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Detection of green coffee oil adulteration using time-domain nuclear magnetic resonance relaxometry and infrared spectroscopies

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ABSTRACT

Green coffee oil (GCO) is a high-value product widely used in the food, cosmetic, and pharmaceutical industries, being susceptible to adulteration with low-cost vegetable oils. This study aimed to develop rapid and non-destructive methods based on time-domain nuclear magnetic resonance (TD-NMR) relaxometry and Fourier transform infrared (FTIR) spectroscopy to detect adulteration of GCO with sunflower oil (SO). Calibration samples containing different proportions of GCO and SO (0-100%) were analyzed using low-field ^{1}H TD-NMR relaxometry, FTIR spectroscopy, and high-resolution ^{1}H NMR as a reference method. TD-NMR measurements were performed using CPMG pulse sequence, and relaxation parameters were evaluated through inverse Laplace transform (ILT) and three-exponential fitting approaches. Among the relaxation components, $T_{2(3)}$ showed the highest sensitivity to compositional changes, presenting a linear correlation with GCO concentration (R^2 = 0.9839). FTIR univariate models based on the band at 1670 cm^{-1}, associated with unsaturation-related vibrational modes, and the band at 3008 cm^{-1}, attributed to cis = C–H stretching of unsaturated lipid chains, also demonstrated good performance, achieving correlation coefficients of 0.9649 and 0.8866, respectively. Commercial samples analyzed by TD-NMR and FTIR revealed spectral and relaxation profiles inconsistent with authentic GCO in two products, which was further confirmed by high-resolution ^{1}H NMR through the absence of cafestol and kahweol markers. The results demonstrate that TD-NMR and FTIR provide rapid, simple, and accessible screening approaches for detecting adulteration in green coffee oil, with potential applications in routine quality control and food fraud detection.

1. Introduction

The detection of adulteration has become a major concern for both industry and consumers, especially with the increasing demand for high-quality, authentic, and traceable products. Green coffee oil (GCO), extracted by cold pressing of unroasted coffee beans, is a high-value ingredient widely used in cosmetic formulations and increasingly explored in food and pharmaceutical applications due to its bioactive compounds, antioxidant activity, and functional properties (Wagemaker et al., 2011; Wagemaker et al., 2011; Ribeiro et al., 2024). However, its high market valuation also makes it a frequent target for fraud, such as adulteration with low-cost vegetable oils like sunflower oil (SO), which compromises product integrity and authenticity (Kanwal et al., 2024). Ensuring the authenticity of GCO is crucial to maintaining industry and consumer confidence and supporting compliance by regulatory agencies.

Coffee is one of the most expensive agricultural commodities, with *Coffea arabica* and *C. canephora* being the primary species cultivated for commercial purposes (Santos et al., 2017). Brazil, as a leading producer, plays a central role in global coffee supply chains (Sera et al., 2025). The economic importance of coffee extends beyond its beverage form, as botanical ingredients such as GCO have gained importance for their functional applications (Chiari et al., 2014). GCO is extracted from green coffee beans before roasting, preserving its rich lipid composition, including diterpenes, tocopherols, and polyphenols, which contribute to its antioxidant and photoprotective properties (Wagemaker et al., 2011; Wagemaker et al., 2011; Ribeiro et al., 2024). Due to these benefits, GCO is increasingly used in cosmetic formulations, particularly as a natural

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alternative in sunscreens and anti-aging products (Chiari et al., 2014; Moeenfard et al., 2020).

High-value oils, such as olive oil and green coffee oil, are particularly susceptible to fraudulent practices, including dilution with lower-cost oils like sunflower, soybean, canola, corn, or even hazelnut oil, which can partially mimic the chemical profile of premium oils and make detection more challenging. These adulterations compromise the oil's bioactive properties and, consequently, its efficacy in cosmetic and nutritional applications, constituting a clear form of consumer fraud by misrepresenting product quality and value. Therefore, the development of rapid, reliable, and accessible analytical methods for authentication and routine quality control has become increasingly important for both industry and regulatory agencies. In addition, differences in lipid composition and degree of unsaturation between vegetable oils may influence their physicochemical and relaxation properties. Sunflower oil is rich in polyunsaturated fatty acids (PUFA), particularly linoleic acid, whereas green coffee oil contains a more complex lipid composition with saturated (SFA), monounsaturated (MUFA), and unsaturated compounds, in addition to diterpenes and tocopherols. These compositional differences are expected to influence molecular mobility and intermolecular interactions, supporting the application of spectroscopic techniques for adulteration detection.

Conventional techniques for detecting oil adulteration include gas chromatography (GC), which is effective in identifying changes in fatty acid composition (Esteki et al., 2018; González-Pereira et al., 2021). Despite its accuracy, GC is time-consuming and laborious method that requires extensive sample preparation, specialized laboratories, and costly consumables, limiting its applicability for rapid routine screening analyses (Bartle & Myers, 2002).

Several other analytical methods such as ultraviolet–visible spectroscopy (UV-IS) (Didham et al., 2020), Near (NIR) and middle infrared spectroscopy (FT-IR), high-resolution nuclear magnetic resonance (HR-NMR) (D'Amelio et al., 2013; Gunning et al., 2018; Portaluri et al., 2020), and time-domain nuclear magnetic resonance (TD-NMR) (Mitchell et al., 2014; Colnago et al., 2021; Moraes et al., 2026) have been employed as rapid screening methods to detect adulteration in high-values vegetable oils.

TD-NMR, also referred to in the literature, as low-field nuclear magnetic resonance (LF-NMR), is a well-established technique in food research, particularly valued for its speed, simplicity, and non-destructive nature (Santos et al., 2021; Cobo et al., 2017; Muniz et al., 2023; Zhao et al., 2022; Basso et al., 2025). Near- (NIR) and middle- (FTIR) infrared spectroscopies are also widely used in food analyses. The main advantages of TD-NMR and infrared methods are simple, rapid and with minimum sample preparation and use of toxic chemicals. Notably, TD-NMR can perform measurements directly through non-metallic packaging, enabling fast and reliable screening for vegetable oil adulteration, even in sealed, intact bottles (Zhang et al., 2013; Pereira et al., 2015; Santos et al., 2021; Moraes et al., 2026).

TD-NMR is widely used to characterize food and oil samples based on signal and echo intensities, relaxation times (T_1 and T_2), and molecular diffusion parameters, which reflect molecular mobility, phase distribution, and physicochemical interactions within complex matrices. Particularly, T_1 and T_2 relaxation times reflect the dynamics of proton populations and their interactions with the surrounding environment, being highly sensitive to variations in composition, such as water and lipid distribution, as well as changes induced by processing or adulteration (Almeida, 2026). In vegetable oils, these relaxation parameters are strongly influenced by lipid composition and degree of unsaturation, since these factors affect molecular mobility and intermolecular interactions. Diffusion measurements further complement this information by enabling the differentiation of molecular species based on their mobility, thereby enhancing the analytical capability of TD-NMR for food quality assessment.

Such TD-NMR parameters can be correlated with physicochemical properties, as oil and moisture content in foods, grains, or other biological materials, following established ASTM, ISO 10565-1998 and ISO 8292-2008 reference protocols. In the context of food fraud, this calibration approach enables the distinction between pure and adulterated samples without the need for extensive preprocessing (Muniz et al., 2023), making TD-NMR a valuable technique for rapid screening and fraud detection.

NIR and FTIR spectroscopy are also widely used in the analysis of vegetable oil. The NIR analysis are normally performed with chemometric method as the spectra are hard to assigned to a specific product due strong overlap of the overtone and combination bands (Raba et al., 2015; Li et al., 2020). On the other hand, FTIR analysis can be performed using univariate or multivariate statistics. The major advantage for qualitative and univariate analysis is the assignment of the bands to chemical function and consequently to the major components of the sample. While multivariate methods may improve predictive accuracy, the use of univariate models in this study was intentional, aiming to demonstrate that reliable screening can be achieved using simple and accessible approaches without advanced data processing. This strategy is particularly attractive for industrial quality control applications, where rapid, low-cost, and easy-to-implement analytical methods are highly desirable.

In this context, this study aims to develop and evaluate ^{1}H TD-NMR relaxometry and FTIR-based approaches for the detection and quantification of adulteration in green coffee oil (GCO) with sunflower oil (SO). The proposed methods are based on relaxation parameters and spectral features that are sensitive to compositional changes, and their performance is assessed using calibration strategies and analysis of commercial samples. The results are further compared with high-resolution ^{1}H NMR as a reference technique, providing a framework for rapid, non-destructive, and reliable detection of oil adulteration. Furthermore, the study emphasizes the use of simple and accessible analytical approaches without extensive sample preparation or advanced chemometric processing, aiming to support routine quality control and rapid screening applications in the food and cosmetic industries.

2. Materials and methods

2.1. Sample preparation and calibration curves

Four different commercial green coffee oil (GCO) were acquired at local stores in the city of Piracicaba, SP, Brazil, and labeled as C1, C2, C3, and C4. The samples were stored and analyzed at room temperature. Sunflower oil (SO) was selected as the model adulterant due to its widespread use as a carrier oil in commercial formulations of green coffee oil, as reported in the literature and observed in market products. The SO used in this study was classified as Type 1 oil, obtained from high-linoleic sunflower seeds, with linoleic acid, a polyunsaturated fatty acid, representing approximately 60-70% of its fatty acid composition. Because Type 1 sunflower oil is an economically lower-value vegetable oil and is commonly used as a carrier oil, it represents a realistic adulterant for fraudulent dilution practices involving high-value oils such as GCO. This choice was also supported by its commercial availability, low cost, and physicochemical compatibility with edible vegetable oils commonly used in adulteration practices.

Calibration curves were produced using green coffee oil and sunflower oil obtained from certified suppliers. The purity of the oils was confirmed through gas chromatography reports. To construct the ^{1}H TD-NMR and FT-IR calibration curves for representing different levels of GCO adulteration, GCO was mixed with SO at varying concentrations: 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100%, totaling 11 samples, each containing a total volume of 5 mL. All calibration mixtures were homogenized prior to analysis and measured in triplicate to ensure experimental reproducibility.

Details of the experimental design and dataset size, including the number of samples, concentration levels, analytical replicates,

Table 1
Summary of sample sets, analytical replicates, measurements, and scans used for TD-NMR, FTIR and ^{1}H HR-NMR analyses.

Set	Ratio/sample	n	Rep	Meas.	Method	Scans
Calibration mixtures	0:100 to 100:0, at 10% intervals	11	3	33	TD-NMR	32
Calibration mixtures	0:100 to 100:0, at 10% intervals	11	3	33	FTIR	32
Commercial samples	C1, C2, C3, and C4	4	3	12	TD-NMR	32
Commercial samples	C1, C2, C3, and C4	4	3	12	FTIR	32
Authentication samples	GCO + C1, C2, C3 and C4	5	1	5	^{1}H HR-NMR	28

Note: For calibration mixtures, ratios are expressed as GCO:SO. n = number of concentration levels for calibration mixtures or number of commercial samples; Rep. = analytical replicates per level or sample; Meas. = total number of measurements. Scans = Total number of scans used in each measurement.

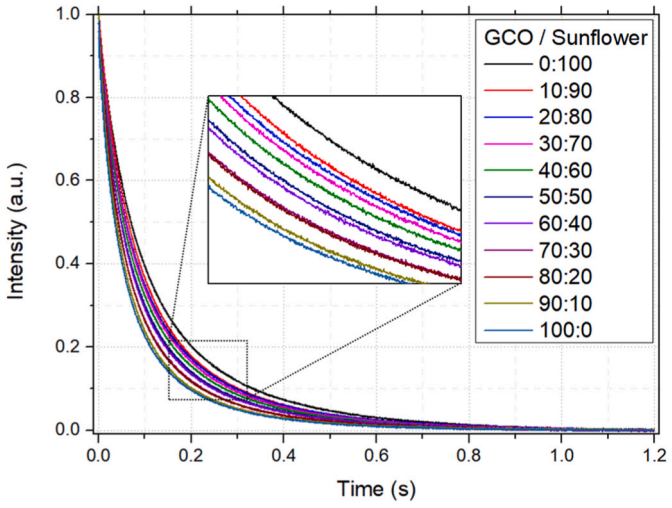

Fig. 1. CPMG decay curves for the eleven samples containing varying concentrations of green coffee oil (GCO) and sunflower oil (SO), measured at 30°C. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

measurements, and scans used for TD-NMR, FTIR and ^{1}H HR-NMR analyses, are summarized in Table 1.

The limit of detection (LOD) and limit of quantification (LOQ) were estimated based on the standard deviation of the response (σ) and the slope of the calibration curve (S), using the expressions LOD = 3.3σ/S and LOQ = 10σ/S (Olivieri, 2014). In this study, σ was obtained from the standard deviation of the residuals of the calibration model.

2.2. Time Domain-NMR relaxometry

TD-NMR measurements were performed using a low-field benchtop spectrometer, SLK-200 (SpinLock Magnetic Resonance Solutions, Córdoba, Argentina), operating at 11.3 MHz and equipped with a 30 mm probe at 30°C. A sample volume of 5 mL was used for each measurement. The T_2 relaxation curves were obtained by the CPMG pulse sequence, with calibrated pulses of 90° and 180° with 9.0 and 19.0 μs, respectively, echo time τ = 100 μs, recycle delay of 2 s, 8000 echoes and 32 scans using cyclops phase cycling. All TD-NMR measurements were performed under identical acquisition conditions to minimize instrumental and temperature-related variations, Table 1.

The CPMG signal was analyzed using OriginLab 9.0 software (OriginLab Corporation, Northampton, MA, USA) to obtain amplitude values

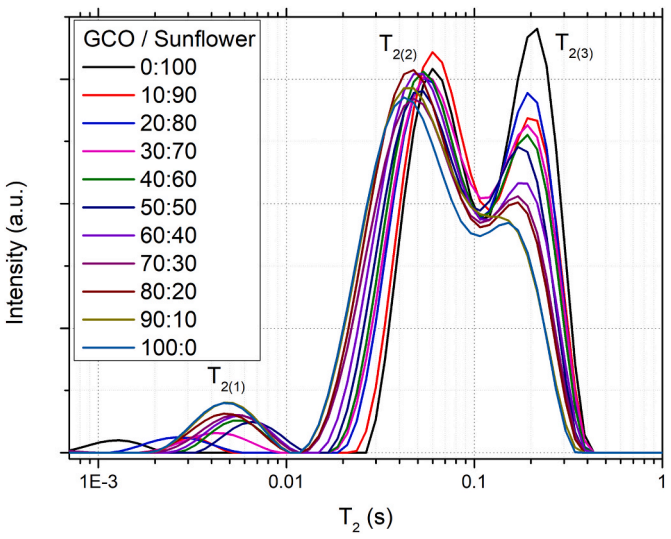

Fig. 2. T_2 distributions profiles obtained from the Inverse Laplace Transform (ILT) of the CPMG decay curves of Fig. 1. Three main relaxation components were identified: $T_{2(1)} \approx 10$ ms, $T_{2(2)} \approx 50$ ms, and $T_{2(3)} \approx 200$ ms.

for constructing the calibration curve (Monaretto et al., 2021; Moraes & Colnago, 2022). Subsequently, the Inverse Laplace Transform (ILT) was applied to derive the T_2 relaxation spectra (Moraes, 2021; Moraes et al., 2026). The inversion procedure employed Tikhonov regularization combined with singular value decomposition, with non-negativity constraints imposed via a non-negative least squares (NNLS) method. A regularization parameter equal to 1 was adopted, and relaxation time distributions were computed using 100 discrete points. Tri-exponential fitting was additionally applied to the relaxation decays to evaluate changes in proton mobility domains associated with adulteration levels.

2.3. Fourier Transform Infrared (FT-IR) analysis

Fourier Transform Infrared (FT-IR) spectroscopy was conducted using a Vertex 70 FT-IR spectrometer (Bruker Optics GmbH, Ettlingen, Germany) equipped with a diamond attenuated total reflectance (ATR) accessory. Spectra were recorded over the wavenumber range of 4000-400 cm^{-1}, with 32 scans collected at a resolution of 4 cm^{-1}, Table 1. Background spectra were collected before each analytical sequence under the same experimental conditions. All reflectance spectra were processed using OriginPro 9.0 software. Spectral preprocessing included baseline correction and normalization prior to data interpretation and calibration curve construction.

2.4. High-resolution ^{1}H NMR spectroscopy

High-resolution proton nuclear magnetic resonance (^{1}H NMR) analyses were performed using a Bruker Avance III 600 MHz NMR spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany) equipped with a 5 mm probe, operating at 30°C. Spectra were acquired with 28 scans (NS), a spectral width of 15 ppm, an acquisition time (AQ) of 1.50 s, and a relaxation delay (D1) of 40 s, using 64k data points, Table 1. Samples were prepared by mixing 100 μL of oil with 580 μL of deuterated chloroform ($CDCl_3$), and 20 μL of a dimethyl sulfone ($DMSO_2$) solution (10.43 mg mL^{-1}) as an internal standard. The zg pulse sequence was applied to obtain the chemical profiles, and all spectra were processed using TopSpin software (Bruker BioSpin GmbH, Rheinstetten, Germany). The presence or absence of characteristic diterpene signals, particularly cafestol and kahweol, was used as a chemical reference for evaluating the authenticity of commercial GCO samples and validating the screening results obtained by TD-NMR and FT-IR analyses.

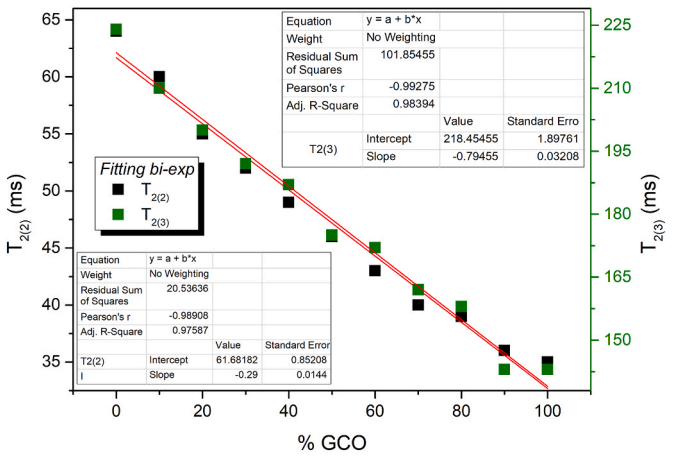

Fig. 3. Calibration curves of the GCO content, diluted with SO, in function of the $T_{2(2)}$ and $T_{2(3)}$ relaxation times, measured at 30°C.

Table 2
Calibration parameters, root mean square error (RMSE), and estimated limits of detection (LOD) and quantification (LOQ) for the T_2 relaxation models.

Model	RSS	RMSE (σ)	Slope (S)	LOD (%)	LOQ (%)
$T_{2(2)}$	20.53636	1.51	0.29	17.18	52.10
$T_{2(3)}$	101.85455	3.36	0.79	13.96	42.30

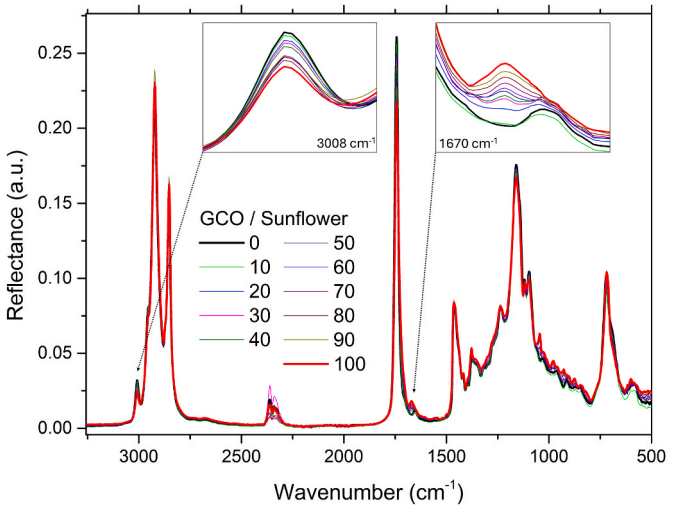

Fig. 4. FTIR spectra (4000 to 400 cm^{-1}) of the eleven samples containing varying concentrations of GCO and SO. The black line corresponds to pure sunflower oil, whereas the red line corresponds to pure GCO. Notably, two main peaks show consistent changes with increasing GCO content: the band at 1670 cm^{-1} increases progressively, while the band at 3008 cm^{-1} decreases. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3. Results and discussion

3.1. Analysis of the GCO/SO samples by TD-NMR

Fig. 1 presents the normalized CPMG decay curves for the eleven samples prepared with different percentages of GCO/SO oil, determined at 30°C. It was observed that as the GCO concentration increases, the T_2 relaxation curves decay faster. The observed variation in T_2 relaxation behavior is associated with differences in molecular mobility and intermolecular interactions, which are influenced by the fatty acid composition of the oils. Green coffee oil is less unsaturated than SO, explaining the reduction of T_2 with the increase of GCO. This behavior is consistent with recent studies correlating T_1 and T_2 relaxation parameters of edible oils with iodine values and degree of unsaturation, in which oils with higher polyunsaturated fatty acid content tend to exhibit greater molecular mobility and longer relaxation times due to reduced intermolecular packing constraints (Remiro et al., 2024).

Fig. 2 shows the respective T_2 distribution profile obtained through the inverse Laplace transform algorithm (Moraes, 2021, Moraes et al., 2026). Three distinct components were identified, denoted as $T_{2(1)}$, $T_{2(2)}$, and $T_{2(3)}$. As the GCO concentration increases, the relaxation peaks shift to lower values, reflecting changes in chemical composition and viscosity. The three T_2 components may be interpreted as proton populations with distinct molecular mobility and intermolecular interaction environments within the lipid matrix, rather than as individual chemical compounds. The shortest component, $T_{2(1)}$, may be associated with less mobile proton domains, including more restricted or highly viscous molecular environments characterized by stronger intermolecular interactions. The intermediate component, $T_{2(2)}$, may be related to proton populations with intermediate mobility in triacylglycerol-rich domains. In contrast, the longest component, $T_{2(3)}$, is associated with the most mobile proton population and is therefore more sensitive to variations in fatty acid composition, viscosity, and degree of unsaturation. The pronounced variation observed for $T_{2(3)}$ with increasing SO content suggests that this component may represent the most informative relaxation marker for monitoring compositional changes associated with GCO adulteration. Since sunflower oil contains a higher proportion of polyunsaturated fatty acids, particularly linoleic acid, the increase in molecular mobility associated with higher SO concentrations is consistent with the observed shift of $T_{2(3)}$ toward longer relaxation times.

It can be noted in Fig. 2 that $T_{2(1)}$ and $T_{2(2)}$ have remained almost unchanged, while $T_{2(3)}$ increases and shifts to the higher T_2 values when the content of sunflower oil content increases. Based on this behavior, our proposed calibration curve monitors the $T_{2(3)}$ component. Thus, the calibration curve can be obtained by processing the CPMG data with ILT algorithm to obtain the $T_{2(3)}$ values. However, ILT algorithms are not extensively available in routine TD-NMR software. Therefore, a proposed simpler way to produce the calibration curve, is to perform the three-exponential decay fitting of CPMG data, that is a fit method available in several software, as OriginLab, Excel, Matlab and Python routines.

It is important to note that ILT was used mainly as an interpretative tool to visualize the distribution of relaxation components and to identify which proton population was most affected by the GCO/SO ratio. Therefore, ILT is not strictly required for adulteration screening. The discrimination between pure and adulterated samples can also be performed using direct fitting of the CPMG decay curves. A single global T_2 value, commonly provided by routine TD-NMR instruments, may also provide useful preliminary discrimination; however, it may reduce sensitivity when multiple relaxation populations contribute to the decay. Thus, the tri-exponential approach represents a compromise between interpretability, sensitivity, and practical accessibility, avoiding the need for specialized ILT software while preserving information on distinct proton mobility domains.

Fig. 3 presents two calibration curves constructed using the $T_{2(2)}$ and $T_{2(3)}$ relaxation times obtained by three-exponential fitting method. A linear relationship was observed in both cases between the percentage of GCO and the relaxation times, with a correlation coefficient (R^2) of 0.97587 for the curve based on the $T_{2(2)}$ relaxation time and 0.98394 for the curve based on the $T_{2(3)}$ relaxation time.

This result demonstrated that both T_2 values can be used to establish a calibration curve for a TD-NMR model, each yielding a high correlation coefficient. Therefore equation (1) represents the calibration model based on $T_{2(2)}$:

$$\%GCO = -3.45\ T_{2(2)} + 212.69 \quad (1)$$

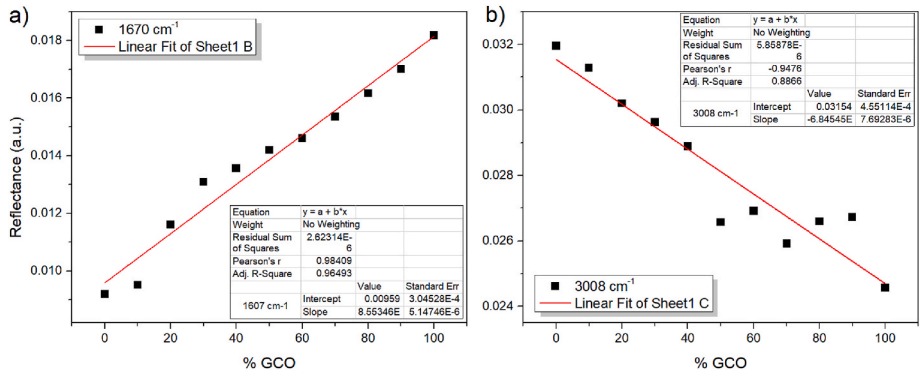

Fig. 5. FTIR calibration curves of the GCO content in function of the reflectance at a) 1670 cm^{-1} (unsaturation-related vibrational modes) and b) 3008 cm^{-1} (cis = C–H stretching vibration of unsaturated lipid chains).

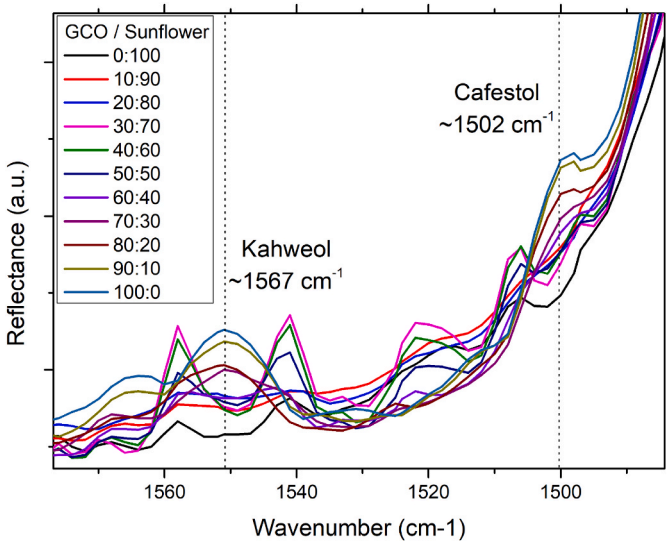

Fig. 6. FTIR spectra from 1480 to 1570 cm^{-1} highlighting diterpene markers of GCO. Dotted lines indicate the characteristic absorption bands of kahweol (~1567 cm^{-1}) and cafestol (~1502 cm^{-1}).

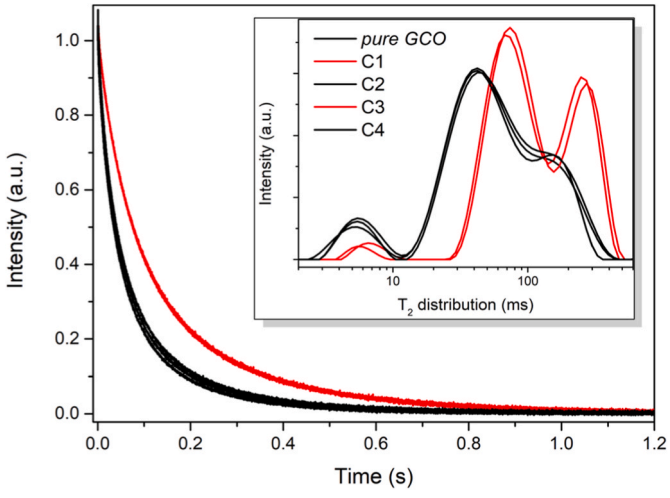

Fig. 7. a) CPMG decay curves for commercial samples (C1-C4); b) its respective T_2 relaxation times distribution.

and equation (2) based on $T_{2(3)}$ to determine the GCO content:

$$\%GCO = -1.26\ T_{2(3)} + 274.78 \quad (2)$$

These TD-NMR models were obtained using a univariate approach, directly correlating the GCO content with the relaxation times. However, it is important to note that multivariate methods, such as partial least squares (PLS) or principal components regression (PCR), among many other methods could also be applied for the same purpose. In this study, a multivariate model was not constructed due to the limited number of commercial samples available, and to emphasize the simplicity and practicality of the univariate approach.

The estimated limit of detection (LOD) and limit of quantification (LOQ) are shown in Table 2, indicating that the proposed models are sensitive to moderate and high levels of adulteration, supporting their applicability as screening tools.

The calibration models based on T_2 relaxation times were further evaluated in terms of sensitivity by estimating the limit of detection (LOD) and limit of quantification (LOQ). These parameters were calculated using the standard deviation of the residuals (σ) and the slope of the calibration curves (S). For the $T_{2(3)}$ model, LOD and LOQ values were 13.96% and 42.30%, respectively. For the $T_{2(2)}$ model, LOD and LOQ were 17.18% and 52.10%, respectively. The lower LOD observed for $T_{2(3)}$ indicates a higher sensitivity compared to $T_{2(2)}$, suggesting that this component is more suitable for detecting adulteration in GCO.

The estimated LOD and LOQ values indicate that the proposed models are primarily suitable for detecting moderate to high levels of adulteration. It is important to note that LOD values are associated with higher uncertainty, as they correspond to signal levels close to the noise, whereas LOQ represents a more reliable threshold for quantitative analysis. In this context, the models show greater robustness for quantification at concentrations above the LOQ. The $T_{2(3)}$ component exhibited greater sensitivity, likely due to its stronger response to compositional changes. Although the sensitivity is lower than that of chromatographic techniques, the method offers advantages such as rapid, non-destructive analysis, supporting its use as a screening tool.

The present study focused on T_2 relaxometry because transverse relaxation is highly sensitive to molecular mobility and intermolecular interactions, which are directly affected by changes in lipid composition and degree of unsaturation. In addition, T_2 measurements obtained using the CPMG pulse sequence are experimentally faster and operationally simpler for routine screening applications. Preliminary exploratory T_1 measurements were also performed; however, only minor variations were observed among the analyzed samples compared to the stronger discrimination obtained using T_2 parameters. For this reason, T_1 relaxometry was not further explored in the present study, although future investigations may evaluate its potential as a complementary parameter for vegetable oil adulteration detection.

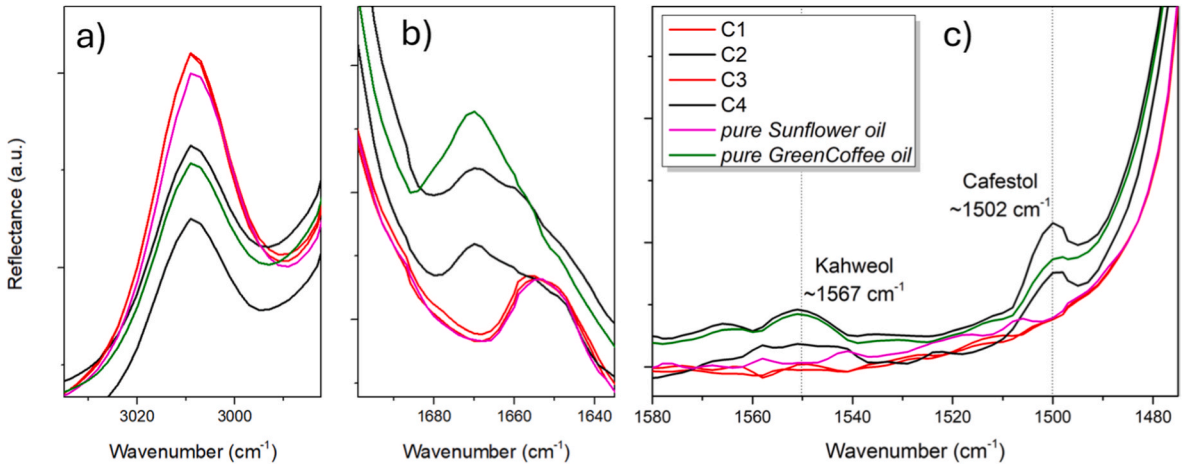

Fig. 8. Comparison of FTIR spectra of commercial samples C1-C4 with pure GCO and pure sunflower oil. a) and b) shows the bands 3008 and 1670 cm^{-1}; c) shows the spectral region (1470-1570 cm^{-1}) highlighting diterpene markers of green coffee oil, with characteristic absorption bands of kahweol (~1567 cm^{-1}) and cafestol (~1502 cm^{-1}). Commercial samples C2 and C4 show absorption profiles closer to pure GCO, while C1 and C3 closely resemble pure sunflower oil (SFO), lacking the typical diterpene signals. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.2. Analysis of the GCO/SO samples by FTIR spectroscopy

To complement the TD-NMR results, FTIR spectroscopy was also evaluated as a rapid, simple, and versatile technique for detecting GCO adulteration with SO.

Fig. 4 shows the FT-IR spectra of GCO samples adulterated with SO, ranging from 0 to 100%. In the spectral region between 4000 and 400 cm^{-1}, the most pronounced spectral change was observed in the band at 3008 cm^{-1}, attributed to cis unsaturated = C–H stretching associated with unsaturated lipid chains, which decreased progressively as the GCO content increased. Additional spectral changes were observed around 1670 cm^{-1}, possibly associated with unsaturation-related vibrational modes (C=C stretching) arising from differences in lipid composition between GCO and SO.

These results demonstrate that FT-IR is sensitive to compositional differences between the two oils and that selected band intensities can be employed to construct univariate calibration models, similar to those developed for the TD-NMR data in the previous section.

FT-IR spectroscopy revealed characteristic spectral differences, particularly at 3008 cm^{-1}, associated with cis unsaturated = C–H stretching of unsaturated lipid chains, and around 1670 cm^{-1}, possibly related to differences in lipid composition and unsaturation-associated vibrational modes between GCO and SO. In addition, spectral regions associated with diterpene-related markers contributed to the chemical differentiation between authentic and suspect commercial samples.

A visible feature was also observed in the spectral region between 2400 and 2300 cm^{-1}. This band was not used for calibration because it is mainly attributed to residual atmospheric CO_2 absorption, commonly observed near 2350 cm^{-1} in FTIR spectra when slight differences occur between background and sample acquisition conditions. Since vegetable oils do not present a major diagnostic absorption band in this region, this feature was interpreted as an instrumental/atmospheric contribution rather than a chemical marker related to GCO or SO composition. Therefore, the calibration models focused on chemically meaningful lipid bands, particularly those at 3008 and 1670 cm^{-1}.

Fig. 5 shows two univariate FTIR models to determine the GCO content based on the reflectance of the bands 1670 cm^{-1} and 3008 cm^{-1}. For the 1670 cm^{-1}, the linear correlation obtained is:

$$\%GCO = 11691.20\, R_{1670} + 112.12 \quad (3)$$

with a correlation coefficient R^2 of 0.9649 and for the 3008 cm^{-1} band (R^2 = 0.8866), the GCO content is given by:

$$\%GCO = -14608.20\, R_{3008} + 460.74 \quad (4)$$

These results show that TD-NMR and FTIR can be used to construct univariate models to estimate GCO content, achieving a correlation coefficient greater than 0.9. However, multivariate models could also be developed to potentially improve performance.

The two diterpenes with biological properties present in GCO, kahweol and cafestol (Kitzberger et al., 2013; Raba et al., 2015; Ren et al., 2019), exhibit characteristic absorption bands in the region between 1470 and 1570 cm^{-1}. Specifically, kahweol shows a prominent band at approximately 1567 cm^{-1}, while cafestol exhibits a band near 1502 cm^{-1}. Fig. 6 highlights the increased amplitude of these bands in the GCO-blended samples. However, due to the low concentration of these diterpenes in pure GCO, typically less than 5%, their bands tend to reach the noise level with increase of SO, making visual identification more challenging.

Similarly, the analyses of these blended samples were also conducted using a Fourier Transform Near-Infrared (FT-NIR) spectrometer (Antaris II, Thermo Scientific™) with 32 scans and a resolution of 16 cm^{-1}. However, the results are not presented here, as no noticeable visual band variations were observed in the spectral region between 10,000 and 4000 cm^{-1}.

3.3. Analysis of commercial GCO samples

To provide a preliminary assessment of real-market applicability, four commercial GCO samples were acquired at local stores in the municipality of Piracicaba, SP, Brazil, and labeled as C1, C2, C3, and C4 to be analyzed by TD-NMR and evaluated in order to validate rapid screening tools for detecting inconsistencies in labeled products.

Therefore, CPMG data of these samples were obtained with the same pulse sequence parameters used in the calibration curve. Fig. 7 illustrates the CPMG decay curves of these commercial samples, while the inset presents its respective T_2 relaxation times distributions (ILT spectra).

These results showed that samples C2 and C4 exhibit T_2 relaxation times distribution similar to those of the pure GCO sample, while C1 and C3 very have different CPMG and ILT distribution, suggesting compositions inconsistent with authentic GCO formulations. These finds can also be illustrated by the relaxation times obtained, where pure GCO sample exhibited the shortest $T_{2(3)}$ value (~143 ms), consistent with the calibration curve and its known molecular dynamics. C1 and C3 showed considerably higher relaxation times (~243 ms and ~256 ms),

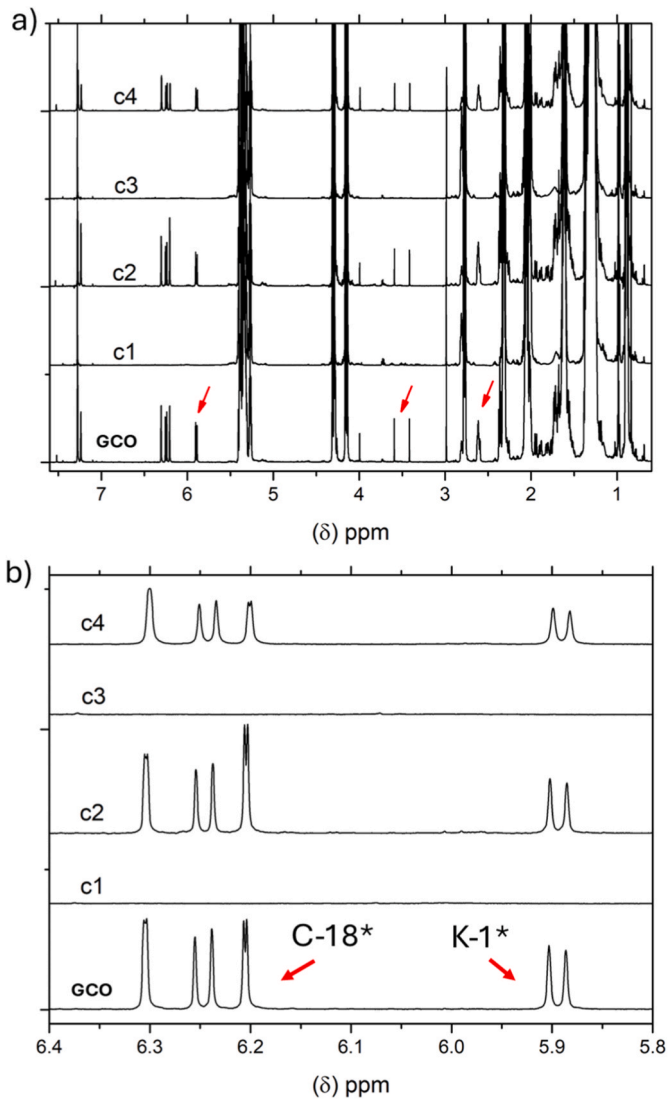

Fig. 9. ^{1}H HR-NMR spectra of commercial C1, C2, C3 and C4 and pure GCO samples. Red arrows indicate the main characteristic signal of Cafestol (C-18*) and Kahweol (K-1*). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

suggesting compositions that deviate from authentic GCO and indicating potential substitution by different vegetable oils.

Notably, sample C3 was the only one that explicitly declared in the bottle the uses of sunflower oil as carrier oil on its label, thus being not fraudulent. However, the product is marketed with the phrase "Green Coffee Oil 250 mL Cold-Pressed with Certification", without clearly mentioning the proportion of SO in its composition. This discrepancy reinforces the need for rapid and effective analytical methods, such as TD-NMR, for verifying the authenticity of products available in the market.

These commercial samples were also evaluated with the FTIR spectroscopy, where C1 and C3 did not present any band in the cafestol and kahweol region (1502 cm^{-1} and 1567 cm^{-1}), while C2 and C4 showed similar spectral features than the pure GCO sample. Furthermore, C1 and C3 exhibit spectra nearly identical to pure SO, with no visible absorption in the diterpene marker regions. These results can be observed in Fig. 8.

These results support the hypothesis that samples C1 and C3 contain substantially reduced amounts of GCO or compositions inconsistent with authentic green coffee oil formulations, consistent with previous findings from TD-NMR analyses. Although both techniques (TD-NMR and FTIR) independently demonstrated the ability to detect adulteration, their combined use provides complementary information. TD-NMR is sensitive to molecular mobility and bulk physical properties, while FTIR provides chemical fingerprinting. This dual approach increases confidence in screening results and reduces false positives associated with single-method analysis.

3.4. Analysis of suspect commercial GCO samples by certified high-resolution NMR method

To confirm the suspected commercial fraud certified analytical method such as gas chromatography (CG) and/or High-Resolution NMR can be used. Thus, High-resolution nuclear magnetic resonance (HR-NMR) spectroscopy was employed as a reference analytical method to verify the authenticity of commercial green coffee oil samples, complementing the results obtained by TD-NMR and FTIR.

Fig. 9 displays the ^{1}H HR-NMR spectra of the commercial samples (C1–C4) and the control sample (*pure GCO*), highlighting the spectral regions corresponding to the diterpenes cafestol (C-18*) and kahweol (K-1*), which are exclusive and characteristic compounds of GCO (D'Amelio et al., 2013; Gunning et al., 2018; Portaluri et al., 2020).

It can be noted that in samples C2 and C4, the signals for cafestol and kahweol were clearly observed, supporting their consistency with authentic GCO formulations. In contrast, samples C1 and C3 showed a complete absence of these compounds, indicating that green coffee oil is not present in their formulations. Instead, another type of vegetable oil appears to be present, lacking chemical features typical of GCO.

These findings corroborate the suspicions raised by the TD-NMR and FTIR analyses and highlight the effectiveness of HR-NMR in distinguishing authentic products from those lacking the characteristic chemical markers of green coffee oil.

3.5. Study limitations and future perspectives

Although sunflower oil was selected as a model adulterant due to its frequent use as a carrier oil in commercial formulations, other vegetable oils such as soybean, palm, or canola oil may also be used for adulteration. The proposed TD-NMR and FTIR approaches are sensitive to differences in molecular mobility and chemical composition, suggesting that they could also detect other adulterants.

In addition to relaxation times, the amplitudes of T_2 components also contain relevant quantitative information regarding proton populations associated with different molecular environments. Although the present study focused primarily on relaxation times and simplified univariate approaches for practical screening purposes, future investigations should explore amplitude-based parameters and multivariate strategies to improve model robustness and sensitivity.

A more robust validation would require a larger dataset, including different oil batches, multiple adulterants, and independent validation samples. Therefore, the present study should be considered a proof-of-concept demonstration of the feasibility of TD-NMR and FTIR as rapid, accessible, and non-destructive tools for screening green coffee oil adulteration.

4. Conclusions

This study demonstrated the potential of TD-NMR relaxometry and FTIR in detecting and quantifying adulteration in green coffee oil, using sunflower oil as a model adulterant. The T_2 relaxation time, obtained through simple exponential fitting, proved to be a reliable parameter for distinguishing between pure and adulterated samples. In addition, FTIR spectroscopy revealed characteristic spectral differences, particularly in spectral regions associated with diterpenes and unsaturated lipids, allowing discrimination based on chemical composition. Both methods showed strong linearity and correlations, reinforcing their applicability in routine analyses.

The reliability of the TD-NMR and FTIR methods was supported through complementary analyses using high-resolution NMR (HR-NMR). FTIR and HR-NMR identified the absence of the chemical markers cafestol and kahweol in two commercial samples, suggesting compositions inconsistent with authentic GCO. Additionally, one of these samples contained sunflower oil but did not clearly declare its proportion on the label. While this does not legally constitute fraud, the lack of transparency may mislead consumers and compromise product trust. This scenario highlights the importance of accessible and rapid analytical tools for verifying the authenticity of oils on the market, supporting both consumer protection and regulatory enforcement.

CRediT authorship contribution statement

Vinicius Silva Paiva: Formal analysis, Investigation, Methodology, Writing – original draft. **Isabel Duarte Coutinho:** Conceptualization, Data curation, Formal analysis, Software, Writing – review & editing. **Luiz Antônio Dutra:** Data curation, Formal analysis, Investigation, Writing – review & editing. **Marina Barros Zacharias:** Formal analysis, Investigation, Methodology, Software, Writing – review & editing. **Luiz Alberto Colnago:** Conceptualization, Investigation, Supervision, Writing – review & editing. **Tiago Bueno de Moraes:** Conceptualization, Formal analysis, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodcont.2026.112430.

Data availability

Data will be made available on request.

References

Bartle, K. D., & Myers, P. (2002). History of gas chromatography. *TrAC, Trends in Analytical Chemistry, 21*(9–10), 547–557. https://doi.org/10.1016/S0165-9936(02)00919-3

Basso, B. H., Garcia, R. H. S., Cardoso, M. A., Simões, F. R., Moras, D. J., Lima, E. R. D., Colnago, L. A., Barbosa, L. L., et al. (2025). Using time-domain nuclear magnetic resonance (TD-NMR) for quantification of diesel adulteration with ethanol. *Applied Magnetic Resonance, 56*(4), 441–452. https://doi.org/10.1007/s00723-024-01736-x

Chiari, B. G., Trovattti, E., Pecoraro, E., Correa, M. A., Cicarelli, R. M. B., Ribeiro, S. J. L., & Isaac, V. L. (2014). Synergistic effect of green coffee oil and synthetic sunscreen for health care application. *Industrial Crops and Products, 52*, 389–393. https://doi.org/10.1016/j.indcrop.2013.11.011

Cobo, M. F., Deublein, E. J., Haber, A., Kwamen, R., Nimbalkar, M., Decker, F., et al. (2017). TD-NMR in quality control: Standard applications. In *Modern magnetic resonance* (pp. 1–18). https://doi.org/10.1007/978-3-319-28275-6_12-1

Colnago, L. A., Wiesman, Z., Pages, G., Musse, M., Monaretto, T., Windt, C. W., Rondeau-Mouro, C., et al. (2021). Low field, time domain NMR in the agriculture and agrifood sectors: An overview of applications in plants, foods and biofuels. *Journal of Magnetic Resonance, 323*, Article 106899. https://doi.org/10.1016/j.jmr.2020.106899

D'Amelio, N., De Angelis, E., Navarini, L., Schievano, E., Mammi, S., et al. (2013). Green coffee oil analysis by high-resolution nuclear magnetic resonance spectroscopy. *Talanta, 110*, 118–127. https://doi.org/10.1016/j.talanta.2013.02.024

Didham, M., Truong, V. K., Chapman, J., Cozzolino, D., et al. (2020). Sensing the addition of vegetable oils to olive oil: The ability of UV–VIS and MIR spectroscopy coupled with chemometric analysis. *Food Analytical Methods, 13*(3), 601–607. https://doi.org/10.1007/s12161-019-01680-8

Esteki, M., Simal-Gandara, J., Shahsavari, Z., Zandbaaf, S., Dashtaki, E., Heyden, Y. V., et al. (2018). A review on the application of chromatographic methods, coupled to chemometrics, for food authentication. *Food Control, 93*, 165–182. https://doi.org/10.1016/j.foodcont.2018.06.015

González-Pereira, A., Otero, P., Fraga-Corral, M., Garcia-Oliveira, P., Carpena, M., Prieto, M. A., Simal-Gandara, J., et al. (2021). State-of-the-art of analytical techniques to determine food fraud in olive oils. *Foods, 10*(3), 484. https://doi.org/10.3390/foods10030484

Gunning, Y., Defernez, M., Watson, A. D., Beadman, N., Colquhoun, I. J., Le Gall, G., Philo, M., Garwood, H., Williamson, D., Davis, A. P., Kemsley, E. K., et al. (2018). 16-O-methylcafestol is present in ground roast Arabica coffees: Implications for authenticity testing. *Food Chemistry, 248*, 52–60. https://doi.org/10.1016/j.foodchem.2017.12.034

Kanwal, N., Musharraf, S. G., et al. (2024). Analytical approaches for the determination of adulterated animal fats and vegetable oils in food and non-food samples. *Food Chemistry, 460*(3), Article 140786. https://doi.org/10.1016/j.foodchem.2024.140786

Kitzberger, C. S. G., Scholz, M. B. S., Pereira, L. F. P., Vieira, L. G. E., Sera, T., Silva, J. B. G. D., Benassi, M. T., et al. (2013). Diterpenes in green and roasted coffee of Coffea arabica cultivars growing in the same edapho-climatic conditions. *Journal of Food Composition and Analysis, 30*(1), 52–57. https://doi.org/10.1016/j.jfca.2013.01.007

Li, X., Zhang, L., Zhang, Y., Wang, D., Wang, X., Yu, L., Zhang, W., Li, P., et al. (2020). Review of NIR spectroscopy methods for nondestructive quality analysis of oilseeds and edible oils. *Trends in Food Science & Technology, 101*, 172–181. https://doi.org/10.1016/j.tifs.2020.05.002

Mitchell, J., Gladden, L. F., Chandrasekera, T. C., Fordham, E. J., et al. (2014). Low-field permanent magnets for industrial process and quality control. *Progress in Nuclear Magnetic Resonance Spectroscopy, 76*, 1–60. https://doi.org/10.1016/j.pnmrs.2013.09.001

Moeenfard, M., Alves, A., et al. (2020). New trends in coffee diterpenes research from technological to health aspects. *Food Research International, 134*, Article 109207. https://doi.org/10.1016/j.foodres.2020.109207

Moraes, T. B. (2021). Transformada inversa de Laplace para análise de sinais de ressonância magnética nuclear de baixo campo. *Química Nova*. https://doi.org/10.21577/0100-4042.20170751

Moraes, T. B., Von Atzingen, G. V., Mazzero, L. P., Mendes, W. S., Zacharias, M. B., Cardinali, M. C. B., et al. (2026). An open-access WebApp for Inverse Laplace Transform analysis of TD-NMR signals. *Magn. Reson. Discuss., 2026*, 1–20. https://doi.org/10.5194/mr-2026-2

Moraes, T. B., & Colnago, L. A. (2022). Noninvasive analyses of food products using low-field time-domain NMR: A review of relaxometry methods. *Brazilian Journal of Physics, 52*(2), 43. https://doi.org/10.1007/s13538-022-01055-1

Muniz, R. O., Gonzalez, J. L., Toci, A. T., Freitas, J. C. C., et al. (2023). Using ^{1}H low-field NMR relaxometry to detect the amounts of Robusta and Arabica varieties in coffee blends. *Food Research International, 174*, Article 113610. https://doi.org/10.1016/j.foodres.2023.113610

Olivieri, A. C. (2014). Analytical figures of merit: From univariate to multiway calibration. *Chemical Reviews, 114*(10), 5358–5378. https://doi.org/10.1021/cr400455s

Pereira, F. M. V., Rebellato, A. P., Pallone, J. A. L., Colnago, L. A., et al. (2015). Through-package fat determination in commercial samples of mayonnaise and salad dressing using time-domain nuclear magnetic resonance spectroscopy and chemometrics. *Food Control, 48*, 62–66. https://doi.org/10.1016/j.foodcont.2014.02.028

Portaluri, V., Thomas, F., Guyader, S., Jamin, E., Bertrand, B., Remaud, G. S., Schievano, E., Mammi, S., Guercia, E., Navarini, L., et al. (2020). Limited genotypic and geographic variability of 16-O-methylated diterpene content in Coffea arabica green beans. *Food Chemistry, 329*, Article 127129. https://doi.org/10.1016/j.foodchem.2020.127129

Raba, D. N., Poiana, M. A., Borozan, A. B., Stef, M., Radu, F., Popa, M. V., et al. (2015). Investigation on crude and high-temperature heated coffee oil by ATR-FTIR spectroscopy along with antioxidant and antimicrobial properties. *PLoS One, 10*(9), Article e0138080. https://doi.org/10.1371/journal.pone.0138080, 14.

Remiro, V., Romero-de-Ávila, M. D., Segura, J., Cambero, M. I., Fernández-Valle, M. E., & Castejón, D. (2024). Rapid and non-invasive determination of iodine value by magnetic resonance relaxometry in commercial edible oils. *Applied Sciences, 14*(24), 11530. https://doi.org/10.3390/app142411530

Ren, Y., Wang, C., Xu, J., Wang, S., et al. (2019). Cafestol and kahweol: A review on their bioactivities and pharmacological properties. *International Journal of Molecular Sciences, 20*(17), 4238. https://doi.org/10.3390/ijms20174238

Ribeiro, R. C., Mota, M. F. S., Silva, R. M. V., Silva, D. C., Novaes, F. J. M., Junior, V. F. V., Bizzo, H. R., Teixeira, R. S. S., Rezende, C. M., et al. (2024). Coffee oil extraction methods: A review. *Foods, 13*(16), 2601. https://doi.org/10.3390/foods13162601

Santos, E. M., Macedo, L. M., Tundisi, L. L., Ataide, J. A., Camargo, G. A., Alves, R. C., Oliveira, M. B. P. P., Mazzola, P. G., et al. (2021). Coffee by-products in topical formulations: A review. *Trends in Food Science & Technology, 111*, 280–291. https://doi.org/10.1016/j.tifs.2021.02.064

Santos, P. M., Kock, F. V. C., Santos, M. S., Lobo, C. M. S., Carvalho, A. S., Colnago, L. A., et al. (2017). Non-invasive detection of adulterated olive oil in full bottles using time-domain NMR relaxometry. *Journal of the Brazilian Chemical Society, 28*(2), 385–390. https://doi.org/10.5935/0103-5053.20160188

Sera, G. H., Volsi, B., Junior, V. M., Pereira, C. T. M., Telles, T. S., et al. (2025). Production and trade of specialty coffee in Brazil. *Scientific Reports, 15*, 42403. https://doi.org/10.1038/s41598-025-26620-x

Wagemaker, T. A. L., Carvalho, C. R. L., Maia, N. B., Baggio, S. R., Filho, O. G., et al. (2011). Sun protection factor, content and composition of lipid fraction of green coffee beans. *Industrial Crops and Products, 33*(2), 469–473. https://doi.org/10.1016/j.indcrop.2010.10.026

Zhang, Q., Saleh, A. S. M., Shen, Q., et al. (2013). Discrimination of edible vegetable oil adulteration with used frying oil by low field nuclear magnetic resonance. *Food and Bioprocess Technology, 6*, 2562–2570. https://doi.org/10.1007/s11947-012-0826-5

Zhao, L., Zhang, M., Wang, H., Mujumdar, A. S., et al. (2022). Monitoring of free fatty acid content in mixed frying oils by means of LF-NMR and NIR combined with BP-ANN. *Food Control, 133*, Article 108599. https://doi.org/10.1016/j.foodcont.2021.108599