Vegetable oils

Ramón Aparicio, Diego Luis García González, Ramón Aparicio-Ruiz*
Instituto de la Grasa, Consejo Superior de Investigaciones Científicas (CSIC), Sevilla, Spain
**E-mail corresponding author: aparicioruiz@cica.es*

General overview of the products

Oilseeds are among the most important agricultural commodities worldwide. Edible oils are obtained from the crushing of oilseeds from species that belong to various botanical groups, some of which are perennials (e.g. argan, avocado, olive) with a majority being herbaceous plants (e.g. maize, sunflower, soya). Although these species have been traditionally cultivated for centuries, some of them have been recently modified by conventional breeding programs or by genetic modification. The development of a worldwide market has led to the fact that 80 % of oilseed traded has been soya in the past years (Table 1), whereas it was mainly used in East Asia (China) only two centuries ago. Today the United States is the largest producer of soybean (together with Brazil), peanut and maize. The Russian Federation and Ukraine are major producers of sunflower while India, China and Canada are the largest producers of rapeseed. However, new species have been modified to adapt to diverse environmental conditions and they are progressively colonising geographical areas that were unthinkable only a few decades ago; i.e. olive trees planted in Australia or Argentina. One exception is the argan tree, which is well adapted to the extremely dry climate of Southwestern Morocco.

Agricultural practices have revolutionized vegetable oil production by increasing yields per hectare to incredible figures and molecular biology has been able to modify chemical composition up to a point that many of the major oilseeds have varieties with a profile of fatty acids (e.g., high oleic acid) in line with the consumers' appeal for healthier foods. The increase in oilseed world production has also contributed to a diversification of their use beyond the manufacture of oils; well thought-out, the oil is not the only by-product of oilseeds. Thus, olive products include table olives, skin care products and olive oil soap among others. Varnish, leather and furniture polish, paint, insecticides and lubricating oil are among the uses of peanut oil while rapeseed oil is used in the manufacture of biodiesel for powering motor vehicles and just as many other vegetable oils are used in bio-gas production. The use of soya has become a primary ingredient in dairy products. In fact, infant formulas based on soya are used for lactose-intolerant babies and for babies that are allergic to cow milk proteins. The corn flour is among the most preferred for human nutrition and for feeding farm animals (i.e. chicken and pigs). Likewise, sunflower plants have been used in phytoremediation to remove chemical pollutant is soils such as lead, arsenic and uranium [1].

The production of oilseeds is strongly linked to geographical areas where the farms are evolving towards monoculture cropping. There is not only the well-known link between olive and the Mediterranean basin, or peanut and Georgia (US) or argan and Morocco but also the great productions of oilseeds like soybean and the Central States of the USA and Amazonia (Brazil) or

https://doi.org/10.32741/fihb.19.vegetableoil

sunflower and the Ukrainian steppes [2]. Geographical provenance and the characterization of oils produced in particular geographical areas are not aspects of minor importance as this information can help in health warnings (e.g. Ukrainian sunflower oil contamination).

This chapter does not deal with all the vegetable oils but a set of them: arachis, cottonseed, evening primrose, maize, palm, palm kernel, rapeseed, safflower, soya, sunflower and argan; olive oil is studied in an independent chapter.

Table 1: World production of selected edible oils (harvest 2016/17) in 1 000 mT

Oilseed	Production	1st producer	2nd producer
Arachis[1]	5.910	China (2.896)	India (1.238)
Argan	0.005	Morocco (0.005)	-
Cottonseed[1]	4.419	India (1.160)	China (1.115)
Maize	3.189	USA (1.818)	China (0.267)
Palm[1]	65.068	Indonesia (36.000)	Malaysia (18.858)
Palm kernel[1]	7.596	Indonesia (4.400)	Malaysia (2.300)
Rapeseed[1]	28.841	EU (10.119)	China (7.059)
Safflower	0.674	Kazakhstan (0.175)	India (0.109)
Soya bean[1]	53.861	China (15.770)	United States (10.035)
Sunflower[1]	18.220	Ukraine (5.590)	Russia (4.089)

Note: [1] figures from USA Oilseeds: World Markets and Trade, April 2018 (www.fas.usda.gov). In the case of evening primrose, China accounts for approximately 90 % of world production.

Sources: USDA Foreign Vegetable Oils (www.fas.usda.gov), indexmundi (www.indexmundi.com) and world atlas (www.worldatlas.com).

1. Product Identity

1.1. Definition of the product and manufacturing process

Codex Alimentarius (henceforth, Codex) defines edible vegetable oils as foodstuffs which are composed primarily of glycerides of fatty acids being obtained only from vegetable sources. They may contain small amounts of other lipids, such as phosphatides, of unsaponifiable constituents and of free fatty acids naturally present in the fat or oil. These kinds of oils are labelled as virgin oils, cold pressed oils or refined oils according to their manufacturing process. Codex also defines these designations. Thus, virgin oils are obtained, without altering the nature of the oil, by mechanical procedures (e.g. expelling or pressing) and the application of heat only; they may have been purified by washing with water, settling, filtering and centrifuging only. Cold pressed oils, according to Codex, are obtained, without altering the oil, by mechanical procedures only (e.g. expelling or pressing) without the application of heat; they may have been purified by washing with water, settling, filtering and centrifuging only. Refined edible vegetable oils result from oilseeds or solvent-extracted oils which have undergone a comprehensive processing to be deacified in one of the following ways: a) with alkali; b) by physical refining or both; c) by miscella refining using a permitted food grade solvent, followed by bleaching with absorbent earth and/or

activated carbon or both of them and deodorised with steam without using any other chemical agent; and d) also including the process of degumming using phosphoric/citric acid. Applying appropriate quality management systems, the refining process produces oils with consistent quality.

Oilseeds for producing edible vegetable oils selected for this chapter can have different synonyms for the same name or various species can be associated to the same name. Following definitions of oilseeds help to oil identity (Codex):

Arachis oil (synonyms: peanut oil; groundnut oil) is derived from groundnuts (seeds of *Arachis hypogaea* L.). More than 70 % of this oil is produced in China (50.4 %) and India (20.3 %).

Cottonseed oil is derived from the seeds of various cultivated species of *Gossypium spp*. China (26.8 %) and India (25.2 %) produce more than 50 % of this oil.

Evening primrose oil is derived from the seeds of the evening primrose (*Oenothera biennis*) plant.

Maize oil (synonym: corn oil) is derived from maize germ (the embryos of *Zea mays* L.). It is produced all over the world but USA (55.2 %), China (8.2 %) and Turkey (5.9 %) are major producer countries.

Palm oil is derived from the fleshy mesocarp of the fruit of the oil palm (*Elaeis guineensis*). Note: Palm olein is the liquid fraction derived from the fractionation of palm oil while palm stearin is the high-melting fraction derived from the fractionation of palm oil. Two countries supply more than 80 % of palm oil: Indonesia (55.2 %) and Malaysia (29.4 %).

Palm kernel oil is derived from the kernel of the fruit of the oil palm (*Elaeis guineensis*). The production of this oil in Indonesia (54.2 %) and Malaysia (28.3 %) accounts for more than 80 % of world production.

Rapeseed oil - low erucic acid (synonyms: low erucic acid turnip rape oil; low erucic acid colza oil; canola oil) is produced from low erucic acid oil-bearing seeds of varieties derived from the *Brassica napus* L., *Brassica campestris* L. and *Brassica juncea* L. species. The European Union is the major producer of this oil (40.4 %) followed by China (26.4 %) and Canada (15.5 %).

Safflower seed oil (synonyms: safflower oil; carthamus oil; kurdee oil) is derived from safflower seeds (seeds of *Carthamus tinctorius* L.). Safflower seed oil - high oleic acid (synonyms: high oleic acid safflower oil; high oleic acid carthamus oil; high oleic acid kurdee oil) is produced from high oleic acid oil-bearing seeds of varieties derived from *Carthamus tinctorius*. The main producer of these oils is the USA followed by India and Mexico.

Soya bean oil (synonym: soybean oil) is derived from soya beans (seeds of *Glycine max* (L.) Merr.). USA has a dominant position in soybean (39 %) followed by Brazil (23.8 %) and Argentina (17.9 %).

Sunflower seed oil (synonym: sunflower oil) is derived from sunflower seeds (seeds of *Helianthus annuus* L.). Sunflower seed oil - high oleic acid (synonym: high oleic acid sunflower oil) is produced from high oleic acid oil-bearing seeds of varieties derived from sunflower seeds (seeds of *Helianthus annuus* L.). Russia is the largest producer of sunflower oil (17.8 %) followed by Ukraine (16.7 %) and Argentina (14.8 %).

Argan oil is derived from the kernel of the fruit of the spiny argan tree (*Argania spinosa*). Morocco is the exclusive producer country of argan oil.

Edible vegetable oils are mainly consumed after being submitted to a refining process although the market for crude oils - either virgin or cold pressed oils - has recently increased. Refining is a homogenous well-established process that has peculiarities for some of the selected oils. Thus, arachis oil cannot be winterised because of its high melting point – it solidifies at 3°C. Besides, peanut oil may contain aflatoxin B1 that can be removed in the refining process whether the standard alkali refining and the washing of the oil are used – detoxifying can then lower the aflatoxin content to 10-14 ppb – so that a subsequent bleaching operation is essential to reduce it to less than 1 ppb. The refining of safflower oil has the peculiarity of increasing the content of free sterols – due to the acid-catalysed hydrolysis of steryl esters in the degumming and bleaching processes – and a significant reduction of the content of total sterols during the bleaching process because of reduction of esterified sterol fraction. Crude maize oil has a high content of phosphorous and a wet degumming process at low temperature is recommended; degumming at 10-30 °C results in the removal of more phosphorous than at 70 °C.

The identity of edible vegetable oils usually requires its characterization with information of the most defining/characteristic physical-chemical parameters. As the refining process may modify the original chemical composition (e.g. tocopherols, sterols), the changes of which depend on the refining process used, the following tables show the values related to crude vegetable oils.

The distribution of fatty acid methyl esters (Table 2), which account for more than 95 % of edible oil chemical composition, is used most frequently to characterize oils and confirm their authenticity. The second source of information is the composition of sterols, which is the major series of the unsaponifiable matter of vegetable oils and as important as fatty acids in food authentication. In fact, some sterols may be unique to an oil (i.e. brassicasterol). Sterol composition as shown in Table 3 covers 4-desmethylsterols or also so-called phytosterols or simply sterols. Table 3 also displays the composition of methyl tocols (tocopherols and tocotrienols) not only because they are powerful lipid-soluble antioxidants and a major dietary component but also because their profiles can be used to distinguish vegetable oils; e.g., sunflower seed oil is a good source of α-tocopherol and palm oil of the tocotrienols. In addition to the detailed chemical composition specification, essential physical-chemical characteristics of selected crude vegetable oils (relative density, refractive index, saponification value, iodine value, unsaponifiable matter content) are given in Table 4, which may be also used as identity criteria. Finally, the stable carbon isotope ratio is also included but only for maize oil as it is believed that this measurement provides a better means of detecting foreign oils in this type of oil than other more traditional techniques.

1.2. Current standards of identity or related legislation

1.2.1. EU Legislation

Unlike olive oil, which is extensively covered in EU regulations, there is no specific EU legislation for other edible vegetable oils. The only vertical legislation relevant in this area, is Directive 76/621/EEC which limits the level of erucic acid permitted in oils and fats intended for human consumption, and Directive 80/891/EEC that describes the method for the analysis of erucic acid. National legislation, in particular in the producing countries, defines permitted processing conditions such as neutralization, bleaching, hydrogenation, deodorization, and so on. In fact, EU laws do not provide for a “generally acknowledged definition of food fraud” but there is an extensive EU legislative framework focused on food safety. Only a general guideline is found in EU regulations requiring that food labelling, advertising, presentation and packaging “shall not mislead consumers” [3].

1.2.2. Codex Alimentarius

A number of Codex standards for edible fats and oils was published individually as Recommended Standards until 1981 but unified since then as: Codex Alimentarius. Volume 8. Fats, oils and related products. Information here reported corresponds to: Standards for Named Vegetable Oils Codex Stan 210-1999. Adopted in 1999. Revision: 2001, 2003, 2009. Amendment: 2005, 2011, 2013 and 2015. Last modified: 2017.

This standard contains identity and quality characteristics together with provisions relating to food additives, contaminants, hygiene and labelling. Methods of analysis are also specified. The identity characteristics, which include fatty acid composition, iodine value and relative density etc., essentially define the product and can be used as the basis for determining purity. The standard contains only those provisions essential for public health and safety and consumer protection, as well as other elements needed to ensure fair trade and to prevent fraud.

Tables 2-4 include information of physical-characteristics of the selected crude vegetable oils; evening primrose and argan oils are not described by Codex Stan 210-1999 yet. Thus, those crude vegetable oils for which characteristics fall within the appropriate ranges of the Standard are in compliance with Stan 210-1999 [6]. However, Codex also includes particular values of some indicators, tests and chemical compounds that have to be fulfilled for some of the selected crude edible vegetable oils. Thus, (i) the ranges of the Reichert and Polenske values for palm kernel should lie between 4-7 and 8-12 respectively; (ii) the Halphen test for cottonseed oil should be positive; (iii) arachidic and higher fatty acid content of arachis oil should not exceed 48 g/kg; (iv) total carotenoids (as beta-carotene) for unbleached palm oil should be in the range 500-2000 mg/kg; (v) the Crismer value for low erucic acid rapeseed oil should be in the range 67-70; (vi) the concentration of brassicasterol in low erucic acid rapeseed oil should be greater than 5 % of total sterols; (vii) low-erucic acid rapeseed oil must not contain more than 2 % erucic acid (as % of total fatty acids); (viii) high oleic acid safflower oil must contain not less than 70 % oleic acid (as a % of total fatty acids); and (ix) high oleic acid sunflower oil must contain not less than 75 % oleic acid (as % of total fatty acids).

Codex, however, keeps the door open to consider supplementary criteria based on geographical provenance of crude edible vegetable oils because of climatic variations. Ranges of chemical compounds and physical-parameters vary according to the geographical provenance of crude vegetable oils as shown in the Annex Table of the Chapter of Fats and Oils of the first edition of this book [7]. Geographical traceability is still an important issue of the authenticity of crude vegetable oils.

2. Authenticity issues

2.1. Identification of current authenticity issues

2.1.1. Adulteration by addition of other products

While olive oil is one of the most expensive oils and therefore a prime target for adulteration or misrepresentation, other less expensive oils and fats are also at times fraudulently adulterated. This obviously involves adding a cheaper oil. There is not usually any problem of food safety but there is one of misrepresentation and false labelling if the resulting blend is offered or traded as a pure or genuine oil. An individual analysis of authenticity problems of these oils is analysed next

although the number of documented incidents may be a small fraction of the actual number since they usually do not result in a food safety risk and consumers often do not notice them.

Groundnut and sunflower seed oils.

The contamination or adulteration of groundnut and sunflower seed oils with cheaper soya bean oil has been identified for several years in traded oils containing low concentrations of linolenic acid whereas according to chemical information pure sunflower seed and groundnut oils should be free of this acid (≤0.3), unlike the high content of this fatty acid in soya bean oils (4.5-10 %). More recently (November 2015) the adulteration of groundnut oil was reported in India, the second major producer of this oil, because the demand for this oil had increased leading to an abrupt spike in its average price. The Consumer Association of India found that a majority of a large set of groundnut oil samples was adulterated with palmolein and cottonseed oils among other cheaper oils. Thus, 7 % of the samples contained less than 10 % of groundnut oil and 43 % contained less than 20 %. Furthermore, the Food and Drug Administration (FDA) of India reported that traders blended sunflower seed, groundnut and soybean oil with cheaper cottonseed oil. As regards groundnut, this is one of the major edible oils in China, besides soybean oil and rapeseed oil, but it is more expensive than the other two making it prone to adulteration. In January 2012 it was reported that unscrupulous dealers had mixed cottonseed oil and flavour-enhanced soybean oil and marked it as peanut oil. In addition, oils such as soybean oil, sunflower oil, canola oil, and palm oil are also blended into peanut oil in several proportions.

Safflower oil

Safflower oil is a high-priced oil, favoured as a result of its high content of linoleic (C18:2) acid and almost zero content of the easily oxidised linolenic (C18:3) acid. Sunflower seed oil is closely related to it, with a high content of linoleic acid but a very low content of linolenic acid. The similarity of the fatty acid composition and other properties of the two oils has meant that it is difficult to detect the adulteration of safflower seed oil with sunflower seed oil. The main producers of sunflower seed oil are adjacent to the main producer of safflower oils, which might not help end this fraudulent practice.

Other adulterations have been described using safflower oils as an adulterant of virgin olive oil in scientific papers. However, it is unlikely since safflower oil should be refined first, and then the determination of stigmastadienes would make that adulteration unprofitable.

Palm oil

A major problem in the early 1980s was the so-called Singapore Cocktail. This was a reconstituted palm oil made by blending unrelated palm stearin and olein fractions. The blend was much more severely oxidised than unprocessed whole palm oil. Unfortunately, as both the fractions had originated from Malaysian palm oil and were usually blended back in something approaching the right ratio, it was almost impossible to prove by conventional analytical methods that the manipulation had taken place. Another adulteration with a toxic effect is the addition of the artificial dye Sudan IV to some palm oil brands from Ghana; Sudan IV is known to cause cancer. The addition of artificial colouring to palm oil is so widely used that it can be rare to buy any palm oil that has not artificially coloured. In fact, Solvent red 24, which is used in colouring plastics, or Anatol dye are added to palm oil by the nefarious traders to improve its redness.

The Roundtable on Sustainable Palm Oil has reported that palm oil made with sustainable and ethical sourcing claims is at high risk of food fraud; it has been claimed that some manufactures of palm oil use child labour in harvesting or refining processes.

Recently, oleic-enhanced palm oil interesterified with high oleic acid components, followed by fractionation using a patented MPOB (Malaysian Palm Oil Board) process, has been product. However name of “high oleic acid palm oil” is still under consideration for Codex (Codex Alimentarius, REP17/FO-Rev, 3 March 2017) as are value ranges for its chemical compounds and physical-chemical parameters.

Palm kernel oil

Another concern is the co-mingling of lauric oils, usually palm kernel and coconut oils. These two oils have closely related chemical compositions (both contain about 47 % lauric acid) and low levels of unsaturation. Coconut oil usually trades at a higher price, however, so there is a temptation to adulterate it with small amounts of palm kernel oil. An equally worrying, if less prevalent, problem is associated with an oil called babassu. This oil is produced mainly in Brazil and has no international market. However, its chemical and physical properties are similar to those of palm kernel oil. There has therefore been a temptation to bring babassu oil into the edible oil trade by blending it with palm kernel oil.

Palm kernel oil can be fractionated into hard and soft fractions in much the same way as palm oil. In this case, however, it is the hard fraction that is valuable, as a confectionery butter or cocoa butter substitute. The by-product is palm kernel olein, which, as in the case of palm stearin, has only a limited number of outlets and it therefore trades at a lower price than whole unfractionated palm kernel oil. There is a temptation to dispose of the palm kernel olein by blending it into palm kernel oil. Levels of about 10 % are difficult to detect. If the palm kernel oil is then used for the production of hydrogenated palm kernel oil, another useful confectionery fat, the addition of up to 40 % prior to hydrogenation is difficult to detect.

Cottonseed oil

A related case of adulteration occurred in 1983, when cottonseed oil was diluted with palm olein [8]. The incident was widely publicised by the Malaysian Palm Oil Processing Industry at the time [8,9] since, although the Malaysians had supplied the palm olein, they had done so as part of an honest transaction and had not been part of the deception. Cotton is one of the top four GMO crops produced in the world (83 %) - along with soybean (89 %), canola (75 %), and corn (61 %) - and approx. 90 % of all US cotton is genetically engineered. GM products are not labelled in some countries since manufacturers are not required by National Safety Authorities to list the existence nor the quantity of GM food in a producer’s products (i.e. cottonseed oil) on their labels. Thus, it is a potential, if not actual, authenticity problem for consumers concerned about consuming GM foods.

Table 2: Composition of fatty acids of the selected crude edible vegetable oils from authentic samples. Sources: [4-6]

FAME	1	2	3	4	5	6	7a	7b	8	9a	9b	10	11
C6:0	nd	nd	nd	nd	≤0.8	nd	nd	nd	nd	nd	nd	nd	nd
C8:0	nd	nd	nd	nd	2.4-6.2	nd	nd	nd	nd	nd	nd	nd	nd
C10:0	nd	nd	nd	nd	2.6-5.0	nd	nd	nd	nd	nd	nd	nd	nd
C12:0	≤0.1	≤0.2	≤0.3	≤0.5	45.0-55.0	nd	nd	≤0.2	≤0.1	≤0.1	nd	nd	nd
C14:0	≤0.1	0.6-1.0	≤0.3	0.5-2.0	14.0-18.0	≤0.2	≤0.2	≤0.2	≤0.2	≤0.2	≤0.1	≤0.2	≤0.1
C16:0	8.0-14.0	21.4-26.4	8.6-16.5	39.3-47.5	6.5-10.0	2.5-7.0	5.3-8.0	3.6-6.0	8.0-13.5	5.0-7.6	2.6-5.0	11.5-15.0	6.0-10.2
C16:1	≤0.2	≤1.2	≤0.5	≤0.6	≤0.2	≤0.6	≤0.2	≤0.2	≤0.2	≤0.3	≤0.1	≤0.2	nd
C17:0	≤0.1	≤0.1	≤0.1	≤0.2	nd	≤0.3	≤0.1	≤0.1	≤0.1	≤0.2	≤0.1	≤0.1	nr
C17:1	≤0.1	≤0.1	≤0.1	nd	nd	≤0.3	≤0.1	≤0.1	≤0.1	≤0.1	≤0.1	nd	nr
C18:0	1.0-4.5	2.1-3.3	≤3.3	3.5-6.0	1.0-3.0	0.8-3.0	1.9-2.9	1.5-2.4	2.0-5.4	2.7-6.5	2.9-6.2	4.3-7.2	1.5-3.5
C18:1	35.0-69	14.7-21.7	20.0-42.2	36.0-44.0	12.0-19.0	51.0-70.0	8.4-21.3	70.0-83.7	17-30	14.0-39.4	75-90.7	43.0-50.1	5.0-12.1
C18:2	12.0-43.0	46.7-58.2	34.0-65.6	9.0-12.0	1.0-3.5	15.0-30.0	67.8-83.2	9.0-19.9	48.0-59.0	48.3-74.0	2.1-17	23.3-36.0	65.0-85.4
C18:3	≤0.3	≤0.4	≤2.0	≤0.5	≤0.2	5.0-14.0	≤0.1	≤1.2	4.5-11.0	≤0.3	≤0.3	≤0.3	8.0-14.1
C20:0	1.0-2.0	0.2-0.5	0.3-1.0	≤1.0	≤0.2	0.2-1.2	0.2-0.4	0.3-0.6	0.1-0.6	0.1-0.5	0.2-0.5	≤0.5	≤0.3
C20:1	0.7-1.7	≤0.1	0.2-0.6	≤0.4	≤0.2	0.1-4.3	0.1-0.3	0.1-0.5	≤0.5	≤0.3	0.1-0.5	≤0.6	nr
C20:2	nd	≤0.1	≤0.1	nd	nd	≤0.1	nd	nd	≤0.1	nd	nd	nd	nr
C22:0	1.5-4.5	≤0.6	≤0.5	≤0.2	≤0.2	≤0.6	≤1.0	≤0.4	≤0.7	0.3-1.5	0.5-1.6	≤0.2	nd
C22:1	≤0.3	≤0.3	≤0.3	nd	nd	≤2.0	≤1.8	≤0.3	≤0.3	≤0.3	≤0.3	nd	nd
C22:2	nd	≤0.1	nd	nd	nd	≤0.1	nd	nd	nd	≤0.3	nd	nd	nr
C24:0	0.5-2.5	≤0.1	≤0.5	nd	nd	≤0.3	≤0.2	≤0.3	≤0.5	≤0.5	≤0.5	nd	nd
C24:1	≤0.3	nd	nd	nd	nd	≤0.4	≤0.2	≤0.3	nd	nd	nd	nd	nr

Note: FAME, fatty acid methyl esters. 1, Arachis oil; 2, Cottonseed oil, 3, Maize oil; 4, Palm oil; 5, Palm kernel oil; 6, Rapeseed (Canola) oil; 7a, Safflower oil; 7b, Safflower high oleic oil; 8, Soya oil; 9a, Sunflower oil; 9b, Sunflower high oleic oil; 10, argan oil; 11, evening primrose oil; nd, non-detectable, defined as <0.05 %; nr, not reported.

Table 3: Levels of 4-desmethylsterols as a percentage of total sterols (in mg/kg), tocopherols and tocotrienols in mg/kg in the selected crude edible vegetable oils from authentic samples. Sources: [4-6]

	1	2	3	4	5	6	7a	7b	8	9a	9b	10	11
Cholesterol	≤3.8	0.7-2.3	0.2-0.6	2.6-6.7	0.6-3.7	≤1.3	≤0.7	≤0.5	0.2-1.4	≤0.7	≤0.5	nd	nd
Brassicasterol	≤0.2	0.1-0.3	≤0.2	nd	≤0.8	5.0-13.0	≤0.4	≤2.2	≤0.3	≤0.2	≤0.3	nd	nd
Campesterol	12.0-19.8	6.4-14.5	16.0-24.1	18.7-27.5	8.4-12.7	24.7-38.6	9.2-13.3	8.9-19.9	15.8-24.2	6.5-13.0	5.0-13.0	≤0.4	8-9
Stigmasterol	5.4-13.2	2.1-6.8	4.3-8.0	8.5-13.9	12.0-16.6	0.2-1.0	4.5-9.6	2.9-8.9	14.9-19.1	6.0-13.0	4.5-13.0	nd	nd
β-sitosterol	47.4-69.0	76.0-87.1	54.8-66.6	50.2-62.1	62.6-73.1	45.1-57.9	40.2-50.6	40.1-66.9	47.0-60	50-70	42.0-70	nd	87-90
Δ^5-avenasterol	5.0-18.8	1.8-7.3	1.5-8.2	≤2.8	1.4-9.0	2.5-6.6	0.8-4.8	0.2-8.9	1.5-3.7	≤6.9	1.5-6.9	nd	≤4
Δ^7-stigmastenol	≤5.1	≤1.4	0.2-4.2	0.2-2.4	≤2.1	≤1.3	13.7-24.6	3.4-16.4	1.4-5.2	6.5-24.0	6.5-24.0	20.5-35.9	≤2
Δ^7-avenasterol	≤5.5	0.8-3.3	0.3-2.7	≤5.1	≤1.4	≤0.8	2.2-6.3	≤8.3	1.0-4.6	3.0-7.5	≤9.0	1.2-4.4	nd
Others	≤1.4	≤1.5	≤2.4	nd	≤2.7	≤4.2	0.5-6.4	4.4-11.9	≤1.8	≤5.3	3.5-9.5	59.0-78.0[a]	nr
Total sterols	900-2900	2700-6400	7000-22100	300-700	700-1400	4500-11300	2100-4600	2000-4100	1800-4500	2400-5000	1700-5200	1300-3190	nr
α-tocopherol	49-373	136-674	23-573	4-193	≤44	100-386	234-660	234-660	9-352	403-935	400-1090	14-78	76-356
β-tocopherol	≤41	≤29	≤356	≤234	≤248	≤140	≤17	≤13	≤36	≤45	10-35	≤5.2	nd
γ-tocopherol	88-389	138-746	268-2468	≤526	≤257	189-753	≤12	≤44	89-2307	≤34	3-30	322-810	187-358
Δ-tocopherol	≤22	0-21	23-75	≤123	nd	≤22	nd	≤6	154-932	≤7.0	≤17	28-113	≤19
α-tocotrienol	nd	nd	≤239	4-336	nd	nd	nd	nd	≤69	nd	nd	nr	nr
γ-tocotrienol	nd	nd	≤450	14-710	≤60	nd	≤12	≤10	≤103	nd	nd	nr	nr
Δ-tocotrienol	nd	nd	≤20	≤377	nd	nd	nd	nd	nd	nd	nd	nr	nr
Total (mg/kg)	170-1300	380-1200	330-3720	150-1500	≤260	430-2680	240-670	250-700	600-3370	440-1520	450-1120	597-880	263-661

Note: 1, Arachis oil; 2, Cottonseed oil, 3, Maize oil; 4, Palm oil; 5, Palm kernel oil; 6, Rapeseed (Canola) oil; 7a, Safflower oil; 7b, Safflower high oleic oil; 8, Soya oil; 9a, Sunflower oil; 9b, Sunflower high oleic oil; 10, argan oil; 11, evening primrose oil; nd, non-detectable, defined as <0.05 %; nr, not reported. Maize oil also contains ≤52 mg/kg β-tocotrienol; [a], stigmasta-8,22-diene-3-ol (3-6 %), spinasterol (34-44 %), schottenol (44-49 %) and sigmasta-7,24-diene-3-ol (4-7 %).

Table 4: Physical-chemical characteristics of the selected crude edible vegetable oils from selected samples. Sources: [4-6]

	1	2	3	4	5	6	7a	7b	8	9a	9b	10	11
RD	0.912-0.920 x=20 °C	0.918-0.926 x=20 °C	0.917-0.925 x=20 °C	0.891-0.899 x=50 °C	0.899-0.914 x=40 °C	0.914-0.920 x=20 °C	0.922-0.927 x=20 °C	0.913-0.919 x=20°C[a]	0.919-0.925 x=20 °C	0.918-0.923 x=20 °C	0.909-0.915 x=25°C	0.906-0.919 x=20 °C	nr
RI	1.460-1.465	1.458-1.466	1.465-1.468	1.454-1.456 at 50 °C	1.448-1.452	1.465-1.467	1.467-1.470	1.466-1.470 at 25 °C[b]	1.466-1.470	1.461-1.468	1.467-1.471 at 25 °C	1.463-1.472 at 25 °C	14791 at 20 °C
SV	187-196	189-198	187-195	190-209	230-254	182-193	186-198	186-194	189-195	188-194	182-194	189.1-199.1	192-198
IV	86-107	100-123	103-135	50.0-55.0	14.1-21.0	105-126	136-148	80-100	124-139	118-141	78-90	91-110	147-155
UM	≤10	≤15	≤28	≤12	≤10	≤20	≤15	≤10	≤15	≤15	≤15	≤11	≤2

Note: 1, Arachis oil; 2, Cottonseed oil, 3, Maize oil; 4, Palm oil; 5, Palm kernel oil; 6, Rapeseed (Canola) oil; 7a, Safflower oil; 7b, Safflower high oleic oil; 8, Soya oil; 9a, Sunflower oil; 9b, Sunflower high oleic oil; 10, argan oil; 11, evening primrose oil; nd, non-detectable, defined as <0.05 %; nr, not reported. RD, relative density (x °C/water at 20 °C); RI, refractive index (ND 40 °C); SV, saponification value (mg KOH/g oil); IV, iodine value; UM, unsaponifiable matter (g/kg). [a], 0.910-0.916 x=25°C; [b], 1.460-1.464 at 40°C. Stable carbon isotope ratio for maize oil should oscillate between -13.71 and -16.26.

Maize oil

Maize oil is a premium oil which may also be adulterated but, because its fatty acid composition overlaps that of other vegetable oils, blending is difficult to detect. Similarly, although maize oil has a much higher level of sterols than other oils, the ratios of the concentrations of the individual sterols (useful in resolving purity issues with most other oils) hardly change at all in blends of maize oil with minor amounts of other vegetable oils. For these reasons, it is difficult to detect adulteration of maize oil by conventional analytical techniques. This is the case for the reported addition of cheaper rapeseed oil to maize oil at high percentages which is an economically motivated adulteration. There are, however, many scientific papers that describe the addition of maize oil to virgin olive oil which would, in fact, be easily detected by only tasting the hypothetical mix if crude maize oil is added, or by the quantification of stigmastadienes if refined maize oil is added to virgin olive oil. The fraud of adding refined maize oil to refined olive oil has been detected at very low percentages using stable carbon isotope ratio analysis since the beginning of 1990's. Although any kind of adulteration is always possible if there is a profit for fraudsters, some types of adulteration put forward by some scientists may not be supported by facts and may be far from the actual oil market.

Rapeseed and soya-bean oil

Rapeseed and soya-bean oils have similar fatty acid compositions. Although they are among the cheaper vegetable oils, they are traded at slightly different prices, soya-bean oil usually being the more expensive. Blends of the two may alleviate a temporary shortage of one or other of the oils or provide a small commercial advantage but such blends have been difficult to identify when the levels of addition are below 20 %. Conversely, soya bean oil can be adulterated with rapeseed oil. The type of adulteration depends on the market demands for one or the other edible oil, and the tariffs to be paid for the declared edible oil in the destination market. Whenever large tariffs are payable in the destination country, there is a high risk of cross-border smuggling operations, including various proportions of the adulterated mixture.

Evening primrose oil (EPO)

EPO is produced, at a high cost, because of its moderate content of gamma-linolenic acid (GLA, i.e. all *cis*-6,9,12 octadecatrienoic acid), which is distinguished from normal or alpha-linolenic acid (all *cis*-9,12,15 octadecatrienoic acid). GLA is normally formed in the human body by the metabolism of linoleic acid (all *cis*-9,12 octadecadienoic acid). However, some people have a deficiency in their delta-6 desaturase enzyme system leading to a deficiency of GLA and subsequent metabolic products. It is claimed that this results in a number of human aliments that can be alleviated by consuming preformed GLA. Thus, evening primrose is produced commercially as a source of GLA [10]. Borage and blackcurrant seed oils are also considered as valid sources of GLA [11]. As an unofficial standard requires that EPO should contain at least 10 % GLA, these other oils have been considered as possible adulterants of evening primrose in order to reach the required concentration of GLA. Although consumers thus receive the required amount of GLA, it is fraudulent to describe the oil as pure EPO.

Sunflower seed oil

Although sunflower seed oils are produced at a low price, they have not been free from adulteration with other food products. In 2017, for example, the Security Service of Ukraine carried out inspections of sunflower seed oil market operators because it had been alleged that producers adulterated this oil with chicken fat. In the past, the enzymatic interesterification of lard and high-oleic sunflower oil was used for the legal development of new products [12], which

increased the stability of the vegetable oil and its bland flavour in fried foods [13]. During winter/spring 2007/2008, in Ukraine, nearly 100 000 t of sunflower oil were contaminated with mineral oil at concentrations often above 1 000 mg/kg. Fortunately, the European Food Safety Authority (EFSA) concluded that "exposure to such oil, although undesirable, would not be a public health concern" since no additives for lubricating oils or pesticides were detected – the risk assessment was exclusively based on the hydrocarbons - but the complete absence of n-alkanes suggested that the contaminant consisted of a base oil for the manufacture of lubricants or hydraulic oils [14].

Argan oil

Argan oil is expensive, its current price in Europe is above 100 euros per litre. Thus, such a price is likely to incite unscrupulous behaviour and illegal practices are not uncommon (i.e. dilution with olive oil coloured with paprika or other substances). In addition, the detection of its adulteration is sometimes a complex problem [15]. Historically, detecting such fraud has been difficult because of the small databases establishing appropriate purity criteria. Today, argan oil is widely sold in Western-Europe, North-America and Japan, and the set of potential adulterants include now soya bean and sunflower seed oils among others.

Coconut oil

The current edible oil market shows a fast-rising demand for coconut oil in developed countries (e.g., USA), whereas at the same time coconut production is falling in producer countries, mostly the Caribbean and Central America, because of a lethal yellowing disease which is threatening coconut crops [16]. An immediate consequence has been widespread adulteration and counterfeiting of retail coconut oil brands, alleged to be occurring in large amounts (50 %) in India [17]. The expected fraudulent activity could not be circumscribed to the dilution of coconut oils with cheaper edible oils but also includes aspects such as the misrepresentation of the organic coconut oil status and country of origin (geographical provenance) or the addition of undeclared ingredients for flavouring or colouring possibly resulting in an allergen risk.

Oil processing

Oils prepared by mechanical means alone, without the application of extra heat and in the absence of further processing, are described as cold-pressed. These normally have a fine flavour, depending on the quality of the seeds used as raw material. They are produced in relatively low yields and are therefore more expensive. Oils obtained by hot-pressing and/or solvent extraction are obtained in higher yields and are therefore cheaper. Furthermore, oils can be solvent-extracted from inferior seeds and then refined and deodorised to give bland, manufactured oils which are even cheaper than those produced, for example, by hot-pressing from high grade seeds.

Processing of poor-quality oilseeds or poor storage conditions may lead to an unwelcome increase of free fatty acids (FFA) in the oil. Crude oils are often purchased on contracts that specify a maximum FFA content. If, as a result of some mishap, an oil has an FFA above the contractual maximum, there is a temptation to refine part of the oil to remove the FFA and then to blend back unprocessed oil to give a supposed crude oil that is now within the contractual limit.

As a further consideration, partially hydrogenated oils (PHOs) are going to be banned in several countries in 2018 (e.g. Final Determination Regarding Partially Hydrogenated Oils, FDA- 80 FR 34650). The demand for PHOs will fall and the price of replacement oils expected to rise, with a medium risk that unscrupulous suppliers may use PHOs in edible oils and other food materials that are claimed to be free of such compounds.

2.1.2. Geographical origin

Values of the physical-chemical parameters characterising crude vegetable oils are influenced by the variety of the harvested plant and the pedoclimatic characteristics of their orchards; for example, West African groundnut oil has a low iodine value, which makes it preferred by buyers. In fact, the existence of some discrepancies in the authenticity of edible oils and errors among laboratories are mostly due to the scarcity of information on the samples analysed (e.g. cultivar and geographical origin) that can be remedied by databases that store information for most of the chemical compounds and physical-chemical parameters relevant to authenticity-characterisation. Thus, Leatherhead Food RA (UK) put a lot of effort into collecting a set of authentic vegetable oilseed samples that were representative of world trade. Annex of Oils and Fats Chapter in Food Authenticity: Issues and Methodologies [7] displays the ranges of a series of crude edible vegetable oils (coconut, cottonseed, maize, groundnut, palm kernel sesame, rapeseed as canola, sunflower seed, soya bean, safflower and palm) from their different geographical origins that were characterised by their fatty acids, main phytosterols, triglyceride carbon number, tocopherols, iodine value, slip melt point, fatty acids at the 2-position and enrichment factors.

The importance of characterization of crude edible oils by their geographical origin is becoming more and more important as some oilseeds and edible oils are being smuggled along “drug” routes between origin and destination countries to avoid the high tariffs payable on original destination. Although the ratio between domestic production and export volumes is the main parameter to imply that an imported food might be fraudulent, it is not always easy to get this information and the values of analytical parameters can be of help.

2.1.3. Organic edible oils

It is well-known that the demand for organic edible oils has grown rapidly and now outstrips the figures of production for some edible oils (e.g., corn and soybeans), up to the point that accredited certifying agents for organic foodstuffs have increased surveillance of organic edible oils in order to detect possible fraudulent organic certifications. American commentators have claimed that the volumes of imports from certain producer countries exceed the legitimate oilseed organic production volumes that could be produced by those countries. In developed countries, paradoxically an organic edible oil may be qualified as conventional oil just because the organic verification process is too expensive (> 1 000 EUR) whereas, at the same time, an imported edible oil can be qualified as organic using a fraudulent certification. Sometimes, the problem of organic oils arises from pesticides from neighbouring farms or from polluted soil and water (e.g. China organic farms). Conversely, after oilseeds or crude vegetable oils are washed, the concentration of pesticide residues can reach similar values to those of organic food products.

2.2. Identification of potential issues

Food fraud, or the act of defrauding buyers of food has vexed the food industry throughout history, and edible oils are not an exception. Thus, the adulteration of edible vegetable oils goes beyond the label on their bottles as many of the oils described in this chapter are very common ingredients present in many food products including chips, margarine, mayonnaise, salad oils and dressings, pasta sauces, packed foods, baked and many more. Thus, the adulteration of edible vegetable oils for direct consumption could be just the visible part of an iceberg of the adulteration if the Control Authorities for Food Fraud turn a blind eye to the adulteration of edible oils as ingredients in food formulations, only reacting when risks to public health are detected in the food chain.

The combined action of databases with information on genuine crude vegetable oils with analytical methodologies that are able to detect additions of cheaper edible oils to expensive ones at low concentrations is making classical adulteration less profitable, at least in developed countries (e.g., EU, USA, Canada). However, it does not guarantee that the adulteration of seed oils does not exist if international and national control organisms lift legal barriers.

There are, however, relatively new adulterations like the addition of “gutter oils” to edible oils [18]. Gutter oils are used edible oils or waste cooking oils, which are collected from restaurant fryers, grease traps, slaughterhouse waste etc. and re-labelled as normal edible oils. Unfortunately, the very diverse sources (e.g., processes, kind of oils, mixtures) of the gutter oils mean that the identification of a good marker for their detection in adulterated edible oils is an analytical challenge. In addition, the detection of the toxic substances might not be reliable if one carefully analyses the variability of the origin of the oil and also the fact that these oils are treated with chemicals prior to being sold back to restaurants in Asia. In September 2014, a scandal was reported involving 240 tons of gutter oil in Taiwan, some of which may have been exported overseas. Although, this kind of adulteration is currently limited to Asia, finding it in developed countries in the next years cannot be ruled out.

Another adulteration that is expected to continue is the illegal colouring of palm oils in developing nations which remains a challenge for the enforcement authorities. The Migration of populations often leads to an increase in the imports of food products that were common in the home countries of the migrants, and these are then bought in markets used by foreign traders. There have been recent reports (4 March 2018) of palm oil that is been adulterated with artificial colouring [19] in such markets.

Other consumer concerns that are likely to increase include the demand for sustainably-grown palm oil, with the high risk that this sustainability status is fraudulently misrepresented. Consumers in some countries are also worried about consuming edible oils extracted from GM oilseeds because of possible mislabelling not only of their containers but also as they are ingredients in a number of food products. The high complexity of national and international regulations dealing with genetically modified organisms adds furthers difficulties to effective authentication in this regard.

An attempt at identifying potential issues in authentication should also focus on the abrupt changes in price and a break in the value balance between edible oils. A common rule is that larger harvests of an oilseed often lead to lower prices, which usually means a decreased risk of fraudulent activity for this particular oil; whereas the availability of cheap and abundant amounts of the oil make it attractive as an adulterant, a diluent or filler. For example, a large harvest of hazelnuts makes refined hazelnut oil a potential adulterant of olive oil but, on the contrary, a large harvest of olives may make roasted hazelnut oil the object of adulteration with virgin olive oil.

Food fraud can include economic adulteration, economically motivated adulteration, intentional adulteration, or food counterfeiting, according to the United States Pharmacopeial Convention (USP). Given the diversity of possible types of fraud, it is necessary to register real cases of adulteration to understand the actual incidence of a fraud type and go beyond hypothetical cases described in analytical studies. Today, the coordination between institutions for registering these cases is assumed as a critical tool for detecting new fraud types.

2.3. Potential threat to public health

Vegetable oil adulteration involves the substitution of a high-value product with a less expensive or lower quality alternative that deprives the food buyer of the product they think they are getting. However, the vast majority of fraud incidents does not pose a public health risk or food safety crisis although some journals have published alarmist headlines such as “deep-frying with sunflower oil and corn oil releases toxic chemicals linked to cancer”.

The consumption of edible oils either adulterated with gutter oils or even 100 % gutter oil is a source of potential health concerns. As gutter oil contains many kinds of toxic waste material, arsenic being one of them, it can have a serious impact on gastrointestinal diseases and digestive disorders. Gutter oil also contains a large variety of detergents and chemical cleaning substances (e.g., lead content is surprisingly high), which can cause abdominal cramps and anaemia and even liver function damage. Besides, gutter oil is usually extracted from sewers, but also refining the rotten animal meat and rotten animal offal, and the immediate consequence in the consumers is diarrhoea [20].

Today's rising food prices and the global nature of the food chain offer the opportunity for criminals to sell counterfeit and substandard food in a multi-billion criminal industry, and sometimes it has the consequence of health risk. These health risks, when happening, are of several degrees of importance. Thus, for example, cottonseed oil, if partially hydrogenated, as found in margarines or solid shortenings, contains high amounts of trans-fats, which are considered dangerous for health. When consumed in regular small amounts, the effect on health is negligible. However, consumer preference is for non-hydrogenated oils. In other cases, when the oil is adulterated, and it is out of the regular market chain, the health risk may be more important. Sometimes this importance is justified by a toxic effect of an unexpected compound. In other cases, allergic reactions are involved, sometimes due to minor compounds present in the oil. Thus, allergic reactions to cotton as food, may also involve physiological responses to the presence of harmful pesticides, herbicides, fungicides, and GMOs. Gossypol may be another factor related to cottonseed food allergies.

It is essential, in order to protect public health, to consider also the contaminants at levels which are toxicologically acceptable [21]. In regard to authenticity, contaminants can be related with additions of other oils or with processes that are not commonly applied. It is true that the chemical 3-monochloropropane diol (3-MCPD) and its esters are formed unintentionally during the refining process of vegetable oils, mainly palm oil, as high temperatures are applied in order to achieve quality and safety specifications. These substances are genotoxic and carcinogenic (i.e. they can damage DNA and cause cancer) although the consumption levels of 3-MCPD in food are considered safe for most consumers. However, EFSA has determined the maximum 3-MCPD tolerable daily intake at 2.0 *micrograms per kilogram of body weight* to prevent high consumers in younger age groups from a potential health concern (e.g., male fertility).

The progress in analytical techniques has provided advanced knowledge of chemical composition, focusing attention on particular some compounds for their health implications. The detection of the presence of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) in foods in general, and in edible oils in particular, has started a debate about which is the best method to control their presence and the best and realistic limits to be included in regulation. The European Food Safety Authority (EFSA) has published a scientific opinion on this topic [22] in which it was stated that the major sources of MOH in food are food packaging and additives, processing aids, and lubricants. The health concern on these compounds is explained by the observation that these compounds may accumulate and cause micro-

granulomas in several tissues. Currently modifications in the production process are under discussion to avoid the sources of this contamination. Similar problems can be identified with other migrating contaminants, such as phthalates [23].

3. Analytical methods used to test for authenticity

3.1. Officially recognised methods

Edible vegetable oils that are misdescribed, insufficiently described or adulterated or deceptive by any combination of these factors can all be detected, in theory, by analysis and comparison of the resulting data with those from an authentic population. This means that these oils are characterised by their most relevant chemical compounds and physical-chemical parameters in regards to each authenticity issue. The information from those variables requires a set of standardised methods to be implemented in control laboratories. Table 5 summarises the determinations that are relevant to edible oil authenticity and characterisation and possible methods validated by international institutions.

3.2. Other used methods

With such a variety of oils and an extensive scientific literature, identifying alternative methods require selecting those approaches that permit to tackle real cases and adulteration percentages. A high proportion of literature reports, understandably perhaps, relate to obscure varieties of oilseeds that had been analysed simply because they were unusual. In other cases, samples for analysis had been "picked" and were superior examples of the variety under study. The full stock of literature information is, as a result, not always related to the vegetable oils traded for use as food on world markets. The alternative methods that are proposed beyond those described in trade standards are mostly based on non-targeted techniques, such as vibrational spectroscopy, nuclear magnetic resonance and isotopic techniques. The fundamentals and methods are very similar to those described for olive oil.

Infrared absorption and Raman scattering give complementary information about molecular vibrations, yielding a vibrational fingerprint of the molecules [24]. Both the mid-infrared (MIR) (4000-400 cm^{-1}, 2.5-25 µm) and near-infrared (NIR) (15000-4000 cm^{-1}, 0.72-2.5 µm) regions have been used in the study of fats and oils.

The IR spectroscopy and multivariate approach [25] has been applied to authentication of non-edible oils [26,27], and today the combination of non-targeted techniques and Chemometrics seem to be an alternative to solve sophisticated cases of adulteration [28]. Thus, this approach has been used to detect contaminants and additives from lubricating oils and diesel in edible oils resulting from the use of diesel tankers and lubricating oil drums for transportation [29]. Such contaminants have serious health implications.

Further developments in the analysis of the spectral data through computer-aided techniques have opened up new opportunities for use in the on-line analysis of industrial processes. Thus, these analytical approaches can be used to measure several properties, which are described below.

Table 5: Summary of the relevant methods proposed in Codex Alimentarius [6]

Determination	Method
Fatty acid composition	IUPAC 2.301, 2.302 and 2.304 or ISO 5508: 1990 and 5509: 2000 or AOCS Ce 2-66, Ce 1e-91 or Ce 1f-96
Sterol content	ISO 12228:1999, or IUPAC 2.403
Tocopherol content	IUPAC 2.432 or ISO 9936: 1997 or AOCS Ce 8-89
Total carotenoids	BS 684 Section 2.20
Acidity	IUPAC 2.201 or ISO 660: 1996 or AOCS Cd 3d-63
Unsaponifiable matter	IUPAC 2.401 (part 1-5) or ISO 3596: 2000 or ISO 18609: 2000
Peroxide value	IUPAC 2.501 (as amended), AOCS Cd 8b - 90 (97) or ISO 3961: 1998
Matter Volatile at 105°C	IUPAC 2.601 or ISO 662: 1998
Arsenic content	AOAC 952.13, IUPAC 3.136, AOAC 942.17, or AOAC 985.16
Insoluble impurity	IUPAC 2.604 or ISO 663: 2000
Trace metals of copper and iron	ISO 8294: 1994, IUPAC 2.631 or AOAC 990.05 or AOCS Ca 18b-91
Determination of traces of heavy metals	Lead: IUPAC 2.632, AOAC 994.02 or ISO 12193: 1994 or AOCS Ca 18c-91 Arsenic: AOAC 952.13; AOAC 942.17; AOAC 985.16
Slip point	ISO 6321: 1991 and Amendment 1: 1998 for all the edible oils, or AOCS Cc 3b-92 or Ce 3-25 (97) for palm oils only
Crismer value	AOCS Cb 4-35 (97) and AOCS Ca 5a-40 (97)
Badoiun test[1]	AOCS Cb 2-40 (97)
Halphen test	AOCS Cb 1-25 (97)
Reichert and Polenske values	AOCS Cd 5-40 (97)
Refractive Index	IUPAC 2.102 or ISO 6320: 2000 or AOCS Ce 7-25
Iodine value	Wijs - according to IUPAC 2.205/1, ISO 3961: 1996, AOAC 993.20, or AOCS Cd 1d-92 (97), or by calculation - AOCS Cd 1b-87 (97)
Saponifiable value	IUPAC 2.202 or ISO 3657: 1988
Soap content	BS 684 Section 2.5
Relative density	IUPAC 2.101[a]
Apparent density	ISO 6883: 2000[a] or AOCS Cc 10c-95

Note: [a], with the appropriate conversion factor; [1], modified Villavecchia test or sesame seed oil test; AOCS, American Oil Chemists Society; ISO, International Organization for Standardization; FOSFA, Federation of Oils, Seeds and Fats Associations Ltd; IUPAC, International of Union of Pure and Applied Chemistry.

The majority of the unsaturated fatty acids that make up edible oils are found in the *cis* form. When oils are hardened by hydrogenation (to formulate margarine), or partially hydrogenated to stabilise against oxidation, there is a conversion of some *cis* to *trans* double bonds. FTIR can be used to determine the *trans* isomer content of oils and fats with a good agreement with GC results [24]. Actually, FTIR has demonstrated good performance in this determination and a IUPAC method was developed with this objective [30]. Raman spectroscopy has also been used to determine the *cis/trans* isomer content of edible vegetable oils, as well as to determine the total unsaturation of oils and margarines. Furthermore, Fourier transform mid infrared (FT-MIR) has

been used in the detection of adulteration of virgin coconut oil [31], the mixtures of sesame and corn oils [32], and the presence of lard in some vegetable oils [33] also analysed by differential scanning calorimetry [34]; a large set of applications is described by [7].

FTIR analysis also provides a rapid means of evaluating the oxidative state of an oil or of monitoring changes in oils undergoing thermal stress [35]. Rapid methods based on FTIR have also been developed for the quantitative determinations of the iodine value and saponification number, free fatty acids, peroxide value and solid fat index.

In terms of oil authenticity, FTIR, NIR and Raman spectroscopy coupled with multivariate analysis techniques have been used to characterise edible oils, according to their degree of unsaturation and other characteristics [25,27]. The basis for the discrimination between fats is often the concentration of unsaturated fatty acids, and different concentrations of linoleic acid in the case of oils (sunflower, olive and peanut oils) [25,36].

^{1}H-NMR has also been applied to the study of the triacylglycerol structure of palm oils, seed oils, some hydrogenated fats and vegetable margarines as, for instance, the adulteration of peanut oil [37].

Quantitative ^{13}C-NMR data of the acyl profile have been reported to be in good agreement with GC for other edible vegetable oils, fats and lipids. Thus, a profiling strategy with ^{13}C-NMR, ^{1}H-NMR and the analysis of results by chemometrics [38,39] has shown satisfactory results in detecting the presence of different vegetable oils, although always with the involvement of a database that can affect these results.

Isotopic analysis has already been carried out with respect to the isotope ratio of individual fatty acids in an oil and it has been shown that there are slight differences [40]. Any contamination of an oil will upset these slight differences, the nature of the distortion from the established pattern revealing the cause of the impurity. Thus, for example, carbon isotope ratio was used, in combination with GC-FID, to detect the presence of corn oil in sesame oil [41].

The technique of site-specific isotope fractionation studied by NMR (SNIF-NMR) has been applied to alcoholic beverages and fruit juices. There is every possibility that it may also show advantages in the evaluation of edible seed oils.

The main applications of spectroscopic techniques in authenticating edible oils has been focused on detecting their presence in olive oil categories as described in the chapter on olive oil. Sometimes, however, authors imagine a virtual world in which any kind of adulteration can be possible, some ones even being unprofitable for fraudsters, and they study cases that do not exist in the real world even being published in reputed scientific journals.

4. Overview of methods for authenticity testing

In the investigation of suspect oils, it is usual that fatty acid compositions are studied first as they are easy to determine and are sufficiently different to clarify the majority of uncertainties of food authenticity. However, many other methods can provide chemical or physical-chemical information that can be also useful in authentication. The following table provides an overview of common methods for the detection of seed oil adulteration. The reader is referred to previous tables provided for chemical differences among edible oils (Tables 2-3) and analytical methods suggested by Codex (Table 5).

Analytical Method	Analyte - Indicative data	Applicability
Fatty acid profile by GC	Linolenic acid (C18:3) Fatty acid concentration at the triglyceride-2 position	Contamination of groundnut and sunflower seed oils with soybean and rapeseed oils
Sterol profile by GC	Brassicasterol	Detection of rapeseed oil in sunflower seed or groundnut oils
Tocopherol content by HPLC	Gamma-tocopherol	Detection of soybean oil in sunflower seed oil
Tocopherol content by HPLC	Delta-tocopherol	Detection of soybean oil in groundnut oil
Carbon number triglyceride composition by HPLC	C60/C58 ratio	Detection of sunflower seed oil in safflower seed oil
Slip melting point/Iodine values		Detection of stearins or oleins in palm oil
Carbon number triglyceride composition by HPLC	C48 concentration * palmitic acid enrichment factor	Detection of stearins or oleins in palm oil
ICP-OES	Elemental content	Detection of olive oil and soybean oil in argan oil
Sterol profile by GC	Campesterol	Detection of olive oil in argan oil
HPLC	Triacylglycerols	Detection of sunflower seed, soybean and olive oils in argan oil
1H LF-NMR	Ratios	Detection of soybean, palm and rapeseed oils in peanut oil
Fatty acid profile by GC	Palmitic acid (C16 :0)	Adulteration of cottonseed by palm olein
Carbon number triglyceride composition by HPLC	C50 and C54	Detection of palm olein oil in cottonseed oil
Carbon number triglyceride composition by HPLC	Various purity criteria	Mixtures of palm kernel and coconut oils
Fatty acid profile by GC and Iodine values	Oleic acid (C18 :1)	Detection of palm kernel olein in palm kernel oil
Differential Scanning Calorimetry	Thermogram profiles	Detection of animal fat in sunflower seed oil
Stable isotope analysis	$^{13}C/^{12}C$ ratios	Detection of commercial oils in maize oils and vice versa
Stable isotope analysis	$^{13}C/^{12}C$ ratios	Detection of maize oil in olive, sesame and soybean oils
Fatty acid profile by GC	Oleic and linoleic acids	Detection of rapeseed and soybean blends
Fatty acid profile by GC	Linoleic and erucic acids	Detection of borage oil in evening primrose oil
Fatty acid profile by GC	Linoleic and stearidonic acids	Detection of blackcurrant seed oil in evening primrose oil

5. Conclusion

A large number of the problems in identifying more than 10 % adulteration or contamination of bulk edible oils have been clarified. However, changes in commercial trade patterns and in consumer eating habits, together with increasing application of genetic engineering to improve oil crops mean that tomorrow's problems may not be the same as those encountered today. Thus, using genetic modification it is possible to obtain oils from different botanical sources with chemical characteristics that are similar to those oils that are targets for adulteration. In consequence, authentication strategies should consider this fact to be efficient in detecting frauds.

As regards analytical developments, the difficulty is that some of the methods, such as sterol analysis, are long, tedious and therefore expensive. Others, such as some spectroscopic analysis (e.g. NMR, isotopic analysis), require sophisticated equipment which are only available in a limited number of laboratories.

The challenge for the future is still the identification and detection of adulteration, but at lower levels of impurity, and by simpler routine methods. In global terms, the analysts predict that the greatest increase in vegetable oil consumption will take place in South East Asia and South America. North America, Australia and Japan will experience a moderate increase in the demand for vegetable oils mostly as a result of health concerns. Thus, abrupt changes in demand may also bring some new chances for adulteration that will need to be controlled with coordinated and efficient tools that combine analytical enhancement and data management. Since vegetable oils are essential in the human diet and they form part of many food formulations, they cannot be omitted or substituted by other ingredients. Thus, any problem of fraud is magnified and can have a significant impact on health and consumer concern. Therefore, an oriented strategy on vegetable oils authentication is always necessary and it should be on the table of food safety authorities, without forgetting the news on food frauds reported on media (https://ec.europa.eu/jrc/en/food-fraud-and-quality/monthly-summary-articles).

6. Bibliographic references

1. Lyubun Y.V., Kosterin P.V., Zakharova E.A., Shcherbakov A.A. & Fedorov E.E. (2002). – Arsenic-contaminated soils. Phytotoxicity studies with sunflower and sorghum. *J. Soils Sediment.*, **2** (3), 143–147. doi:10.1007/BF02988466.
2. Plourde J.D., Pijanowski B.C. & Pekin B.K. (2013). – Evidence for increased monoculture cropping in the Central United States. *Agric, Ecosyst. Environ.*, **165**, 50–59. doi:10.1016/j.agee.2012.11.011.
3. European Union. (2002). - Commission Regulation (EC) No 178/2002 of 28 January 2002 laying down the general principles and requirements of food law, establishing the European Food Safety Authority and laying down procedures in matters of food safety, *Official Journal of the European Union L31/1*.
4. Firestone D. & Reina R.J. (1996). - Authenticity of vegetable oils. In: *Food Authenticity* (P.R. Ashurst & M.J. Dennis, eds), Blackie Academic & Professional, London, pp 198-258.
5. Russo G.L. (2009). - The Scientific Handbook. Mapping and Comparing Oils (MAC-Oils) Project. European Commission 6th Framework Programme Priority 5. Food Quality and Safety Priority, Call 4-C.
6. Codex Stan (2015). - Codex Alimentarius International Food Standards. Standard for amendment vegetable oils. CODEX STAN 210-1999. Amendment 2015.
7. Lees M. (2013). - *Food authenticity and traceability*. Eurofins Scientific Analytics- Woodhead Pub. Nantes, France. DOI: 10.1533/9781855737181.
8. Lazarus R. (1983) Cottonseed Rip-Off. Our Refineries Cleared. New Straits Times of Wednesday, March 2nd, 1983.
9. Lazarus R., & Bala K. (1983) $14M Export swindle. New Straits Times of Wednesday, March 2nd, 1983.

10. Eskin N.A.M. (2008). – Borage and evening primrose oil. *Eur. J. Lipid Sci. Technol.*, **110** (7), 651–654. doi:10.1002/ejlt.200700259.

11. Eskin N.A.M. (2002). - Authentication of evening primrose, borage and fish oils. In *Oils and Fats Authentication* (M. Jee, ed), CRC Press Blackwell Publishing, Boca Raton, FL, pp 95-114.

12. Rodríguez A., Castro E., Salinas M.C., López R. & Miranda M. (2001). – Interesterification of tallow and sunflower oil. *J. Am. Oil Chem. Soc.*, **78** (4), 431–436. doi:10.1007/s11746-001-0280-5.

13. Seriburi V. & Akoh C.C. (1998). – Enzymatic interesterification of lard and high-oleic sunflower oil with candida antarctica lipase to produce plastic fats. *J. Am. Oil Chem. Soc.*, **75** (10), 1339–1345. doi:10.1007/s11746-998-0181-x.

14. Biedermann M. & Grob K. (2009). – How "white" was the mineral oil in the contaminated Ukrainian sunflower oils? *Eur. J. Lipid Sci. Technol.*, **111** (4), 313–319. doi:10.1002/ejlt.200900007.

15. Ourrach I., Rada M., Pérez-Camino M.C., Benaissa M. & Guinda Á. (2012). – Detection of argan oil adulterated with vegetable oils: New markers. *Grasas Aceites*, **63** (4), 355–364. doi:10.3989/gya.047212.

16. Gurr G.M., Johnson A.C., Ash G.J., Wilson B.A.L., Ero M.M., Pilotti C.A., Dewhurst C.F. & You M.S. (2016). – Coconut lethal yellowing diseases: A phytoplasma threat to palms of global economic and social significance. *Front. Plant Sci.*, **7** (October 2016). doi:10.3389/fpls.2016.01521.

17. Food Fraud Advisors. (2018). URL: https://trello.com/b/aoFO1UEf/food-fraud-risk-information

18. Wee H.M., Budiman S.D., Su L.C., Chang M. & Chen R. (2016). – Responsible supply chain management – an analysis of Taiwanese gutter oil scandal using the theory of constraint. *Int. J. Logist-Res. App.*, **19** (5), 380–394. doi:10.1080/13675567.2015.1090964.

19. Food Standards Agency. (2018). Surya Foods recalls Mother Africa Palm Oil because it contains illegal dye Sudan IV. URL: https://www.food.gov.uk/news-alerts/alert/fsa-prin-20-2018. Food Alert 13 April 3018.

20. Li J., Cui N. & J. Liu. (2017). - Gutter oil: an overview of Chinese food safety issues and policies. *Glob. Health Promot.* **24**(3), 75-78. https://doi.org/10.1177/1757975915623733.

21. European Union. (2006). - Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs, Official Journal of the European Union L364/5.

22. European Food Safety Authority (EFSA). (2012). Scientific Opinion: Scientific Opinion on Mineral Oil Hydrocarbons in Food. EFSA Panel on Contaminants in the Food Chain (CONTAM) EFSA Journal, 10(6):2704.

23. Sungur S., Okur R., Turgut F.H., Ustun I. & Gokce C. (2015). – Migrated phthalate levels into edible oils. *Food Addit. Contam. B*, **8** (3), 190–194. doi:10.1080/19393210.2015.1041065.

24. García-González D.L., Baeten V., Fernández Pierna J.A. & Tena N. (2013). – Infrared, Raman, and fluorescence spectroscopies: Methodologies and applications. In: *Handbook of Olive Oil. Analysis and Properties, second ed.* (R. Aparicio & J. Harwood, eds), Springer, New York, pp 335–393 doi:10.1007/978-1-4614-7777-8_10.

25. Baeten V. & Aparicio R. (2000). – Edible Oils and Fats Authentication by Fourier Transform Raman Spectrometry. *Biotechnol. Agron. Soc. Environ.*, **4** (4), 196–203.

26. Rohman A. & Man Y.B.C. (2012). – Application of Fourier transform infrared spectroscopy for authentication of functional food oils. *Appl. Spectrosc. Rev.*, **47** (1), 1–13. doi:10.1080/05704928.2011.619020.

27. Hourant P., Baeten V., Morales M.T., Meurens M. & Aparicio R. (2000). –Oil and fat classification by selected bands of near-infrared spectroscopy. *Appl. Spectrosc*., **54** (8), 1168-1174. doi: 10.1366/0003702001950733.

28. Javidnia K., Parish M., Karimi S. & Hemmateenejad B. (2013). – Discrimination of edible oils and fats by combination of multivariate pattern recognition and FT-IR spectroscopy: A comparative study between different modelling methods. *Spectrochim. Acta A*, **104**, 175–181. doi:10.1016/j.saa.2012.11.067.

29. Voort F.R. van de, Ghetler A., García-González D.L. & Li Y.D. (2008). – Perspectives on quantitative Mid-FTIR spectroscopy in relation to edible oil and lubricant analysis: Evolution and integration of analytical methodologies. *Food Anal. Methods*, **1** (3), 153–163. doi:10.1007/s12161-008-9031-6.

30. IUPAC (1987) Method 2.207 in Standard Methods for the Analysis of Oils and Fats (7th Ed.), Pergamon Press.

31. Rohman A. & Che Man Y.B. (2011). – The use of Fourier transform mid infrared (FT-MIR) spectroscopy for detection and quantification of adulteration in virgin coconut oil. *Food Chem.*, **129** (2), 583–588. doi:10.1016/j.foodchem.2011.04.070.

32. Yang R., Dong G., Sun X., Yang Y., Liu H., Du Y., Jin H. & Zhang W. (2017). – Discrimination of sesame oil adulterated with corn oil using information fusion of synchronous and asynchronous two-dimensional near-mid infrared spectroscopy. *Eur. J. Lipid Sci. Technol.*, **119** (9). doi:10.1002/ejlt.201600459.

33. Rohman A., Che Man Y.B., Hashim P. & Ismail A. (2011). – FTIR spectroscopy combined with chemometrics for analysis of lard adulteration in some vegetable oils. *CYTA - Journal of Food*, **9** (2), 96–101. doi:10.1080/19476331003774639.

34. Marikkar J.M.N., Dzulkifly M.H., Nadiha M.Z.N. & Man Y.B.C. (2012). – Detection of animal fat contaminations in sunflower oil by differential scanning calorimetry. *Int. J. Food Prop.*, **15** (3), 683–690. doi:10.1080/10942912.2010.498544.

35. Tena N., Aparicio R. & García-González D.L. (2018). – PhotooxidationEffect in Liquid Lipid Matrices: Answers from an Innovative FTIR Spectroscopy Strategy with "mesh Cell" Incubation. *J. Agric. Food Chem.*, **66** (13), 3541–3549. doi:10.1021/acs.jafc.7b05981.

36. Lv M.Y., Zhang X., Ren H.R., Liu L., Zhao Y.M., Wang Z., Wu Z.L., Liu L.M. & Xu H.J. (2016). – A rapid method to authenticate vegetable oils through surface-enhanced Raman scattering. *Sci. Rep-UK*, **6**. doi:10.1038/srep23405.

37. Zhu W., Wang X. & Chen L. (2017). – Rapid detection of peanut oil adulteration using low-field nuclear magnetic resonance and chemometrics. *Food Chem.*, **216**, 268–274. doi:10.1016/j.foodchem.2016.08.051.

38. Sacchi R., Addeo F., Musso S.S., Paolillo L. & Giudicianni I. (1995). - A high resolution ^{13}C-NMR study of vegetable margarines. *Ital. J. Food Sci.,* **7,** 27-36.

39. Guyader S., Thomas F., Portaluri V., Jamin E., Akoka S., Silvestre V., Remaud G. (2018). - Authentication of edible fats and oils by non-targeted ^{13}C INEPT NMR spectroscopy. *Food Control,* **91**, 216-224. doi:10.1016/j.foodcont.2018.03.046.

40. Woodbury S.E., Evershed R.P., Barry Rossell J., Griffith R.E. & Famell P. (1995). – Detection of Vegetable Oil Adulteration Using Gas Chromatography Combustion/Isotope Ratio Mass Spectrometry. *Anal. Chem.*, **67** (15), 2685–2690. doi:10.1021/ac00111a029.

41. Seo H.Y., Ha J., Shin D.B., Shim S.L., No K.M., Kim K.S., Lee K.B. & Han S.B. (2010). – Detection of corn oil in adulterated sesame oil by chromatography and carbon isotope analysis. *J. Am. Oil Chem. Soc.*, **87** (6), 621–626. doi:10.1007/s11746-010-1545-6.