Journal of Oleo Science

doi : 10.5650/jos.ess17130
J. Oleo Sci. **67**, *(1) 1-10 (2018)*

JOURNAL OF OLEO SCIENCE
Jos

REVIEW

Analytical Methods to Evaluate the Quality of Edible Fats and Oils: The JOCS Standard Methods for Analysis of Fats, Oils and Related Materials (2013) and Advanced Methods

Yasushi Endo*

School of Bioscience and Biotechnology, Tokyo University of Technology, 1401-1 Katakuramachi, Hachioji, Tokyo 192-0982, JAPAN

Abstract: Edible fats and oils are among the basic components of the human diet, along with carbohydrates and proteins, and they are the source of high energy and essential fatty acids such as linoleic and linolenic acids. Edible fats and oils are used in for pan- and deep-frying, and in salad dressing, mayonnaise and processed foods such as chocolates and cream. The physical and chemical properties of edible fats and oils can affect the quality of oil foods and hence must be evaluated in detail. The physical characteristics of edible fats and oils include color, specific gravity, refractive index, melting point, congeal point, smoke point, flash point, fire point, and viscosity, while the chemical characteristics include acid value, saponification value, iodine value, fatty acid composition, trans isomers, triacylglycerol composition, unsaponifiable matters (sterols, tocopherols) and minor components (phospholipids, chlorophyll pigments, glycidyl fatty acid esters). Peroxide value, *p*-anisidine value, carbonyl value, polar compounds and polymerized triacylglycerols are indexes of the deterioration of edible fats and oils. This review describes the analytical methods to evaluate the quality of edible fats and oils, especially the Standard Methods for Analysis of Fats, Oils and Related Materials edited by Japan Oil Chemists' Society (the JOCS standard methods) and advanced methods.

Key words: analytical methods, edible fats and oils, quality, standard method

1 Introduction

Edible fats and oils are among the basic components of the human diet, along with carbohydrates and proteins. Edible oils mainly include vegetable oils such as soybean, canola, palm, and corn oils, etc., while fish oils such as sardine and tuna oils are often supplemented to processed foods. Fats and oils are the source of high energy (9 kcal/g) and essential fatty acids such as linoleic (18:2), linolenic acid (18:3), EPA (20:5) and DHA (22:6) to human. Edible fats and oils are used in for pan- and deep-frying, and in salad dressing, mayonnaise and processed foods such as chocolates, cream and bakery products. The physical and chemical properties of fats and oils can affect the sensory attributes and nutritional quality of foods. Melting and congeal points, viscosity and consistency of edible fats and oils are responsible for the hardness and softness of food products, while the color and cloud point may affect the appearance of the food products. On the other hand, chemical characteristics such as saponification and iodine values based on the fatty acid composition can affect the stability of fats and oils during heat cooking and storage. Minor components such as sterols and tocopherols contained in vegetable oils can affect the nutritional value of products and their oxidative stability. Chlorophyll pigments and phospholipids may also affect the appearance and oxidative stability of edible fats and oils. Among the minor components, toxic metals and other harmful chemicals should not be present in edible fats and oils. Moreover, thermal deterioration of fats and oils due to oxidation, cyclization, polymerization and hydrolysis occurs during heat cooking, although pan- and deep-frying process impart the desirable flavor and taste to foods. Various low- and/or

*Correspondence to: Yasushi Endo, School of Bioscience and Biotechnology, Tokyo University of Technology, 1401-1 Katakuramachi, Hachioji, Tokyo 192-0982, JAPAN
E-mail: endo@stf.teu.ac.jp
Accepted July 5, 2017 (received for review June 5, 2017)
Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online
http://www.jstage.jst.go.jp/browse/jos/ http://mc.manusriptcentral.com/jjocs
This is the review by the winner of 51th Award for Prominent Studies, The Japan Oil Chemists' Society (JOCS).

high-molecular weight chemicals are formed during heat cooking. Particularly, by-products harmful to human health, such as hydroperoxides and polymers are formed during frying, which reduce the nutritional value of fats and oils. Moreover, some volatile low-molecular weight compounds with functional groups (aldehydes, ketones and alcohols) may impart undesirable flavor. Fats and oils in oil foods are also susceptible to auto- and photo-oxidation reactions during storage, and the products may lead to undesirable flavor and taste. Thus, it is very important to evaluate the degree of deterioration in fats and oils during heat cooking and storage to ensure and maintain the quality of the food products. Some internationally known standard methods are used to evaluate the quality of edible fats and oils such as the AOCS official methods[1], IUPAC standard methods[2] and Standard Methods for Analysis of Fats, Oils and Related Materials published by Japan Oil Chemists' Society (named as the JOCS standard methods)[3]. This review describes the analytical methods to evaluate the quality of edible fats and oils, especially the JOCS standard methods and advanced methods.

2 Physical characteristics[1–6]

A list of physical characteristics of edible fats and oils described in the JOCS standard methods is shown in Table 1. The physical characteristics of edible fats and oils include color (2.2.1), specific gravity (2.2.2), refractive index (2.2.3), melting point (2.2.4), congeal point (2.2.5), smoke point, flash point, fire point (2.2.11), and viscosity (2.2.10). Solid fat content (2.2.9) and consistency (2.2.15) are measured for processed oils such as margarine and shortening. Moreover, cold test (2.2.8) is carried out for salad oil.

Generally vegetable oils are transparent and have a yellowish or greenish color due to the presence of carotenoids and chlorophyll pigments. Color is usually estimated by the Lovibond spectrophotometric colorimeter. The specific gravity, refractive index, melting point and fatty acid composition of major vegetable oils are shown in Table 2. The specific gravity of edible fats and oils such as corn, olive and soybean oils are in the range of 0.90-0.92 at 25℃, although palm oil and the related oil had slightly lower specific gravity (0.89-0.90) at 25℃. The refractive index is in the range of 1.44-1.47, and it depends on the fats and oils variety. Palm oil has a refractive index of 1.44-1.45, while other vegetable oils have a refractive index of 1.47 at 25℃.

The melting point of vegetable oils depends on the fatty acid composition, as shown in Table 2. Olive and rapeseed oils rich in oleic acid (18:1) have melting points ≥ 0℃, while corn and soybean oils rich in linoleic acid (18:2) have melting points ≤ 0℃. Palm oil and coconut oil, which are rich in saturated fatty acids, especially palmitic acid (16:0) have higher melting points. The viscosity of edible fats and oils is measured using the Brookfield method. The kine-

Table 1 Physical characteristics of edible fats and oils.

Analysis	JOCS Standard Methods	Factor
Color	2.2.1	Pigment
Specific gravity	2.2.2	
Refractive index	2.2.3	Fatty acid (unsaturation)
Melting point	2.2.4	Fatty acid
Congeal point	2.2.5	Fatty acid
Cold test	2.2.8	Wax
Solid Fat content	2.2.9	Saturated fatty acid
Viscocity	2.2.10	Fatty acid, Polymer
Smoke point, Flash point	2.2.11	Fatty acid
Fire point		
Consistency	2.2.15	Saturated fatty acid

Table 2 Physical and chemical properties and fatty acid composition of vegetable oils.

Vegetable oil	Specific gravity (25℃)	Refractive index (25℃)	Melting point (℃)	Saponification value	Iodine value	Fatty acid composition (%)				
						16:0	18:0	18:1	18:2	18:3
Corn	0.920–0.928	1.473–1.476	−18〜−10	187–198	88–147	11	2	33	52	1
Olive	0.914–0.929	1.465–1.468	0〜−6	185–197	75–90	10	3	73	11	<1
Palm	0.921–0.948	1.453–1.459	27〜50	196–210	43–60	43	5	41	10	–
Soybean	0.922–0.934	1.472–1.475	−7〜−8	188–196	114–138	10	4	24	54	8

See Ref. 6

matic viscosity of edible fats and oils ranges from 6 to 10 mPa·s at 210°F(98.9℃). In addition, viscosity is an index used to determine the extent of oxidation and thermal deterioration of oils, because deteriorated oils have high viscosity due to polymers formation. Smoke point, flash point and fire point are often measured with a Cleveland open-cup tester. The flash point of vegetable oils is almost 320℃ in regardless of the variety. However, the smoke point depends on the types of edible fats and oils.

The solid fat content in processed oil and cacao fat is measured by the nuclear magnetic resonance(NMR)spectroscopy[7]. Consistency is often measured to determine the rheological properties of processed oils such as margarine and shortening.

3 Chemical characteristics[1–6, 8]

A list of chemical characteristics of edible fats and oils cited in the JOCS standard methods is given in Table 3. The chemical characteristics of edible fats and oils include acid value(2.3.1), saponification value(2.3.2), iodine value(2.3.4), fatty acid composition(2.4.2), trans isomers(2.4.4), triacylglycerol composition(2.4.6), unsaponifiable matter(2.4.8), sterols(2.4.9), tocopherols(2.4.10), phospholipids(2.4.11), chlorophyll pigments(2,4.12)and glycidyl fatty acid esters(2.4.13).

Acid value(AV)is a measure of the concentration of free fatty acids in fats and oils. AV is determined by the titration method based on the neutralization reaction with potassium hydroxide in ethanol. AV is an index for the purification of fats and oils, and a value ≤ 0.1 is desirable for refined edible fats and oils. Saponification value(SV)and iodine value(IV)are determined by the fatty acid composition of edible fats and oils, as shown in Table 2. Both SV and IV are measured by the titration methods. For measuring the SV, edible fats and oils are refluxed together with known quantity of potassium hydroxide in ethanol solution, and then the unreacted potassium hydroxide is titrated against standard hydrochloric acid. SV means the average molecular weight of triacylglycerols. A higher SV is a measure of low-molecular weight triacylglycerols of edible fats and oils. Most vegetable oils such as corn, olive, rapeseed and soybean oils have an SV of about 190, whereas the SV of palm oil and coconut oil, rich in palmitic acid(16:0), myristic acid(14:0)and lauric acid(12:0)is more than 200. IV is based on the extent of unsaturation of fatty acids located in triacylglycerol. When a constant amount of iodine solution is added to edible fats and oils, addition of the iodine molecule to the double bonds occurs on the acyl chain in triacylglycerols. The residual iodine is titrated with standard sodium thiosulfate to a starch endpoint. IV is an effective index for characterizing vegetable and fish oils. Olive oil, which is rich in monounsaturated fatty acids(18:1), has an IV ranging from 75 to 90, while soybean and corn oils rich in polyunsaturated fatty acids(18:2)have IV in the range of 120-140. Both SV and IV of vegetable oils can also be estimated from their fatty acid composition obtained by gas liquid chromatography(GLC)[9, 10].

Fatty acid composition is a useful parameter to distinguish between different edible fats and oils. The fatty acid composition of edible fats and oils is estimated by GLC with a flame ionization detector(FID)and a capillary column after derivatization from fatty acids in triacylglycerols to the corresponding methyl esters.

The trans isomers of unsaturated fatty acids in edible fats and oils are also quantified by GLC using a capillary column[11]. Hardened oil and hydrogenated oil such as margarine and shortening may contain considerable amounts of *trans* fatty acids. The presence of *trans* fatty acids in edible fats and oils has raised concerns among consumers as they may increase the LDL-cholesterol levels in blood. The infrared(IR)spectrum of *trans* fatty acids shows in IR peak at 966 cm^{-1}[12].

Table 3 Chemical characteristics of edible fats and oils.

Analysis	JOCS Standard Methods	Method	Index
Acid value (AV)	2.3.1	Titration	Free fatty acid
Saponification value (SV)	2.3.2	Titration	Average molecular weight
Iodine Value (IV)	2.3.4	Titration	Unsaturated fatty acid
Fatty acid composition	2.4.2	GLC	Fatty acid
Trans isomers	2.4.4	GLC	Trans fatty acid
Triacylglycerol composition	2.4.6	HPLC	Triacylglycerol
Unsaponifiable matter	2.4.8	Gravimetric	Unsaponifiables (sterol, tocopherol)
Sterols	2.4.9	GLC	Sterol
Tocopherols	2.4.10	HPLC	Tocopherol
Phospholipids	2.4.11	Colorimetric	Phosphorus
Chlorophyll pigments	2.4.12	HPLC	Pheophytin, pyropheophytin
Glycidyl fatty acid esters	2.4.13	LC–MS	Glycidyl fatty acid ester

The triacylglycerol composition may affect the physical properties such as melting and freezing properties and the crystalline structure of edible fats and oils. Triacylglycerol moieties are determined by high-performance liquid chromatography (HPLC). They are separated using the C18 (ODS), C22 or C30 reversed phase column and detected with a refractive index detector (Fig. 1)[13].

Most edible fats and oils contain minor components, especially unsaponifiable matters containing sterols and tocopherols[14], along with triacylglycerols Sterols are quantified by GLC with FID after saponification of edible fats and oils[15]. The major sterol in vegetable oils is β-sitosterol, whereas that in animal fats such as lard and beef tallow is cholesterol. Tocopherols are determined by HPLC with a fluorescence detector[16]. Tocopherols in vegetable oils include α-, β-, γ- and δ-isomers. The tocopherol composition depends on the types of vegetable oils. Palm oil and rice bran oil have tocotrienols in addition to tocopherols.

Crude oils sometimes contain phospholipids. The phospholipid values are reported as phosphorus contents, which are estimated colorimetrically by the reaction between phosphorus and ammonium molybdate[17].

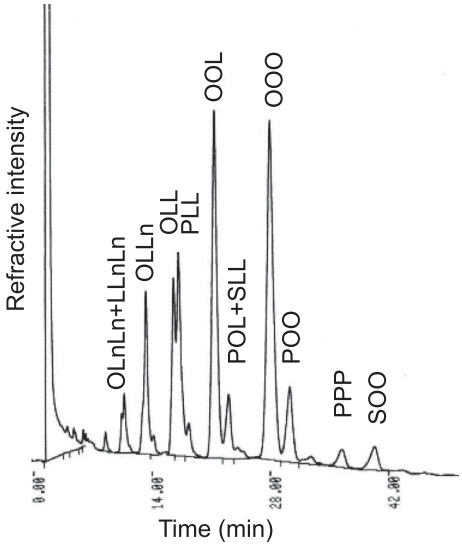

Fig. 1 Triacylglycerol composition of rapeseed oil. P, 16:0; S. 18:0; O, 18:1; L, 18:2; Ln, 18:3.

Some of the vegetable oils are rich in chlorophyll pigments, mainly pheophytins a and b and pyropheophytins a and b. Olive oil and rapeseed oils often contain considerable amounts of chlorophyll pigments that may induce photosensitized oxidation of unsaturated fatty acids. Chlorophyll pigments are measured by HPLC with a UV or fluorescence detector[18].

Recently, glycidyl fatty acid esters have been found as undesirable minor components in palm oil and some processed oils rich in di- and mono-acylglycerols. Glycidol may be carcinogenic to humans[19], although there is no conclusive evidence as yet. Glycidyl fatty acid esters may be the by-products of mono- and di-acylglycerols under high-temperature refining conditions, such as the deodorization process of edible fats and oil. These esters are quantified by direct and indirect methods. In the JOCS standard methods, glycidyl fatty acid methyl esters are determined by HPLC coupled with mass spectrometry (MS)[20].

Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) are sometime added as synthetic antioxidants to enhance the stability of edible fats and oils. Both BHA and BHT are measured by GLC after reflux extraction (2.6.1). Undesirable and toxic metals such as lead, cadmium, and arsenic are detected by atomic absorption spectrometry (2.6.3).

4 Methods to determine the extent of deterioration[21–23]

The most common methods used to determine the extent of oxidation and thermal deterioration of edible fats and oils are cited in the JOCS Standard Methods, as described in Table 4. The detailed procedure to analyze the oxidation products of fats and oils are also discussed in other books[21] and reviews[22, 23]. Methods to determine the oxidative stability of edible fats and oils include the active oxygen method (AOM; 2.5.1.1) and conductmetric determination method (CDM; 2.5.1.2). Fats and oils are exposed to accelerated oxidation in both stability tests. In the case of AOM[24], fats and oils are heated in a special glass test tube at 98.8 ± 0.2℃, and air is bubbled through the heated liquid at a rate of 2.3 mL/min. Samples are periodically collected,

Table 4 Methods to determine the extent of oxidation and thermal deterioration.

Analysis	JOCS Standard Methods	Method	Index
Fat stability (AOM)	2.5.1.1	Titration	Stability
Fat stability (CDM)	2.5.1.2	Conductivity	Stability
Peroxide value (PV)	2.5.2	Titration, Potentiometric	Hydroperoxide
p-Anisidine value (*p*-AnV)	2.5.3	Colorimetric	Carbonyls (aldehyde, ketone)
Carbonyl value (CV)	2.4.4	Colorimetric	Carbonyls (aldehyde, ketone)
Polar compounds	2.5.5	Column chromatography	Non-triacylglycerol
Polymerized triacylglycerols	2.5.7	HPLC	Polymer

and their peroxide value (PV) is measured. The induction period is described as the time required to attain 100 meq/kg of PV. The CDM[25] also uses the special apparatus. In this experiment, 3 g of the fats and oils sample is heated in a glass container at 120℃, and air is bubbled through the liquid at a rate of 20 L/h. This air eluate from the glass container is trapped in 50 mL deionized water and the conductivity is measured. The induction period in conductivity measurements is described as the time at which the inflection point occurs, as the conductivity is increased by the presence of volatile low-molecular weight compounds such as free fatty acids, alcohols and carbonyls.

The methods to determine the extent of oxidation and thermal deterioration of edible fats and oils include measurement of PV (2.5.2), *p*-anisidine value (2.5.3) and carbonyl value (2.5.4), as well as the amount of polar compounds (2.5.5) and polymerized triacylglycerols (2.5.7).

PV is the most popular index of the oxidation of oils. Ttitration[26] and potentiometric[27] methods are used to measure the PV. The principle underlying both methods is the oxidation-reduction reaction of hydroperoxides with potassium iodide. Accordingly, potassium iodide is added to the sample oils, and the liberated iodine is titrated with standard sodium thiosulfate. PV is useful in evaluating the initial step of oxidation of edible fats and oils. In Japan, the permissible limit for PV is 30 meq/kg for fats and oils in instant noodles and confectionary. However, the determination of PV is not applicable for heated oils used for deep- and pan-frying, because hydroperoxides are rapidly decomposed at temperature ≥ 100℃.

p-Anisidine value (*p*-AnV)[28] and carbonyl value (CV)[29] describes the total amount of carbonyl compounds, which are the secondary oxidation products of edible fats and oils. When carbonyl compounds such as aldehydes and ketones produced from hydroperoxides by the oxidation of fats and oils are reacted with *p*-anisidine in isooctane solution, colored compounds formed: these are measured spectrophotometrically at 350 nm. *p*-AnV is defined as the absorbance of the resultant solution when the reaction is complete, and is given by the following equation.

$$p\text{-}AnV = 25(A - B)/C$$

where A is the absorbance of the solution resulting after the reaction is complete, B is the absorbance of sample oil in isooctane solution, and Cis the weight of sample oil in 25 mL isooctane solution

However, *p*-AnV does not always show the accurate carbonyl compounds contents, because *p*-anisidine is sensitive only to alkenal and alkadienal compounds but not alkanal compounds in the aldehyde series.

In CV[29] studies, the total carbonyl compounds can be determined by the reaction with 2,4-dinitrophenylhydrazine, and the colored hydrazone derivatives are measured spectrophotometrically at 420 nm. CV is estimated as the corresponding amount of 2-decenal per gram of oil (μmol/g). Both AnV and CV are effective tools to evaluate the quality of frying oil. In Japan, the permissible limit is CV 50 by the benzene method (corresponding to CV 75 by the butanol method) for frying oils.

When edible fats and oils are heated for deep- and pan-frying, several kinds of decomposition compounds are produced. Free fatty acids and di- and mono-acylglycerols produced by the hydrolysis of triacylglycerols, and hydroxy- and oxo-fatty acids and polymerized compounds produced by the thermal oxidation are all polar compounds. Polar compounds are measured by column chromatography using silicic acid[30]. When sample oils are loaded on the silicic acid column and developed with a mixture of *n*-hexane and diethyl ether (87:13, v/v) as the mobile phase, only unoxidized triacylglycerols are eluted and then weighed. The polar compounds content is defined as follows.

$$Polar\ compounds\,(\%) = 100 \times (A - B)/A$$

where A is the weight of loaded sample oil (g) and B is the weight of unoxidized triacylglycerols (g).

The permissible limit of polar compounds is 24-27% for frying oil in Europe. Thin layer chromatography with FID is useful to quantify polar compounds in oils[31]. This method also uses a mixture of *n*-hexane and diethyl ether (87:13, v/v) as the mobile phase. It allows for the direct determination of polar compounds, because these compounds are observed at positions below triacylglycerol on the chromatogram. Recently, a portable digital edible oil-tester to estimate polar compounds by measuring the dielectric constant has been used for frying oil.

Polymerized triacylglycerols are often produced during deep frying with edible fats and oils. These triacylglycerols are measured by the gel permeation chromatography[32]. Sample oils are injected into gel permeation column, and then developed with tetrahydrofuran. Polymerized and unoxidized triacylglycerols are monitored with a refractive index detector. Polymerized triacylglycerols are eluted prior to unoxidized triacylglycerols. Polymerized triacylglycerols in oils are defined as follows.

$$Polymerized\ triacylglycerols\,(\%) = 100 \times C/\Sigma B$$

where ΣB is the total areas on the chromatogram and Cis the area of polymerized triacylglycerols on the chromatogram.

The permissible limit of polymerized triacylglycerols in frying oils is 10-16% in Europe.

5 Sensory characteristics

Sensory evaluation is often conducted to evaluate the quality of foods containing edible fats and oils. Humans are

very sensitive to taste and smell, and the sensory attributes not only depend on the panel reports but are also influenced by external factors, such as the room temperature, lightning in the room, and number of samples. In addition to the results from experienced panel members, standardization of score and expression are required to obtain accurate results. Hence, the instrumental analysis has been used instead of sensory evaluation.

GLC is often used to evaluate the sensory characteristics and extent of oxidation in edible fats and oils. GLC is capable of determining volatile compounds, which are responsible for imparting flavor in fats and oils. GLC methods for volatile compounds include the statistic headspace method[33], dynamic headspace method[34] and direct injection method[35]. The statistic method consists of 4 steps: 1) measuring and sealing a sample into a suitable container or vial, 2) heating to vaporize the components at a given temperature, 3) injecting an aliquot of the headspace gas directly into the gas chromatographic column, and 4) separating the volatile compounds on capillary column by temperature programming and FID or MS detection. This is such simple and rapid technique that it is suitable for routine analyses in succession, even though its sensitivity is low. Figure 2 shows the gas chromatogram of volatile compounds from oxidized and unoxidized rice bran oils[36]. Recently, the solid phase microextraction (SPME) method[37] using dimethylpolysiloxane as the solid phase is popular because of its high sensitivity.

Dynamic headspace method[34] is also called "purge-and-trap" method, and it is more elaborate than the static headspace method. Volatile compounds are trapped in a short column containing porous polymer (Tenax or Porapaq) or charcoal and purged with nitrogen or helium gas and then desorbed from the trap at elevated temperature into the capillary inlet of the gas chromatograph. However, the types and quantities of volatile compounds from sample oils depend on the trap variety.

Another method is the direct injection method where the sample oil is directly transferred into the gas chromatograph apparatus[35].

Recently, "electronic noses" using sensor arrays and pattern recognition systems that can detect and recognize odors and flavors have been developed, and used to classify different types of edible oils and evaluate the extent of deterioration of oils and oil foods[38, 39].

6 Non-destructive analytical methods

Spectrophotometric methods such as IR, near-infrared (NIR), and terahertz (THz) spectrophotometry as well as NMR are often used as non-destructive methods.

The titration method is generally used to determine the SV and IV of edible fats and oils; however, it is difficult to obtain reliable results, because skilled analysts are required and it takes more than 1 h to complete a sample evaluation. The SV and IV of vegetable oils can be calculated by the fatty acid composition estimated by GLC. However, the GLC method is time consuming and involves methylation pretreatment. Moreover, the GLC method can not be used for fish oils because their fatty acid composition is highly complex.

NIR spectroscopy can scan the absorbance or reflectance of molecules at the region between 800 and 2500 nm. This has become a well-accepted method for evaluating the quality of food-related bio-organic materials because it does not require toxic organic solvent and involves rapid measurement. Some researchers have applied the NIR spectroscopy for the differentiation and determination of edible fats and oils[40, 41]. This technique is also useful to de-

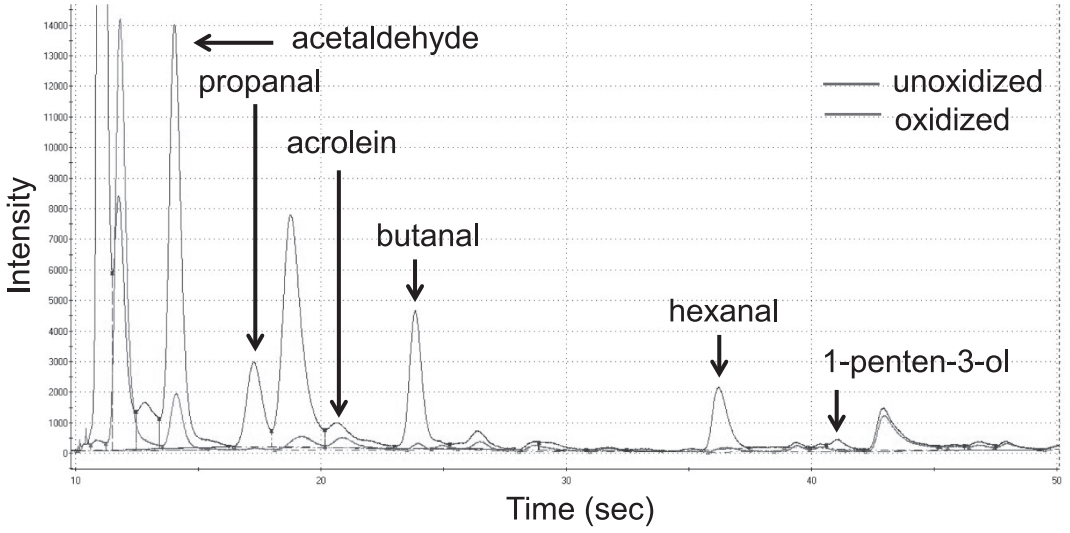

Fig.2 Gas chromatogram of volatile compounds in unoxidized and oxidized rice bran oil.

termine the IV and SV of vegetable[42] and fish[43] oils (Figs. 3 and 4). NIR spectra of edible fats and oils are generally measured using a glass vial at a constant temperature (usually 40℃). SV and IV are calibrated using the spectral data over the region of 7560-9100 cm^{-1} and statistical method of partial least squares regression. NIR spectroscopy is also capable of determining free fatty acids, trans fatty acids and oxidation products such as hydroperoxides, carbonyl compounds and polar compounds in edible fats and oils, although their sensitivity is low. Free fatty acids[44, 45] are determined at 1882, 2010 and 2040 nm based on the C=O overtone, while hydroperoxides (PV)[46] are determined at 1460-1480 nm and 2080 nm. Recently, the THz spectrometry that can scan the region between 10 and 400 cm^{-1} has been developed and applied to food components such as sugars[47], amino acids[48], and drugs[49]. Our group[50] applied THz spectroscopy to evaluate the quality of edible fats and oils. Therefore, THz spectroscopy is capable of determining SV and polymerized compounds of vegetable and fish oils at 77 and 328 cm^{-1} (Figs. 5-8)

^{1}H and ^{13}C NMR spectroscopy are also non-destructive quantitative methods useful to monitor the oxidation and thermal degradation of vegetable oils and to distinguish between different types of vegetable oils[51, 52]. High resolution ^{1}H NMR is capable of providing information on the unsaturation of fatty acids located at glycerol and phytosterols[53]. ^{1}H NMR spectra of fats and oils are scanned in the range of -4 ppm and 8 ppm in a deuterated chloroform solution. It takes usually a few minutes to obtain an NMR spectrum. Thus, ^{1}H NMR spectroscopy is a rapid and convenient method to distinguish between the various types of edible fats and oils. ^{13}C NMR spectroscopy can also determine 2-acyl positional fatty acid distribution in vegetable oil[54], whereas ^{1}H NMR spectroscopy can determine n-3 polyunsaturated fatty acids such as DHA in fish oils[55]. Moreover, ^{1}H NMR can detect oxidation products such as hydroperoxides and aldehydes (alkanal, alkenal, alkadei-

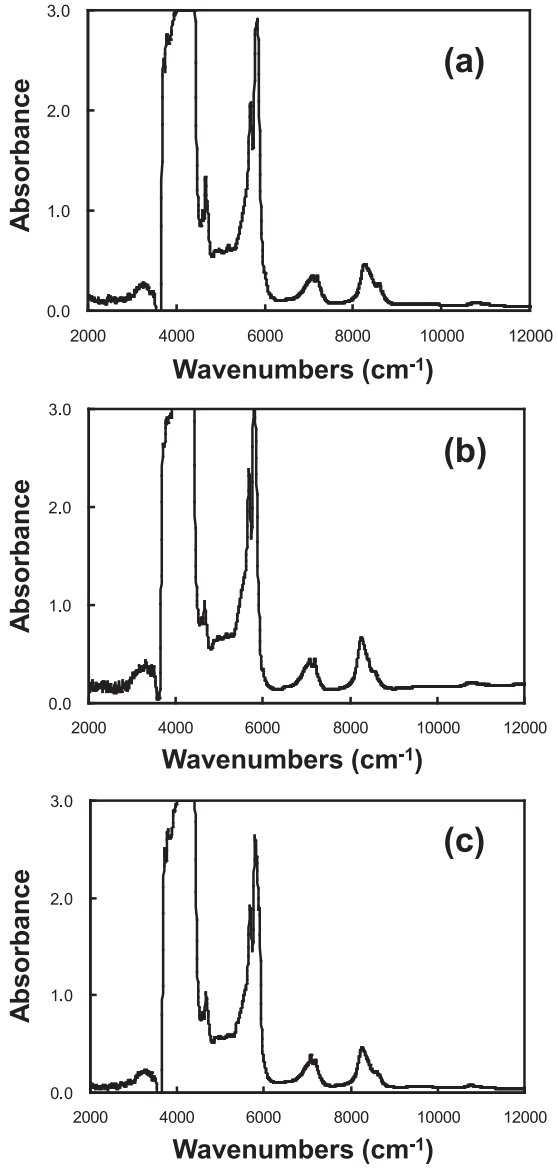

Fig. 3 Near-infrared (NIR) spectra of sardine (a), orange roughy (b) and stromateidei (c) oils.

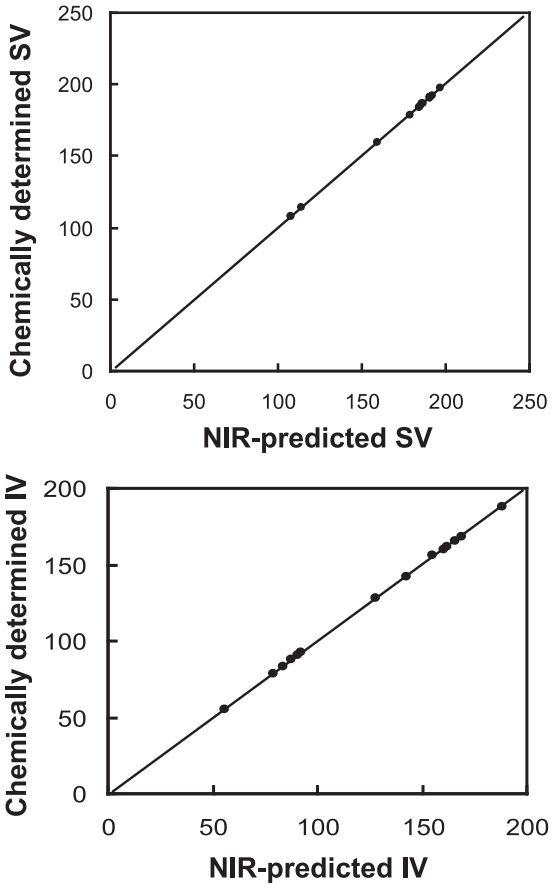

Fig.4 NIR-predicted SV and IV plotted against chemically determined SV and IV of fish oils.

enal)[56, 57]. ^{1}H NMR is also effective in investigating the oxidation mechanism of edible fats and oils during storage, although the quantification of oxidation products is difficult.

7 Conclusion

This review describes the analytical methods to evaluate the quality of edible fats and oils, especially the Standard Methods for Analysis of Fats, Oils and Related Materials edited by Japan Oil Chemists' Society (the JOCS standard methods) and other advanced methods. Many physical and chemical characteristics are used to evaluate the quality of edible fats and oils. Although different types and quantities of solvents are used in the JOCS standard methods, non-destructive methods using no solvents and harmful chemicals such as NIR and THz spectroscopy and other portable sensors are expected to become more popular.

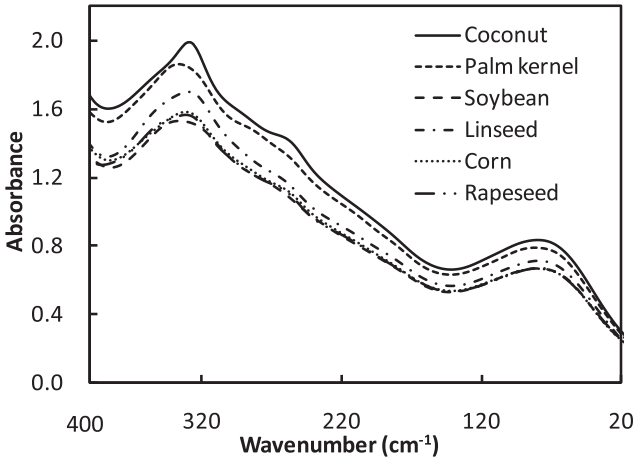

Fig. 5 Terahertz absorption spectra of vegetable oils.

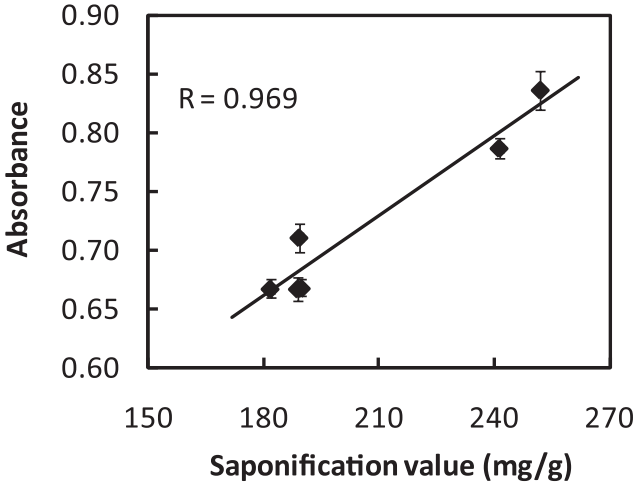

Fig. 6 Correlation curve between terahertz absorbance and saponification value of vegetable oils.

Acknowledgment

Most of studies were carried out in Tohoku University and Tokyo University of Technology. The author thanks Prof. Kaneda, Prof. Fujimoto, Prof. Miyazawa, Prof. Ikeda, and many research colleagues besides the committee of the JOCS standard methods for their valuable discussion and support.

References

1) The American Oil Chemists' Society. *Official Methods and Recommended Practices of the AOCS*. 7th ed.
2) International Union for Pure and Applied Chemistry, Applied Chemistry Division, Commission on Oils, Fats and Derivatives. *The Standard Methods for the Anal-*

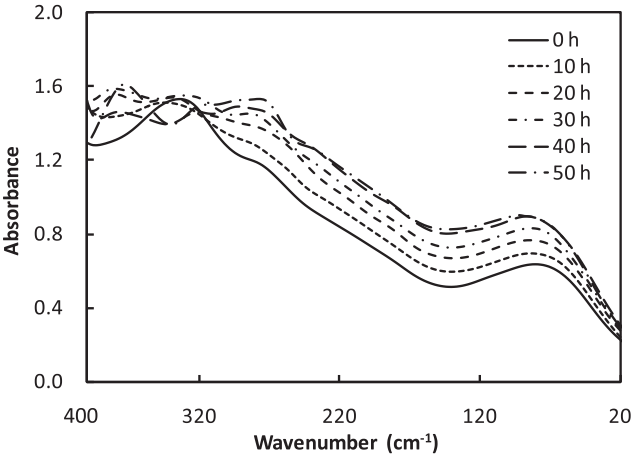

Fig. 7 Terahertz absorption spectra of heated high-oleic safflower oils.

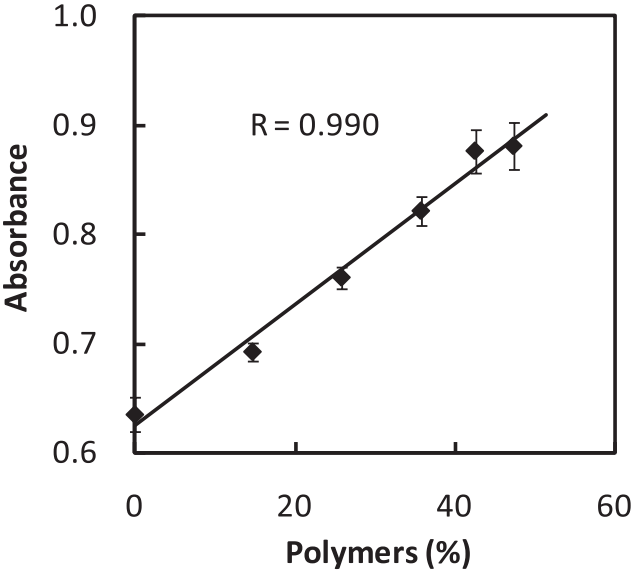

Fig. 8 Correlation curve between terahertz absorbance and polymers in heated high-oleic safflower oils.

ysis of Oils, Fats, and Derivatives, Section 2: Oils and Fats. 7th ed.
3) The Japan Oil Chemists' Society. *Standard Methods for the Analysis of Fats, Oils, and Related Materials (2013)*.
4) Totani, Y. *Properties and Utilization of Oils and Fats*. Saiwaishobo, Tokyo (2012).
5) Totani, Y.; Hara, S. *Science of Fats and Oils*. Asakurashoten, Tokyo (2015).
6) The Japan Oil Chemists' Society. *Oleochemistry Data Book*. Maruzen, Tokyo (2012).
7) Kawada, T.; Kato, C.; Suzuki, K.; Kanematsu, H.; Abeshima, T.; Tatsuo Shikama, T.; Kako, M.; Hirata, Y.; Mori, H.; Sakata, M. Determination of solid fat content by NMR. *J. Jpn. Oil Chem. Soc.* **33**, 162-165 (1984).
8) Totani, Y. Analytical methods of fats and oils. *Oleoscience* **1**, 657-665 (2001).
9) AOCS Official Method Cd 3a-94: Saponification Value, Calculated (oils and fats).
10) AOCS Official Method Cd1c-85: Iodine Value (calculated from GLC).
11) Shiramasa,, S.; Shiota, M.; Arakawa, H.; Shigematsu, Y.; Yokomizo, K.; Shioya, N.; Okamato, T.; Miyazaki, Y.; Takahashi, S.; Himata, K. Quantitative determination of trans-fatty acids in oils and fats by capillary gas chromatography: Results of a JOCS collaborative study. *J. Oleo Sci.* **56**, 405-415 (2007).
12) AOCS official Method Cd14d-99: *Trans* isomers in triglycerides by ATR/FTIR.
13) Endo, Y.; Ohta, A.; Kido, H.; Kuriyama, M.; Sakaguchi, Y.; Takebayashi, S.; Hirai, H.; Murakami, C.; Wada, S. Determination of triacylglycerol composition in vegetable oils using high-performance liquid chromatography: A collaborative study. *J. Oleo Sci.* **60**, 451-456 (2011).
14) Yoneyama, S.; Yamakawa, Y.; Oohashi, H.; Okamoto, T.; Ogata, Y.; Kawamato, T.; Yokochi, T. Collaborative studies on the determination of unsaponifiable. *J. Jpn. Oil Chem. Soc.* **42**, 523-528 (1993).
15) Tamura, T.; Maruyama, T.; Isoda, Y.; Sato, S.; Suzuki, K.; Murui, T.; Yoneyama, S.; Watanabe, M. Determination of sterols in fats and oils. *J. Jpn. Oil Chem. Soc.* **25**, 853-859 (1976).
16) Nakasato, S.; Hoshida, H.; Maruyama, T.; Ujiie, T.; Ohta, Y.; Kawaguchi, Y.; Shibo, K.; Watanabe, S.; Wada, S.; Hirayama, H.; Sawada, M. High-performance liquid chromatographic determination of tocopherols in vegetable oils and fats. *J. Jpn. Oil Chem. Soc.* **36**, 506-514 (1987).
17) AOCS Official Method Ca 12-55: Phosphorus (colorimetric).
18) Endo, Y.; Kouzui, H.; Shibuya, N.; Suzuki, K.; Takahashi, S.; Tsuchida, S.; Nakamura, K. High-performance liquid chromatographic determination of chlorophyll pigments in vegetable oils and fats : Collaborative study. *J. Jpn. Oil Chem. Soc.* **47**, 1225-1232 (1998).
19) IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. *Glycidol*. World Health Organization Press, Lyon, pp. 469-485 (2000).
20) Masukawa Y.; Shiro, H.; Nakamura, S.; Kondo, N.; Jin, N.; Suzuki, N.; Ooi, N.;and Kudo N. A new analytical method for the quantification of glycidol fatty acid esters in edible oils. *J. Oleo Sci.* **59**, 81-88 (2010).
21) Frankel, E.N. *Lipid Oxidation*. The Oily Press Ltd, Scotland (1998).
22) Dobarganes, M.C.; Velasco, J. Analysis of lipid hydroperoxides. *Eur. J. Lipid Sci. Technol.* **104**, 420-428 (2002).
23) Endo, Y. Analytical methods for deteriorated oils and oil foods. *New Food Industry* **58**, 41-47 (2016).
24) Kajimoto, G.; Horikawa, K.; Ota, M.; Nakayama, T.; Yoneyama, S.; Hirano, J.; Yuki, E.; Fujiwara, M.; Thiba, S.; Masuyama, S. Studies on a standardization of fat stability tests on autoxidation. I. II. *J. Jpn. Oil Chem. Soc.* **25**, 525-533 (1976); 27, 38-43 (1978).
25) Kato, C.; Makabe, K.; Katayama, H.; Kumita, S.; Takizawa, Y.; Hara, M.; Tanaka, S.; Wanaka, K.; Watanabe, K.; Ohishi, A.; Kojima, K.; Toukairin, S. Fat stability test on autoxidation by conductmetric determination method. *J. Jpn. Oil Chem. Soc.* **42**, 55-62 (1986).
26) Takeshita, Y.; Yoneyama, S.; Tanabe, S.; Miki, S.; Arakawa, A.; Iimura, K.; Shikama, T.; Shimizu, Y.; Suzuki, O.; Tanaka, A.; Hara, S. Determination of peroxide value by acetic acid-isooctane method. *J. Jpn. Oil Chem. Soc.* **43**, 586-593 (1994).
27) Hara, S.; Kohno, Y.; Aoyama, M.; Abe, S.; Isobe, T.; Kakuta, M.; Kuriyama, K.; Nakamura, K.; Hirata, Y.; Miyake, Y.; Watanabe, Y. Determination of peroxide value by potentiometry. *J. Jpn. Oil Chem. Soc.* **46**, 671-682 (1994).
28) IUPAC Standard Method 2.504.
29) Endo, Y.; Tominaga, M.; Tagiri-Endo, M.; Kumozaki, K.; Kouzui, H.; Shiramasa, H.; Miyakoshi, K. A modified method to estimate total carbonyl compounds in frying oils using 1-butanol as a solvent. *J. Oleo Sci.* **52**, 353-358 (2003).
30) Yoneyama, S.; Suzuki, O.; Iimura, K.; Kumozaki, K.; Takeshita, H.; Tanaka, A.; Tanabe, S.; Tanno, H.; Yamazaki, M.; Wanaka, Y. Determination of polar compounds in frying fats and oils. *J. Jpn. Oil Chem. Soc.* **40**, 159-163 (1991).
31) Hara, K.; Hasegawa, K.; Endo, Y.; Fujimoto, K. Polymer and polar material content determination as basis for assessing thermally oxidative deterioration of soybean oil for potato heat cooking. *J. Jpn. Oil Chem. Soc.* **43**, 57-60 (1994).
32) Komoda, M.; Ishikawa, O.; Inoue, M.; Hatanaka, H.;

Hattori, T.; Satoh, C.; Murakami, C.; Yamada, K.; Tsutsumi, T. Quantitative determination of polymerized triacylglycerols in frying oils and fats by size exclusion chromatography: A collaborative study. *J. Oleo Sci.* **54**, 529-536(2005).

33) Snyder, J.M.; Frankel, E.N.; Selke, E. Capillary gas chromatographic analyses of headspace volatiles from vegetable oils. *J. Am. Oil Chem. Soc.* **62**, 1675-1679 (1985).

34) Lee, I.; Fatemi, S.H.; Hammond, E.G.; White, P.J. Quantitation of flavor volatiles in oxidized soybean oil by dynamic head space analysis. *J. Am. Oil Chem. Soc.* **72**, 539-546(1995).

35) Dupuy, H.P.; Flick, G.J.; Bailey, M.E.; Angelo, A.J.S.; Legendre, M.E.; Sumrell, G. Direct sampling capillary gas chromatography of volatiles in vegetable oils. *J Am. Oil Chem. Soc.* **62**, 1690-1693(1985).

36) Endo, Y.; Hayashi, C.; Yamanaka, T.; Takayose, K.; Yamaoka, M.; Tsuno, T.; Nakajima, S. Linolenic acid as the main source of acrolein formed during heating of vegetable oils. *J. Am. Oil Chem. Soc.* **90**, 959-964 (2013).

37) Steenson, D.F.; Lee, J.H.; Min, D.B. Solid phase microextraction of volatile soybean oil and corn oil compounds. *J. Food Sci.* **67**, 71-76(2002).

38) Oliveros, M.C.C.; Pavon, J.L.P.; Pinto, C.G.; Laespada, M.E.F.; Cordero, B.M.; Forina, M. Electronic nose based on metal oxide semiconductor sensors as a fast alternative for the detection of adulteration of virgin olive oils. *Anal. Chim. Acta* **45**, 219-228(2002).

39) Dymerski, T.M.; Chmiel, T.M.; Wardecki, W. Invited Review Article: An odor-sensing system-powerful technique for foodstuff studies. *Rev. Sci. Instrum.* **82**, 1-32(2011).

40) Bewig, K.M.; Clarke, A.D.; Roberts, C.; Unklesbay, N. Discriminant analysis of vegetable oils by near-infrared reflectance spectroscopy. *J. Am. Oil Chem. Soc.* **71**, 195-200(1994).

41) Sato, T. Application of principal-component analysis on near-infrared spectroscopic data of vegetable oil for their classification. *J. Am. Oil Chem. Soc.* **71**, 293-298 (1994).

42) Li, H.; van de Voort, F.R.; Sedman, J.; Ismail, A.A. Rapid determination of cis and trans content, iodine value, and saponification number of edible oils by Fourier transform near-infrared spectroscopy. *J. Am. Oil Chem. Soc.* **76**, 491-497(1999).

43) Endo, Y.; Tagiri-Endo, M.; Kimura, K. Rapid determination of iodine value and saponification value of fish oils by near-infrared spectroscopy. *J. Food Sci.* **70**, 127-131(2005).

44) Ismail, A.A.; van de Voort, F.R.; Emo, G.; Sedman, J. Rapid quantitative determination of free fatty acids in fats and oil by Fourier transform infrared spectroscopy. *J. Am. Oil Chem. Soc.* **70**, 335-341(1993).

45) Man, Y.B.C.; Moh, M.H. Determination of free fatty acids in palm oil by near-infrared reflectance spectroscopy. *J. Am. Oil Chem. Soc.* **75**, 557-562(1998).

46) Hong, J.; Yamaoka-Koseki, S.; Yasumoto, K.; Yasumoto, K. Analysis of peroxide values in edible oil by near-infrared spectroscopy. *Nippon Shokuhin Kogyo Gakkaishi* **41**, 277-280(1994).

47) Upadhya, P.C.; Shen, Y.C.; Davies, A.G.; Linfield, E.H. Terahertz time-domain spectroscopy of glucose and uric acid. *J. Biol. Phys.* **29**, 117-121(2003).

48) Yamamoto, K.; Tominaga, K.; Sasakawa, H.; Tamura, A.; Murakami, H.; Ohtake, H.; Sarukura, N. Terahertz time-domain spectroscopy of amino acids and polypeptides. *Biophys. J.* **89**, L22-L26(2005).

49) Kawase, K.; Watanabe, Y.; Ogawa, Y.; Ito, H. Component spatial pattern analysis of chemicals using terahertz spectroscopic imaging. *IEEJ Trans. EIS* **124**, 1339-1344(2004).

50) Jiang, F.L.; Ikeda, I.; Ogawa, Y.; Endo, Y. Rapid determination of saponification value and polymer content of vegetable and fish oils by terahertz spectroscopy. *J. Oleo Sci.* **61**, 531-535(2012).

51) Guillen, M.D.; Ruiz, A. High resolution ^{1}H nuclear magnetic resonance in the study of edible oils and fats. *Trends Food Sci. Technol.* **12**, 328-338(2001).

52) Hidalago, F.J.; Zamora, R. Edible oil analysis by high-resolution nuclear magnetic resonance spectroscopy: recent advances and future perspectives. *Trends Food Sci. Technol.* **14**, 499-506(2003).

53) Kurata, S.; Yamaguchi, K.; Ohtsuka, S.; Nagai, M. Rapid and convenient discrimination of various types of fats and oils by proton nuclear magnetic resonance spectroscopy. *BUNSEKI KAGAKU* **54**, 1083-1090(2005).

54) Miyake, Y.; Yokomizo, K. Determination of 2-acyl positional fatty acid distribution in vegetable oils by high resolution 13C nuclear magnetic resonance spectroscopy. *J. Jpn. Oil Chem. Soc.* **47**, 179-185(1998).

55) Igarashi, T.; Aursand, M.; Hirata, Y.; Gribbestad, I.S.; Wada, S.; Nonaka, M. Nondestructive quantitative determination of docosahexaenoic acid and n-3 fatty acids in fish oils by high-resolution 1H nuclear magnetic resonance spectroscopy. *J. Am. Oil Chem. Soc.* **77**, 737-748(2000).

56) Guillen, M.D.; Ruiz, A. Formation of hydroperoxy- and hydroxyalkenals during thermal oxidative degradation of sesame oil monitored by proton NMR. *Eur. J. Lipid Sci. Technol.* **106**, 680-687(2004).

57) Guillen, M.D.; Ruiz, A. Monitoring the oxidation of unsaturated oils and formation of oxygenated aldehydes by proton NMR. *Eur. J. Lipid Sci. Technol.* **107**, 36-47(2005).