Liling_Combination Chemometrics

by

Submission date: 02-May-2023 07:22PM (UTC-0400)
Submission ID: 2082505197
File name: 1-s2.0-S2949771X23000105-main_3.pdf (5.55M)
Word count: 11099
Character count: 58870

Journal of Pharmaceutical and Biomedical Analysis Open 1 (2023) 100010

Contents lists available at ScienceDirect

Journal of Pharmaceutical and Biomedical Analysis Open

journal homepage: www.journals.elsevier.com/journal-of-pharmaceutical-and-biomedical-analysis-open

Combination quantitative ^{1}H NMR and chemometric approaches for the assessment of quality control in commercially available products of red fruit (*Pandanus conoidues*, Lam.) oil

Liling Triyasmono[a,b], Ulrike Holzgrabe[a,*]

[a] Institute for Pharmacy and Food Chemistry, University of Würzburg, 97074 Würzburg, Germany

[b] Department of Pharmacy, Faculty of Mathematics and Natural Sciences, Lambung Mangkurat University, 70713 Banjarbaru, Indonesia

ARTICLE INFO

Keywords:
Red fruit oil
Quantitative ^{1}H NMR
Internal standards
Chemometric
Fat parameters

ABSTRACT

assessment of fat acid parameters (acid value, saponification value, ester value, iodine value, composition of monounsaturated fatty acids, polyunsaturated fatty acids, and total unsaturated fatty acids) in edible oils, including red fruit oil, delivers essential indices to guarantee their quality. This index also holds true for excipients as well as for traditional medicines. NMR spectroscopy is an alternative tool to the conventional methods for the determination of these quality parameters, offering attractive advantages. Here, the approach reported in the literature based on the ^{1}H NMR quantitative method is illustrated, highlighting the application procedure strategy and suggested sample processing. Chemometric applications on ^{1}H NMR spectra are also discussed. Furthermore, this review can support the role of ^{1}H NMR and chemometrics in routine analysis for oil quality control.

1. Introduction

Traditional medicine has been widely recognized and used as a support or alternative to modern medicine as a therapy, especially for degenerative diseases [1]. As is the case in Indonesia, around 24–32% of the population in Indonesia consumes traditional medicines every month, including urban and rural communities [2]. Hence the quality assessment of such traditional medicines is of utmost importance. As a representative, we have chosen the oil quality parameter determination of Red Fruit Oil (RFO) being a raw material for traditional medicine in Papua, Indonesia, which is the oil extracted from red fruit (*Pandanus conoideus*, Lam.).

Traditionally, Papuans use red fruit oil (RFO) to increase energy and strengthen the immune system. RFO contains active components such as phenols, carotenoids, tocopherols, and unsaturated fatty acids. The reported characteristics of RFO differ from those of other Indonesian vegetable oils, such as coconut and palm oil. The composition of RFO is dominated by saturated fatty acids (10–20%), monounsaturated fatty acids (oleic) (60–70%), and polyunsaturated fatty acids (2–10%) [3,4].

The literature records some pharmacological studies on RFO, as demonstrated by Rohman and Windarsih [5]. Several studies have been reported on the biological activities of RFO, including anticancer activity [6,7], antioxidants [8,9], and treating various degenerative diseases such as arteriosclerosis, rheumatoid arthritis, and stroke [10] as well as HIV, malaria, cholesterol, and diabetes mellitus [11–13].

The quality requirement of RFO products is one of the critical factors in the sustainability of these products. The variants of raw materials from red fruit that vary due to geographical factors, harvest time and processing methods are the reasons for the potential differences in the content of components of red fruit oil [14]. Subsequently, the differences in red fruit types have been shown by Susanti et al. [15] (Fig. 1).

Therefore, quality assurance is required by regulation of the Indonesian Food and Drug Authority and all food and drug authorities in ASEAN countries to ensure that RFO products have standards that qualify them as alternatives to traditional medicines or functional foods. Some of the main quality parameters used for oil quality control are commonly known as fat parameters, including the acid number, saponification number, iodine number, ester number, and the composition of fatty acids.

Established methods for measuring acid value (AV), saponification value (SV) and iodine value (IV) are volumetric methods (i.e., titration), whereas for the determination of fatty acid components, gas chromatographic methods are applied [16,17]. Unfortunately, the classical methods have several drawbacks. Volumetric ones are usually visually dependent and their accuracy can be compromised, for example, in the

* Correspondence to: Institute for Pharmacy and Food Chemistry, University of Würzburg, Am Hubland, 97074 Würzburg, Germany.
E-mail address: ulrike.holzgrabe@uni-wuerzburg.de (U. Holzgrabe).

https://doi.org/10.1016/j.jpbao.2023.100010
Received 10 February 2023; Received in revised form 5 April 2023; Accepted 9 April 2023

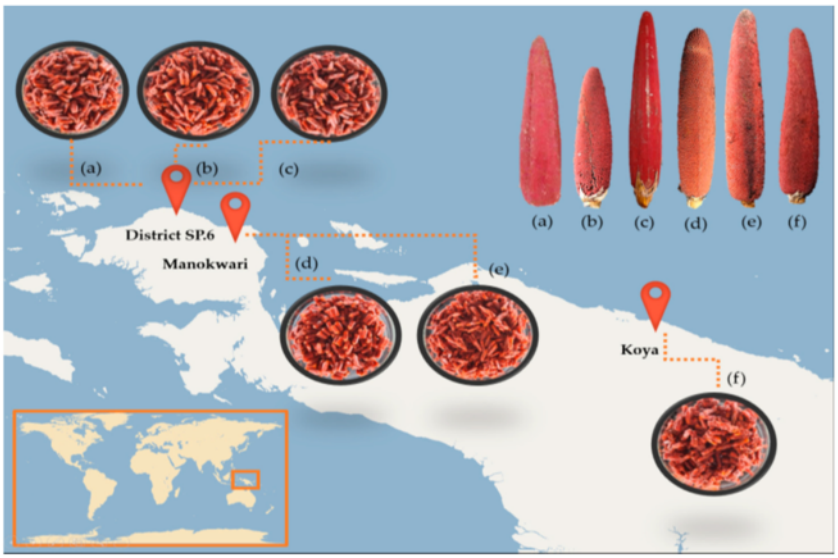

Fig. 1. Red fruit drupe of six red fruit clones: (a) Edewewits clone; (b) Menjib clone; (c) Memeri clone; (d) Monsor clone; (e) Monsrus clone; and (f) Mbarugum clone. [15].

case of highly colored samples as it is the case with RFO. Although the introduction of technologies such as potentiometric endpoint determination significantly improved the methods, there are still some disadvantages: they are usually slow, require large sample sizes, large amounts of organic solvents and hazardous chemicals, and need more specificity. Regarding the gas chromatography (GC) method, an esterification step to convert oil triglycerides to volatile fatty acid methyl esters (FAME) still requires more lengthy procedures and time [18].

Alternative analytical techniques have been proposed for the determination of the classical oil quality parameters (AV, SV, IV, and fatty acid composition), including potentiometry [19], GC [20,21], HPLC [18,22], FTIR [23–27], and electrophoresis [28,29]. In addition, quantitative NMR (qNMR) spectroscopy methods [30–35] are also increasing in popularity. The qNMR method has the advantage of being a non-destructive, non-invasive method, allows for a relatively fast sample preparation, and can provide the composition of the sample mixture in one single spectrum.

Due to physics of NMR spectroscopy, the integral of a signal is directly proportional to the corresponding number of nuclei [36], making molar concentration directly accessible. Hence, NMR has become prominent as favoured fatty acid characterization technique, obtaining and predicting composition and the ratio of fatty acids contained in oils based on the profiles of the different acyl groups. In addition, the NMR method has also proven helpful for classifying edible oils, monitoring the occurrence of hydrolysis, oxidation, or deterioration processes, and detecting oil adulteration [37–39].

In addition, to support the potential of the described NMR technique, some authors also use chemometric methods combined with NMR [40–43]. The primary purpose of using chemometrics is to reduce the amount of NMR data, achieve better visualization of the system, and emphasize the differences and similarities of the samples. Kowalski and Reilly [44] first introduced the combination of both methods. Furthermore, this combination has been actively used for analyzing biological and pharmaceutical matrices since the 1990s [45,46]. Meanwhile, the first comprehensive review dedicated to oil analysis was published in the early 2003s [47].

Therefore, the purpose of the review is to describe the applicability of qNMR and chemometrics to assess the quality of oils and in particular of RFO. We will discuss the NMR experimental procedures, emphasizing on spectral processing and data analysis, and compare them with results of AV, EV, IV, and SV determination with regard to the composition of monounsaturated fatty acids (MUFA), polyunsaturated fatty acids (PUFA), and total unsaturated fatty acids (Total UFA). At the same time, applying chemometrics on proton NMR spectra data for visualizing grouping oil quality differences also were discussed.

2. NMR practical considerations

The use of NMR in analytical evaluation, especially in determining oil parameters (AV, SV, IV, MUFA, PUFA, and Total UFA composition), aims to simplify the preparation and analysis procedures, for example, without extraction, derivatization, or sample separation. Because each specific oil product will contain component species in different concentrations, any concentration differences must be detected precisely. Therefore, the qNMR techniques can be used to evaluate all parameters, provided the spectrometer has specific performance characteristics.

One of the critical keys is the magnetic field strength, as signal separation is proportional to the magnetic field strength. In addition, NMR is intrinsically known as a method with low sensitivity. This disadvantage can be partially overcome by using high magnetic field instruments [48]. However, in oil quality assessment, low sensitivity is not a problem as oil components are usually present in sufficient concentrations. Nevertheless, a higher field strength [31,49,50] provides a better resolution, and thus relatively little signal overlap. Most studies use medium strength and the 300–400 MHz magnetic field shows satisfactory results [32,33,35].

2.1. Parameter acquisition

For quantitative NMR measurements, some parameters have to be considered and, if needed, to be adopted. Holzgrabe [36], Bharti, and Roy [51] generally discussed in detail all the essential parameters to be considered in the qNMR experiment. Furthermore, in this context, some decisive parameters are briefly summarized and commented, particularly on oil applications.

Temperature. The temperature during the experiment is essential with regard to the reproducibility of the quantitative results. Thus, the temperature must be kept constant throughout the study. Furthermore,

temperature variations can affect the relaxation properties of molecules, including air temperature flow which must also be kept constant and stable during the acquisition time because it can cause "wobble" artifacts in the baseline of strong signals at high flow rates [51]. On the other hand, Holzgrabe [36] also described temperature settings as having a significant impact on the resolution of the spectra. In particular, settings at higher temperatures can induce an upfield shift of the HOD signal. Therefore, in the case of oil applications, maintaining a controlled and constant temperature of 20–30 °C is recommended to obtain optimal molecular relaxation and decent signal resolution [35,39,52].

Pulse width. Most usable pulse angles are between 30° to 90° in spectrum recording. A 90° pulse gives the maximum signal intensity, but in practice, pulse widths less than 90° are more often used to obtain good qNMR data in a reasonable time [53]. Furthermore, the uniformity of pulse width usage during measurement is a significant concern. Hence, during the majority of oil applications, 30° pulses are more widely used with complete relaxation of resonance in a shorter experiment time [35,52].

Repetition time. Repetition time is the total time spent acquiring a single scan spectrum, which is obtained from the sum of the relaxation delay and the acquisition time required. It is an essential parameter for quantitative purposes and plays a crucial role in obtaining accurate integration. Since the repetition time depends on the longest longitudinal relaxation time T1 of the signal considered to reach more than 99% equilibrium, the repetition time is generally required to be five times the longest TI value [36]. In this context, the relaxation delay depends on the T1 relaxation time in the triglyceride molecule which also applies to the methylene proton of the glyceryl group. Furthermore, the relaxation delay time also considers T1 of the internal standard (IS) used [36].

Determination of T1. The inversion recovery pulse sequence method is a commonly used method for determining T1 [36,54], as was performed by Triyasmono et al. [35] on RFO (Fig. 2). As described by Holzgrabe [36], the IS signal applied should also be considered, as many IS are often characterized by long T1 times; for example, the standard compound 1,2,4,5-tetrachloro-3-nitrobenzene (TCNB) obtained a T1 of 10.7 s, while dimethyl sulfone ($DMSO_2$) has a T1 of 2.7 s, as shown by Skiera et al. [32] and Triyasmono et al. [35], respectively.

Number of scans. The number of scans is one of the parameters highly dependent on the sample concentration and is governed by the desired S/N ratio and the LOQ to be achieved. This parameter also changes most frequently during NMR experiments. For quantitative purposes with accuracy and precision better than 1%, the S/N ratio should be 1:250 [36]. On the other hand, the increase in S/N ratio is proportional to the square root of the number of scans, so the increase in S/N ratio will affect the time consumption, especially for analytes which are present in low concentrations. However, for oil analysis applications, the recommended number of scans between 32 and 128 shows good accuracy and precision values within a reasonable time [32,34,35] because concentration is not an issue.

Spectral width. The spectral width (SW) parameter determines the size of the observed frequency window. As reported by Monakhova and Diehl [55], an SW of more than 3.0 ppm is recommended. A too narrow SW = 1.8–2.5 ppm can cause spectrum intensity disturbances, especially at the edge of the spectrum, distorted baselines, and folded signals; so it will have a negative impact on the desired signal integration process. Usually, in standard experimental setups, a suitable SW is set as the default value (20–30 ppm) so this parameter is mostly kept in qNMR experiments, including for oil applications [32,35].

Frequency offset. In addition to the spectral width parameter, the transmitter (frequency) offset (O1P) is also a critical interrelated parameter. For qNMR, the O1P parameter can also produce other bias factors. This parameter determines the center point of the spectrum. For SW 30.00 ppm, O1P values generally vary between 5 and 8 ppm [51,53]. When the excitation pulse is in the middle of the desired spectral window, the relative purity will reach its maximum value [55]. It is also applied for most of the oil samples [32,35].

Receiver gain. Furthermore, to maximize the ability to obtain the right signal-to-noise ratio, the selection of the receiver gain value is also

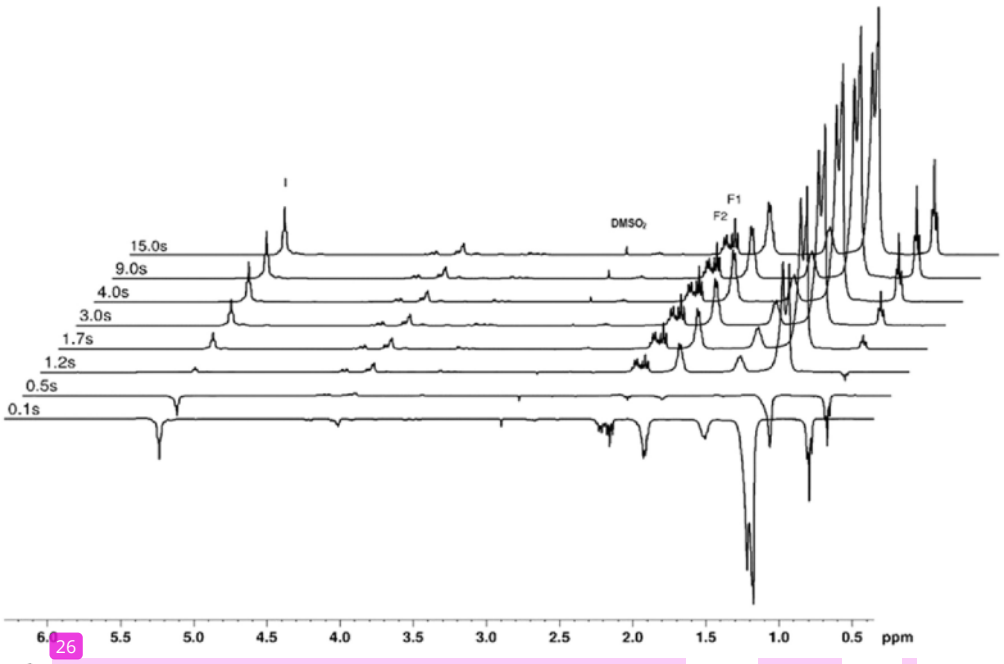

Fig. 2. 400 MHz ^{1}H NMR; an inversion-recovery pulse sequence of experiments used to measure the values of T1 for the protons of RFO in $CDCl_3$: DMSO-d_6 (5:1, v/v), a 90° flip angle-T-90° pulse sequence was applied [35].

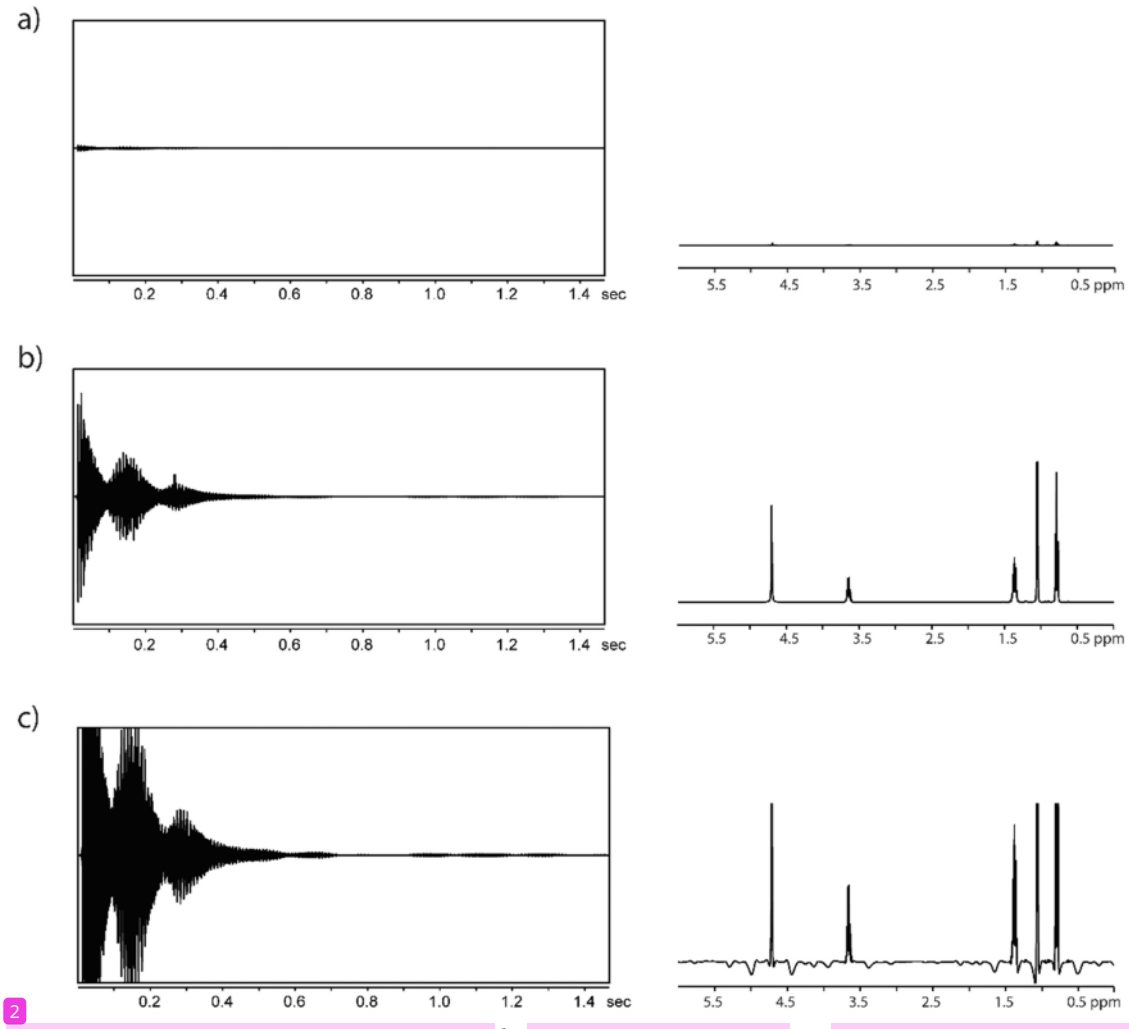

Fig. 3. Effect of receiver gain setting on the FID and the resulting 1D ^{1}H spectrum of 10%(v/v) 2-butanol in D_2O at 400 MHz. The FIDs (left column) and their corresponding NMR spectra (right column) are displayed with the same scaling. (a) receiver gain set too low leading to a very small (poorly digitized) FID and small NMR peaks, (b) receiver gain set to optimum leading to a large well digitized FID and large undistorted NMR peaks, and (c) receiver set too high leading to a "clipped" FID and with distorted NMR peaks and baseline [56]; thanks to the authors providing the figure.

fundamental. According to Torres et al. [56], the receiver gain (RG) should not be too high, otherwise it will be "clipped" the large signal (Fig. 3).

This means that the most powerful early part of the Free Induction Decay (FID) will be truncated because it is beyond the capabilities of the analog-to-digital converter. In short, FID will have a rectangular-like signal profile resulting in a difference rather than the usual exponential decay. Data from Triyasmono et al. [35] show that RG in the range of 4–5 gives the optimal S/N value (S/N > 1000).

2.2. Sample preparation

The sample preparation is relatively simple because a certain amount of oil or fat has to be dissolved in a suitable deuterated solvent in specific proportions only. Deuterated chloroform ($CDCl_3$) is most commonly used as a solvent [34,37,57], as well as DMSO-d_6 [38,39], and a mixture of both (DMSO-d_6 with $CDCl_3$) [34,41,58]. As discussed by Holzgrabe [36], Bharti and Roy [51], the assignment of baseline separated and unambiguous signals is an absolute prerequisite for quantitative NMR techniques. Therefore, Skiera et al. [32] and Hafer et al. [34] used solvent mixtures which guarantee signal separation. In addition, for the RFO sample a mixture of $CDCl_3$:DMSO-d_6 (5:1, v/v) was applied which gave clear results for the presence of a specific proton from the methylene group α-CH_2 at δ = 2.37–2.20 ppm [35]. The beneficial effect of adding DMSO-d_6 to $CDCl_3$ is due to the formation of NMR complexes between DMSO and fatty acid groups [59,60].

2.3. ^{1}H Spectral assignment

The ^{1}H NMR spectrum of RFO is shown in Fig. 4, the assignment of the spectra of RFO was performed according to previous literature [61–63] on oil analysis.

As discussed by Ravaglia et al. [64], the addition of standards of olive oil can assist in confirming signal assignment in the spiked spectra [41,48]. This method has been used to assign the full proton spectrum of RFO. Palmitic and oleic acid standards were added to the RFO [35]. As can be seen in Fig. 5, the addition of both standard substances is proven by the regression data showing an increase in the integration

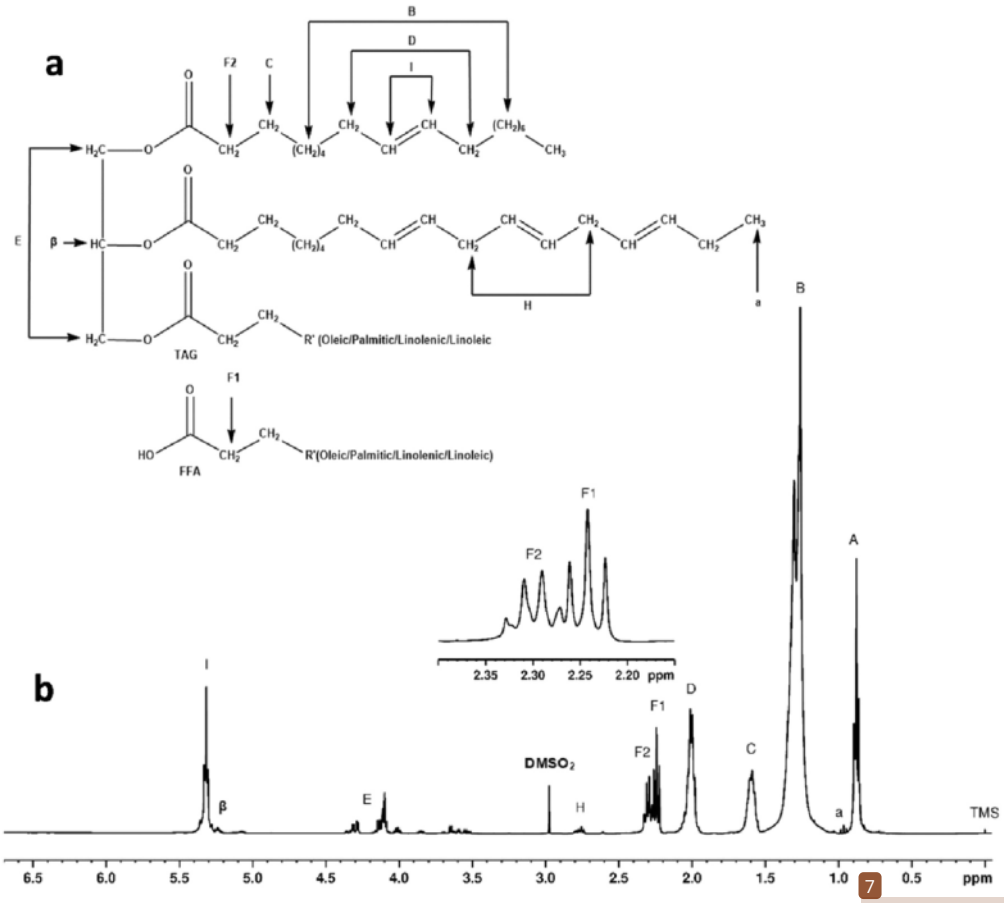

Fig. 4. **a** Representative structures of triacylglyceride (TAG) and free fatty acid (FFA) and **b** ^{1}H NMR spectrum of RFO dissolved in a mixture of $CDCl_3$ and DMSO-d_6 (5:1 v/v) containing TMS 0.1% with enlargement signal at δ = 2.20–2.37 ppm (are labeled by F1 and F2) [35].

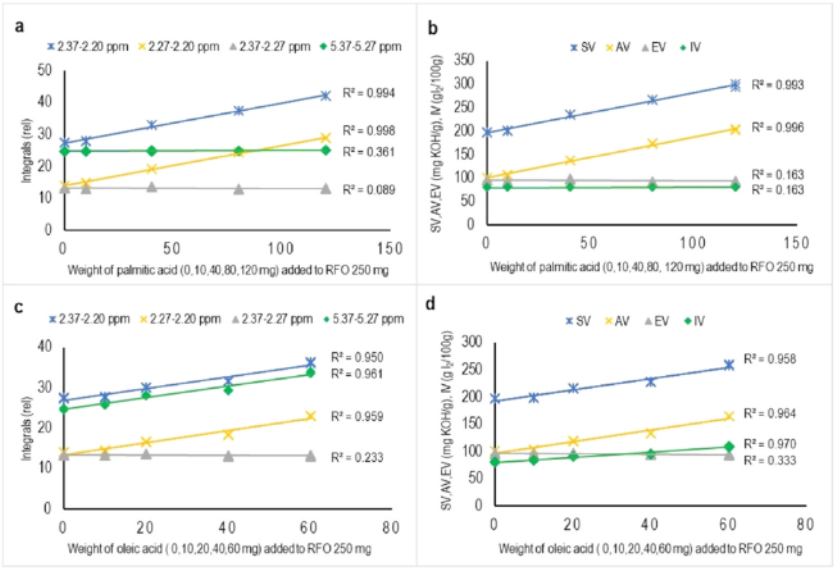

Fig. 5. Correlation between RFO with palmitic acid addition versus Integral of ^{1}H NMR RFO (δ = 5.37–5.27 ppm, δ = 2.37–2.27 ppm, δ = 2.27–2.20 ppm, δ = 2.37–2.20 ppm) and **b** Correlation between RFO with palmitic acid addition versus SV, AV, EV, and IV by qNMR calculation. **c** Correlation between RFO with oleic acid addition versus integral of ^{1}H NMR (δ = 5.37–5.27 ppm, δ = 2.37–2.27 ppm, δ = 2.27–2.20 ppm, δ = 2.37–2.20 ppm) and **d** correlation between RFO with oleic acid addition versus SV, AV, EV, and IV by qNMR calculation [35].

Table 1
Chemical shift assignment of the ^{1}H NMR signals of the main components of RFO [35].

Signal	Functional group	Chemical shift (ppm)	
		TAG	FFA
A	(-CH_3) saturated, oleic and linoleic acyl chains	0.93–0.83	0.93–0.83
a	(-CH_3) linolenic acyl chains	1.03–0.93	1.03–0.93
B	(-$(CH_2)_n$-) methylene groups	1.42–1.22	1.42–1.22
C	(-CH_2-CH_2-CH_2-) β-methylene protons	1.70–1.52	1.70–1.52
D	(-CH_2-CH=C) allyl methylene protons	2.14–1.94	2.14–1.94
E	(-CH_2OCOR) methylene protons in the glyceryl group	4.32–4.10	-
F1	(-OCO-CH_2-) α-methylene protons	-	2.27–2.20
F2	(-CH_2-CH_2-) α-methylene protons	2.37–2.27	-
H	(=CH-CH_2-CH=) divinyl methylene protons	2.84–2.70	2.84–2.70
β	(-CHOCOR) methine proton at C2 of glyceride	5.26–5.20	5.26–5.20
I	(-CH=CH-) olefinic protons	5.37–5.27	5.37–5.27

value of the corresponding signal and the correlated fat value parameter.

In Table 1, the assignment of proton signals of all compounds is reported.

2.4. Post-processing parameters

For reliable quantification results, each NMR spectrum generated must be processed considering post-processing parameters including referencing chemical shift (previously described), phasing, baseline correction, and integration. For example, Emwas et al. [65] illustrate the influence of post-processing parameters in Fig. 6.

Phase correction. The first step is phase correction; the signal phase must be precise to get an accurate intensity measurement. If an error occurs while phasing, it will result in a significant error in the measurement of the peak ratio, and thus, it will be also correlated to the error in the absolute or relative concentration of the qNMR compound. Often manual phase correction is preferable to automatic phase correction because small signals could be distorted. This demonstrates that a negative deviation of the x% signal can produce an area error of 2x% compared to other signals. Therefore, the application of manual phase correction will increase optimal precision [65].

Baseline correction. The second step is the baseline correction; automatic baseline correction is generally performed, but it is nevertheless necessary to look at the resulting spectral profile. There is a number of algorithms built into the NMR analysis software that can be selected to facilitate the process of correcting the baseline so that accurate calculations are obtained [65]. As for processing the spectra of the RFO sample using the ABSG polynomial [35], a narrow full width at half maximum value (FWHM) is obtained for the selected signal [66].

Integration. The third step is integration. This step is one of the most crucial steps in qNMR analysis. The integral area range, slope, and bias greatly influence the quantitative accuracy as the integration should be obtained over 99% of the total signal area. Monakhova and Diehl [55] suggest integrating 64 x FWHM to obtain high accuracy. All signals should be harmonized for area range, slope setting, and bias included or excluded, e.g., all integrals are measured over a range of + /- 5 Hz around each signal. Setting manual integration parameters and selecting the "exact coordinates integrated area" is regarded as a reliable integration process [35].

Since integrals are very sensitive to baseline differences, the baseline correction should be done very carefully to minimize biases and errors. Therefore, performing 5–10x integrations per spectrum to obtain an average of all values to reduce analysis errors is highly recommended [65].

2.5. Quantification method

Quantitative techniques with NMR include two main types, namely: relative methods, which are commonly used in quantitative NMR [67,68], and absolute methods using internal standards which are gaining popularity [32,35,69]. The quantification technique requires standard compounds to calculate the concentration of the analyte. The internal standard selected for measurement must be available in a high pure form, be relatively inexpensive, stable, inert, nonvolatile, and be available in a non-hygroscopic form and soluble in the solvent used. The signals from the standard compounds must be completely separated from the signals of the analyte and should preferably be a singlet. Furthermore, the relaxation time is relatively short so that the measurement time does not increase, which will reduce the effectiveness and efficiency of the method in terms of time [36,70]. In the same solvent mixture ($CDCl_3$:DMSO-d_6 (5:1 v/v) Skiera et al. [32] used TCNB as the standard compound with a singlet proton signal at 7.70 ppm, whereas Triyasmono et al. [35] used $DMSO_2$ as a standard with a singlet proton signal at 2.90 ppm.

On the basis of their use, reference compounds can be classified as internal and external standards. In this context, we provide a particular review of internal standard quantification techniques. The internal standard procedure is carried out with a known concentration or weighted amount of a reference compound dissolved in a known volume of analyte solution for quantitative estimation, as shown in Fig. 7. The most critical conditions for an internal standard are its solubility and chemical interaction with the analyte.

Subsequently, the quantification of each sample's quality parameter value is directly calculated from the integral of the selected NMR signal, together with the initial weight of the sample and reference compound, molecular mass, and the number of protons which contribute to the respective signal and certified purity of the reference compound, as shown in the following formula [36]:

$$P_x = \frac{I_x}{I_{std}} \cdot \frac{N_{std}}{N_x} \cdot \frac{M_x}{M_{std}} \cdot \frac{m_{std}}{m} \cdot P_{std} \quad (1)$$

where, I, N, M, W and P are integral area, number of nuclei, molar mass, gravimetric weight and purity of analyte (x) and standard (std), respectively.

Skiera et al. [32] and Triyasmono et al. [35] developed the quantification method in relation to the calculation of oil quality parameters with the modification of the above formula.

3. Application to RFO quality control

According to the compendial method, the chemical characteristics of edible fats and oils can be determined by measuring the AV, SV, EV, and IV using titrations, whereas the determination of MUFA, PUFA, and total UFA content is done by using Gas Chromatography. This value also determines the shelf-life quality and therefore influences the economic value of the oil. On the other hand, Skiera et al. [32] and Triyasmono et al. [35] demonstrated that several fat parameters can be assessed by qNMR using an internal standard, including:

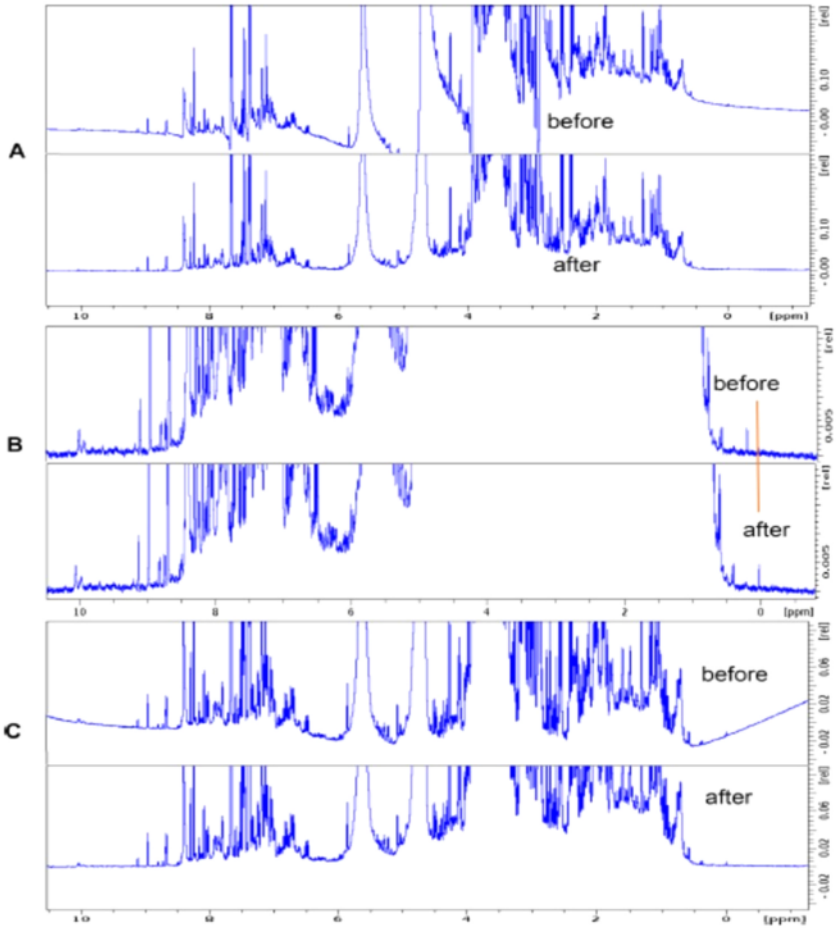

Fig. 6. A simple visualization of the effects of **a** phasing, **b** referencing and **c** baseline correction and on an NMR spectrum [65].

3.1. Acid value / Free fatty acid

The ^{1}H NMR spectrum of the RFO in the solvent mixture of $CDCl_3$:DMSO-d_6 allows directly obtaining this information; this value was obtained from the assessment of the integral of methylene alpha signal (α-$CH_{2\text{-acid}}$) resonance at δ = 2.20–2.27 ppm (F1), see Fig. 3. The pattern of signals obtained from different RFO products showed different intensities. This signal assignment has also been confirmed by hydrolysis experiments [35]. Furthermore, with the internal standard method described above, the calculation of the AV value can be obtained using the following formula:

$$AV_{NMR} = \frac{M_{KOH}}{m_s} \cdot \frac{m_{DMSO2} \cdot P_{DMSO2}}{M_{DMSO2}} \cdot \frac{N_{DMSO2}}{N_s(2)} \cdot \frac{I_{\alpha-CH2\,(acid)}(2.27\text{-}2.20\,ppm)}{I_{DMSO2}(2.98\,ppm)} \cdot 1000 \quad (2)$$

According to Skiera et al. [32], the AV of rapeseed oil can be determined by integrating the COOH signal at δ = 11.4 ppm and TCNB signal at δ = 7.70 ppm and AV NMR in mg KOH/g calculated based on Eq. 3:

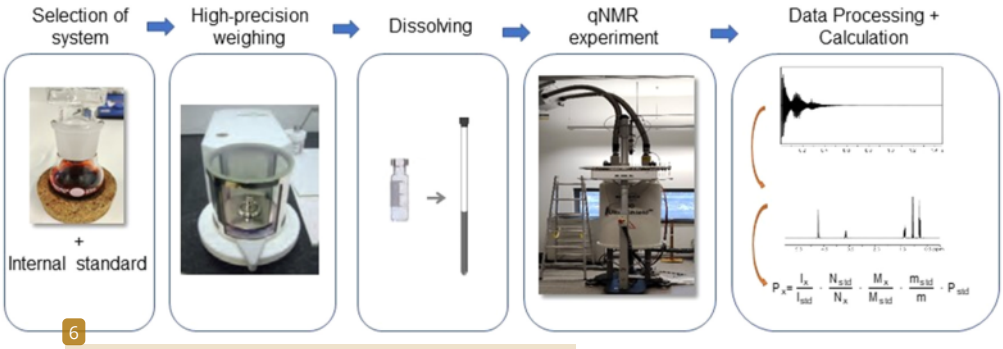

Fig. 7. General procedure of a qNMR experiment using an internal standard with modification and according to Sigma-Aldrich [71].

Table 2
Statistics F-test, Student's t-test, and RSD results for four quality parameters of RFO calculated from qNMR method versus titration method [35].

Parameter	F-Test	F-critical value	P (T <= t) one-tail	t critical one-tail	P (T <= t) two-tail	t critical two-tail	RSD (%)
SV	0.47	1.65	0.47	1.66	0.94	1.99	1.74
AV	0.47		0.47		0.93		1.65
EV	0.48		0.44		0.89		2.15
IV	0.50		0.46		0.92		0.90

$$AV_{NMR} = \frac{M_{KOH}}{m_s} \cdot \frac{m_{TCNB} \cdot P_{TCNB}}{M_{TCNB}} \cdot \frac{N_{TCNB}}{N_s(2)} \cdot \frac{I_{COOH}}{I_{TCNB}} \cdot 1000 \quad (3)$$

Unfortunately, the COOH singlet signal (δ = 10–11 ppm) does not always appear clearly in every oil spectrum. As described by Skiera et al. [32], since carboxyl groups are protic groups, their presence is strongly influenced by other protic groups in the sample solution (e.g., oil matrix components or the presence of impurities from the solvent). The rapid proton exchange process in the pure $CDCl_3$ solvent can cause the COOH signal line to broaden; it is not clearly visible with a low S/N ratio (insensitive for quantification). It can also be affected by the presence of alcohol groups in the sample solution, leading towards a substantial broadening of the COOH signal. Even using $CDCl_3$:DMSO-d_6 as a solvent (5:1, v/v), the COOH signal remains invisible clearly due to the high amount of alcohol groups in the sample solution, as shown for castor oil. On the other hand, it can also be naturally influenced by less FFA content, as found in the spectrum of repressed oil [32].

3.2. Saponification value

As with the determination of the AV, the ^{1}H NMR spectrum of RFO (Fig. 4) makes it possible to directly calculate the SV value; this value was obtained from the integral of the resonance of the methylene alpha (α-CH_2 total) at δ = 2.20–2.37 ppm (F1 and F2) which correlates with the structure of triglycerides and free fatty acids. Furthermore, SV can be calculated using the following formula [35]:

$$SV_{NMR} = \frac{M_{KOH}}{m_s} \cdot \frac{m_{DMSO_2} \cdot P_{DMSO_2}}{M_{DMSO_2}} \cdot \frac{N_{DMSO_2}}{N_s(2)} \cdot \frac{I_{\alpha-CH_2(total)}(2.37\text{-}2.20ppm)}{I_{DMSO_2}(2.98ppm)} \cdot 1000 \quad (3)$$

Skiera et al. [32] succeeded in demonstrating a quantitative NMR method with internal standards for determining SV in which the integrated methylene alpha proton signal is the same as the one used by Triyasmono et al. [35]. Only the signal of a different standard substance was used for comparison. The calculation formula used is as follows:

$$SV_{NMR} = \frac{M_{KOH}}{m_s} \cdot \frac{m_{TCNB} \cdot P_{TCNB}}{M_{TCNB}} \cdot \frac{N_{TCNB}}{N_s(2)} \cdot \frac{I_{\alpha-Carbonyl-CH2}}{I_{TCNB}} \cdot 1000 \quad (4)$$

3.3. Ester value

According to the results of ^{1}H NMR spectra of RFO obtained by Triyasmono et al. [35], the F2 signal (Fig. 4) can be assigned to the alpha methylene proton (α-CH_2 TAG) adjacent to the triacylglycerol carbonyl. This approach was also checked by the hydrolysis step and compared with the findings of Nieva et al. [37]. Therefore, the EV can also be calculated through the RFO spectra using the formula:

$$EV_{NMR} = \frac{M_{KOH}}{m_s} \cdot \frac{m_{DMSO_2} \cdot P_{DMSO_2}}{M_{DMSO_2}} \cdot \frac{N_{DMSO_2}}{N_s(2)} \cdot \frac{I_{\alpha-CH2(ester)}(2.37\text{-}2.27ppm)}{I_{DMSO_2}(2.98ppm)} \cdot 1000 \quad (5)$$

3.4. Iodine value

The IV is one of the oil quality parameters used to evaluate the degree of unsaturation. From the ^{1}H NMR spectra, as shown in Fig. 3, IV can also be determined directly, using the diagnostic signal of the resonance at δ = 5.27–5.37 ppm, which correlates with -CH = CH- in unsaturated fatty acids. IV can also be calculated using the formula:

$$IV_{NMR} = \frac{M_{Iod}}{m_s} \cdot \frac{m_{DMSO_2} \cdot P_{DMSO_2}}{M_{DMSO_2}} \cdot \frac{N_{DMSO_2}}{N_s(2)} \cdot \frac{I_{-CH=CH-}(5.37\text{-}5.27ppm)}{I_{DMSO_2}(2.98ppm)} \cdot 100 \quad (6)$$

3.5. Polyunsaturated fatty acid, monounsaturated fatty acid, and total unsaturated fatty acid

Recent developments related to the determination of MUFA, PUFA, and Total UFA that can also be determined by NMR spectra. The corresponding signal assignment for the determination of unsaturated fatty acid values was adopted from Hama et al. [33], namely, the signal at δ = 2.80–2.71 ppm, which correlates with the bis-allylic proton (= CH-CH_2-CH =) of PUFA; the integration of this signal can be used for quantification of PUFA values. The signal integration at δ = 2.10–1.90 ppm, associated with methylene allylic protons (-CH_2-CH = CH-), can be used to calculate the Total UFA value. Furthermore, by adopting the previous equation, the values of PUFA, Total UFA, and MUFA can be calculated using the following formula:

$$PUFA_{NMR} = \frac{M_{PUFA}}{m_s} \cdot \frac{m_{DMSO2} \cdot P_{DMSO2}}{M_{DMSO2}} \cdot \frac{N_{DMSO_2}}{N_s(2)} \cdot \frac{I_{CH_2(bisallylic)}(2.80\text{-}2.71ppm)}{I_{DMSO_2}(2.98ppm)} \cdot 100\% \quad (5)$$

$$TotalUFA_{NMR} = \frac{M_{TotalUFA}}{m_s} \cdot \frac{m_{DMSO2} \cdot P_{DMSO2}}{M_{DMSO2}} \cdot \frac{N_{DMSO_2}}{N_s(2)} \cdot \frac{\frac{1}{2} \cdot I_{CH2(allylic)}(2.10\text{-}1.90ppm)}{I_{DMSO_2}(2.98ppm)} \cdot 100\% \quad (6)$$

$$MUFA_{NMR} = \text{Total } UFA_{NMR} - PUFA_{NMR} \quad (7)$$

The benefit obtained from the use of this quantification technique using NMR is that all of these parameters can be determined simultaneously because one proton NMR measurement will produce all corresponding NMR spectral profiles. Therefore, the analyst can carry out the determination process of the quality parameter value in a single experiment, confirming that qNMR using the standard internal method is relatively effective and efficient in RFO quality control.

Furthermore, a comparison method is required by testing the same sample using the standard method to show the accuracy of the NMR method measurements obtained. For example, Triyasmono et al. [35] have compared the results of determining the AV, IV, SV, and EV values using the NMR method and the standard method (titration); both methods show comparable results on each sample after being tested with t-test and F-test statistics (Table 2). Both methods have the same precision.

4. Chemometric methods in NMR spectroscopic analysis of RFO

In general, chemometrics is defined as a scientific discipline that combines mathematical, statistical, and other methods based on formal logic for modeling and selecting optimal methods and experimental designs, as well as extracting important information in multivariate data analysis [72]. Chemometrics has become a primadonna worldwide as a data analysis technique, especially in combination with spectroscopy during the last decade [73]. This condition cannot be unlinked

from the development of high-tech and more sophisticated hardware and the ability to measure large amounts of repeated data.

Monakhova et al. [74] published a review on the application of combined chemometric algorithms to NMR spectral data, especially for food samples, where the usefulness of various chemometric algorithms is discussed, along with examples of their application. These techniques can generally be grouped according to the practical objectives to be achieved [75]. First, the principal component analysis (PCA) can simplify complex and massive multi-data and search for a group of hidden influences [76]. Second, the classification and discrimination methods can be divided into classification without training and classification with training in the next step, in which the partial least squares (PLS) is an example of a type of this second group. The application of the second method is preferable because in this case, a training sample set with known a priori information about its classification is used [73].

On the other hand, NMR spectroscopy itself and NMR analysis of the components of complex food/oil mixtures are not trivial. As explained above, the proton NMR sample spectra produce intensity positions and signal widths which are influenced by the type of mixed components present in the sample, the corresponding spin-coupling patterns, and various other sample parameters [36]. NMR settings and processing parameters can also have a significant impact on the quality of the NMR spectrum and subsequent interpretation [65,66]. Several strategies for handling and processing sample spectra are widely discussed. However, there still is relatively little consensus on what to do after NMR spectra have been collected, i.e., postprocessing steps, particularly for chemometric follow-up analysis [74]. Therefore, several types of software were developed for deconvoluting NMR spectra, using statistical approaches to the alignment of multiple NMR spectra, to scale or normalize aligned spectra, and then to identify spectral regions of interest (e.g., binning) or signals that differentiate cases from control [77].

In this context, Fig. 8 shows an outline of the NMR data processing steps referring to the spectral processing, post-processing, and analysis data carried out as applied by Triyasmono et al. [43] to RFO samples.

In spectra processing, several algorithms are used. One of them is the Bucketing technique. The operation of this technique is to reduce data and group the divided spectral spectra into equally spaced windows, called bins, or buckets, whose width usually ranges empirically between 0.005 and 0.05 ppm, consistent with typical spectra obtained [78]. Therefore, a new smaller set of variables is generated with intensities remaining the same as the original spectrum as the new variables are the result of summing the intensities with the area under each region used as individual intensities.

Furthermore, the width of the bucket is also adjusted to cover the variability of chemical shifts around the signal, so the problem of misalignment tends to be overcome [77]. Lachenmeier et al. [78] also suggested this strategy to generate a matrix consisting of integrals, which can be further analyzed with the help of chemometric methods. Likewise, Triyasmono et al. [43] used an alignment strategy with 0.009 ppm bucketing to obtain a sample spectral matrix sufficient for chemometric analysis, as shown in Fig. 9.

At the same time, this method is effective in terms of time consumption while maintaining the fine structure of the spectrum. However, the disadvantage of such a method is that a stable signal at the chemical shift scale in the initial spectrum is required. Despite this, it is fact that binning/bucketing is the most successful and frequently used method of choice for the pretreatment of experimental NMR spectroscopy data [43,78–80]. Therefore, subsequent statistical analyses are always carried out on a bucket basis rather than by direct use of individual intensities or integrals. This is a basic special feature of the chemometric approach to NMR spectral treatment.

It should be noted that the majority of NMR signal intensities in different regions of the spectrum can be different, as explained by Monakhova et al. [74]. The construction of models for different regions of the spectrum and the subsequent search for optimal models is a common practice. In addition, the internal standard signal is negligible because random changes in the concentration of these compounds have no effect on the analytical results.

Moreover, any statistical procedure suitable for generating product groupings according to specific criteria should be performed after proper variable selection. In the context of RFO sample analysis, the selection of correlated signals for each oil quality parameter has been determined [54]. Furthermore, a bucketing algorithm is used to generate an adequate variable matrix for data pre-processing. After obtaining an appropriate matrix, the Principle Component Analysis (PCA) technique is applied for grouping the samples.

PCA is a statistical technique widely used for analyzing large multidimensional data sets such as the NMR spectral data point. This technique can identify the direction of the most significant variation in the data via principal components (P1;P2;...) and represent the data in a coordinate system determined by the PCs [76].

The application of PCA for quantization in spectral discrimination is entirely analogous: suppose that in the case of RFO spectra, coherent types of variation in the spectral dataset include the amplitude of a fixed line shape, then the first PC identifies this shape, regardless of whether it is Lorentzian, Gaussian, or a more complex shape. Furthermore, higher-order PC shapes will also indicate the type of variation (other than amplitude) in the data, including frequency and/or chemical shifts as well as linewidth variations. Therefore, the entire spectral data set can be approximated by a projection of data points along P1 (called a score) with minimal loss of information [76].

Consequently, PCA is suitable for data sets containing spectra acquired under the same conditions-same instrument, same acquisition parameters (e.g. number of points in FID, spectral bandwidth, saturation pulses, decoupling) to avoid analysis interference.

In the case of most oil analyses, PCA applied to NMR spectra is used to find classes or groupings of classes that have the same object in common. For example; grouping based on geographical position and authentication and presence of adulterants [40–42,64]. Triyasmono et al. [43] demonstrated PCA to visualize grouping the quality of RFO based on two main parameters, namely, the degree of unsaturation using 13 matrix variables signals at δ = 5.27–5.37 ppm and the FFA value using 18 matrix variables signal at δ = 2.20–2.37 ppm, as shown in Fig. 10.

According to the results of the PCA plots above, there are differences in the group visualization of the RFO products analyzed using NMR based on the categories used. For example, in Fig. 10**A**, the RFO products are distributed in each PC and divided into six groups of the degree of unsaturation values, respectively. In Fig. 10**B**, RFO products are scattered along the PC, which can be differentiated into seven groups of FFA values, respectively. Thus, the PCA algorithm applied to the ^{1}H NMR spectra of a sample can be an effective alternative solution in determining the quality of an oil.

As discussed earlier, PCA including exploratory analysis is the first and fundamental step in processing chemometric data. In some cases, it may be the only approach required to characterize the sample under investigation. However, due to the limitations of its unsupervised method, to support and provide solutions that occur more frequently in quality control practices, it is necessary not only to rely on qualitative control but also to provide quantitative estimates [75]. Therefore, PLS regression [81–83] was proposed as an alternative method to calculate a reliable multivariate calibration model.

Briefly, as discussed by Biancolillo and Marini [73], the PLS technique is based on extracting a set of T scores by projecting a block X on the latent variable subspace, which is relevant for calibration issues. In PLS, the latent variable (that is, the direction to where the data are projected) is defined in such a way that maximizes the covariance between the score and the fit response(s): maximizing the covariance makes it possible to obtain a score which at the same time describes the relevant part of X's variance and correlates with the response Y. In simple terms, in the PLS method, the simultaneous decomposition of two matrices is performed: an analytical signal matrix (X) and a matrix

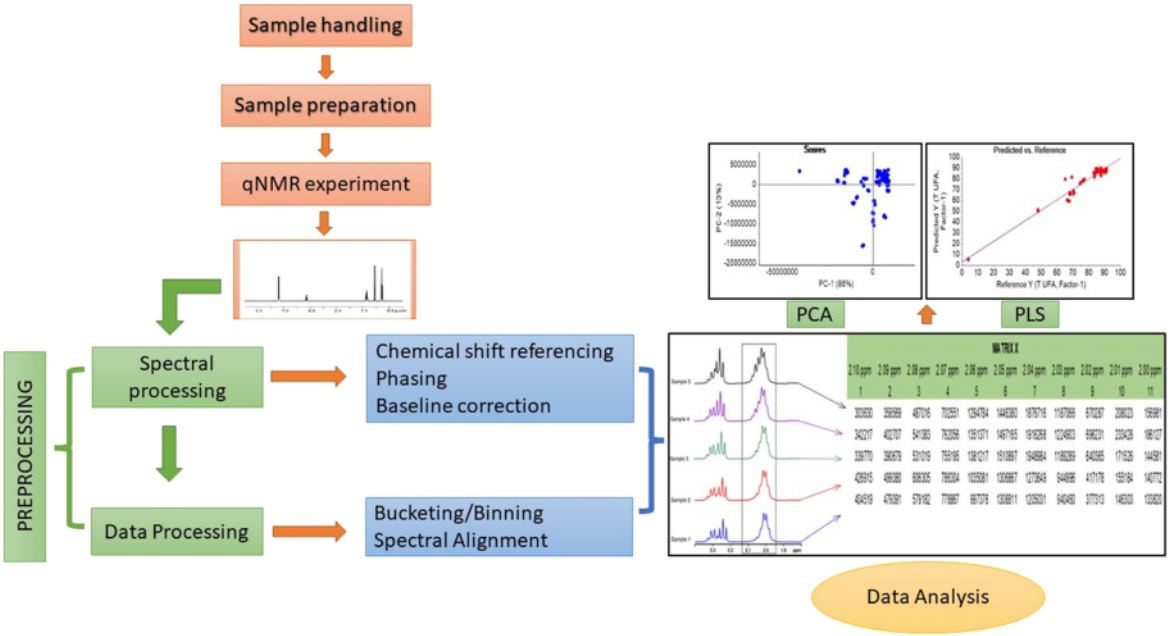

Fig. 8. Summary of spectral processing, post-processing, and analysis data steps on RFO NMR-spectra with modification and permission from Emwas et al. [65].

of corresponding chemical indices (Y). Furthermore, Masili et al. [84] demonstrated the success of NMR and PLS modeling in the physico-chemical characterization test of 64 pure crude oil samples obtained from 28 different extraction fields with the majority of the coefficient of determination not less than 0.85 and a relatively low standard error.

In preparing the calibration and prediction sets, most of the sample proportion divided into 70:30 adhere to the Kennard–Stone algorithm [41,85]. However, at the same time, the number of samples available to create a calibration model is usually limited due to the cost of analysis and/or sample availability. Therefore, the number of calibration samples is often much lower than the number of variables used for prediction. As discussed by Kvalheim et al. [86], using a Monte Carlo

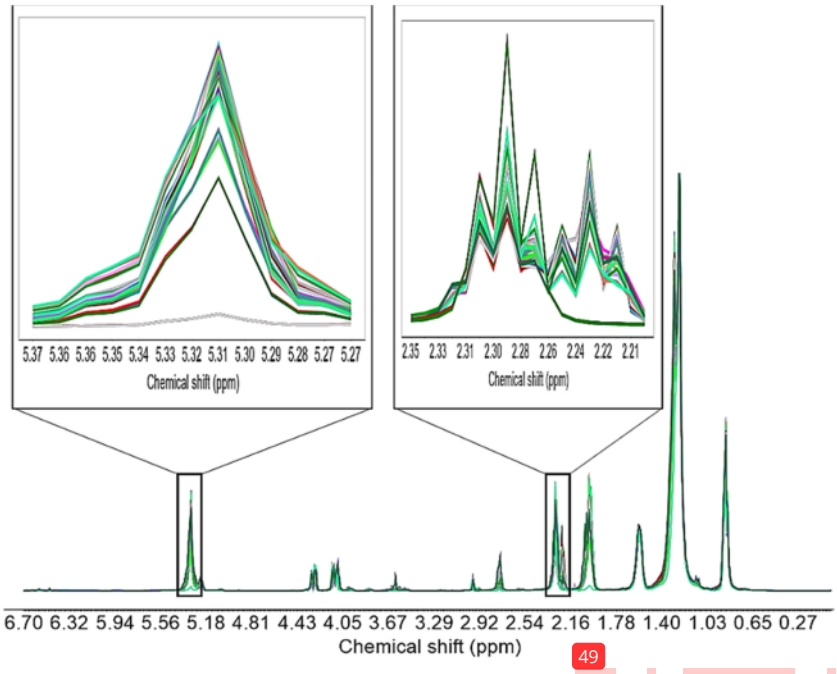

Fig. 9. Reduced of bucketing ^{1}H NMR spectra of all RFO samples with an enlarged spectral range of δ = 5.37–5.27 ppm and δ = 2.37–2.20 ppm. The spectra are color-coded according to the brand. [43].

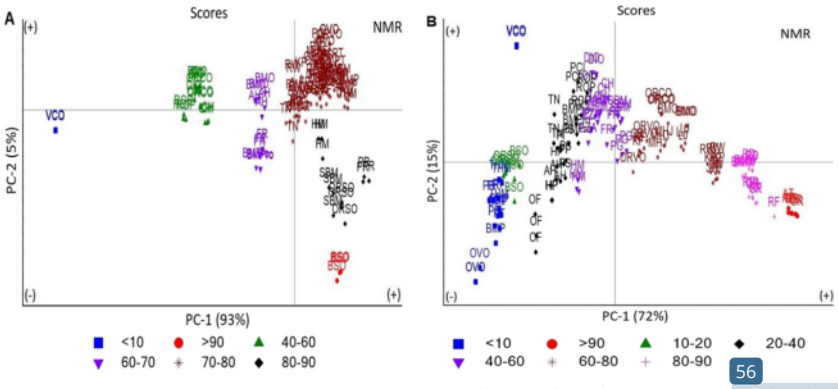

Fig. 10. Plot scores of all samples (120 spectra) on the main components PC1 and PC2 on the selected signal 1H NMR spectra based on the degree of unsaturation (A) and the FFA value category with modification and permission from Triyasmono et.al [43].

approach [87], two methods were developed and compared to select the optimal number of PLS components which is defined as the number where no statistically significant increase in prediction error is observed when additional components are introduced into the model. Both methods define probability measures and give similar results for model selection in this application. As applied by Triyasmono et al. [43] on RFO spectra samples, PLS model with a composition of calibration and prediction ratio close to 50:50 still gives a relatively small error value (< 4%).

In addition, the comparison of NMR spectroscopy results with data obtained by other spectroscopic methods is also interesting. For example, the PLS model to determine the quality parameters of RFO (unsaturated degree and FFA) is built based on its spectrum. However, the R^2 values for independent assay sets (0.83 and 0.94) and root mean square errors of (5.50 and 5.10), respectively, were much lower than those for NMR spectroscopy [43]. This is probably due to the much more significant amount of spectroscopic (structural) information obtained from the NMR spectrum rather than in the IR range [74]. Thus, although NMR spectroscopy is relatively expensive and the measurement time is longer (about 15 min, compared to 2 min for IR spectroscopy), we believe that NMR spectroscopy provides more reliable quantitative analytical results and is a highly efficient technique, as shown in Table 3.

On the other hand, Giese et al. [88] reported that the results of cod liver oil authentication using NMR and FTIR spectra combined with artificial neural networks algorithms showed that the detection limit of FTIR was lower (0.22%) with a root mean square error of predict (RMSEP) of 0.86% than ^{1}H NMR (3.0%) and ^{13}C NMR (1.8%) with RMSEP 2.7% and 1.8%, respectively. However, the comparison of the ^{13}C NMR and FTIR models yielded the highest accuracy with 100% of correct classification in a series of calibrations, tests, and validations. In addition, they stated that the ^{1}H NMR signal is essential for one of the counterfeitings of cod liver oil predictions that can be identified by analyzing its PLS factor loading.

Furthermore, to meet the quality and reliability of the investigated model, it is necessary to carry out a validation process with an appropriate diagnostic definition, most of which is based on residual calculations [75]. In this context, to avoid over-optimism and to get a fair estimate as much as possible, it is necessary to calculate the errors from different data sets, which is generally referred to as cross-validation [89]. On the other hand, cross-validation can be based on repeated resampling training and test data sets. Cross-validation, in particular, is suitable when the number of samples available is small and there is no possibility of constructing an external test set. However, the potential for bias can still occur as calibration and validation are not completely independent of one another [90]. Nevertheless, cross-validation can still be effectively used to estimate the optimal values of the model meta-parameters (e.g.the number of hidden variables in PLS regression or PLSDA classification) [89,91].

5. Conclusion

Some of the descriptions outlined in this perspective indicate that the quantitative ^{1}H NMR method using internal standards is able to directly and simultaneously assess several oil quality parameters (AV, EV, IV, SV, and the composition of MUFA, PUFA, and Total UFA). In addition, the combination of ^{1}H NMR spectroscopy and chemometrics is a reliable tool for the routine analysis of oil products, including RFO samples. PCA can demonstrate exploratory or visualized grouping from multivariate data and PLS, providing buildings with reliable calibration and classification strategies to predict quantitatively based on the collected ^{1}H NMR spectral profile experiments.

Unfortunately, currently NMR spectroscopy is not widely used in official product analysis (compendial method) and oil quality control laboratories because it is considered complicated and too expensive. In practice, one NMR spectrum can be obtained very fast within approximately 15 min and subsequent chemometrics analysis of the entire spectrum can be done quickly and automatically done with chemometric software such as Unscrambler, so that PCA and PLS operations can also be carried out very quickly (about 10 min). Therefore, in the future, it is necessary to increase the role of cheaper and smaller benchtop NMR instrumentation and software in order to make NMR

Table 3
Results of PLS modeling and prediction of the RFO properties based on both methods (1 H NMR and FTIR) [43].

Parameter	Method	Value	Factor	R^2			Root Mean Square Error (RMSE)		
				Calibration	Validation	Prediction	RMSEC	RMSEV	RMSEP
Unsaturated degree	^{1}H NMR	0–90	1	0.972	0.967	0.915	3.08	3.29	4.18
	FTIR	0–90	1	0.919	0.914	0.834	5.31	5.49	5.50
FFA value	^{1}H NMR	0–100	2	0.988	0.986	0.982	3.49	3.76	3.12
	FTIR	0–100	2	0.977	0.977	0.948	4.88	5.15	5.10

spectroscopy more suitable and accessible for routine analysis in oil quality control.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Liling Triyasmono reports financial support was provided by Lambung Mangkurat University.Acknowledgements

This work was supported by the supporting finance of Lambung Mangkurat University (Grant No. 3894/UN8/KP/2019). The authors warmly thank Dr. Ludwig Höllein for editorial support during writing and preparation for submission this publication.

Author contributions

The manuscript was written through contributions from both authors. All authors h approved the final version of the manuscript. Liling Triyasmono: Methodology, writing – original draft, Writing – review & editing, and Projec administration. Ulrike Holzgrabe: methodology, Writing – review & editing, and Funding acquisition.

References

[1] S. Joos, K. Glassen, B. Musselmann, Herbal medicine in primary healthcare in Germany: the patient's perspective, Evid. -Based Complement. Altern. Med (2012) 1–10, https://doi.org/10.1155/2012/294638
[2] S. Pengpid, K. Peltzer, Utilization of traditional and complementary medicine in Indonesia: results of a national survey in 2014–15, Complement. Ther. Clin. Pract. 33 (2018) 156–163, https://doi.org/10.1016/j.ctcp.2018.10.006
[3] A. Rohman, R. Sugeng, Y.B. Che Man, Characterizaton of red fruit (Pandanus conoideus Lam) oil, Int. Food Res. J. 19 (2) (2012) 563–567.
[4] Z.L. Sarungallo, P. Hariyadi, N. Andarwulan, E.H. Purnomo, Characterization of chemical properties, lipid profile, total phenol and tocopherol content of oils extracted from nine clones of red fruit (Pandanus conoideus), J. Nat. Sci. 49 (2) (2015) 237–250.
[5] A. Rohman, A. Windarsih, Characterization, biological activities, and authentication of red fruit (*Pandanus conoideus* Lam) oil, Food Res 2 (2) (2017) 134–138.
[6] O.P. Astirin, M. Harini, N.S. Handajani, The effect of crude extract of Pandanus conoideus Lamb. var. yellow fruit on apoptotic expression of the breast cancer cell line (T47D), Biodiversitas 10 (1) (2009) 44–48.
[7] R. Siagian, Effect of red fruit (*Pandanus conoideus*) on the growth of breast cancer, J. Agromed Unila 2 (4) (2015) 500–503.
[8] S.A. Sangkala, M.R. Jura, I.M. Tangkas, Antioxidant activity test of red fruit (Pandanus baccari L) extractsi Poso area Central Sulawesi, J. Akad. Kim. 3 (4) (2014) 198–205.
[9] A. Rohman, S. Riyanto, N. Yuniarti, W.R. Saputra, R. Utami, W. Mulatsih, Antioxidant activity, total phenolic, and total flavaonoid of extracts and fractions of red fruit (*Pandanus conoideus*, Lam.), Int. Food Res. J. 17 (2010) 97–106.
[10] M. Budi, F.R. Paimin, Red fruit (Pandanus conoideus Lam), Penebar Swadaya 3–26 (47–56) (2004) 67–68.
[11] Y. Astuti, L.L.R. Dewi, The effect of red fruit extract (*Pandanus conoideus* L.) to the blood glucose level, Mutiara Med. 7 (1) (2007) 01–06.
[12] K. Khiong, O.A. Adhika, M. Chakravitha, Inhibition of NF-κB pathway as the therapeutic potential of red fruit (*Pandanus conoideus* Lam.) in the treatment of inflammatory bowel disease, JKM (J. Kedokt. Maranatha). 9 (1) (2009) 69–75.
[13] T. Tambaip, M.B. Karo, M. Hatta, R. Dwiyanti, R. Natzir, M.N. Massi, A.A. Islam, K. Djawad, Immunomodulatory Effect of Orally Red Fruit (*Pandanus conoideus*) Extract on the Expression of CC Chemokine Receptor 5 mRNA in HIV Patients with Antiretroviral Therapy, J. Immunol. Res. 11 (2018) 15–21, https://doi.org/10.3923/rji.2018.15.21
[14] Sarungallo Z.L. Murtiningrum, N.L. Mawikere, The exploration and diversity of red fruit (*Pandanus conoideus*, Lam.) from Papua based on its physical characteristics and chemical composition, J. Biol. Divers. 13 (3) (2012) 124–129.
[15] E.P. Susanti, A. Rohman, W. Setyaningsih, Dual response optimization of ultrasound-assisted oil extraction from red fruit (Pandanus conoideus): Recovery and Total Phenolic Compounds, Agronomy 12 (523) (2022) 1–16, https://doi.org/10.3390/agronomy12020523
[16] Y. Endo, Analytical methods to evaluate the quality of edible fats and oils: the JOCS standard methods for analysis of fats, oils and related materials and advanced methods, J. Oleo Sci. 67 (1) (2018) 1–10, https://doi.org/10.5650/jos.ess17130
[17] European Pharmacopoeia 10th. European Department for the Quality of Medicines. 2020.Strasbourg. France: chapt. 2.5.1, 2.5.2, 2.5.4, 2.5.6.
[18] H.H. Chiu, C.H. Kuo, Gas chromatography-mass spectrometry-based analytical strategies for fatty acid analysis in biological samples, J. Food Drug Anal. 28 (1) (2020) 60–73, https://doi.org/10.1016/j.jfda.2019.10.003
[19] Y.I. Tur'yan O.Y. Berezin I. Kuselman A. Shenhar pH-metric determination of acid values in vegetable oils without titration J. Am. Oil Chem. Soc. 73 1996 295 301.
[20] W.Q. Xiea, X.-S. Chai, An efficient method for determining the acid value in edible oils by solvent-assisted headspace gas chromatography, Anal. Methods 8 (2016) 5789-579.
[21] N. Bazina, J. He, Analysis of fatty acid profiles of free fatty acids generated in deep-frying process, J. Food Sci. Technol. 55 (2018) 3085–3092.
[22] M. Tarvainen, J.P. Suomela, H. Kallio, Ultra high performance liquid chromatography-mass spectrometric analysis of oxidized free fatty acids and acylglycerols, Eur. J. Lipid Sci. Technol. 113 (2011) 409–422.
[23] F.R. Van de Voort, J. Sedman, G. Emo, A.A. Ismail, Rapid and direct iodine value and saponification number determination of fats and oils by attenuated total reflactance/fourier transform infrared spectroscopy, J. Am. Oil Chem. Soc. 69 (11) (1992) 1118–1123.
[24] M.D. Guill'en, N. Cabo, Fourier transform infrared spectra data versus peroxide and anisidine values to determine oxidative stability of edible oils, Food Chem. 77 (2002) 503–510, https://doi.org/10.1016/S0308-8146(01)00371-5
[25] C. Gertz, H.J. Fiebig, J.N.S. Hancock, FT-near infrared (NIR) spectroscopy screening analysis of used frying fats and oils for rapid determination of polar compounds, polymerized triacylglycerols, acid value and anisidine value [DGF C-VI 21a (13)], Eur. J. Lipid Sci. Technol. 115 (2013) 1193–1197, https://doi.org/10.1002/ejlt.201300221
[26] L. Triyasmono, S. Riyanto, A. Rohman, Determination of iodine value and acid value of red fruit oil by infrared spectroscopy and multivariate calibration, Int. Food Res. J. 20 (6) (2013) 3259–3263.
[27] A. Rohman, L. Triyasmono, S. Riyanto, L. Andina, Rapid determination of saponification value in red fruit oil by infrared spectroscopy and partial least square calibration, Res. J. Med. Plant. 9 (8) (2015) 442–448.
[28] R.T. Sato, R. de Jesus Coelho Castro, P.M. de Castro Barra, M.A.L. de Oliveira, Rapid separation of free fatty acids in vegetable oils by capillary zone electrophoresis, Phytochem. Anal. 25 (2014) 241–246, https://doi.org/10.1002/pca.2499
[29] T.L. Amorim, L.M. Duarte, E.M. da Silva, M.A.L. Oliveira, Capillary electromigration methods for fatty acids determination in vegetable and marine oils: A review, Electrophoresis 42 (3) (2020) 289–304, https://doi.org/10.1002/elps.202000260
[30] M.D. Guillén, A. Ruiz, High resolution ^{1}H nuclear magnetic resonance in the study of edible oils and fats, Trends Food Sci. Technol. 12 (9) (2001) 328–338, https://doi.org/10.1016/S0924-2244(01)00101-7
[31] A.S. Sarpal, S.R. Silva, P.R.M. Silva, T.V. Monteiro, J. Itacolomy, V.S. Cunha, R.J. Daroda, Direct method for the determination of the iodine value of biodiesel by quantitative nuclear magnetic resonance (q1H NMR) spectroscopy, Energy Fuels 29 (12) (2015) 7956–7968, https://doi.org/10.1021/acs.energyfuels.5b01462
[32] C. Skiera, P. Steliopoulos, T. Kuballa, B. Diehl, U. Holzgrabe, Determination of free fatty acids in pharmaceutical lipids by ^{1}H NMR and comparison with the classical acid value, J. Pharm. Biomed. Anal. 93 (2014) 43–50, https://doi.org/10.1016/j.jpba.2013.04.010
[33] J.R. Hama, V. Fitzsimmons-Thoss, Determination of unsaturated fatty acids composition in walnut (Juglans regia L.) oil using NMR spectroscopy, Food Anal. Methods 15 (5) (2022) 1226–1236, https://doi.org/10.1007/s12161-021-02203-0
[34] E. Hafer, U. Holzgrabe, S. Wiedemann, K.M. Adams, B. Diehl, NMR spectroscopy: determination of peroxide value in vegetable and krill oil by using triphenylphosphine as tagging reagent, Eur. Food Res. Technol. 122 (5) (2020) 1–11, https://doi.org/10.1002/ejlt.201900442
[35] L. Triyasmono, C. Schollmayer, J. Schmitz, E. Hovah, C. Lombo, S. Schmidt, U. Holzgrabe, Simultaneous determination of the saponification value, acid value, ester value, and iodine value in commercially available red fruit oil (Pandanus conoideus, Lam.) using ^{1}H qNMR spectroscopy, Food Anal. Methods (2022) 1–13, https://doi.org/10.1007/s12161-022-02401-4
[36] U. Holzgrabe, Quantitative NMR spectroscopy in pharmaceutical applications, Prog. Nucl. Magn. Reson. Spectrosc. 57 (2010) 229–240, https://doi.org/10.1016/j.pnmrs.2010.05.001
[37] B. Nieva-Echevarría, E. Goicoechea, M.J. Manzanos, M.D. Guillén, A method based on ^{1}H NMR spectral data useful to evaluate the hydrolysis level in complex lipid mixtures, Food Res. Int. 66 (2014) 379–387, https://doi.org/10.1016/j.foodres.2014.09.031
[38] A. Sacco, M.A. Brescia, V. Liuzzi, F. Reniero, C. Guillou, S. Ghelli, P. Van Der Meer, Characterization of Italian olive oils based on analytical and nuclear magnetic resonance determinations, J. Am. Oil Chem. Soc. 77 (6) (2000) 619–625, https://doi.org/10.1007/s11746-000-0100-y
[39] R.I.M. Almoselhy, M.H. Allam, M.H. El-Kalyoubi, A.A. El-Sharkawy, ^{1}H NMR spectral analysis as a new aspect to evaluate the stability of some edible oils, Ann. Agric. Sci. 59 (2) (2014) 201–206, https://doi.org/10.1016/j.aoas.2014.11.006
[40] L. Mannina, F. Marini, M. Gobbino, A.P. Sobolev, D. Capitani, NMR and chemometrics in tracing European olive oils: the case study of Ligurian samples, Talanta 80 (2009) 2141–2148, https://doi.org/10.1016/j.talanta.2009.11.021
[41] C. Ingallina, A. Cerreto, L. Mannina, S. Circi, S. Vista, D. Capitani, F. Marini, Extra-virgin olive oils from nine italian regions: An ^{1}H NMR-chemometric characterization, Metabolites 9 (4) (2019) 1–12, https://doi.org/10.3390/metabo9040065
[42] R. Popescu, D. Costinel, O.R. Dinca, A. Marinescu, I. Stefanescu, R.E. Ionete, Discrimination of vegetable oils using NMR spectroscopy and chemometrics, Food Control 48 (2015) 84–90, https://doi.org/10.1016/j.foodcont.2014.04.046
[43] L. Triyasmono, C. Schollmayer, U. Holzgrabe, Chemometric analysis applied to ^{1}H NMR and FTIR data for a quality parameter distinction of red fruit (*Pandanus conoideus*, lam.) oil products, Phytochem. Anal. (2022) 1–12, https://doi.org/10.1002/pca.3196
[44] B. Kowalski, C. Reilly, Nuclear Magnetic Resonance, Spectr. Interpret. Pattern Recognit. J. Phys. Chem. 75 (10) (1971) 1402–1411.

[45] H. Grahn, F. Delaglio, M.A. Delsuc, G.C. Levy, Multivariate data analysis for pattern recognition in two-dimensional NMR, J. Magn. Reson. 77 (1988) 294–307.

[46] R.E. Hoffman, G.C. Levy, Modern methods of NMR data processing and data evaluation, Prog. NMR Spectrosc. 23 (1991) 211–258.

[47] G. Le Gall, I.J. Colquhoun, NMR Spectroscopy in Food Authentication (in Food Authenticity and Traceability), Woodhead, New York, 2003, pp. 131–155.

[48] L. Mannina, A.P. Sobolev, A. Segre, Olive oil as seen by NMR and chemometrics, Spectrosc. Eur. 15 (3) (2003) 6–14.

[49] K.K. Ketshajwang, J. Holmback, S.O. Yeboah, Quality and compositional studies of some edible leguminosae seed oils in Botswana, J. Am. Oil Chem. Soc. 75 (1998) 741–743.

[50] V. Thoss, P.J. Murphy, R. Marriott, T. Wilson, Triacylglycerol composition of British bluebell (Hyacinthoides non-scripta) seed oil, RSC Adv. 2 (12) (2012) 5314–5322, https://doi.org/10.1039/c2ra20090b

[51] S.K. Bharti, R. Roy, Quantitative ^{1}H NMR spectroscopy, TrAC - Trends Anal. Chem. 35 (2012) 5–26, https://doi.org/10.1016/j.trac.2012.02.007

[52] D. Castejón, P. Fricke, M.I. Cambero, A. Herrera, Automatic ^{1}H NMR screening of fatty acid composition in edible oils, Nutrients 8 (2) (2016) 1–10, https://doi.org/10.3390/nu8020093

[53] T. Beyer, B. Diehl, U. Holzgrabe, Quantitative NMR spectroscopy of biologically active substances and excipients, Bioanal. Rev. 2 (2010) 1–22, https://doi.org/10.1007/s12566-010-0016-8

[54] S. Sun, M. Jin, X. Zhou, J. Ni, X. Jin, H. Liu, Y. Wang, The application of quantitative^{1}H NMR for the determination of orlistat in tablets, Molecules 22 (9) (2017) 1–10.

[55] Y.B. Monakhova, B.W.K. Diehl, Practical guide for selection of ^{1}H qNMR acquisition and processing parameters confirmed by automated spectra evaluation, Magn. Reson. Chem. 55 (11) (2017) 996–1005, https://doi.org/10.1002/mrc.4622

[56.] A.M. Torres, W.S. Price, Common problems and artifacts encountered in solution-state NMR experiments, Concepts Magn. Reson. Part A 45A (2) (2016) 1–16, https://doi.org/10.1002/cmr.a.21387

[57] M.D. Guillén, A. Ruiz, Rapid simultaneous determination by proton NMR of unsaturation and composition of acyl groups in vegetable oils, Eur. Food Res. Technol. 105 (11) (2003) 688–696, https://doi.org/10.1002/ejlt.200300866

[58] C. Skiera, P. Steliopoulos, T. Kuballa, U. Holzgrabe, B. Diehl, ^{1}H NMR approach as an alternative to the classical p-anisidine value method, Eur. Food Res. Technol. 235 (6) (2012) 1101–1105, https://doi.org/10.1007/s00217-012-1841-5

[59] R.J. Abraham, J.J. Byrne, L. Griffiths, M. Perez, ^{1}H chemical shifts in NMR: Part 23, the effect of dimethyl sulphoxide versus chloroform solvent on ^{1}H chemical shifts, Magn. Reson. Chem. 44 (5) (2006) 491–509, https://doi.org/10.1002/mrc.1747

[60] T. Beyer, C. Schollmayer, U. Holzgrabe, The role of solvents in the signal separation for quantitative ^{1}H NMR spectroscopy, J. Pharm. Biomed. Anal. 52 (1) (2010) 51–58, https://doi.org/10.1016/j.jpba.2009.12.007

[61.] B. Nieva-Echevarría, E. Goicoechea, M.J. Manzanos, M.D. Guillén, Usefulness of ^{1}H NMR in assessing the extent of lipid digestion, Food Chem. 179 (2015) 182–190, https://doi.org/10.1016/j.foodchem.2015.01.104

[62] M. Guillén, I. Carton, E. Goicoechea, P.S. Uriarte, Characterization of cod liver oil by spectroscopic techniques. New approaches for the determination of compositional parameters, acyl groups, and cholesterol from ^{1}H Nuclear Magnetic Resonance and Fourier transform infrared spectral data, J. Agric. Food Chem. 56 (19) (2008) 9072–9079.

[63.] L.F. Johnson, J.N. Schoolery, Determination of unsaturation and average molecular weight of natural fats by nuclear magnetic resonance, Anal. Chem. 34 (1962) 1136–1139.

[64] L.M. Ravaglia, A.B.C. Pizzotti, G.B. Alcantara, NMR-based and chemometric approaches applicable to adulteration studies for assessment of the botanical origin of edible oils, J. Food Sci. Technol. 56 (1) (2019) 507–511, https://doi.org/10.1007/s13197-018-3485-3

[65] A.H. Emwas, E. Saccenti, X. Gao, R.T. McKay, dos Santos VAPM, R. Roy, D.S. Wishart, Recommended strategies for spectral processing and post-processing of 1D ^{1}H NMR data of biofluids with a particular focus on urine, Metabolomics 14 (31) (2018) 1–23, https://doi.org/10.1007/s11306-018-1321-4

[66] C. Deborde, J.X. Fontaine, D. Jacob, A. Botana, V. Nicaise, F. Richard-Forget, R. Molinié, Optimizing 1D ^{1}H NMR profiling of plant samples for high throughput analysis: extract preparation, standardization, automation and spectra processing, Metabolomics 15 (28) (2019) 1–12, https://doi.org/10.1007/s11306-019-1488-3

[67] Y. Miyake, K. Yokomizo, N. Matsuzaki, Rapid determination of iodine value by ^{1}H nuclear magnetic resonance spectroscopy, J. Am. Oil Chem. Soc. 75 (1998) 15–19.

[68] G. Knothe, J.A. Kenar, Determination of the fatty acid profile by ^{1}H NMR spectroscopy, Eur. J. Lipid Sci. Technol. 106 (2) (2004) 88–96, https://doi.org/10.1002/ejlt.200300880

[69] C. Yu, Q. Zhang, P.Y. Xu, Y. Bai, W.B. Shen, B. Di, M.X. Su, Quantitative determination and validation of octreotide acetate using ^{1}H NMR spectroscopy with internal standard method, Magn. Reson Chem. 56 (1) (2018) 37–45, https://doi.org/10.1002/mrc.4665

[70] R.J. Wells, J. Cheung, J.M. Hook, Dimethylsulfone as a universal standard for analysis of organics by QNMR, Accredit. Qual. Assur. 9 (8) (2004) 450–456, https://doi.org/10.1007/s00769-004-0779-0

[71] Sigma-Aldrich. QUANTITATIVE NMR - Technical Details and TraceCERT® Certified Reference Materials. Sigma-Aldrich. 2017;8. Retrieved from 〈https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/SigmaAldrich/Brochure/1/qnmr-brochure-rjo.pdf〉.

[72] Y.O. Rodionova, L.A. Pomerantsev, Chemometrics: achievements and prospects, Russ. Chem. Rev. 75 (4) (2006) 271–287.

[73] A. Biancolillo, F. Marini, Chemometric methods for spectroscopy-based pharmaceutical analysis, Front. Chem. 6 (576) (2018) 1–16, https://doi.org/10.3389/fchem.2018.00576

[74] Y.B. Monakhova, T. Kuballa, D.W. Lachenmeier, Chemometric methods in NMR spectroscopic analysis of food products, J. Anal. Chem. 68 (9) (2013) 755–766, https://doi.org/10.1134/S1061934813090098

[75] R.G. Brereton, J. Jansen, J. Lopes, F. Marini, A. Pomerantsev, O. Rodionova, Chemometrics in analytical chemistry—part II: modeling, validation, and applications, Anal. Bioanal. Chem. 410 (2018) 6691–6704, https://doi.org/10.1007/s00216-018-1283-4

[76] R. Stoyanova, T.R. Brown, NMR spectral quantitation by principal component analysis, NMR Biomed. 14 (2001) 271–277, https://doi.org/10.1002/nbm.700

[77] S.A. Sousa, A. Magalhães, M.M.C. Ferreira, Optimized bucketing for NMR spectra: three case studies, Chemom. Intell. Lab. Syst. 122 (2013) 93–102, https://doi.org/10.1016/j.chemolab.2013.01.006

[78] D.W. Lachenmeier, W. Frank, E. Humpfer, H. Schäfer, S. Keller, M. Mörtter, M. Spraul, Quality control of beer using high-resolution nuclear magnetic resonance spectroscopy and multi-variate analysis, Eur. Food Res. Technol. 220 (2) (2005) 215–221.

[79] P. Maes, Y.B. Monakhova, T. Kuballa, H. Reusch, D.W. Lachenmeier, Qualitative and quantitative control of carbonated cola beverages using ^{1}H NMR spectroscopy, J. Agric. Food Chem. 60 (11) (2012) 2778–2784.

[80] H. Köbler, Y.B. Monakhova, T. Kuballa, C. Tschiersch, J. Vancutsem, G. Thielert, A. Mohring, D.W. Lachenmeier, Nuclear magnetic resonance spectroscopy and chemometrics to identify pine nuts that cause taste disturbance, J. Agric. Food Chem. 59 (13) (2011) 6877–6881.

[81] P. Geladi, B.R. Kowalski, Partial least squares regression: a tutorial, Anal. Chim. Acta 185 (1986) 1–17, https://doi.org/10.1016/0003-2670(86)80028-9

[82] Martens H., Geladi P. "Multivariate Calibration," in Encyclopedia of Statistical Sciences, eds eds S. Kotz, C. B. Read, N. Balakrishnan, B. Vidakovic, and N. L. Johnson (Hoboken, NJ: Wiley), 5177–5189.

[83] S. Wold, H. Martens, H. Wold, "The multivariate calibration problem in chemistry solved by the PLS methods, in: A. Ruhe, B. Kagstrøm (Eds.), in Matrix Pencils: Proceedings of A Conference Held at Pite Havsbad, Sweden, Springer Verlag, Heidelberg, 1983, pp. p286–p293.

[84] A. Masili, S. Puligheddu, L. Sassu, P. Scano, A. Lai, Prediction of physical-chemical properties of crude oils by ^{1}H NMR analysis of neat samples and chemometrics, Magn. Reson. Chem. 50 (11) (2012) 729–738, https://doi.org/10.1002/mrc.3872

[85] R.W. Kennard, L.A. Stone, Computer aided design of experiments, Technometrics 11 (1969) 137–148, https://doi.org/10.1080/00401706.1969.10490666

[86] O.M. Kvalheim, B. Grung, T. Rajalahti, Number of components and prediction error in partial least squares regression determined by Monte Carlo resampling strategies, Chemom. Intell. Lab. Syst. 188 (2019) 79–86, https://doi.org/10.1016/j.chemolab.2019.03.006

[87] Q.S. Xu, Y.Z. Liang, Monte Carlo cross validation, Chemom. Intel. Lab. Syst. 56 (2001) 1–11.

[88] E. Giese, S. Rohn, J. Fritsche, Chemometric tools for the authentication of cod liver oil based on nuclear magnetic resonance and infrared spectroscopy data, Anal. Bioanal. Chem. 411 (2019) 6931–6942.

[89] Stone M.Cross-Validatory Choice, and Assessment of Statistical Predictions, J. *R. Stat. Soc.* 36 (1974) 111–147.

[90] F. Westad, F. Marini, Validation of chemometric models—a tutorial, Anal. Chim. Acta 893 (2015) 14–24, https://doi.org/10.1016/j.aca.2015.06.056

[91] A. Biancolillo, F. Marini, C. Ruckebusch, R. Vitale, Chemometric strategies for spectroscopy-based food authentication, 1-34, Appl. Sci. 10 (18) (2020) 6544, https://doi.org/10.3390/app10186544

Liling_Combination Chemometrics

ORIGINALITY REPORT

18%	8%	16%	%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	Yu. B. Monakhova, T. Kuballa, D. W. Lachenmeier. "Chemometric methods in NMR spectroscopic analysis of food products", Journal of Analytical Chemistry, 2013 Publication	3%
2	Allan M. Torres, William S. Price. "Common problems and artifacts encountered in solution-state NMR experiments", Concepts in Magnetic Resonance Part A, 2016 Publication	1%
3	A. S. Sarpal, Samantha R. Silva, Paulo R. M. Silva, Thays V. Monteiro, Júlia Itacolomy, Valnei S. Cunha, Romeu J. Daroda. " Direct Method for the Determination of the Iodine Value of Biodiesel by Quantitative Nuclear Magnetic Resonance (q H NMR) Spectroscopy ", Energy & Fuels, 2015 Publication	1%
4	Zeyun Li, Edward Welbeck, Li Yang, Chunyong He, Haijun Hu, Ming Song, Kaishun Bi, Zhengtao Wang. "A quantitative 1H nuclear	<1%

magnetic resonance (qHNMR) method for assessing the purity of iridoids and secoiridoids", Fitoterapia, 2015
Publication

5	umu.diva-portal.org Internet Source	<1 %
6	www.sigmaaldrich.com Internet Source	<1 %
7	mdpi.com Internet Source	<1 %
8	ddd.uab.cat Internet Source	<1 %
9	Endah Prasetia Susanti, Abdul Rohman, Widiastuti Setyaningsih. "Dual Response Optimization of Ultrasound-Assisted Oil Extraction from Red Fruit (Pandanus conoideus): Recovery and Total Phenolic Compounds", Agronomy, 2022 Publication	<1 %
10	mafiadoc.com Internet Source	<1 %
11	Alessandra Biancolillo, Federico Marini, Cyril Ruckebusch, Raffaele Vitale. "Chemometric Strategies for Spectroscopy-Based Food Authentication", Applied Sciences, 2020 Publication	<1 %

12	hal.univ-grenoble-alpes.fr Internet Source	<1 %
13	Maŕia D Guillén, Ainhoa Ruiz. "High resolution 1H nuclear magnetic resonance in the study of edible oils and fats", Trends in Food Science & Technology, 2001 Publication	<1 %
14	dipot.ulb.ac.be Internet Source	<1 %
15	Editha Giese, Sascha Rohn, Jan Fritsche. "Chemometric tools for the authentication of cod liver oil based on nuclear magnetic resonance and infrared spectroscopy data", Analytical and Bioanalytical Chemistry, 2019 Publication	<1 %
16	b-ok.org Internet Source	<1 %
17	journal.ugm.ac.id Internet Source	<1 %
18	pt.scribd.com Internet Source	<1 %
19	theses-test.ncl.ac.uk Internet Source	<1 %
20	www.bisac.com.pe Internet Source	<1 %

21	"NMR-Based Metabolomics", Springer Science and Business Media LLC, 2019 Publication	<1 %
22	A. Carrington, A.R. Fabris, B.J. Howard, N.J.D. Lucas. "Electron resonance studies of the renner effect", Molecular Physics, 1971 Publication	<1 %
23	Chen Yu, Qian Zhang, Peng-yao Xu, Yin Bai, Wen-bin Shen, Bin Di, Meng-xiang Su. " Quantitative determination and validation of octreotide acetate using H-NMR spectroscopy with internal standard method ", Magnetic Resonance in Chemistry, 2018 Publication	<1 %
24	M S Sirait, E Warsiki, D Setyaningsih. "Potential of red fruit oil (Pandanus conoideus Lam.) as an antioxidant active packaging: A review", IOP Conference Series: Earth and Environmental Science, 2021 Publication	<1 %
25	medworm.com Internet Source	<1 %
26	Holzgrabe, U.. "Quantitative NMR spectroscopy in pharmaceutical applications", Progress in Nuclear Magnetic Resonance Spectroscopy, 201008 Publication	<1 %

27	tjnpr.org Internet Source	<1%
28	Euth Ortiz Ortega, Hamed Hosseinian, María José Rosales López, Andrea Rodríguez Vera, Samira Hosseini. "Chapter 4 Characterization Techniques for Chemical and Structural Analyses", Springer Science and Business Media LLC, 2022 Publication	<1%
29	María D. Guillén. "Monitoring the oxidation of unsaturated oils and formation of oxygenated aldehydes by proton NMR", European Journal of Lipid Science and Technology, 01/2005 Publication	<1%
30	S. Yu. Ryabova, L. M. Alekseeva, V. G. Granik. "Acetals of acid lactams and amides. 70. Reactions of 2-aminomethyleneindolin-3-one with CH-acids. Synthesis of substituted pyrrolo[1,2-a]indoles", Chemistry of Heterocyclic Compounds, 1991 Publication	<1%
31	repositorium.sdum.uminho.pt Internet Source	<1%
32	Ravindra Kumar, Veena Bansal, M. B. Patel, A. S. Sarpal. " H Nuclear Magnetic Resonance (NMR) Determination of the Iodine Value in	<1%

Biodiesel Produced from Algal and Vegetable Oils ", Energy & Fuels, 2012
Publication

33	s3-eu-west-1.amazonaws.com Internet Source	<1 %
34	brage.bibsys.no Internet Source	<1 %
35	Lalit Goswami, R. Vinoth Kumar, Kannan Pakshirajan, G. Pugazhenthi. "A novel integrated biodegradation—microfiltration system for sustainable wastewater treatment and energy recovery", Journal of Hazardous Materials, 2019 Publication	<1 %
36	Malet-Martino, M.. "NMR techniques in biomedical and pharmaceutical analysis", Journal of Pharmaceutical and Biomedical Analysis, 20110428 Publication	<1 %
37	Marina Cocchi, Alessandra Biancolillo, Federico Marini. "Chemometric Methods for Classification and Feature Selection", Elsevier BV, 2018 Publication	<1 %
38	Yunfei Liao, Huiming Fan, Yongli Zhang, Hongyan Mou, Fengyu Li, Ziyin Zhou, Jianan Liu. "Conservation and enhancement of	<1 %

naturally aged paper using bi-functionalized polyamidoamine (SiPAAOH)", Nordic Pulp & Paper Research Journal, 2022
Publication

39	Jitendra K. Satyarthi, D. Srinivas, Paul Ratnasamy. " Estimation of Free Fatty Acid Content in Oils, Fats, and Biodiesel by H NMR Spectroscopy ", Energy & Fuels, 2009 Publication	<1 %
40	kclpure.kcl.ac.uk Internet Source	<1 %
41	Sharifah Shahira Syed Putra, Wan Jefrey Basirun, Adeeb Hayyan, Amal A.M. Elgharbawy. "Enzymatic hydrolysis for the removal of 3- monochloropropanediol esters in edible oils using Candida rugosa lipase in the presence of deep eutectic solvents and nanocellulose", Biochemical Engineering Journal, 2023 Publication	<1 %
42	daneshyari.com Internet Source	<1 %
43	www.freepatentsonline.com Internet Source	<1 %
44	www.rafa2015.eu Internet Source	<1 %

45	Alessandra Biancolillo, Federico Marini. "Chemometrics Applied to Plant Spectral Analysis", Elsevier BV, 2018 Publication	<1 %
46	Hassen Mohamed Sbihi, Imededdine Arbi Nehdi, Saud Ibrahim Al-Resayes. "Characterization of Hachi (Camelus dromedarius) fat extracted from the hump", Food Chemistry, 2013 Publication	<1 %
47	Nobuhiro Matsumoto, Takuya Shimosaka. "Purity analyses of high-purity organic compounds with nitroxyl radicals based on the Curie–Weiss law", Journal of Applied Physics, 2015 Publication	<1 %
48	Tanja Beyer, Curd Schollmayer, Ulrike Holzgrabe. "The role of solvents in the signal separation for quantitative 1H NMR spectroscopy", Journal of Pharmaceutical and Biomedical Analysis, 2010 Publication	<1 %
49	Wenjiang Dong, Qidi Hong, Jinhuan Cheng, Hongyan He, Yanan Li, Rongsuo Hu, Yuzhou Long. "Simultaneous analysis of the oxidation of solvent-extracted and cold-pressed green coffee oil during accelerated storage using 1H	<1 %

NMR and 13C NMR spectroscopy", Food Research International, 2023
Publication

50	addi.ehu.es Internet Source	<1 %
51	assets.researchsquare.com Internet Source	<1 %
52	eprints.soas.ac.uk Internet Source	<1 %
53	forestecosyst.springeropen.com Internet Source	<1 %
54	ouci.dntb.gov.ua Internet Source	<1 %
55	www.nature.com Internet Source	<1 %
56	www.unboundmedicine.com Internet Source	<1 %
57	"Handbook of Olive Oil", Springer Nature, 2013 Publication	<1 %
58	AHMED AHMED, MOHAMMED SAYED, SAHAR KAMAL, OMAR AHMED ABDEL-HAFEEZ. "PHYSICOCHEMICAL EVALUATION OF COOKING BUTTER AND HYDROGENATED OILS", Assiut Veterinary Medical Journal, 2022 Publication	<1 %

59	Atitiya Saedan, Jutiporn Yukird, Nadnudda Rodthongkum, Sarute Ummartyotin. "Graphene oxide modified cellulose paper-based device: A novel platform for cooking oil quality evaluation", Food Control, 2023 Publication	<1 %
60	Bou, R.. "Determination of hydroperoxides in foods and biological samples by the ferrous oxidation-xylenol orange method: A review of the factors that influence the method's performance", Analytical Biochemistry, 20080601 Publication	<1 %
61	Bárbara Nieva-Echevarría, María J. Manzanos, Encarnación Goicoechea, María D. Guillén. "Changes provoked by boiling, steaming and sous - vide cooking in the lipid and volatile profile of European sea bass", Food Research International, 2017 Publication	<1 %
62	Cerceau, Cristiane I., Luiz C.A. Barbosa, Elson S. Alvarenga, Antonio G. Ferreira, and Sérgio S. Thomasi. "A validated 1H NMR method for quantitative analysis of α-bisabolol in essential oils of Eremanthus erythropappus", Talanta, 2016. Publication	<1 %

63	Emmanouil Veroutis, Steffen Merz, Rüdiger A. Eichel, Josef Granwehr. "Intra- and inter-molecular interactions in choline-based ionic liquids studied by 1D and 2D NMR", Journal of Molecular Liquids, 2021 Publication	<1 %
64	Guy Beavis, Martin Rusilowicz, James Donarski, Adrian Charlton, Julie Wilson. "Chemometrics Applied to Nuclear Magnetic Resonance Analysis", Wiley, 2019 Publication	<1 %
65	Jinlong Zhang, Shanshan Wu, Runmin Xu, Chenxin Wang, Chuangye Li, Junbin Hao, Xuecheng Du, Shangwei Yang, Yong Guo, Yuxia Chen. "A study on natural luffa seed oil as a potential source of polymers and bioactive compounds", Industrial Crops and Products, 2021 Publication	<1 %
66	Jose Luis Izquierdo-Garcia, Daniel Padro, Palmira Villa, Lucia Fadon. "NMR-Based Metabolomics", Elsevier BV, 2019 Publication	<1 %
67	Michał Szmatoła, Justyna Chrobak, Rafał Grabowski, Jolanta Iłowska et al. "Spectroscopic Methods in the Evaluation of Modified Vegetable Base Oils from Crambe abyssinica", Molecules, 2018	<1 %

Publication

68	Olav Martin Kvalheim, Reidar Arneberg, Bjørn Grung, Tarja Rajalahti. "Determination of optimum number of components in partial least squares regression from distributions of the root-mean-squared error obtained by Monte Carlo resampling", Journal of Chemometrics, 2018 Publication	<1 %
69	R S Prasad, D Mishra, J Swarnkar, O Kumawat, M Pandey, A Gupta. "Fatigue analysis of SAE8620: Synergistic effect of thermal treatments and surface roughness", Advances in Materials and Processing Technologies, 2022 Publication	<1 %
70	Serge Rezzi, Ivan Giani, Károly Héberger, David E. Axelson, Vittorio M. Moretti, Fabiano Reniero, Claude Guillou. " Classification of Gilthead Sea Bream ( ) from H NMR Lipid Profiling Combined with Principal Component and Linear Discriminant Analysis ", Journal of Agricultural and Food Chemistry, 2007 Publication	<1 %
71	Song, X.H.. "Source apportionment of gasoline and diesel by multivariate calibration based on single particle mass spectral data", Analytica Chimica Acta, 20011119 Publication	<1 %

72	Westad, Frank, and Federico Marini. "Validation of chemometric models – A tutorial", Analytica Chimica Acta, 2015. Publication	<1 %
73	Yi Liu, Laijun Sun, Chengsi Du, Xing Wang. "Near-infrared prediction of edible oil frying times based on Bayesian Ridge Regression", Optik, 2020 Publication	<1 %
74	pubs.rsc.org Internet Source	<1 %
75	scholarworks.bwise.kr Internet Source	<1 %
76	www.bigdatagrapes.eu Internet Source	<1 %
77	www.jove.com Internet Source	<1 %
78	www.jstage.jst.go.jp Internet Source	<1 %
79	www.jtmtg.org Internet Source	<1 %
80	María D Guillén, Ainhoa Ruiz. " Edible oils: discrimination by H nuclear magnetic resonance ", Journal of the Science of Food and Agriculture, 2003 Publication	<1 %

81	Rosa M., Margaret V., Claude Guillou, Kroly Hberger. "Chapter 2 Quality Assessment of Olive Oil by 1H-NMR Fingerprinting", IntechOpen, 2012 Publication	<1 %
82	"Ethnobotany of the Mountain Regions of Southeast Asia", Springer Science and Business Media LLC, 2021 Publication	<1 %
83	Hinrichsen, Nils, and Hans Steinhart. "Techniques and Applications in Lipid Analysis", Lipid Analysis and Lipidomics NewTechniques and Applications, 2006. Publication	<1 %
84	Kent, Erin E., Julia H. Rowland, Laurel Northouse, Kristin Litzelman, Wen-Ying Sylvia Chou, Nonniekaye Shelburne, Catherine Timura, Ann O'Mara, and Karen Huss. "Caring for caregivers and patients: Research and clinical priorities for informal cancer caregiving : Informal Cancer Caregiving", Cancer, 2016. Publication	<1 %

Exclude quotes	On	Exclude matches	Off
Exclude bibliography	On		