Food controls for nuts: product batch rancidity assessment

The following paragraphs describe a complete analytical method that enables the monitoring of the quality of dried fruit before it reaches the final consumer. This proprietary extraction and analysis system is the result of CDR's chemical and engineering knowhow.
Dried fruit is a food product rich in fat content. For this reason, routine analyses of free fatty acids and peroxide value are performed by producers of dried fruit to obtain precious information regarding oil and fat rancidity levels.
The analytical method developed by CDR is practical, rapid and reliable and allows for an efficient food quality control on extractable fats contained in dried fruit.

1. Dried fruit: characteristics and industry

Dried fruit is a widely marketed product. The 'dried fruit family' includes sweet dried fruit, rich in sugars and low in fat content (plums, figs, raisins, dates, etc.) and oily dried fruit, rich in fats and low in sugar content, commonly known as 'nuts'.
This leaflet specifically refers to oily dried fruit and encompasses all types of hard-shelled nuts, such as walnuts, peanuts, hazelnuts, pistachios, almonds, pine nuts, cashews, etc.
The varieties of oily dried fruit are numerous and diversified, but using a cold press method, it is possible to extract the oil specific to each variety. By testing the extracted oil, it is possible to obtain the chemical characteristics of the dried fruit and key production and marketing information.
Statistical data on nut consumption indicate a market growth in upcoming years and further expansion in Asian countries.
For businesses active in this sector there will be an increased demand for production and the need to fine tune distribution processes. In this regard, assessment of chemical characteristics of single product batches will be fundamental.
The monitoring of chemical components of the fruit affects the quality, shelf life and appearance of the product.
One of the most important parameters to keep under control is the quantity of free fatty acids. Nuts are, in fact, rich in polyunsaturated fatty acids and, as with all fatty substances, are subject to rapid rancidity process.
This applies to any variety of the dried fruit family, even though each of them has its own specific characteristics and different percentages of triglyceride content.
Following is a brief description of the most commonly marketed nuts in the world and their related industry.

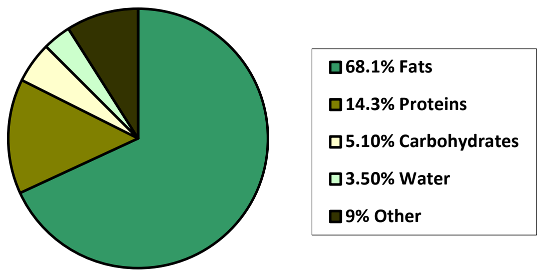
1.1 Walnuts

There are many varieties of walnuts. The most common and important from an economic point of view is the *Juglans Regia*. Fruit is harvested between September and October. Mechanical harvesting machines shake the tree for a few seconds, letting the drupes fall, which are gathered immediately to avoid contamination with molds or mushrooms. Before being put on the market, walnuts undergo:

- Husk removal to prevent the shell from blackening;
- Washing to remove all husk residues;
- Whitening with sulfur dioxide;
- Gradual drying to lower its humidity rate to 4-5%;
- Selection, calibration and packing;
- Products can be stored at 0°C, 60-75% relative humidity to prevent rancidity.

Fatty acids (%):

Walnut nutrient profile



Saturated fatty acids	5.57
Monounsaturated fatty acids	9.54
Polyunsaturated fatty acids	40.66
Others	44.23

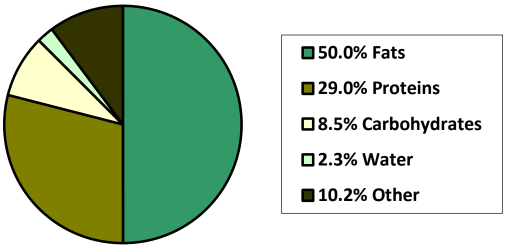
Values for 100g of product

1.2 Peanuts

Peanuts are the seeds of a plant growing up to 30-50 cm tall. The fruit develops into a 3-7 cm long legume pod containing 2 or 3 seeds. The stalks of the plant push the pod underground where the fruit ripens. The scientific name *Arachis hypogaea* derives from this particularity of the plant commonly known as the "groundnut".
Harvesting is carried out with machines that uproot the plants, which are then spread out on the soil and allowed to dry.
The seeds contain up to 50% oil and are generally toasted prior to consumption.

Fatty acids (%):

Peanut nutrient profile



Saturated fatty acids	**7.13**
Monounsaturated fatty acids	23.05
Polyunsaturated fatty acids	14.19
Others	55.63

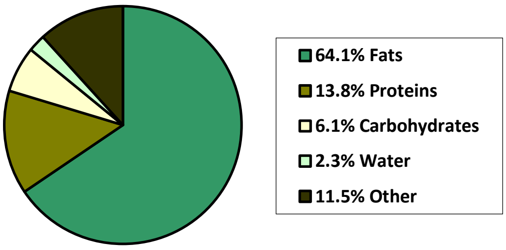
Values for 100g of product

1.3 Hazelnuts

Hazelnuts grow on a plant that belongs to the birch family, *Betulaceae*. The varieties selected and cultivated for commercial purposes belong to the *Corylus Avellana* species, a shrub that generally does not grow taller than 3-5 meters. Harvesting is carried out in August-September, while the nuts are marketed throughout the remaining months. In fact, after harvesting and before being marketed, nuts are stored in dry and aired warehouses at a temperature ranging between 8 and 10°C, 60% relative humidity.
Hazelnuts have a high calorie concentration, and a buttery taste due to a very high fat content (approximately 65%) and a massive presence of sugars and proteins.

Fatty acids (%):

Hazelnut nutrient profile



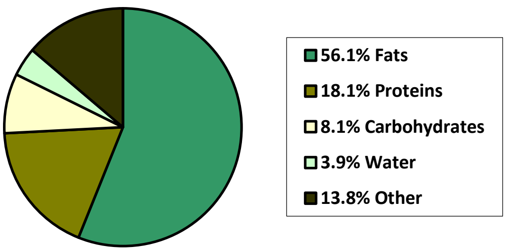
Saturated fatty acids	**4.16**
Monounsaturated fatty acids	38.62
Polyunsaturated fatty acids	5.2
Others	52.02

Values for 100g of product

1.4 Pistachios

Pistachios are the long flat seeds contained in the fruit of the pistachio tree. The plant is a member of the cashew family, whose most common variety for pistachio production is the *Pistacia vera*, a bush that grows up to an average of 4-5 meters. The fruit of the pistachio tree is a drupe with a thin oval husk. The seeds, typically pale green in color, are rich in oil and proteins.
Harvesting generally takes place in September. After removal of the husk, the fruit is allowed to dry. Pistachios have a high fat content, with a fairly high percentage of both monounsaturated and polyunsaturated fatty acids.

Pistachio nutrient profile



Fatty acids (%):

Saturated fatty acids	5.61
Monounsaturated fatty acids	36.47
Polyunsaturated fatty acids	10.66
Others	47.26

Values for 100g of product

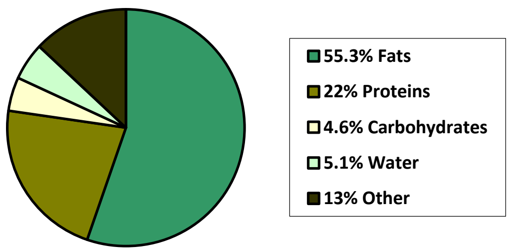
1.5 Almonds

The almond tree is a member of the *Rosaceae* family. *Prunus dulcis*, a small tree growing up to 5 meters tall, produces the edible and widely marketed nuts known by the name of almonds. Based on the type of fruit, distinction is made between the toxic *amara* seed variety, the *fragilis* variety, characterized by sweet seeds and a membranous endocarp, and the *dulcis* variety, whose seeds are used in the foodstuffs and confectionery industry and for the extraction of medicinal almond oil.
The fruit of the almond is a drupe. The outer covering (exocarp) is green and fleshy, sometimes with reddish hues; the endocarp is a hard woody shell that contains the seed (almond). A smooth or corrugated husk, whose color ranges from brown to ochre, surrounds the seed. Occasionally two seeds are present inside the endocarp, which is detrimental from a commercial standpoint.
Harvesting takes place between August and September. The fruit is then allowed to dry in the open air, the husk is removed and the fruit is allowed to dry completely.

Before storage, shelled almonds are occasionally blanched using sulfur dioxide to improve their appearance. Like all oily seeds, almonds have a high calorie and fat content: packed with over 50% of lipids and a high percentage of monounsaturated fatty acids.

Fatty acids (%):

Almond nutrient profile



Saturated fatty acids	**4.59**
Monounsaturated fatty acids	39.44
Polyunsaturated fatty acids	10.85
Others	45.21

Values for 100g of product

1.6 Pine nuts

Pine nuts are the edible seeds of pine trees, usually from the *Pinus pinea* family, but also from the *Pinus cembra* species. These very tall trees reach up to 25 meters height and produce seeds that are large enough to be worth harvesting. The pine nuts (seeds) are present in the cone, the fruit of the pine tree. Cones are 8-15 cm long and oval; at maturity, they open to release the seeds. Cones take up to 36 months to reach maturity.
Cones are harvested from fall to spring; they are piled and allowed to dry. Heat favors the extraction of pine seeds, which are then shelled, washed, dried, selected and packaged.
Pine nuts are rich in lipids (50-60%) and have a high protein content, as well as a high percentage of unsaturated fatty acids, in particular linoleic acid.

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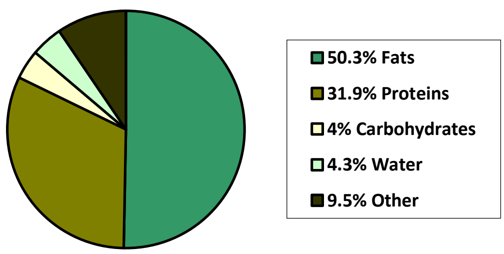
Fatty acids (%):

Pine nut nutrient profile



Saturated fatty acids	**4.8**
Monounsaturated fatty acids	18.7
Polyunsaturated fatty acids	34
Others	42.5

Values for 100g of product

2. Storage: chemical processes and analyses

2.1 Quality control

The characteristics and the origins of certain types of oily dried fruit aid producers in better understanding test requirements and product controls. Businesses that produce, process and package these products are called upon to guarantee the quality and genuineness of raw materials.

An adequate monitoring system foresees:

- Visual control by specialized personnel to the purpose of removing damaged products and monitor hygiene conditions, equipment and transportation;
- Controls during processing as regards the temperature and humidity of cold rooms, the temperature in roasting chambers, the detection of foreign bodies;
- Quality controls to assess product appearance, consistency, color, taste and aroma;
- Physical, chemical and microbiological tests on raw, semi-processed and finished products;
- Other specific analyses for mycotoxins, pesticides and allergenic proteins for environmental protection and compliance with health and safety regulations.

2.2. Rancidification: oxidation and hydrolysis

Tests for product flavor, aroma and appearance are linked with the storage process of nut batches.

It is fundamental to monitor the condition of dried fruit before it reaches the final consumer with a guarantee of standards in appearance, flavor and aroma of the

product. The principal danger is the occurrence of rancidity, since nuts are composed mainly of fats.

Fats are carboxyl compounds made of carbon, hydrogen and oxygen atoms and make up one of the principal classes of organic molecules of biological interest together with carbohydrates, proteins and nucleic acids.
During storage, the quality and characteristics of dried fruit may undergo alterations due principally to two chemical processes that occur with fats: oxidation and hydrolysis. The chemical parameters that allow for the monitoring of these processes are peroxide value and free fatty acids.

2.2.1. Oxidation

In contact with air, fats molecules present in nuts react with oxygen and trigger an oxidation process that produces peroxides, which are chemical compounds containing an oxygen-oxygen single bond (O-O group). The first phase produces peroxides. In the second phase, oxidation produces aldehydes and ketones; these are organic compounds responsible for the characteristic odor of rancidity. The parameter to assess oxidation is therefore the peroxide value.

2.2.2. Hydrolysis

Hydrolysis splits fats by means of water. Some enzymes naturally occurring in food catalyze this reaction and, ultimately, water reacts with fats. Fatty acids detach from the triglyceride backbone and form molecular chains of free fatty acids. The quantity of free fatty acids is measured though the acidity level, the second fundamental parameter for the assessment of the quality of dried fruit.

2.3. Fatty acids

Fatty acids that have carbon-carbon single bonds are known as saturated, while fatty acids that have carbon-carbon double bonds are known as unsaturated.
The presence of saturated or unsaturated fatty acids affects the solidity of fats: the more saturated fatty acids are, the more solid the fat. The single bond, in fact, allows molecules to combine more easily.
Saturated fats aggregate more easily to form solids and their melting point is higher than unsaturated fats.
On the contrary, unsaturated fatty acids are not likely to be solid as the double bond between their carbon atoms prevents molecules from binding into a 'solid structure'. Unsaturated fatty acids are divided into monounsaturated (one double bond between carbon atoms) and polyunsaturated (two or more bonds between carbon atoms).

Fats containing unsaturated fatty acids are always liquid (oils) at room temperature. Their melting point is lower than saturated fats.
Heat and light alter the structure of fats and speed their reaction with oxygen, thus favoring rancidification. Unsaturated fats are more prone to oxidation and the impact of air and light on fats containing unsaturated fatty acids is more aggressive.

Dried fruit is made primarily of unsaturated fats and therefore develops a rancid odor when exposed to air or light. This may alter the appearance and the quality of an entire product batch.

3. CDR extraction and testing system

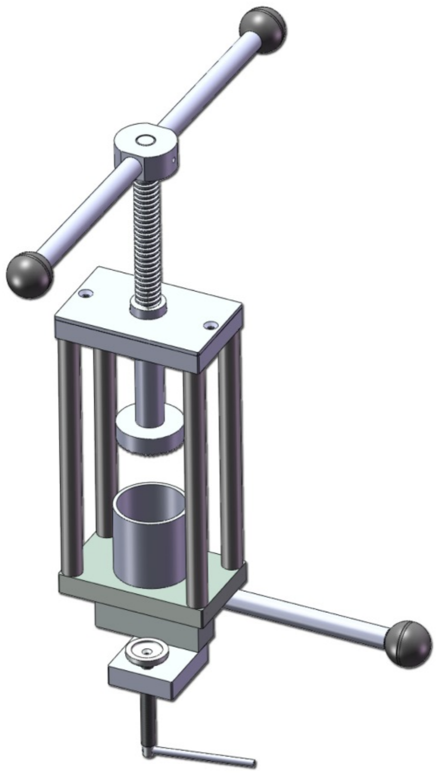
3.1 Components

It is crucial to determine free fatty acids and peroxide value parameters in order to maintain dried fruit characteristics and quality in line with final consumer expectations. The methods by which these tests are conducted affect production stages and procedures.

CDR has developed a rapid, practical, all-inclusive system in order to execute these tests while saving time, raw material and personnel. This system begins with the cold pressing of nuts.

It does not require the use of chemical solvents and foresees three complementary components:

(1) a press (see image);
(2) a centrifuge;
(3) CDR OxiTester or CDR FoodLab tester.



The third component can be either the CDR OxiTester or the CDR Foodlab analyzer, which are both part of the CDR FoodLab set of food testing instruments.

Both instruments are spectrophotometric analyzers based on LED technology and represent the 'analytic core' of the system because they perform acidity and peroxide chemical analyses (**CDR OxiTester**), besides determining more complex parameters such as the p-anisidine (**CDR FoodLab**).

Spectrophotometry is based on the selective absorption by molecules of a light emission at a specific wavelength.

3.2 No need to use toxic solvents

The CDR proprietary extraction and testing system is independent from the first component, which is operated to extract a microquantity of oil from a handful of seeds in a practical and efficient manner.

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The press (1) is comprised of a lever connected to a screw that pushes a piston downward. The piston enters a cylindrical container, a sort of stainless steel ‘cup' where the seeds to be squeezed are placed. The piston has a rough and notched surface and exerts a pressure up to 10,000 kg; it can be used to squeeze any type of unshelled nut easily and efficiently. A connecting structure between the lower and upper parts of the press enables the piston to move. The press can be secured to a table or a workbench by means of a clamp. A lever to balance force may aid in producing pressure, although no great effort is required to turn the upper wheel to obtain the quantity of oil needed to perform the test.
The steel press is a safe and solid instrument, designed entirely by CDR.
Squeezed oil can be easily collected from the steel container and transferred to the centrifuge (2) where liquids are separated from the solid matter. After its transfer into a specific tube the oil is centrifuged.
Oil to be tested is collected by means of a pipette (3).

This system does not require the use of toxic solvents, either during the cold extraction of oil, or during the chemical test.
Cold squeezing of dried fruit by means of the press is an entirely mechanical extraction method that does not require any chemical process. The sample to be tested is not contaminated by other substances and the solid matter of the nut is entirely separated from its oily component, which does not undergo any alteration.
Other methods of extraction available on the market in fact require the use of complex laboratory instruments, such as filters, extraction chambers, condensers, rotary evaporators. One example is the Soxhlet method, developed by Franz Von Soxhlet in 1879.

How does this system work?
First, it requires the use of a chemical solvent, generally diethyl ether, a highly flammable and noxious chemical compound with a low boiling point.
This system is made up of three overlapping glass components: at the bottom, a pot with a beveled edge; in the middle, the actual extractor; at the top, a condenser. The sample is placed in the extraction chamber, while the solvent is placed in the lower pot. The solvent is heated to reflux. The solvent vapor travels up a distillation arm and

floods into the condenser, ultimately dripping back down into the extraction chamber where it is loaded with the solute. It then runs through a thimble made of filter paper and passes into a siphon side arm where the solute concentrates at the bottom while the solvent remains at the top. The cycle continues with the solvent circulating back to the still pot.
Alternatively, both solvent and solute are placed in the still pot, where the solute remains as precipitate and is recovered at the end of the cycle.
This procedure requires attention and expertise, as well as adequate measures to handle and dispose of toxic solvents.

The system involving a mechanical press, rather, remains the cleanest and simplest extraction method with no risk of altering the sample and with little waste of raw material.
The action of the centrifuge accelerates the sedimentation process and completes the extraction procedure by separating solid matter from oil. Analyzers do not require the use of toxic chemicals either, thus offering a simple, all-inclusive solvent-free system for the testing of dried fruit.

4. FFA and peroxide value test with CDR OxiTester or CDR FoodLab

4.1 CDR OxiTester

Test	Testing time
FFA	1 minute
Peroxide value	4 minutes

CDR OxiTester was conceived further to the need expressed by olive oil producers for the assessment of parameters such as free fatty acids, peroxide value, polyphenols, and K270 directly on the premises of the oil business, or in the oil mill, or upon purchasing the product. CDR instruments enable the determination of these parameters in 1 to 6 minutes without the need for an equipped laboratory or specialized personnel.
CDR OxiTester can be used in any phase of the production chain.
The instrument is easy to use, rapid and reliable as it exploits fine tuned methods specifically designed for the required range of tests. Anyone is able to operate this instrument. Its application in oil mills or in oil businesses testifies to its convenience as the businesses themselves carry out these tests even when they are inexperienced in the field of chemical analyses, or when they cannot avail themselves of specialized staff.

Use CDR OxiTester to test any type of vegetable oil. In fact, its use is widespread and applied in the dried fruit sector to determine the acidity and peroxide value of the oil obtained from the squeezed nut.

4.2 CDR FoodLab

Test	Testing time
FFA	1 minute
Peroxide value	4 minutes
p-Anisidine	2 minutes

CDR FoodLab is an instrument designed to test oils and fats. It is used in several industry sectors.
Besides tests carried out on hard-shelled nuts, it can be used to test the quality of fried oil, vegetable or animal extracted oils, refined fats, vegetable oil fuel or biodiesel, and essential oils.
CDR FoodLab allows for a more in-depth examination compared to CDR OxiTester: its testing range also includes the determination of the p-asnisidine parameter. Primary oxidation products are commonly measured by means of the peroxide value test. Secondary oxidation products are measured by means of the p-anisidine test. The p-anisidine value represents the level of aldehydes and ketones present in fats. P-anisidine is an isomer of anisidine and reacts with aldehydes and ketones, which are responsible for the characteristic rancid odor that occurs at an advanced oxidation stage.
The peroxide value test alone may not help to detect damaged or fats that are not fresh, as it does not take into account secondary oxidation products. The p-anisidine test is therefore useful to perform a more in-depth analysis on the oil extracted from dried fruit as it allows for an assessment of the entire oxidation process.

4.3 Tests

The following table reports a comparison between the tests carried out on nuts using the two instruments:

	FFA	Peroxide value	p-Anisidine
Measurement range	0.01 – 1.1 %	0,1 – 11 (mEqO2/Kg)	0.5 – 100 (An V)
Sample volume	2.5 - 5 and 10 µL	5 and 10 µL	20 µL
Accuracy	+/- 5%	+/- 5%	+/- 5%
Repeatability	CV<3%	CV<3%	CV<5%
CDR OxiTester			
CDR FoodLab			

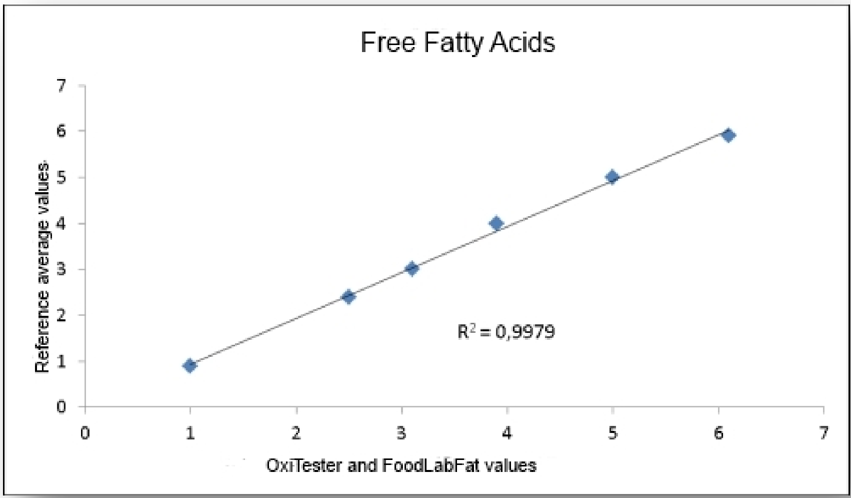
4.4. Simple tests: methods

When examining the parameter of oil acidity, the official method for determining this value is titration (ISO/AOCS reference standards).
Titration is a volumetric analysis, i.e. based on volume measurements. It enables to determine the unknown concentration of a solution by its reaction with a titrant, that is a standard solution whose concentration and volume are known.

This method requires:

- Procedures that can only be performed in a laboratory: the safe handling of noxious substances, such as toxic solvents; the correct washing of glass instruments and components used during the chemical reaction; the use of a fume hood; the compliance with all standard security measures.
- Appropriate equipment and instruments: fume hood, spacious workbenches, burettes, beakers, adequate storage premises for toxic solvents and other chemical substances.
- Specialized personnel: skilled chemists with experience in handling equipment, working in a laboratory in total security, elaborating titration curves and calculating the value of the unknown titer of the solution according to mathematical formulas and statistics foreseen by reference standards.
- Lengthy procedures: titration is a long process that takes at least half an hour.

The CDR OxiTester testing system does not require any of the points above in virtue of its fine tuned methods and, therefore, it accelerates the entire titration procedure while remaining in line with the results obtained through the ISO/AOCS reference standards. In other words, the method changes but not results, guaranteeing accuracy and compliance with official methods.



***Correlation** and **alignment** between the results obtained with **CDR Foodlab analyzers** and the reference standards.*

FFA and peroxide value tests can be performed in a few easy steps and just a few minutes, using one single instrument and saving time. Methods are simple and easy to follow.

5. CONCLUSIONS

The CDR integrated extraction and testing system is widely endorsed and exploited by dried fruit businesses to guarantee the genuineness of the finished product.
The overall characteristics of the system components guarantee the following advantages:

1. Practical and rapid tests
2. Accuracy and reliability
3. No need to rely on external laboratories
4. No maintenance costs

Thanks to its mechanical process and simplified testing methods, this system saves time and offers a flexible range of analyses that can be adjusted to meet the specific demands of the business concerned.

Reference links:

http://www.mark-up.it/

http://www.agraria.org/

http://www.nutfruit.org/en/

http://www.inran.it/646/tabelle_di_composizione_degli_alimenti.html

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