	1–2 % w/w	(Gunning et al., 2023; Gunning et al., 2018)
Beef	Horse meat	- MHz: 60 MHz - scans: variable - texp: variable - T: 37 °C	Targeted		X	X	Naïve Bayes classification model, PCA		(Jakes et al., 2015)
White wine vinegars	Spirit vinegar	- MHz: 60 MHz - scans: 32 - texp: ~5 min - T: 25 °C	Fingerprinting	X			PCA, LDA	5 % v/v	(Grassi et al., 2024)

[1] MHz: proton frequency of the spectrometer; scans: number of collected scans; texp: total acquisition time; T: spectrometer temperature.

[2] US: Untreated sample; NDS: Non-deuterated solvent; DS: Deuterated solvent.

respectively), demonstrated that benchtop NMR could be used for this application. Having met the conditions previously mentioned to choose benchtop NMR for analysis, a good quantification strategy and processing software are essential. The integration method can sometimes give inaccurate results; this sets the need to analyze the factors that influence the detection and quantification of each analyte according to each matrix and the matrix effect. Computer-based integration models offer advantages in this area since they allow spectral deconvolution and are less prone to errors since they do not require human manipulation of the spectra. Using computer-based integration models, it was possible to quantify peaks that were obscured among them, something that cannot be accomplished even with advanced algorithms like global spectral deconvolution (qGSD) in some cases. This methodology has been applied to determine the concentration of analytes in wine samples obtaining errors lower than 10 % and, in some cases, lower than 5 % when the analytes were in high concentration like the case of ethanol.

In another study on wine and other fermented beverages, all the major components of each beverage have been identified and quantified using a 60 MHz benchtop NMR instrument (Matviychuk et al., 2021). The levels of ethanol, glycerol, methanol, 2,3-butanediol, acetic acid, succinic acid, malic acid, lactic acid, citric acid, tartaric acid, sorbitol, maltodextrins, sucrose, fructose, and glucose have been determined by carrying out a complete chemical characterization and the internal standard quantification method on samples in their untreated form and after drying and solubilization in non-deuterated solvent. Moreover, in this study benchtop NMR has been also applied to approximate important aggregate parameters, such as total acidity and alcoholic strength.

5.1.1.4. Spices. Cinnamon is a spice typically used for cuisine around the World. It is mainly subdivided into two types, namely, true or Ceylan cinnamon, and Cassia cinnamon, with diverse botanical origins. True cinnamon possesses low levels of coumarin (around 0.004 % *w*/w), while Cassia cinnamon levels are around 1 %, representing a potential risk for consumers due to its hepatotoxic activity. Cinnamon samples and food supplements claiming to contain cinnamon in the ingredient list were analyzed by both high-field and benchtop NMR through a targeted approach (Wu et al., 2021). The principal compounds in the samples were identified by high-field NMR. For the analysis in benchtop NMR, limits of detection and quantification played a critical role. The authors observed a 60-fold decrease in the signal-to-noise ratio when analyzing by benchtop NMR, hence requiring an acquisition time of over 100 h to obtain results comparable with the high-field instrument. This was a limiting factor in the use of benchtop NMR for completely quantitative approaches. The high-field instrument results allowed the detection of false food supplements where not even the signals of cinnamaldehyde or coumarin were detected (opposite to the label claims). However, this was not based on a mathematical model but rather on the presence/absence of the signals found in the true samples. The benchtop NMR data explored by PCA showed diverse groups based on the coumarin and eugenol content. Thus, a PLS model was constructed with the benchtop NMR spectra of standard (*E*)-cinnamaldehyde and coumarin ($R^2 = 0.98$) and used to test commercial samples. Although it was not a complete quantification and a quite small dataset, the coumarin and cinnamaldehyde content in the samples could be predicted by benchtop NMR analysis with a good linear fit with respect to the high-field NMR results. This served as a fast approach to determine the authenticity of food supplements in the market.

5.1.1.5. Meat products. As the complexity of food matrices increases, so equally do their spectra and signal overlap, that is why initially only simple matrices were analyzed by this technique. Complex matrices require more pre-treatment steps to extract the analytes of interest instead of being analyzed in their raw/natural state. This is the case of Iberic dry-cured ham analyzed by Pajuelo (Pajuelo et al., 2023). The authors proposed a benchtop NMR approach to classify Iberic dry-cured according to the quality labels defined by the Spanish government. Indeed, the high quality commodity distinguished into quality categories according to the pig feeding system and its effect on the fat composition. GC-FID has been the most employed method for the determination of fatty acids after methylation in an acidic medium. The authors showed by a benchtop NMR approach that the diagnostic peaks of fatty acids were easily identified, except for the triplet belonging to omega-3 polyunsaturated fatty acids because of an overlap with the major signal of methyl groups of all fatty acids. Regarding glycerides, only the peak of the methylene group bound to the OH group in 1,2-diacylglycerides was identified in benchtop NMR, requiring high-field instruments to detect all the missing signals. Hence, the quantification of MUFA, PUFA, and SFA in the lipidic fraction of Iberian hams was successfully performed. However, benchtop NMR spectroscopy could not accurately quantify the ratio of TAG, 1,2-DAG, 1,3-DAG, and free Fatty acids due to the low resolution. The developed methodology helped to detect how the feeding system with grass and acorn produced statistically significant differences in the SFA content. The results from the quantification were comparable with those obtained in the high-field instrument, except for compounds in low concentration that could not be quantified in benchtop NMR by this approach, always reminding the need to choose the analytes of interest carefully.

5.1.1.6. Edible oils. Regarding edible oils, two studies demonstrated the potential of benchtop NMR, used in both metabolomic and fingerprinting approaches, combined with chemometric tools to determine essential quality parameters of edible oils.

Gunning and coworkers determined the MUFA, PUFA and SFA composition through calibration with the reference composition values obtained by GC-FID analysis of FAMEs and applying a multiple linear regression method (Gunning et al., 2020). MUFA and PUFA were determined as percentages of the TAG composition through a targeted approach, by integrating the regions of bis-allylic protons (2.54–3.08 ppm), olefinic protons (4.91–5.55 ppm), the double bond protons near the terminal CH_3 in α-linolenic acid (0.96–1.05 ppm), and the glyceride protons arising from protons attached to positions 1 and 3 of the glycerol backbone present in all TAGs (3.60–4.57 ppm). Moreover, the SFA content was also determined through the equation (SFA = 100 – PUFA – MUFA). Applying this approach to a collection of argan oils, typical values for MUFA and PUFA contents of 47 and 32 %w/w were obtained giving information with accuracy and precision suitable for ‘typical value’ food labelling.

The same objective has been pursued by Galvan and coworkers who developed a regression model for MUFA, PUFA, SFA and iodine value determination based on full spectra chemometrics analysis on several edible oils. The authors compared the potential of 43, 60 and 400 MHz NMR spectroscopy and of two calibration models based on linear PLSR and non-linear SVR algorithms. The models obtained with the low-field spectra were equivalent to those obtained by the high field device, and both presented reproducibility values lower than the minimum accepted by the official methods based on GC-FID analysis.

5.1.2. *Online process monitoring*

Both high-field and benchtop NMR spectroscopy are widely applied to control different kinds of processes, offering the possibility to have information about food processes or chemical reactions also online, and this represents an advantage that is not reachable by many other methods (Giraudeau & Felpin, 2018; Levitt, 2008; Sundekilde et al., 2018). Process control is crucial to ensure safe, high-quality products, to comply with regulations, and to optimize production efficiency. It involves monitoring and adjusting critical parameters throughout the production process to minimize hazards and maintain consistency, leading to a reliable food supply chain. The current paragraph investigates the available research articles on the application of benchtop NMR instruments in continuous mode in food industry processes.

5.1.2.1. Hydrolysis process monitoring. The first application of benchtop online monitoring applied to sea foods has been reported by Anderssen and coworkers in 2020 (Anderssen & McCarney, 2020). Five enzymatic hydrolysis processes on sea foods (red cod fillet, salmon fillet and unpeeled shrimps) have been used monitoring the process at regular intervals of five minutes for one hour. To evaluate the reaction rate of each enzymatic hydrolysis, the first order kinetics equation has been used with the concentrations variation of soluble proteins during hydrolysis, using the following equation to obtain the kinetic constants:

$$A = A_f - A_0 e^{-kt}$$

Where A_f is the final NMR signal intensity, A_0 is the difference between initial and final signal intensities, and t and k are respectively time and kinetic constant. To detect proteins, the WET-NOESY sequence has been used to suppress the water signal.

The benchtop NMR methodology has been also applied for on-line monitoring of sucrose hydrolysis to glucose and fructose, under the action of a specific invertase enzyme (Soyler et al., 2020). Experiments have carried out on a 43 MHz benchtop Magritek spectrometer with a 0.5 mL/min flow rate at 29 °C temperature. WET-180-NOESY pulse sequence has been used for water signal suppression, TSP has been used as internal standard, and the sucrose signal at 5.48 ppm has been chosen for sucrose monitoring. To extrapolate the kinetic constant of the sucrose conversion, the following equation was applied:

$$\frac{C - C_\infty}{C_0 - C_\infty} = e^{-kt}$$

where k represents the rate constant, C is the concentration at time t, C_0 represents the initial concentration and C_∞ is the equilibrium concentration.

The lactose hydrolysis in the production of lactose-free milk (Soyler et al., 2021) has been also monitored by benchtop NMR. Lactose is the main sugar of milk, composed of glucose and galactose, and is responsible for lactose intolerance in consumers who do not produce lactase in their organisms. Nowadays, new technologies allow the commercialization of lactose-free milk and milk derivatives, constituting an option for consumers. The hydrolysis of lactose has been monitored through online benchtop NMR following the signal of the β anomeric proton of lactose at 4.4 ppm and knowing that there is a constant α:β ratio. Spectra have been recorded every 6 min for 240 min and concentrations of lactose has been calculated using imidazole as internal standard. The procedure has been firstly optimized on a lactose solution and then on in real milk samples. The kinetic constant of the process has been calculated by the fractional conversion model. The developed method showed a high potential to be adapted for industrial processes.

5.1.2.2. Fermentation processes monitoring. The concentration of ethanol in real time during barley malt mash fermentation has been monitored for 93 h using 3 different methodologies, namely, benchtop NMR, UV, and a commercial kit (Burkhardtsmaier et al., 2021). After 93 h, benchtop NMR has showed the highest reproducibility with respect to the commercial enzymatic kits. The values obtained by UV measurement were not in agreement with date from the other techniques and the SD could not be calculated. Therefore benchtop methodology turned out to be a useful tool for the rapid control of fermentation process.

5.1.2.3. Lipid concentration monitoring. Bouillaud and coworkers applied a 43 MHz Magritek benchtop NMR for the on-line monitoring, quantification and characterization of microalgae lipid fraction directly in the bioreactor (Bouillaud et al., 2019, 2020). W5 version of WATERGATE or WET-180-NOESY has been applied as water suppression method for the spectra acquisition. Moreover, the Benchtop NMR data have been compared with the conventional analysis methods, HPLC and GC, demonstrating good quantitative results with the advantages of real-time calculation.

In the field of lipidomics, benchtop NMR has been also applied for phospholipid identification and quantification, with the work of Gouilleux and coworkers as the first application of ^{31}P benchtop NMR (Gouilleux et al., 2019). In this work, authors shown how benchtop NMR had the capacity to recognize and quantify many different phospholipids, using both 1D ^{31}P-{^{1}H} and 2D ^{1}H—^{31}P TOCSY experiments with ^{31}P detection. Finally, they proposed two alternative benchtop NMR methods for phospholipids quantification. In the first approach DPP was used as reference compound with the addition of DOTAREM to reduce the relaxation time of DPP, whereas in the second approach an external calibration curve for each phospholipid of interest was used through 2D ^{1}H—^{31}P TOCSY experiment. The first approach had the higher accuracy (medium accuracy 5 %), with respect to the second one that suffered from the line broadening caused by DOTAREM.

5.1.2.4. Direct pKa measurement. Benchtop NMR methodology has been also used for direct pK_a measurements (Putko et al., 2024). A devise with a pH gradient directly along the NMR tube has been developed: the pK_a of L-tyrosine, 2,6-lutein as well as of two real samples from the food industry has been measured.

5.1.3. Consideration on quality control by benchtop NMR instrument

The studies here discussed show that quality control is one of the two major sectors of benchtop NMR applications in the food industry in both static and continuous modes. The static mode analysis for quality control, as previously discussed and reported in Table 1, has been mainly carried out using a targeted NMR approach with the aim to characterize and quantify the main metabolites of the foodstuff under investigation. The metabolites were quantified mainly by absolute quantification, through the internal standard method, or relative quantification. Moreover, one article has applied quantification by means of a calibration curve.

On the other hand, the continuous mode allows the online monitoring of reactions, hydrolysis processes and lipid accumulation. This approach could be applied in the future for many other purposes such as the optimization of fermentation processes where the fermentation depends on monitoring sugar consumption and the production of metabolites like alcohol and acids; monitoring enzymatic reactions in food processing such as in the production of syrups from starch; sugar reduction for development of ‘low-calorie’ or sugar-free products; tracking the Maillard reaction in food processing to optimize cooking conditions to achieve desired flavor without over-browning; controlling the lipolysis in fat-based products to control the flavor profile, among other applications.

In the continuous mode, the solvent suppression method has a critical role since the experiments is conducted in non-deuterated solvents. Hence it is of great importance the choice of the solvent suppression sequence. The main sequences rely on a selective suppression of the corresponding resonance or on the selective excitation of all the resonances except the solvent one. The discussed articles used different solvent suppression methods to ensure a proper decrease of the water signal with minimal impact on nearby peaks. Some examples are WATERGATE-5 (Bouillaud et al., 2019, 2020), an improvement of the original WATERGATE (WATER suppression by GrAdient-Tailored Excitation) pulse sequence, WET-180-NOESY (Soyler et al., 2020, 2021) and WET-NOESY (Anderssen & McCarney, 2020) pulse sequences, where a WET block combines a train of selective shaped pulses with spoil gradients to selectively disperse the longitudinal component of the solvent magnetization (Gouilleux et al., 2017).

In conclusion, quantitative online benchtop NMR spectroscopy, thanks to its rapid and non-invasive nature, offers a promising alternative to the traditional analytical methods currently applied in the food processing industry, which often require lengthy procedures and sample pre-treatment. In fact, with its high linearity between absolute signal area and sample concentration, it can be seamlessly integrated into factory process lines.

5.2. Benchtop NMR for adulteration detection

Food adulteration has been practiced for a long time and has become increasingly sophisticated in recent years posing risks to public health, eroding consumer trust, and undermining the integrity of the global food supply chain (Kamal & Karoui, 2015). High value foods and ingredients are particularly vulnerable to adulteration. The partial or complete substitution of original substances with cheaper, more readily available alternatives is the most common practice employed by fraudsters. Other common adulteration practices are the addition of small amounts of a non-authentic substance to mask inferior quality ingredients, and the removal or intentional omission of an authentic and valuable constituent in a food product or food ingredient (Johnson, 2014). The economic and social consequences of food adulteration are far-reaching. Consumers frequently purchase adulterated products without knowledge, while regulatory authorities face difficulties monitoring and preventing such practices. This loss of trust impacts both the industry and producers. Hence, ensuring food authenticity and detecting adulteration have become critical issues in quality control and food safety. Therefore, developing cost-efficient, easily implementable, rapid, and reliable methods for assessing the authenticity of the most adulterated foods is crucial. Benchtop NMR can represent an interesting analytical method to detect a range of non-authentic food products. This section will examine the current role of benchtop NMR in detecting food adulteration and explore practical solutions to address this pressing issue. A high number of articles is available in the literature regarding the adulteration detection by benchtop NMR in many edible oils (ten articles are discussed in paragraph 4.2.1.). Other relevant adulterations among the most consumed items in the market that are successfully unraveled by benchtop NMR analysis included saffron, honey, coffee, meat products and vinegar (seven articles are discussed in paragraph 4.2.2.).

5.2.1. Adulteration of edible oils

Adulteration in edible oils market mainly encompasses the addition of different oils in the declared oil. Usually, expensive oils, such as olive oils, are adulterated by adding cheaper oils, such as hazelnut oils or other seed oils. Hence, adulteration detection and fraud prevention in edible oil market is of high interest for the economic value of these commodities. Benchtop NMR instruments ranged from 43 MHz up to 60 MHz have been used to detect adulteration in extra virgin olive oil, frying oils, perilla oils, argan oils, patchouli oils, rapeseed oils, seed oils and other vegetable oils (Table 3).

Edible oils sample preparation for high field NMR normally consists in the dilution of the edible oil in $CDCl_3$ solvent, with a small addition of DMSO-d_6 (Dais & Hatzakis, 2013; Maestrello et al., 2022). In benchtop NMR the same dilution protocol could be applied to reduce the oil viscosity and lead to sharper spectral peaks. Moreover, in benchtop NMR the edible oil dilution could be performed also with non-deuterated solvents, which are cheaper than the deuterated ones, thanks to the external lock system. It is noteworthy that benchtop NMR can analyze also neat oil avoiding expending time on sample preparation, costs and the environmental concerns associated with solvents. In fact, since benchtop NMR spectra inherently exhibit low resolution, they are much less affected by sample preparation steps.

Regarding the NMR experiment, to reduce the edible oil samples' viscosity, the known cause of line broadening, and ensure consistency across measurements, the temperature inside the probe during acquisition is commonly set over 30 °C, for olive oils and argan oils and around 25 °C for the other types of edible oils like rapeseed oil and perilla oil. Edible oil spectra were typically acquired using a 1D ^{1}H experiment without solvent suppression using a small number of transients (16–32 scans) and with a total acquisition time of less than 5 min, demonstrating the technique's suitability for rapid industrial quality control. One article applied 2D experiments to solve the issue of the overlapping peaks in 1D spectra. Another interesting aspect is the type of NMR spectral processing approach employed. Many studies used a fingerprinting approach, while two studies adopted a targeted/fingerprinting approach and one study a completely targeted approach. Additionally, a variety of chemometric methods were applied to the processed NMR spectra to unravel non-authentic samples.

5.2.1.1. Olive oils. The first article that used benchtop NMR to detect frauds was published in 2014 by Parker and coworkers regarding the adulteration detection of extra virgin olive oil with hazelnut oil (Parker et al., 2014). Using a Pulsar 60 MHz ^{1}H NMR spectrometer, the addition of hazelnut down to a minimum level of 13 % has been detected. A targeted approach has been used measuring the internal ratio of the olefinic-to-glyceride peak areas (the signal at ~4.2 ppm arises from ^{1}H nuclei attached to carbon at positions 1 and 3 on the glycerol backbone and the peaks at ~5.2 ppm arise from all the ^{1}H nuclei attached to carbons involved in a double bond). The lack of other clearly defined isolated peaks in benchtop NMR spectra of olive oils promoted the use of chemometric techniques that analyze the entire spectrum. Hence, the limit of detection has been lowered to 11.2 % *w*/w through the application of a fingerprinting approach on the full NMR spectra of a set of independent test samples by PLS chemometric analysis. Comparing with high field NMR studies, Mannina et al. reported the hazelnut oil adulteration until a limit of detection of 10 %w/w using a 600 MHz spectrometer: a targeted approach based on the quantification of five compounds(linolenic acid, saturated acid, squalene, β-sitosterol and linolenic acid) has been used including LDA and a multiple regression model as statistical tools (Mannina et al., 2009).

The hazelnut oil adulteration in olive oils has been also studied by 2D experiments (Gouilleux et al., 2018). An Ultrafast COSY experiment, based on a homemade pulse sequence, with a total experimental time of 2.4 min for 72 scans on mixtures of olive oil with different percentages of hazelnut oil has been acquired. The aim of this fast 2D NMR spectra was to solve the issue of the overlapping peaks in 1D spectra enabling access to more accurate and detailed information compared to that obtained in one-dimensional NMR spectra. The correlations related to unsaturated fatty acids, polyunsaturated fatty acids and glycerol were key factors to screen the fatty acid composition of the different vegetable oils and are integrable in the 2D spectra. However, for the chemometric analysis, all the peaks present on the 2D spectrum have been considered (metabolomic approach applied to 2D experiment). In particular, the average 2D-peak volume for thirteen signals was computed and normalized by the sum of all the peak volumes. Finally, a PLS model was performed and the detection from 10 %w/w to 100 %w/w of hazelnut oil in olive oil was successfully predicted.

A fingerprinting approach (Gunning et al., 2022) has been applied to detect different grades of sunflower and soya in olive oils . Samples have been analyzed in their pure form, without further preparation, and the obtained spectra have been normalized with various methods to remove unwanted systematic variation: two well-established spectral normalization methods namely piecewise direct standardization (PDS) and standard normal variate (SNV) correction methods, and by rank transformation (RT) method that is less commonly applied on spectral data. Three different classification models have been employed: Partial Least Squares Discriminant Analysis (PLS-DA), Random Forests (RF) and a One Class Classification approach (NN-OCC). Applying the model obtained by the Random Forest method using magnitude data and RT pretreatment, a detection limit of upwards of 10 %w/w has been achieved. Moreover, these findings have been validated with multiple spectrometers in two different laboratories.

Recently, a 60 MHz benchtop NMR (Giebelhaus et al., 2023) has been used to analyze 20 different non-olive oils that could be added fraudulently to olive oils A fingerprinting approach has been applied performing the spectra alignment through icoshift algorithm and PLS regressions: the model allows the detection of most of the used non-olive oil adulterants in extra virgin olive oil below 10 %*v*/v.

5.2.1.2. Edible oils. Besides olive oils, other high market value edible oils, such as perilla oil, argan oil, cold pressed rapeseed oil and patchouli essential oils, are often subjected to adulteration. Benchtop NMR methodology has been used for the adulteration detection of these commodities.

For instance, in the Gunning and coworkers paper (Gunning et al., 2020), the targeted quantification of MUFA, PUFA and SFA has been used to build a ternary plot able to distinguish authentic argan oils from their mixture with sunflower oils. However, since the TAG composition of sunflower oil varied significantly with cultivar and processing methods, a larger dataset would be required to establish a reliable detection limit. To overcome these limitations, a fingerprinting approach has been applied on the same spectra, leveraging information from the full spectral range, a nearest neighbor outlier detection model has been applied. The model was lastly applied to retail-purchased argan oils finding several instances of fraud.

Moreover, the argan oil adulteration with sunflower and soya oil was further studied by Random Forests and rank transformed magnitude data obtaining a better discrimination for soya than sunflower from argan oil, as some mixtures of 20 % w/w sunflower with argan were frequently misclassified, whereas no samples with this level of soya resulted in false positives (Gunning et al., 2022).

The adulteration detection of many different edible oils (rice, crambe, chia, olive, grape seed, peanut, sunflower, avocado, sesame, walnut, linseed, corn, basil, soybean, garlic, and rapeseed oils) mixed in a ratio among 15 and 80 %v/v was successfully studied through the application of calibration models to determine the SFA, PUFA and MUFA contents from the entire spectra of low field instruments, as previously described in paragraph 4.1.1. (Galvan et al., 2021).

Another edible oil adulteration investigated using a fingerprinting approach involved cold-pressed rapeseed oil adulterated with refined rapeseed oil and refined sunflower oil (McDowell et al., 2019). The necessity to use the fingerprinting approach comes from the very small visible spectral variation that was observed by superimposing NMR spectra of different grades of cold pressed rapeseed oil adulteration with refined rapeseed oil (also comparing the equivalent high field NMR spectra). On the other hand, refined sunflower oil had a much more dissimilar fatty acid composition than cold pressed rapeseed oil due to the difference in omega-3 to omega-6 ratios. Several classification techniques, namely PLS-DA, SIMCA, LDA-KNN and LDA-SVM, on selected spectral regions were applied. The best performing classifiers were LDA-KNN and LDA-SVM with classification results of 87 % true positive rate and 3 % false negative rate, which are comparable with high field NMR results of 93 % and 2 % respectively. The adulteration level was studied by PLS-R obtaining a good adulteration detection limit of 12.2 % for refined rapeseed oil, comparable with the 8 % results of high field NMR. However, the limits of detection for refined rapeseed oil adulteration were unacceptably high with results over 70 % for both benchtop and high field NMR analysis, showing that both NMR techniques were inadequate tools for quantifying this type of adulteration.

Regarding the other possible NMR approaches, the metabolomic approach was successfully used for the adulteration detection of perilla oils with soybean oil, a cheaper edible oil. In fact, perilla oil is a rich source of ω3 fatty acids and is mainly obtained by cold pressing and used in dietary supplements and skincare products of high value. Kim and coworkers integrated all 6 major peaks, belonging to fatty acids and glyceryl groups, found in the spectrum between authentic and adulterated perilla oil samples, verifying their identity by high-field NMR analysis (Kim et al., 2018). Authentic perilla oil samples had a significantly smaller integration value for the region 1.064–1.664 ppm than the adulterated perilla oil samples due to the decrease of unsaturated fatty acids in the adulterated samples. Comparing the six integration regions among samples, the authors were able to detect adulteration levels as low as 6 % v/v.

Benchtop NMR has been also tentatively applied for the adulteration detection of essential oils. Krause and coworkers studied samples of patchouli essential oil mixed with several adulterants. Patchouli essential oil was extracted from the leaves of the patchouli plant and consisted for half of sesquiterpene hydrocarbons. The authors performed a similarity analysis (Mahalanobis distance) based on the integration from 0.1 to 8.1 ppm in 0.01 ppm increments obtaining the recognition of good quality patchouli essential oils as well as 15 of 17 deliberate adulterations. Hence, due to these results benchtop NMR could be considered a complementary technique to GC–MS for quality control of essential oils in the fragrance industry.

5.2.2. *Adulteration of foodstuffs*

Benchtop NMR has also been utilized to study the detection of adulteration in other high-value commodities. The European Union and the United States recognized the food products most vulnerable to fraudulent trade practices in 1980–2010: olive oil, fish and seafood, organic foods, milk and dairy products, grains, honey, coffee and tea, spices, wine, meat and meat products and fruit juices (Johnson, 2014). In the present paragraph the benchtop NMR studies on adulteration detection of coffee, honey, meat, vinegar and saffron were reported. Both targeted and fingerprinting approaches were applied based on the food matrices, the specific problem to solve and the adulterant to detect.

5.2.2.1. Coffee. Coffee derived from Arabica species is highly valuable, and the adulteration of Arabica with the less valuable Robusta can be identified by measuring specific fat-soluble diterpenes: kahweol is a compound characteristic of Arabica, while 16-*O*-methylcafestol (16-OMC) is exclusive to Robusta. The official method for testing coffee authenticity is outlined in the German standard DIN 10779, which quantifies 16-OMC through lipid extraction and HPLC analysis (DIN 10779, 2011). This marker can also be detected in the high-field ^{1}H NMR spectrum of chloroform extracts from roasted coffee, with a detection limit of 1–3 % for Robusta in Arabica blends (Monakhova et al., 2015). However, also benchtop NMR spectroscopy has shown potential for verifying coffee authenticity in a targeted manner. A study conducted by Defernez and co-workers demonstrated the effectiveness of benchtop NMR methodology by comparing its results with those from high-field NMR on ground coffee extracts obtained by direct extraction with $CDCl_3$ and 1:3 matrix:solvent ratio (Defernez et al., 2017). In this preliminary study, 81 lipophilic extracts from authenticated coffees and mixtures were analyzed using a benchtop NMR instrument operating at the proton frequency of 60 MHz. The singlet at 3.16 ppm, due to H_{21} protons of the methyl functional group of 16-OMC and free of other nearest resonances, was used to perform a linear regression model to detect the presence of Robusta. The authors also applied the signal processing method of matched filtering obtaining a detection limit of Robusta in Arabica between 10 % and 20 % *w*/w.

The same research group further refined the extraction protocol by adding a concentration step: higher-cost deuterated solvent was substituted with chloroform allowing the use of much larger amounts of coffee and solvent in the extraction step, then the chloroform extract was evaporated and the residue dissolved in a much smaller amount of deuterated chloroform (Gunning et al., 2023; Gunning et al., 2018). The concentrated extract gave an NMR spectrum with enhanced peak intensity and improved signal-to-noise ratio under the same acquisition conditions. Surprisingly the researchers have shown for the first time the presence of both 16-OMC and 16-*O*-methylkahweol (16-OMK), another major coffee diterpenes with the same singlet a 3.16 ppm, in Arabica roasted coffee: a typical Arabica coffee contains approximately 1–2 % of the combined esterified 16-OMC and 16-OMK levels present in a typical Robusta. Considering this finding, the researchers concluded that any authenticity test must account for the natural variation of this compound's levels in authentic Arabica samples, rather than treating it as a straightforward "present/absent" marker. In conclusion, to follow using the 3.16 ppm peak area as a reliable proxy for Robusta content in mixtures, the authors defined a threshold at the upper limit of the normal Arabica range: applying simple linear regressions Robusta could be detected in Arabica samples at levels as low as 1–2 % w/w.

5.2.2.2. Honey. Another largely studied and commonly adulterated product is honey. Two recent studies utilized benchtop FT-NMR spectroscopy for honey adulteration. The first study, carried out by Rhee and coworkers (Rhee et al., 2023), employed a parametric modelling method, described in paragraph 4.1 (Matviychuk et al., 2019), alongside 43 MHz benchtop NMR spectroscopy to analyze the sugar profile of honey samples adulterated with corn syrup, brown rice syrup, glucose syrup, and wheat syrup. The amount of maltose, glucose, fructose, and sucrose were determined in a targeted manner and correlated with the amount of adulterant by linear regression. Then, the study utilized ternary plots to visualize the changes in sugar composition as adulterant concentrations increased. With the increment of adulterant concentration, the sugar profile of the honey became increasingly like that of the adulterant. The findings indicated a proficiency in detecting adulteration with brown rice syrup at a minimum detectable concentration of 5 % w/w, with results consistently reliable over a period of 60 days.

On the other hand, the second study conducted by Ozbay and coworkers has applied a metabolomic approach to detect the adulteration of monofloral, polyfloral and honeydew honeys with glucose, maple and invert sugar syrups (Ozbay et al., 2024). In this case the authors applied a PLS-R model on the spectra region among 0.00–7.50 ppm reaching a minimum detection limit for syrup adulterants of 0.96 % in monofloral honeys, 1.55 % in polyfloral honeys, and 1.93 % in honeydew honeys, with high R^2 values exceeding 0.9970.

5.2.2.3. Spices. Among spices, saffron is one of the major adulterated ones. Saffron is a highly coveted spice renowned for its distinctive color, aroma, and flavor, which are attributed to compounds such as crocins and safranal. Given its high price, resulting from labor-intensive production, fraudsters frequently target saffron. Gunning and coworkers used 60 MHz Benchtop NMR instrument to analyze extracts from saffron spice and common adulterants (Gunning et al., 2023). They employed DMSO-d_6 organic extracts of pure saffron spice alongside various suspected adulterants, including *Arnica montana*, *Calendula officinalis*, *Carthamus tinctoris*, *Curcuma longa*, *Capsicum annuum*, and *Santalum* species in addition to tartrazine. Three different classification models were employed on the acquired NMR spectra analyzed with a fingerprinting approach: NN-OCC, data driven SIMCA (DD-SIMCA) and isolation forests (IF). All three models effectively flagged serial mixtures as anomalous, varying detection limits by adulterant. The performance of all approaches was found to be highly similar, with OCC-NN demonstrating slightly better sensitivity and specificity compared to the others. For instance, tartrazine exhibited the lowest detection limit at 5 % w/w, while specific dried plant materials required concentrations of up to 30 % w/w to be flagged as suspicious. Although these detection limits are significantly higher than typical contamination levels, they may indicate fraudulent substitution aimed at financial gain. When these methods were applied to the spectra of saffron samples purchased from an online marketplace, 7 out of 33 samples were identified as highly anomalous. A comparative analysis with known mixtures' spectra and confirmatory spectral assessment using 600 MHz NMR suggested that these samples likely contained substantial amounts of undisclosed foreign matter.

5.2.2.4. Fermented foods. Another significant application of benchtop NMR in authentication is the analysis of vinegar. Like other food products, vinegar is vulnerable to various types of fraud. One prevalent form of deception is the addition of lower-value products, such as spirit vinegar, to higher-priced items like wine vinegar. In a recently published study, researchers successfully distinguished 32 authentic white wine vinegars from 56 products adulterated with spirit vinegars, with adulteration levels ranging from 5 % to 25 %*v*/v (Grassi et al., 2024). The monodimensional spectral data were segmented into three spectral regions (i.e., 3.75–0.90 ppm, 3.75–2.00 ppm, and 1.50–0.90 ppm). For each region, fifteen variables were selected from the pre-treated spectra. The initial PCA indicated a clear distribution of samples according to the samples adulterated at 25 % v/v from the other samples, mainly due to the disappearance of the signal attributed to acetyl-sugar at 2.07 ppm. Then, the authors developed an LDA model applied to the monodimensional spectra in the 3.75–0.90 ppm range, and achieved a remarkable 100 % correct classification of authentic and adulterated vinegars in predictive assessments.

5.2.2.5. Meat products. Lastly regarding meat products, a common adulteration is the meat replacement with alternative animal species (Johnson, 2014). The research conducted by Jakes et al. (Jakes et al., 2015) aimed to discriminate between beef and horse meat samples, both fresh and freeze-thawed, by employing a 60 MHz Benchtop NMR with a targeted approach. This analysis focused on lipid components, particularly three signals related to the bis-allylic, olefinic, and terminal CH_3 peaks were integrated providing significant insight into the chemical composition of the meat samples. The NMR spectra of horse meat consistently exhibited larger olefinic and bis-allylic peaks than those of beef, indicating a higher unsaturated fat content in horse meat. The integrated peak areas of the triglyceride protons were assessed using PCA and Naïve Bayes classification, both of which enabled effective differentiation of the meat samples. This methodology was successfully applied in two distinct laboratories, each using slightly different protocols: one laboratory used deuterated chloroform for the extraction and optimized the NMR parameters on standardization and cost minimization, while the other used chloroform and optimized the parameters on spectral quality. The results suggested that the spectral variations of the samples aligned with those of the different protocols and instrumentation, indicating that this methodology can be seamlessly adapted across various industrial environments to verify beef authenticity against horsemeat. Moreover, this discrimination study among beef and horsemeat paves the way for studies on the quantification of beef–horse mixtures and the study of other meat adulterations.

5.2.3. Consideration on adulteration detection by benchtop NMR instrument

The discussed articles show that both targeted and fingerprinting approaches can be used in adulteration detection studies based on the type of matrix and problem. Moreover, based on the high number of articles available on edible oil adulteration detection, the benchtop NMR application in this sector is promising.

Discriminative analysis plays a key role in addressing adulteration issues in various food products, particularly edible oils and honey. A notable example is the development of a PLS-DA model by Head et al. (Head et al., 2024), which uses benchtop NMR spectra to distinguish extra virgin olive oil from 16 non-olive oils, with the model focusing on the olefinic and ester protons of unsaturated fatty acids. Such discriminative studies form the foundation for adulteration detection, as many researchers conduct PCA analysis on pure oils to establish baseline profiles before applying adulteration models. Many studies on edible oils adulteration detection performed a prior PCA explorative analysis on all the pure oils before mixing and developing the adulteration detection model (Galvan et al., 2021; Giebelhaus et al., 2023; Gouilleux et al., 2018; Gunning et al., 2022). This methodology was also applied to other foodstuffs, like honey, where Ozbay et al. (Ozbay et al., 2024) used PCA, HCA, and soft SIMCA to differentiate honeys from various botanical origins before proceeding to adulteration detection using PLS-R models.

In conclusion, benchtop NMR is a promising analytical technique for detecting food adulteration, offering a rapid, cost-effective, and environmentally friendly alternative to traditional methods. With its ability to analyze complex food matrices and identify subtle variations in product composition, benchtop NMR has proven to be effective in detecting adulteration in a variety of edible oils and other commonly adulterated foods. The development of robust chemometric models, alongside advancements in NMR spectral processing, has further enhanced the sensitivity and accuracy of adulteration detection, making it an invaluable tool for both quality control and regulatory oversight. As the demand for food authenticity continues to rise, the application of benchtop NMR will likely play an important role in safeguarding public health and restoring consumer confidence in food products.

6. Pipeline for benchtop FT-NMR applications in the food sector

The comparative analysis of the here reported studies allows the methodology behind the benchtop FT-NMR analysis of food matrices to be outlined as reported in Fig. 2. This scheme can be applied to set up benchtop FT-NMR protocols for studying new food matrices or addressing food-related issues. At the same time, it helps to evaluate the feasibility and suitability of the method for each specific case. Additionally, by following this framework, the most appropriate approach (targeted, metabolomic, or fingerprinting) can be selected.

First and foremost, the successful application of benchtop FT-NMR relies on signal assignment and compound identification achieved through high-field NMR spectroscopy (at least 400 MHz). These studies typically combine high-field and low-field FT-NMR instruments, or at the very least, leverage data from previous high-field FT-NMR investigations to design benchtop FT-NMR experiments.

The NMR spectral information relative to the chemical food composition under investigation obtained from the high-field NMR spectra and/or from the literature, gives a solid base for the analysis of benchtop FT-NMR spectra. Moreover, the proper NMR approach must be selected.

If specific compounds of interest are present in the food matrix and their signals do not overlap and are quantifiable, a targeted approach can be developed. This approach, which focuses on the integration of a few key signals, leverages the "high-resolution" capabilities of benchtop NMR to create a simple model. Owing to a small number of variables, the quantified NMR signals can be directly linked to the food characteristics - or aspects under investigation - with a direct industrial application.

Alternatively, if there are no specific metabolites of interest in the

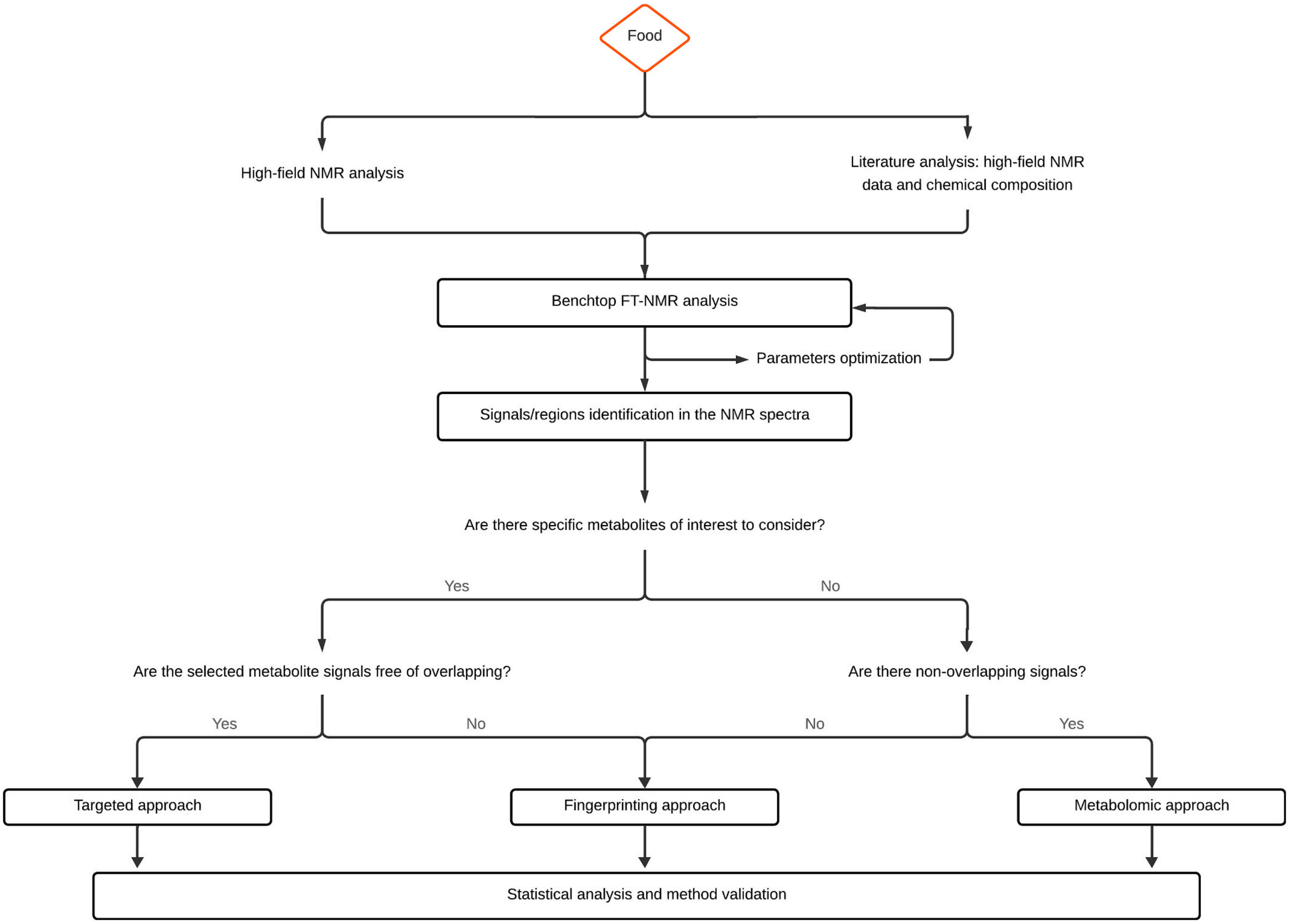

Fig. 2. Scheme of benchtop FT-NMR experimental protocol for the study of new food matrixes or to address food-related problems.

matrix under investigation or if the signals of these metabolites overlap, the fingerprinting approach is the only method for extracting information from the NMR spectra. In this case, the full spectra or binned data, without prior signal identification, are used to compose a data matrix. After appropriate data pre-treatment, this matrix can be used as input for the relevant chemometric method to address the problem.

Lastly, if there are no specific metabolites of interest for the matrix under investigation, but a series of signals are not overlapping and integrable, the metabolomic approach can be attempted. This approach, as the targeted one, takes advantage as well of the “high-resolution” properties of benchtop NMR instruments and seeks to identify and quantify as many metabolites as possible, without relying on a predetermined hypothesis, striving for the most comprehensive description of the NMR spectrum while determining the identity of the signals. In this case, all the quantified metabolites are typically used as input for chemometric analysis.

With the selected NMR processing approach, the proper chemometric analysis, regression, or classification model, can be applied to solve the investigated food related problem. Finally, the developed statistical model must be validated to ensure reliable and reproducible results.

Additionally, some good practices are needed to properly handle the benchtop spectrometers for food applications.

7. Good practices for benchtop FT-NMR applications in the food sector

Due to the novelty of benchtop FT-NMR instruments and the limited articles available on their application for food-related issues, no well-established protocols are available for the analysis and data treatment. In fact, in this review, several steps of the benchtop FT-NMR analysis of foods present differences among articles and research groups. However, it is of great importance to start establishing some good practices for critical steps of the NMR analysis. In particular, the setting of a shimming routine and optimizing the parameters prior to the analysis are fundamental practices to obtain reproducible NMR spectra and use the best NMR parameters for the specific food-related challenges and applications. Moreover, it is important to leverage the peculiarities of benchtop FT-NMR instruments, such as the continuous mode and the analysis without a deuterated solvent, whenever possible, to develop easier-to-use methods. Some of these general good practices are listed below.- Shimming procedure. Schedule a routine shimming protocol to avoid variance in peak heights/areas. The shimming could be performed daily, before every experiment, at a certain time or as and when necessary, based on daily checking.

- Parameters optimization. Prior to benchtop NMR analysis of the samples, optimizing NMR parameters is crucial to fully exploit the capabilities of the instrument for the food matrix under investigation. Key parameters to optimize include the number of scans, relaxation delay, and temperature inside the probe. Additionally, selecting the appropriate NMR sequence is essential, depending on the food matrix and the specific problem being addressed. The choice of solvent suppression method is also crucial when solvent signals obscure neighboring signals.

- Online monitoring. When the food related problem to solve needs continuous monitoring of a process, a benchtop NMR instrument can be equipped to carry out a real-time analysis.

- Non-deuterated solvent. Benchtop NMR can also work with non-deuterated solvents, that are cheaper than the deuterated ones, thanks to the external lock system. The development of food analysis on its untreated form, as in the case of liquid food, can increase the industrial applicability of the procedure.

8. Future perspectives

Modern benchtop FT-NMR instruments appear to be widely applicable for various food-related issues. An application that seems to be promising is the chemical characterization of lipid fraction in lipid-rich foods. In fact, ten articles on edible oils were reviewed and discussed together with two articles on meat products, ham and beef, respectively, and two articles related to lipid accumulation monitoring in microalgae. It is noteworthy that several of these articles apply a targeted/metabolomic approach, since the fatty acid signals are usually well-resolved and integrable even in the low-field NMR spectra. Targeted application in quality control is another prospective approach, relying on specific metabolites with distinct NMR signals that do not overlap and serve as key markers of a product or process. This is the case of 16-*O*-methylcafestol quantification in coffee, alcohol determination in beverages, α:β-acids ratio in hops, and sugars in honey. On the other hand, fingerprinting characterization through the full spectral analysis can be widely used in adulteration detection of many foodstuffs, also thanks to chemometrics. In the future, it is crucial to continue developing advanced solutions to overcome the limitations of benchtop NMR, mainly connected to the low resolution and low sensitivity. As demonstrated in the recent research studies reported in paragraph 4, these solutions could include the development of advanced visualization and processing methods, as well as dedicated databases and web tools to facilitate low-field NMR spectra interpretation and analysis. Finally, it is important to highlight, as a future perspective, the direct industrial applicability of the modern benchtop FT-NMR spectrometers due to their ease of use, deuterated-solvent-free analysis, and their portability. These innovations significantly expanded the accessibility of NMR spectroscopy's powerful diagnostic capabilities to a much broader range of users.

CRediT authorship contribution statement

Giacomo Di Matteo: Writing – original draft, Funding acquisition, Conceptualization. **Silvia Grassi:** Writing – original draft, Methodology, Data curation. **Maria Carmela Emanuele:** Writing – original draft. **Giuseppe Scioli:** Writing – original draft, Methodology. **Federico Ivan Brigante:** Writing – original draft, Data curation. **Luana Bontempo:** Validation. **Cinzia Ingallina:** Writing – original draft. **Claude Guillou:** Validation. **Anatoly P. Sobolev:** Writing – review & editing, Supervision. **Luisa Mannina:** Writing – review & editing, Supervision, Funding acquisition.

Funding

Project funded by 'Mediterranean Diet for Human Health Laboratory' project (MeDiHealthLab) – No. T5-AN-07 (POS 5), CUP: B83C22005580006.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Giacomo Di Matteo reports was provided by University of Rome La Sapienza. - Two authors are Guest Editors of the Special Issue "VSI: Miniaturized Spectroscopy" of Food Research International. Giacomo Di Matteo and Silvia Grassi. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors acknowledge the support from the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3—Call for tender No. 341 of 15 March 2022 of the Italian Ministry of University and Research funded by the European Union—NextGenerationEU. Award Number: Project code PE0000003, Concession Decree No. 1550 of 11 October 2022 adopted by the Italian Ministry of University and Research, CUP D93C22000890001, Project title "Research and innovation network on food and nutrition Sustainability, Safety and Security—Working ON Foods" (ONFoods). Project supported also by 'Mediterranean Diet for Human Health Laboratory' project (MeDiHealthLab) – No. T5-AN-07 (POS 5), CUP: B83C22005580006.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodres.2025.116327.

Data availability

No data was used for the research described in the article.

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