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Original Research Article

An expert system based on ^{1}H NMR spectroscopy for quality evaluation and adulteration identification of edible oils

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ABSTRACT

The advantages of nuclear magnetic resonance (NMR) such as nondestructive and simultaneous detection, high reproducibility and rapidity make it easily develop the objective and credible methods for food analysis and identification. In this study, we developed a computer-aided, MATLAB-scripted expert system which enables NMR data to distinguish different edible oils and evaluate the quality of edible oils. The NMR spectral data of seven species of most popular vegetable edible oils in China were used to establish the assessment criterions including the content percentage of fatty acids and the quality parameters of edible oils. In our case, the identification accuracy of vegetable origin for the pure edible oils is 95.83% and that for the mixed edible oils is 89.58%, and all the recycled waste cooking oils and fried oils were correctly screened out and identified by the expert system. Further, the quality information of the edible oils was also provided. Our results show that the current expert system is a fast, easy-operated and convenient tool for the adulteration identification and quality control of edible oils.

1. Introduction

Healthy diet has always been being the continuous concern in people's lives, and recently the problems in diet enhance national awareness of healthy-eating trends. Vegetable edible oils are daily used in cooking food and flavoring and are regarded as necessity of living because of the relevance to people's lives (Rao, 2001). Edible oils can provide nutrients such as sitostanol, unsaturated fatty acids, oryzanol and so on (Odabasoglu et al., 2008), which are beneficial for human health and health care. The differences in composition of edible oils result in the differences in their health benefits together with the aroma and taste (Ferreiro-González et al., 2017), and further the price of different species of edible oils. However this also makes it prone to falsification or adulteration with less expensive oils in order to profiteer (Lisa et al., 2009). The common adulteration of edible oils involves the use of unqualified edible oils or the mixing of cheaper edible oils with higher-cost edible oils. Unqualified edible oils specify the recycled waste cooking oils and the fried oils after multiple heating by a series of processes including deacidification, decoloration and deodorization, which would inevitably produce a variety of harmful substances such as toxic alkylbenzenes (Uriarte and Guillén, 2010). Even through filtration and purification, many kinds of toxic and harmful substances in the unqualified edible oils cannot be easily removed. It is more difficult to distinguish unqualified edible oils from the appearance or odor, but this kind of edible oils harm badly to the organism (Moreno et al., 2007). Mixed edible oils are the blended edible oils of two kinds or more than two kinds of pure edible oils in a certain proportion. In practice, it usually occurs to mix the more expensive edible oils with less expensive edible oils in order to increase profits, such as olive oil mixed with soybean oil as olive oil. This kind of adulteration is not only the focus of our attention, but also the most commonly used method of reducing costs by illegal traders. This kind of adulteration is more private and cannot harm health of consumers, so it is often ignored by common consumers. The adulteration problem of edible oils not only affects the health of the people but also hold back the international trade of the edible oils. Therefore, the quality control and food safety in edible oils have attracted more and more attention from the governments, the manufacturers and the public.

The diversity of edible oils on the market and the increase in adulteration have made it necessary to establish a reliable method and criteria to identify such adulteration. Nowadays many research groups have provided a number of discriminating methods with regards to the detection and analysis of edible oils (Climaco Pinto et al., 2010; Dupuy et al., 2005; Esteki et al., 2017; Poulli et al., 2009; Zou et al., 2009). However, the traditional chemical methods often require a variety of apparatus and chemical reagents and professional skilled operators. Especially, the detection of quality parameters is time-consuming (Mu et al., 2013; Nunes, 2014) and cannot be used for rapid screening.

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Therefore, the development of a fast analysis of edible oils is meaningful, especially for improving the quality supervision of edible oils enterprises, ensuring the market of edible oils consumption and consumers' rights and interests (Esteki et al., 2019).

Nuclear magnetic resonance (NMR) spectroscopic techniques have been widely applied in the analysis of edible oil (Castejón et al., 2014; Cordella et al., 2012; Vigli et al., 2003; Zhang et al., 2013), and their combination with multivariable statistical analysis provided an advantage in identifying the plant and geographical origin and monitoring quality (Zhang et al., 2018). In our previous research (Zhang et al., 2018), the exact ratios of specific fatty acids in the different vegetable-origin edible oils, including linolenic acid, linoleic acid, oleic acid, saturated fatty acid and iodine value, have been calculated from the corresponding NMR spectral information. Thus, a database could be accordingly established to set the threshold of main nutritional components in the different edible oils for identification. For unqualified edible oils, according to the spectral characteristics of wasting cooking oils, fried oils and the relevant national standards of edible oils, several important parameters, including the iodine value, the carbonyl value, the hydroxyl value (acetyl value), the acid value and the water content, could reflect the quality of the oil and thus serve to discriminate them from the qualified ones.

The aim of this work was to establish a computer-aided expert system to distinguish the unqualified edible oils from the eligibility vegetable oils to administrate the inferior edible oil in the food and drinking trade. ^{1}H NMR spectroscopy (Kuballa et al., 2018; Santos et al., 2018; Zhang et al., 2018), chromatographic and other spectroscopic methods (Esteki et al., 2018a,b) have been conjugated with multivariate data analysis to serve the similar target, and artificial intelligence techniques would strengthen the capabilities (Gonzalez-Fernandez et al., 2019), but we mainly focused on simplifying the process to identify adulteration and detect quality of edible oil in our research.

2. Materials and methods

2.1. Samples

Two sets of edible oil samples were used in this study:

The first set of edible oil samples came from our previous work (Zhang et al., 2018). A total of 48 commercial refined edible oils came from seven different vegetable-origins including 15 samples of sesame oil (SE), 6 samples of soybean oil (SO), 6 of peanut oil (PE), 6 of corn oil (CO) and 6 of sunflower seed oil (SS), 5 samples of rapeseed oil (RA) and 4 samples of olive oil (OL), 43 of which were purchased from the local supermarkets, and 5 of them were certified reference materials (CRMs) for different species of edible oils including soybean oil, peanut oil, sunflower seed oil, corn oil and sesame oil which were obtained from National Institute of Metrology, China. This set of samples covered almost all popular species and brands of edible oils in China.

The second set of edible oil samples included 5 unqualified edible oils and 58 mixed edible oils by two kinds of pure edible oils. In the unqualified edible oils, one sample (sample 1) is a emulsifying edible oil, two samples (samples 2 and 4) are recycled waste cooking oils, sample 3 is a mixed edible oil with 20% recycled waste cooking oil, and sample 5 is a multiple fried sunflower seed oil. In the mixed edible oils, ten samples are the mixed edible oils by the 48 refined edible oils in set 1 by random pairing, and 48 samples were obtained by the simulated mixing of the integral data of the 48 refined edible oils in set 1 by random pairing.

For each sample of different edible oil, 50 μL of edible oils were dissolved in the mixture of 300 μL chloroform-d ($CDCl_3$) with 0.03% TMS and 250 μL dimethyl sulphoxide (DMSO-d_6). After homogenizing, 500 μL of the mixture was introduced into 5-mm NMR tubes for ^{1}H NMR detection.

2.2. Spectral data acquisition and preprocessing

^{1}H NMR spectra of the edible oils were collected at a 600 MHz Bruker AMX NMR spectrometer (Bruker Corporation, Karlsruhe, Germany), which possesses a 5-mm CPBBO probe, and resonant frequency of hydrogen is 600.13 MHz. ^{1}H NMR spectra were acquired by using the following parameters: pulse sequence, zg30; numbers of scan, 32 times; relaxation delay time, 1 s; acquisition time, 4.95 s; acquired size, 32 K; spectral width, 6613.8 Hz. And experimental temperature was controlled at 298 K, and ten edible oil samples could be measured per hour.

Before Fourier transform, the FIDs (free induction decays) were multiplied with a window function of 0.5 Hz line width for increasing SNR (signal-to-noise ratio) on MestReNova software (version: 9.0.1, Mestrelab Research S. L, Spain). NMR spectral phase was adjusted manually and baseline was corrected by multipoint base correction, and then referenced to TMS at 0 ppm. Each ^{1}H NMR spectrum (0.50–7.00 ppm) was integrated with integration interval of 0.01 ppm after the removal of solvent, and then full spectrum was normalized to the sum of the integrals for data analysis.

The normalized data was imported to SIMCA software (version14.1, Umetrics AB, Umea, Sweden) for multivariate statistical analysis including principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA). PCA was performed with mean centering scaling on the ^{1}H NMR data of the 48 refine edible oil samples to visualize the distribution of oil species, and PLS-DA was performed with unit variance scaling to classify the samples according to their plant origins.

2.3. Develop expert system for classification and identification of edible oils

The NMR integral data of the characteristic peaks of different vegetable-origin edible oils were used to calculate the threshold of major components and quality parameters, which would provide the standard for identifying the vegetable origin and adulteration of edible oils when combined with the national standards. Several peaks from the harmful substances in the unqualified edible oils including recycled waste oils and fried oils were served to the identification of unqualified edible oils from ordinary edible oils. Finally, a MATLAB-based software (expert system) was developed to identify the vegetable origin and possible adulteration of edible oils according to the thresholds of major components and quality parameters, and the actual data and simulated data of the different edible oils were used to verify the accuracy and reliability of expert system.

3. Results and discussion

3.1. NMR spectral analysis of different pure edible oils

Edible oils are mainly composed of triglycerides, which are formed by dehydration with different kinds of fatty acid and glycerol, and some low-content components such as vitamins and phenolic compounds also present in edible oils (Santos et al., 2018). The fatty acids can be categorized into saturated fatty acids, monounsaturated fatty acid and polyunsaturated fatty acids according to the degree of unsaturation, position or quantity of carbon-carbon double bonds. The category of major fatty acids in edible oils was listed in Table S1 (Supplemental materials). The different vegetable-origin edible oils demonstrated the individual characteristics in NMR spectra although they hold similar spectra profiles. In our previous study (Zhang et al., 2018) and related data (Almoselhy et al., 2014; Castejón et al., 2014), the individual peaks have been assigned to the specific components. According to their NMR spectra, all edible oils contain saturated fatty acids (SFA), unsaturated fatty acids, triglycerides (TG), 1,3′-diglycerides (1,3′-DG), limonene, β-carotene and β-sitosterol. Nevertheless, some obvious differences in spectral profiles are observed in the different species of

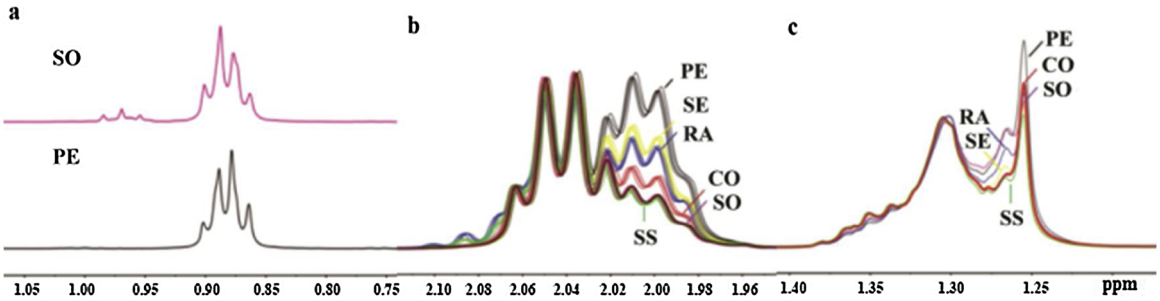

Fig. 1. Characteristic NMR (nuclear magnetic resonance) peaks in the different species of edible oils. (a) linolenic acid in rapeseed oil and soybean oil; (b) the ratio of linolenic acid to oleic acid and linoleic acid in the different species of edible oils; (c) saturated fatty acids in the different species of edible oils. CO, corn oil; PE, peanut oil; RA, rapeseed oil; SE, sesame oil; SO, soybean oil; SS, seed oil.

edible oils. For example, tyrosol was only detected in olive oil, and linolenic acid (a triplet at 0.98 ppm) was more obvious in rapeseed oil and soybean oil than other edible oils (Fig. 1a). The content ratio of linolenic acid (1.98–2.03 ppm) to oleic acid and linoleic acid (2.03–2.08 ppm) in peanut oil (1.5) is higher than in sesame oil (1.15) and other edible oils (below 1.0) (Fig. 1b). The high content (19.26% ± 1.09%) of saturated fatty acids in peanut oil contributes to the significantly higher signals at 1.255 ppm and 1.300 ppm than other edible oils (Fig. 1c). Since sesame oil contains a large amount of phenolic compounds, their characteristic peaks are demonstrated in the aromatic hydrocarbon region between 5.5–7.0 ppm, and the 1,2′-diglyceride peak at 3.8 ppm is also unique for sesame oil (data not shown).

According to our previous research (Zhang et al., 2018), the exact content of fatty acids in edible oils could be derived from their spectral information. Fig. 2 shows the representative ^{1}H NMR spectra of soybean oil and sesame oil, and the marked characteristic peaks could serve to calculate the fatty acid content in edible oils. The spectral information, including peak notation, chemical shift and multiplicity, assignment, and vegetable origin, is described in Table 1.

The content percentage of linolenic acid, linoleic acid, oleic acid and saturated fatty acids can be calculated via the Eqs. (1)–(4).

$$[\text{linolenic acid}]=B/(A+B) \quad (1)$$

$$[\text{linoleic acid}]=(3E-4B)/[2(A+B)] \quad (2)$$

$$[\text{oleic acid}]=3D/[4(A+B)]-[\text{linolenic acid}]-[\text{linoleic acid}] \quad (3)$$

$$[\text{saturated fatty acids}]=A/(A+B)-[\text{linoleic acid}]-[\text{oleic acid}] \quad (4)$$

where A, B, D and E correspond to the integral of spectral peaks in Table 1. The composition contents of fatty acids in edible oils in our study have been provided in our previous research (Zhang et al., 2018) and the results were also listed in Table S2 (Supplemental materials).

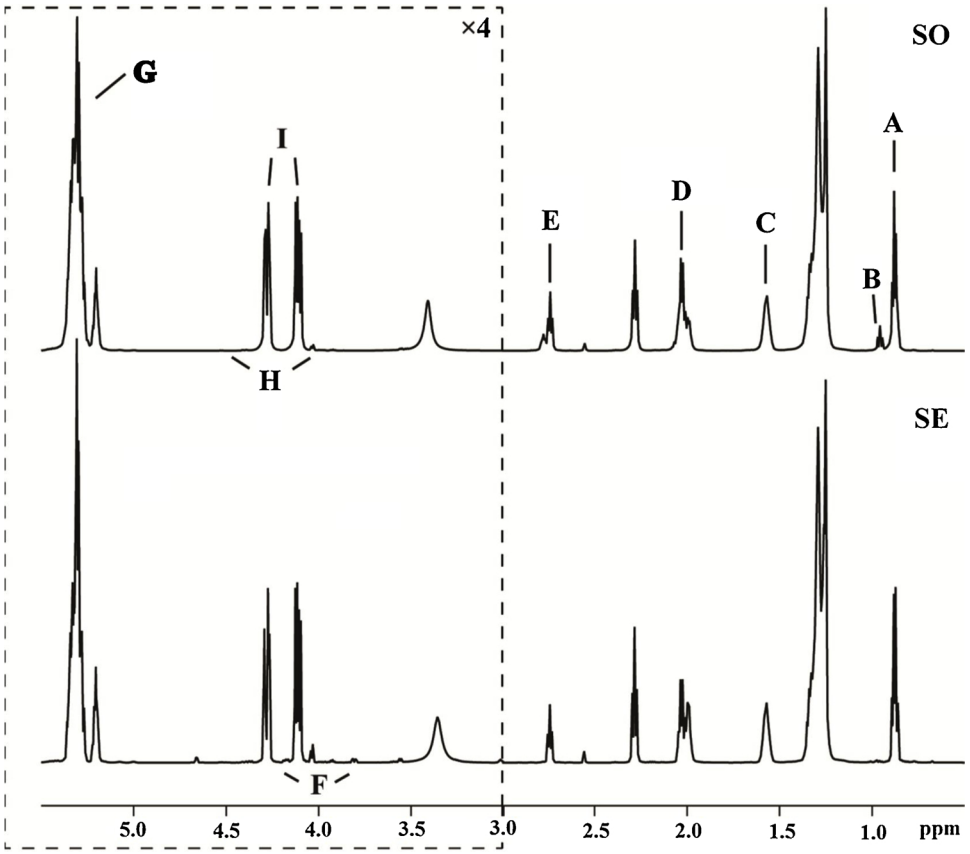

Fig. 2. Representative ^{1}H NMR (nuclear magnetic resonance) spectra (0.5–5.5 ppm) of soybean oil (SO, top panel) and sesame oil (SE, bottom panel). The spectral regions at 3.0–5.5 ppm are longitudinally magnified 4 times compared with the corresponding regions at 0.5–3.0 ppm. The detailed information of the marked peaks was provided in Table 1.

Table 1
The NMR spectral information of edible oils.

Peak notation	δ(ppm) (Multiplicity[b])	Proton	Assignment	Vegetable origin
A[a]	0.88(br)	$CH_2CH_2CH_2-CH_3$	All fatty acid (Except linolenic)	ALL[d]
B	0.96(t)	$CH{=}CH-CH_2-CH_3$	Linolenic	Soybean/Rapeseed
C	1.57(br)	CH_2-CH_2-COO-	All fatty acid	ALL
D	2.03(q)	$CH_2-CH{=}CH$	UFA[c](Except oleic)	ALL
	1.99(q)	$CH_2-CH{=}CH$	Oleic	ALL
E	2.74(t)	$CH{=}CH-CH_2-CH{=}CH$	UFA(Except linolenic)	ALL
F	4.18, 3.81(dd)	CH_2-OCOR, CH_2OH sn-1,3	1,2-DG	Sesame
G	4.28, 4.11(dd)	CH_2-OCOR sn-1,3	TG	ALL
H	4.40, 3.99(dd)	CH_2-OCOR sn-1,3	1,3-DG	ALL
I	5.31(br)	$CH_2-CH{=}CH$	All UFA	ALL

[a] The marks are same as in Fig. 2.
[b] Multiplicity: t, triplet; q, quartet; dd, doublet of doublets; br, broad resonance.
[c] UFA, unsaturated fatty acids; TG, triglyceride; DG, diglyceride.
[d] ALL, all plant origins.

3.2. Quality identification of edible oils by NMR spectral characteristics

3.2.1. Quality parameters for edible oils

The national standard (GB 2716-2018) on the quality of edible oils have formulated some important indexes such as odor, flavor, insoluble impurity, acid value, peroxide value, water content, and solvent residue. In our study, six parameters, including iodine value, acid value, hydroxyl value (acetyl value), aromaticity, carbonyl value and water content, were selected to identify the quality of edible oils based on the characteristics of unqualified edible oils and national standard, which could be quantified via a single NMR measurement. The major concerns in NMR spectra of unqualified oils include aromatic hydrocarbon peak, water peak, double hydrogen bond peak and hydrogen peak near glyceride. By calculating and analyzing those peaks, the corresponding quality parameter above could be obtained.

Iodine value is a significant parameter to illustrate the quality of edible oils (Yan et al., 2018), and it is the percentage by weight of iodine absorbed by unsaturated fatty acids and often used to determine the amount of unsaturation in fatty acids. Thus, iodine value of edible oils can be calculated via Eq. (5).

$$[\text{Iodine value}] = (I/2\text{-}H/4)/[(A+B)/3]\times 86 \quad (5)$$

where A, B, H and I correspond to the integral of spectral peaks in Table 1, respectively. I/2 was chosen as integral value of double bond, H/4 was chosen as the molecular number of all glycerides for data correction, and (A + B)/3 (equal to C/2) was molecular weight of all fatty acids.

Carbonyl value is a good index of oxidative changes in fatty acids (Chen et al., 2010), and it shows the degree of oxidation in fatty acid and measures the amount of secondary decomposition products of oxidation such as aldehydes and ketones (Farhoosh and Moosavi, 2008). The ratio of the integral of aldehyde carbonyl hydrogen to C/2 or (A + B)/3 can be used as a reference value for evaluating the carbonyl content (Eq. 6). The determination of carbonyl compounds in fried oils is very important for evaluating the quality of frying fats and oils because these compounds often contribute to rancid and unpleasant flavors, and reduce the nutritional value of fried foods (Endo et al., 2001).

$$[\text{Carbonyl value}] = AH/[(A+B)/3] \quad (6)$$

where A and B are the integral values corresponding to the signals in Table 1, and AH is the integral values of aldehyde hydrogen at about 9.5 ppm.

Hydroxyl value (acetyl value) is one of the traditional characteristics of fatty acid (Tavassoli-Kafrani et al., 2014), and it is mainly caused by the hydroxyl groups in diacylglycerol which are not chemical dehydrated with the fatty acid. The hydroxyl value is usually expressed in milligrams of potassium hydroxide and corresponds to the number of hydroxyl groups present in 1 g of fatty acid. Hydroxyl value of edible oils can be calculated via Eq. (7).

$$[\text{Hydroxyl value}] = DG/4/[(A+B)/3] \quad (7)$$

where A and B are the integral values corresponding to the signals in Table 1, and DG is the integral values of diacylglycerol hydrogen at about 4.2 ppm, which was divided by 4 to obtain the total number of hydroxyl group molecule. Then the ratio of the total number to C/2 or (A + B)/3 can reflect the proportion of hydroxyl groups in the overall sample.

Acid value is a measure of the number of carboxyl groups in fatty acid. The acid value can be calculated via Eq. (8).

$$[\text{Acid value}] = (C/2\text{-}3G/4\text{-}H/2\text{-}F/2)/(C/2)\times 100\%\times[\text{average molecular weight}]/56 \quad (8)$$

where C/2, 3 G/4, H/2 and F/2 are the contents of all the fatty acids, triglyceride, diglyceride, and monoglyceride, respectively. Their difference (the content of all non-free fatty acids) is divided by the content of all the fatty acids (C/2) to obtain the molecular percentage. The average molecular weight of the samples is usually calculated as 280, and 56 is the molecular weight of potassium hydroxide (KOH).

Water content in edible oils is another sensitive index to distinguish unqualified edible oils from the normal ones. The integral of the water peak was directly compared with the integral of the peaks of all fatty acid. Water content (X%) in edible oils can be obtained via Eq. (9).

$$X\% = [(m_1 - m_0)\times 18]/(m_2\times 280)\times 100 \quad (9)$$

where m_1 is the integral of the normalized water peak by methyl normalization, m_0 is the integral of water peak in solvent, and m_2 is the integral of the β-methylene of carboxyl group (that is C in Table 1). Molar weight of water is 9, and 280 is the average molar weight of edible oils.

Aromaticity is mainly referred to polycyclic aromatic hydrocarbons at 5.5–7.5 ppm which are harmful to human health. Polycyclic aromatic hydrocarbons (PAHs) are a class of compounds in which two or more benzene rings are connected in the form of a fused ring. PAHs in edible oils is mainly produced by direct contact with incomplete combustion or pyrolysis gas, so the content of PAHs would obviously increase in used cooking edible oils. Aromaticity in edible oils can be obtained via Eq. (10).

$$[\text{Aromaticity}] = PAHs/[(A+B)/3] \quad (10)$$

where A and B are the integral values corresponding to the signals in Table 1, and PAHs is the integral values of polycyclic aromatic hydrocarbons at 5.5–7.5 ppm.

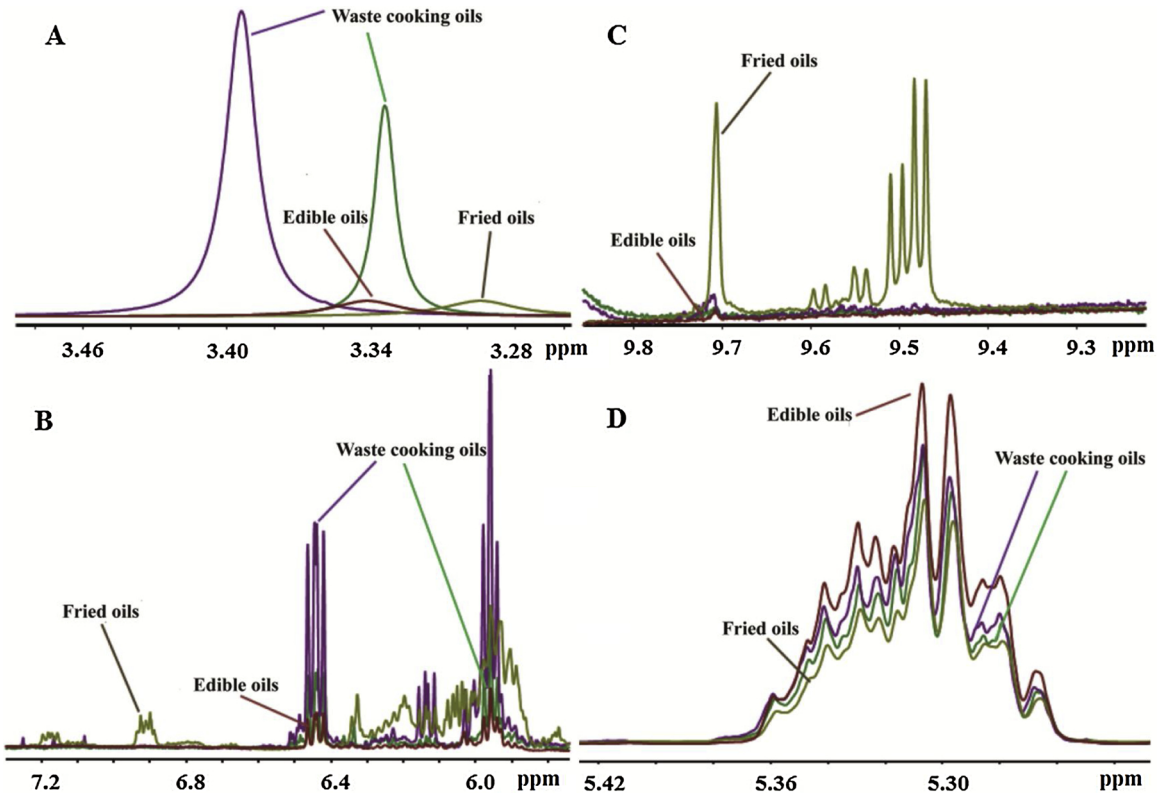

Fig. 3. ^{1}H NMR (nuclear magnetic resonance) spectral characteristics of waste cooking oils, fried oils and qualified edible oil. (A) spectral region of water; (B) spectral region of aromatic hydrocarbon; (C) spectra region of aldehyde; (D) spectra region of methine with double bond.

3.2.2. Quality identification of edible oils by the quality parameters

The unqualified oils such as waste cooking oils and multiple-fried oils will inevitably introduce a variety of harmful substances during the recycling and refining processes, which display the specific profiles in their NMR spectra. Fig. 3 shows the ^{1}H NMR characteristic spectra of unqualified oils (including waste cooking oils and fried oils) compared with ordinary qualified edible oils. Fig. 3A displays the spectral region of water in edible oils at about 3.4 ppm. After methyl normalization, the intensity of water signal directly indicated water content in the sample. Water also appeared in the qualified edible oils because of the solvent and storage environment, but the water peak was relatively gentle and the integral was relatively small, while the water peak of the wasting cooking oils was obviously greater than that of ordinary edible oils due to the water generated by hydrolytic rancidity. This process can also cause the change of pH, which led to the partial offset of water peaks. According to the quantitative analysis (Table 2), the water content of the recycled waste cooking oils (samples 2–4) increased by 5–13 times higher than that of the qualified edible oils, and the water content of the emulsifying edible oil (sample 1) was even surged 130 times. Although the frying processes in the high-temperature (more than 473 K) would make water gasify and evaporate, the water content in the fried oil (sample 5) was also increased (38.5% higher than that of ordinary edible oils) due to absorbing a small amount of water in the process of cooling and preservation.

The spectral region of aromatic hydrocarbon at 5.5–7.5 ppm was displayed in Fig. 3B, which include the peaks both from phenolic compounds that are beneficial to humans and from polycyclic aromatic hydrocarbons that are harmful to humans. It is noticeable that many

Table 2
Quality parameters the qualified and unqualified edible oils.

Quality parameter		Unqualified edible oils					Qualified edible oils	National standard
		No. 1	No. 2	No. 3	No. 4	No. 5		
Iodine value	AV[a]	115.86	114.79	121.16	121.99	103.56	124.81	118–141
	RV(%)[b]	−7.17	−8.03	−2.92	−2.26	−17.02		
Acid value (KOH mg/g)	AV	5.41	3.13	5.99	0.80	6.64	2.96	≤3
	RV(%)	82.68	5.61	102.20	−72.86	124.40		
Hydroxyl value (molar ratio %)	AV	1.54	0.89	1.71	0.23	1.90	0.85	N/A[c]
	RV(%)	81.76	5.08	101.18	−73.00	123.27		
Aromaticity (mole ratio %)	AV	3.14	8.01	2.32	3.24	9.09	1.69	N/A
	RV(%)	85.98	374.19	37.04	91.74	437.84		
Carbonyl Value (molar ratio %)	AV	0.47	0.19	0.22	0.28	2.00	0.32	N/A
	RV(%)	45.42	−40.71	−31.04	−13.60	526.39		
Water content (%)	AV	44.65	4.88	2.97	2.14	0.24	0.11	≤0.2
	RV(%)	13,060.54	1364.06	803.17	558.27	38.50		

[a] Absolute value.
[b] Relative variation to the values of the qualified edible oils.
[c] N/A, not available.

new peaks with strong intensity derived from recycled waste cooking oils and fried oils, which should correspond to the residue aromatic hydrocarbons and impurity during the refining and recycling processes. According to their aromaticity (Table 2), the proportion of aromatic hydrocarbon compounds in the recycled waste cooking oils increased by 37.04% (sample 3, only containing 20% recycled waste cooking oils), 91.74% (sample 4) and 3.7 times (sample 2) that of the ordinary edible oils, and that of emulsifying edible oil (sample 1) increased 85.98%. The proportion of aromatic hydrocarbon compounds in the fried oil (sample 5) increased sharply 4.4 times that of the qualified edible oils. The content of aromatic hydrocarbon compounds was a direct reason of differences in the odor between unqualified and qualified edible oils.

Fig. 3C shows a sudden increase of aldehyde peaks near 9.50 ppm in spectra of fried oils. Aldehydes are volatile substances which are easier to be removed by technical means such as continuous countercurrent extraction process in recycled waste cooking oils (Racheva et al., 2018), but the fried oils sample was made by us without the special treatment. NMR experiment directly retained the damage results in high-temperature to edible oil structures. By the quantitative calculation, the content of aldehydes in the fried oil increased by 5.3 times, while the carbonyl value of the recycled waste cooking oils changed little because of volatilization (Table 2).

Fig. 3D demonstrated the decreased ^{1}H NMR integral of the methine peaks of double bond (at 5.30 ppm) in the fried oils and recycled waste cooking oils, which should be due to the changed hydrogen species of double bond or the decreased content of double bond in fatty acids. From the perspective of reduction range, fried oils decreased most obviously after high-temperature heating, which indicated that multiple high temperatures heating caused structural damage to the carbon-carbon double bonds in ordinary edible oils. The quantitative calculation of iodine value confirmed it (Table 2), where the iodine value of the fried oil dropped by a maximum of 17%, while the decline of the iodine values of the recycled waste cooking oils was not obvious (only varied between 2–8%).

According to the quantitative results of acid value and hydroxyl value (Table 2), they seem not to be the sensitive and reliable parameters to identify the unqualified edible oils from the ordinary edible oils. Although the iodine values and acid values of most unqualified edible oils are higher than that of the qualified edible oils, sample 4 demonstrated the lower values than the qualified edible oils.

In addition to the quality parameters, an obvious difference in the main ingredients was also observed between before and after frying. The results showed that the content of oleic acid in the sunflower seed oils was reduced by 16.1% (from 25.5% to 21.4%), the content of linoleic acid was decreased by 22.8% (from 62.4% to 48.2%) after multiple frying, while the content of saturated fatty acids increased significantly by 110.9% (from 11.9% to 25.1%). It is evident that the carbon-carbon double bonds of unsaturated fatty acids were oxidized during the heating process, thus unsaturated fatty acids were converted into more short chain saturated fatty acids. It could be confirmed by the decreased iodine value (from 124.8 to 103.6), which indicated the decreased degree of unsaturation of edible oil during heating. These parameters are particularly important to the identification of unqualified edible oils because of the irreversibility of heating process. The composition of the recycled waste cooking oils was more complex than that of any ordinary edible oil. Therefore, recycled waste cooking oils can be identified by the combination composition of fatty acids with the quality parameters of the oils.

3.3. Expert system

3.3.1. Settings of expert system

Our expert system was based on MATLAB programming. It can directly read the integrals of NMR spectra exported from MestReNova software, via which removal of solvent peak, retaining of the water peak and normalization of all the integrals could be automatically accomplished. According to Eqs. (1)–(8), the quality parameters of any one kind of edible oil, including the contents of linolenic acid, linoleic acid, oleic acid, SFA and iodine value, acid value, hydroxyl value and carbonyl value, could be obtained. Thus, the edible oil could be identified and the judgment result could be given when compared with our pre-established database.

Identification logic of the expert system was set as follows: firstly, the peaks from surpass-criterion substances such as aldehyde, ketone and aromatic hydrocarbons were paid close attention to. If the surpass-criterion substances were observed, recycled waste cooking oils or fried oils was given as judgment, and the corresponding superscale of each parameter was also provided. Or else, the surpass-criterion test passed, the oils were judged as ordinary edible oils. Secondly, the main composition and the related quality parameters were calculated and compared with those of each pure edible oil. If the parameters satisfied the threshold of parameters of any edible oil, the edible oil was judged as this species of pure edible oils. Otherwise, the logic judgments recurred to mixed edible oils. Finally, according to the linear analysis, the constitution of mixed edible oils was obtained. The specific implementation MATLAB code of system is demonstrated in Appendix.

In practice, two modes of parameter comparison were set up. The first one was that the integral of each peak was directly calculated and stored, and no converting into the composition of edible oil or the value of related parameters is necessary. This mode provided many variables, and therefore it should be able to provide better identification accuracy for the distinguishing of pure edible oils. However, a high requirement for normalization will lead to the misjudgment for edible oils with a large difference in composition. The second mode was that the corresponding contents or parameters such as oleic acid, linoleic acid and iodine value were calculated from the integral of each peak, and then the thresholds for these parameters served as the judgments rule. This mode was appropriate for the discriminant analysis of most edible oils with a higher accuracy rate (about 90%) in our cases. However, the accuracy of judgment will be affected due to few stable variable parameters (a total of five or six in our case).

Table 3
Judgment threshold for every edible oil.

Category	Criterion of judgment
Olive oil	(C18A > = 67)& (C18O > 10)&(C18C < 1)& (C18B < 15)
Soybean oil	(C18A > 18) & (C18A < 30) &(C18C > = 5.5) & (C18B-C18A) > 15 & C18B > 52
Rapeseed oil	(C18A < 70) & (C18A > 60) & (C18C > = 8.5)& (C18A-C18B) > 40 & (C18A-C18B) < 50
Peanut oil	(C18A > 40) & (C18A < 55) &(C18C < 0.2)& (C18O > = 16) & (C18A > C18B)
Corn oil	(C18A > 25) & (C18A < 35) & (C18C < 3)& (C18O < 17) & (C18O > 14) & (C18B-C18A) > 18
Sunflower seed oil	(C18A < 55) &(C18C < 2)&(C18O < = 14) & (C18B-C18A) > 25 & (117 > IV) & (IV > 113)
Sesame oil	(C18A > 38) & (C18A < 42) &(C18C < 1.0) & (C18O < 17) & (C18O > 14) & (C18B-C18A) < 10

C18A, Percentage of monounsaturated fatty acid content; C18B, Percentage of two unsaturated fatty acid content; C18C, Percentage of three unsaturated fatty acid content; C18O, Percentage of saturated fatty acid content; IV, Iodine value.

Table 4
Classification accuracy of expert systems for 48 pure edible oils.

Category	Samples	Correct samples	Accuracy
Sunflower seed oil	6	6	100.00%
Rapeseed oil	5	4[a]	80.00%
Sesame oil	15	14[b]	93.33%
Soybean oil	6	6	100.00%
Peanut oil	6	6	100.00%
Corn oil	6	6	100.00%
Olive oil	4	4	100.00%
Total	48	46	95.83%

[a] C18A (Percentage of monounsaturated fatty acid content) = 36.27% for one of 5 rapeseed oil samples.
[b] C18C (Percentage of three unsaturated fatty acid content) = 1.83% for one of 15 sesame oil samples.

3.3.2. Identification of different oils

In this system, the classification and identification of pure edible oils was based on the relevant conditions and thresholds of main compositions (Table 3). When all of the thresholds of all parameters were met and no exceeded water, aldehyde or ketone, polycyclic aromatic hydrocarbons and monoester of diacylglycerol were observed, the system would judge the sample as pure edible oil, and the corresponding compositional information is also provided. The compositional differences of edible oils lead to their specific distribution in the PCA scores plot (Fig. S1 in the Supplemental materials). The edible oils could be classified by PLS-DA model according to the thresholds of their composition (Fig. S2). In our case, 46 of 48 pure edible oils were identified and classified correctly via single blind experiment (Table 4). One of the two unrecognized edible oils is a high content-oleic acid rapeseed oil, in which the content of oleic acid doubles that of ordinary rapeseed oil. The other one is ultra-high content-linolenic acid sesame oil than the ordinary sesame oil. In general, our expert system demonstrated an accuracy of 95.83% in the identification of pure edible oils (Table 4) without the reference database of high content-oleic acid rapeseed oils or high content-linolenic acid sesame oils. A richer database of ordinary edible oils will improve the accuracy.

The composition of pure edible oils is relatively stable, and their distinction between different vegetable-origin edible oils is relatively obvious, therefore, higher identification accuracy (95.83%) of expert system was reached for the pure edible oils. However, the compositions of mixed edible oils quite varied with the different mixing style of different edible oils, thus leading to more complex judgments. From the PCA scores plot based on ^{1}H NMR data of mixed edible oils (Fig. 4), the scores of each sample on the first two principal components (PC1 and PC2) could be calculated. Accordingly, the scores of mixed edible oils displayed an obvious linear correlation with that of the two pure edible oils such as the mixed oil of soybean oil and olive oil, indicating the certain relevance between component content and mixing ratio. The further calculation of component content after mixing confirmed that all the main components in the mixed edible oils were positively related to the proportion of the pure edible oils involved in the process of mixing. In order to eliminate the interference from the inaccuracy of NMR detection and the instability of the magnetic field, expert system adopted a multi-variable measurement which can automatically remove the fluctuating parameters and retain the relatively stable data, and thus the most accurate mixing ratio of mixing edible oils could be obtained and two kinds of mixing possibilities with the highest confidence level were given by combined with error analysis.

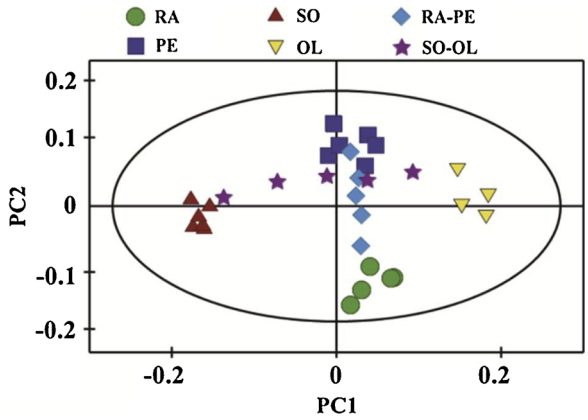

Fig. 4. Principal component analysis (PCA) scores plot based on ^{1}H NMR data of mixed edible oil. RA, rapeseed oil; PE, peanut oil; RA-PE, mixed oil of rapeseed oil and peanut oil; SO, soybean oil; OL, olive oil; SO-OL, mixed oil of soybean oil and olive oil; PC1, the first principal component; PC2, the second principal component.

In the verification test of 10 measured mixed samples of edible oils, 9 of them were correctly identified by the first judgment (the average error was 5.41%), and the remained one was correctly identified at the second judgment (Table 5), which preliminarily met the requirements of the system design. In order to further confirm the accuracy and reliability of the expert system, 48 simulated samples of mixing edible oils by the random-pairing principle. Among them, 43 samples were correctly identified (42 were at the first judgment, and 1 was at the second judgment) (Table S3). The accuracy of the first judgment was 87.50%, and the total accuracy of the two judgments was 89.58%. We noticed that 4 of 5 misjudged mixed edible oils were in the low mixing ratios (one species of edible oil accounted for about 10% of total) and the other was in the medium mixing ratio (one species of edible oil accounted for about 20% of total), and thus the judgment results tended to be the edible oil accounting for greater proportion. This misjudgment may due to the lower level of one edible oil or the similar composition of the two edible oils. We believe that the accuracy could be greatly improved if expert system was adjusted to multichannel style, thus the known mixed edible oil was directly connected to the mixed edible oils system.

The identification of unqualified edible oil was different from that of pure or mixed edible oils which were mainly determined by calculating the proportions of several major components. The identification of unqualified edible oils was focused on those quality parameters such as the content of aldehyde compounds, water content, hydroxyl value and acid value. According to the designed logic of expert system, the abnormal quality parameters are more important than the contents of main components, that is to say, once the sample cannot pass the test of abnormal parameters, expert system can immediately identify the sample as unqualified edible oils, and further analyze the reasons to give all the abnormal parameters.

In our study, all the 5 unqualified edible oils were correctly identified by the expert system. The expert system can quickly identify the recycled waste cooking oils and fried oils, and further analyze the surpass-criterion substances and give possible reasons.

4. Conclusions

Our MATLAB-scripted expert system facilitated the classification and identification of edible oils via ^{1}H NMR spectral data. The characteristic peaks in NMR spectra of the qualified edible oils were used to calculate the components of fatty acids and establish the quality parameters, which provide the basis for the quality determination and adulteration identification of edible oils. The NMR signals of the abnormal substances in unqualified edible oils could serve the identification of unqualified edible oils and provide the exceeded quality parameters via the expert system. In our case, the detection accuracy for the pure edible oils is 95.83%, the detection accuracy for the mixed edible oils is 89.58%, and all the unqualified edible oils made a correct response to the abnormal substance. Thus, the current expert system is applicable for the adulteration identification of edible oils and further

Table 5
Identification results of 10 mixed edible oils.

	Mixing ratio 1	Mixing ratio 2	Mixing ratio 3	Mixing ratio 4	Mixing ratio 5
Rapeseed oil	10%	30%	50%	70%	90%
Peanut oil	90%	70%	50%	30%	10%
First result	46.56% co-ol	29.94% ra-pe	50.92% ra-pe	61.14% ra-pe	85.35% ra-pe
Second result	11.88% ra-pe	35.03% so-ol	48.89% so-ol	56.13% so-ol	93.23% ra-co
Judgement	Second correct	First correct	First correct	First correct	First correct
	Mixing ratio 6	Mixing ratio 7	Mixing ratio 8	Mixing ratio 9	Mixing ratio 10
Oliver oil	10%	30%	50%	70%	90%
Corn oil	90%	70%	50%	30%	10%
First result	86.90% co-ol	69.24% co-ol	49.75% co-ol	32.54% co-ol	12.39% co-ol
Second result	77.67% se-so	37.91% pe-co	62.78% pe-co	85.07% pe-co	8.85% so-ol
Judgment	First correct	First correct	First correct	First correct	First correct

co-ol, corn oil mixed with olive oil; ra-pe, rapeseed oil mixed with peanut oil; so-ol, soybean oil mixed with olive oil; ra-co, rapeseed oil mixed with corn oil; co-ol, corn oil mixed with olive oil; se-so, sesame oil mixed with soybean oil; pe-co, peanut oil mixed with corn oil; so-ol, soybean oil mixed with olive oil.

provides the detailed quality information. Compared with the traditional tedious and complex methods, ^{1}H NMR-based expert system provides a fast, easy-operated and convenient tool for adulteration identification and quality control of edible oils with higher accuracies.

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Declaration of Competing Interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jfca.2019.103316.

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