WHITE PAPER

Stability-based value of natural oils: Easy to determine with the Rancimat test

The value of a product and its quality are inherently linked. In the case of fats and oils, this may be difficult to determine by looks alone. Rancidity of such products, especially expensive natural oils from plant sources, is a factor which can immediately reduce the sale price. Oils which remain stable over longer periods of time are more highly valued as they lead to a higher quality end product, such as for foods or in cosmetics.

Rancidity occurs naturally over time as fats and oils age and oxidize. Depending on the source, some oils already contain antioxidants which increases their lifespan. Others may be more sensitive to aging, and require additional antioxidants to extend shelf life and usability.

Determination of rancidity is possible in several manners, such as by measuring the acid number or peroxide value. However, these tests only give information about the current state of the product, with no indication about the remaining shelf life. One analytical method that can measure this time span until spoilage is the Rancimat method.

Here, the sample is subjected to accelerated aging and the «induction time» determines how long the oil remains usable. This method helps manufacturers to better qualify and guarantee the value and quality of their products to customers in the food and cosmetics industries.

Metrohm

WHAT ARE NATURAL OILS

All oils obtained naturally from plants are considered natural oils. This designation does not say anything about the handling of the oil—whether it was obtained natively, by extraction, or by other means.

Oils are categorized differently depending on how they are processed:

– «**Refined oils**» are e.g. hot-pressed at 100 °C, then refined depending on the oil. Here, the oil is additionally hardened and filtered, and preservatives may be added to increase shelf life.

– «**Unrefined oils**» tend to be cold-pressed, but can be heated up to 60 °C during pressing.

– «**Cold-pressed oils**» are oils that do not undergo any external heat input during pressing. The only heat is that which is generated by friction and pressure.

– «**Virgin oils**» are cold pressed, especially in the case of olive oil, where the quality class of native, extra virgin is awarded on the basis of acidity. In order to label olive oil for sale as extra virgin, the acid value (SC) must be below 0.8 g / 100 g.

In the cosmetics industry, various natural oils are used which do not differ significantly from food oils.

COMPOSITION OF OILS

Oils mainly consist of triglycerides (officially known as triacylglycerols, according to IUPAC). Natural oils are primarily composed of triglycerides, in which a single glycerine molecule is esterified with three fatty acids (**Fig. 1**). These fatty acids can have different chain lengths, and their composition depends strongly on the raw material from which they come.

Fatty acids which contain double bonds are called unsaturated fatty acids. The more double bonds a fatty acid has, the easier it can be oxidized. These unsaturated glycerides are also known as essential fatty acid esters.

Natural oils consist of different mixtures of these triglycerides. If the fatty acids are bound to the

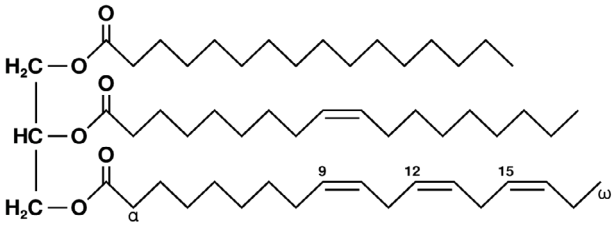

Figure 1. Example of an unsaturated triglyceride ($C_{55}H_{98}O_6$): (L) glycerol, (R) from top to bottom: palmitic acid, oleic acid, and alpha-linolenic acid.

glycerine molecule, they are called bound fatty acids. However, over time these fatty acids decompose – the esters are split, and free fatty acids are obtained. These free fatty acids are determined by the acid number.

The most common fatty acid esters found in natural oils are oleic acids, with a double bond at the ninth C-atom. It is relatively resistant to oxidation, compared to polyunsaturated fatty acids. Linoleic acid is a fatty acid containing two double bonds and is assigned to the class of omega-6 fatty acids. It can be easily oxidized. Linolenic acid is an omega-3 fatty acid and contains three double bonds. It is even easier to oxidize than linoleic acid. Omega-3 and omega-6 fatty acids are both essential fatty acids, i.e. they must be taken in with food as the body cannot produce them itself.

Depending on the type of seed and plant from which they come, the oils obtained differ in composition and in their properties as food oils or cosmetic oils. All vegetable oils mainly consist of oleic acid, linoleic acid, linolenic acid, palmitic acid, and stearic acid. Aside from these fatty acids, the oils also contain various antioxidants such as vitamin A and vitamin E.

RANCIDITY - HOW DOES IT ARISE?

Freshly pressed oils contain unsaturated fatty acids bound to glycerine with different chain lengths and different numbers of double bonds. These are oxidized by the oxygen present in the air. This oxidation process normally proceeds very slowly at room temperature.

All natural oils age over time. Rancidity is caused by oxidation of the fatty acids. This autooxidation of oils and fats is a radical reaction and takes place in three steps.

The first step is the initiation, during which lipid radicals are formed from triacylglycerols. Oils often contain traces of hydroperoxides which may have been formed by lipoxygenase action in the plant before and during oil extraction. Initiation by homolytic cleavage of hydroperoxides is a relatively low-energy reaction, and is therefore normally the major initiation pathway in oils and fats. This reaction is usually catalyzed by metal ions (e.g., iron), and therefore it should be ensured that no metal ions are present in the product.

After initiation, propagation reactions (chain propagation) occur in which one fatty acid radical is converted into other fatty acid radicals. During this reaction, a hydrogen atom is usually removed, or an oxygen radical reacts with the fatty acid. The reaction enthalpy is relatively low compared to the initiation reactions, so that chain propagation is faster in comparison with initiation reactions. Since the bond dissociation energy of the C-H bond is reduced by the adjacent double bonds, the abstraction of hydrogen occurs fastest at the methylene group situated between two alkene groups in a polyunsaturated fatty acid.

Alkoxy radicals formed by hydroperoxide decomposition may decompose and release volatile hydrocarbons, alcohols, or aldehydes that are no longer bound to the glycerol backbone. Volatile aldehydes are particularly important as contributors to the aroma of oxidized oils. One such aldehyde, hexanal, is generally monitored in order to assess the formation of secondary oxidation products during lipid oxidation.

EFFECT OF ANTIOXIDANTS

Antioxidants are defined as substances which are capable of delaying or preventing the development of rancidity or other material deterioration due to oxidation. In general, antioxidants can be said to delay the development of changes in flavor by extending the induction period of oxidation. The addition of antioxidants after this period tends to be ineffective because low molecular weight substances are already present.

Antioxidants can inhibit or delay oxidation in two ways: either by scavenging free radicals, in which case the compound is described as a «primary antioxidant», or by a mechanism that does not involve direct scavenging of free radicals, in which case the compound is a «secondary antioxidant». Primary antioxidants include phenolic compounds such as vitamin E (α-tocopherol). These components are consumed during the induction period. Secondary antioxidants act through a variety of mechanisms, including complexation of metal ions, uptake of oxygen, or conversion of hydroperoxides to non-radical species. Normally, secondary antioxidants only exhibit antioxidant activity when a second component is present. This can be seen with compounds such as citric acid, which are only effective in the presence of metal ions, and reducing agents such as ascorbic acid, which are effective in the presence of tocopherols or other primary antioxidants.

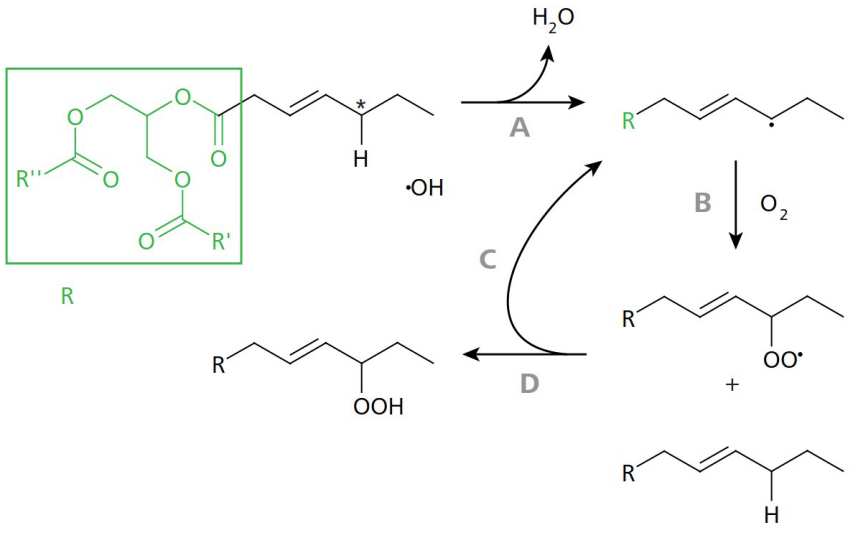

Figure 2. Scheme of peroxidation of a monounsaturated fatty acid. **A:** The methylene group (marked with an asterisk) is particularly susceptible to the cleavage of an H atom due to its position adjacent to the double bond. This leads to a reaction with the hydroxyl radical. **B:** The reactive radical binds to molecular oxygen from the ambient air. **C, D:** A reaction with a "fresh" fatty acid produces a peroxide on the one hand and a free radical on the other – a chain reaction begins.

In addition to synthetic antioxidants, natural antioxidants (e.g., rosemary extract and tea extracts) are also available on the market. When these are added to the natural oils, the oxidation stability of the natural oils can be prolonged if necessary.

A characteristic effect of antioxidants of this type is that they produce a delay time, called the induction period IP, which is usually proportional in duration (or «length») to their concentration, and which lasts until approximately 90% of the antioxidant is destroyed. During this delay time, fatty acid oxidation proceeds very slowly, but once this is used up, oxidation proceeds very quickly.

DETERMINATION OF THE OXIDATION STABILITY WITH THE RANCIMAT

The determination of the oxidation stability is an accelerated oxidation test. In this test, a sample is kept at a constant temperature in a closed reaction vessel, and a continuous flow of air is passed through the sample. Peroxides are formed as primary oxidation products via oxidation of fatty acids in the sample. After some time, the fatty acids are completely destroyed and low-molecular weight organic acids (especially formic and acetic acid) are formed as secondary oxidation products, in addition to other volatile organic compounds.

These secondary oxidation products are conducted by the airflow into a measuring vessel which contains distilled water as an absorption solution. The conductivity of this water is continuously recorded. As soon as volatile carboxylic acids are formed in the sample, this is registered by the increase in conductivity in the measuring vessel. The time until the secondary oxidation products occur is called the «induction time» and is a measure of the oxidation stability of the sample.

The 892 Rancimat has two independent measuring blocks that allow up to eight samples to be measured simultaneously. The measurement of each sample can be started individually. A measuring station is thus immediately available for a new sample at the end of the measurement, and the instrument can therefore be used to its full capacity. The simple and clear design of the measuring instrument also helps to keep track of a larger number of samples. The airflow through the sample is generated by a built-in pump and automatically controlled according to the method settings. Gas pressure lines for the air supply are not necessary.

Preparations for a measurement on the Metrohm 892 Professional Rancimat are very simple: The sample is weighed into the reaction vessel and the measuring cell is filled with distilled water. After connecting two tubes, the determination can be started.

The 892 Professional Rancimat uses inexpensive disposable reaction vessels. On the one hand, this eliminates the usually time-consuming cleaning procedure at the end of the measurement, and on the other hand, it improves the reproducibility of the determinations and thus the reliability of the results.

The conductivity measuring cell is integrated in the lid of the measuring vessel. When the lid is put on, the cell is immersed in the distilled water. At the same time, electrical contact is made with the measuring electronics in the instrument, eliminating the need for cumbersome wiring of the measuring input. The conductivity electrode also impresses with its robust design. It does not mind a thorough cleaning with a brush.

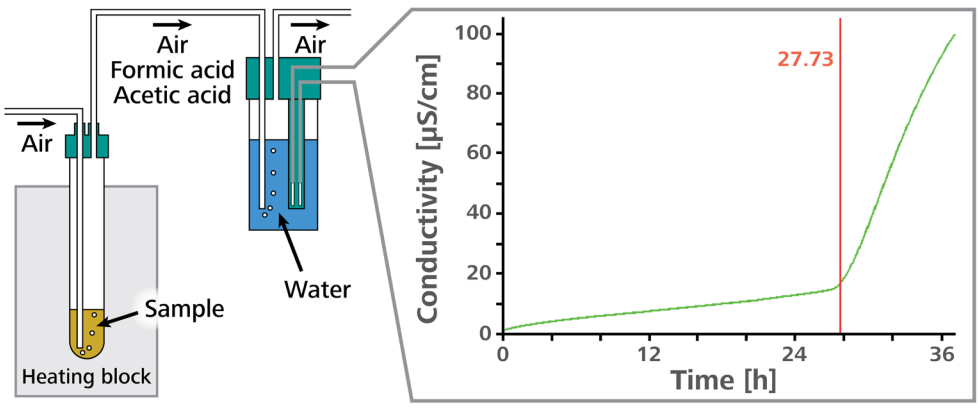

Figure 3. Schematic representation of a measurement with the Rancimat.

Figure 4. By using inexpensive disposable reaction vessels, the 892 Rancimat can be used efficiently, as time-consuming cleaning steps are no longer necessary.

What can take weeks, months, or even years on the shelf can be done in the Rancimat within mere hours.

There is a causal relationship between the induction time and the composition of the oil: the more unsaturated fatty acids present, the higher the acid number, and the less antioxidants (vitamin E, vitamin A) present in the oil, the shorter the induction time.

Depending on the natural oil age of the sample and composition, a different induction time is obtained.

OXIDATION STABILITY OF COSMETICS

Many natural cosmetics, but also other high-quality cosmetic products, contain a high proportion of vegetable oils and fats. For example, cocoa butter is a component of many lip and body care products. Unlike paraffin-based products, these cosmetics spoil over time, among other reasons due to oxidation of the vegetable fats they contain. Depending on the fat content, the samples can either be measured directly with the 892 Professional Rancimat, or the isolated fat after cold extraction with petroleum ether. Natural oils used can be measured directly.

The following table shows induction times for various natural oils. The results can be used as an indication of what the respective oil delivers in terms of results with the respective method.

Natural oil	Temp. (°C)	Induction period (h)
Acai fruit oil, org.	120	16.46
Algae oil	120	2.63
Almond oil cold-pressed, org.	120	3.10
Almond oil cold-pressed, org. and demeter	120	2.64
Apricot kernel oil cold-pressed, org.	120	7.51
Argan oil cold-pressed, org.	120	7.14
Argan oil deodorized, org.	120	5.56
Argan oil, org.	120	6.52
Avocado oil	120	2.34
Avocado oil cold-pressed, org.	120	8.39
Avocado oil, org.	120	4.70
Baobab, org.	120	3.34
Beeswax	160	1.87
Black seed oil, org.	120	1.58
Cashew oil CO_2 extraction, org.	120	6.55
Castor oil	150	10.02
Chia oil cold-pressed, org.	120	0.15
Coconut oil, org.	160	3.49
Coconut oil, org.	120	76.05
Cranberry seed oil cold-pressed, org.	120	1.70
Evening primrose oil	120	0.64
Evening primrose oil, org.	120	0.72
Hemp oil, org.	120	0.97
Hemp seed oil cold-pressed, org.	120	1.23
Hexadecan-1-ol, cetyl alcohol	140	2.90
Jojoba oil cold-pressed, org.	120	24.33
Jojoba oil cold-pressed, org. and demeter	120	25.01
Jojoba oil refined, org.	120	16.26
Jojoba oil, org.	120	23.73
Jojoba oil, org.	140	4.18
Lanolin, wool wax	120	3.11
Linseed oil, org.	120	0.80
Macadamia nut oil, org.	120	10.99
Mango butter, refined	120	11.15
Mango butter, refined	130	5.14
Marula oil cold-pressed, org.	120	44.11
Neem oil, org.	110	5.74
Octadecan-1-ol, stearyl alcohol	140	3.47
Pomegranate oil, org.	100	0.86
Sacha inchi oil cold-pressed, org.	120	1.11
Sea buckthorn oil, org.	120	35.58
Sea buckthorn seed oil CO_2 extraction, org. (n = 3)	120	0.39
Sesame oil	120	3.75
Sesame oil, org.	120	3.65
Shea butter raw, org.	120	0.91
Shea butter refined, org.	120	3.91

Shea butter, org.	120	9.18
Shea butter, refined	120	8.39
Shea butter, unrefined	120	2.85
Shea nut oil, refined	120	1.51
Sweet almond oil, org.	120	1.47
Wheat germ oil CO_2 extraction, org.	120	1.73

CONCLUSION

Classical fat parameters such as the acid number or peroxide value only describe the current status of oils and fats. However, they can only be used to make limited predictions about the remaining shelf life of the product, which is an important factor to determine the value of oils produced for food or cosmetic uses. This knowledge gap can be closed with the induction time as an additional fat index parameter, which is easily measured with the Rancimat from Metrohm.

The induction time reflects the interaction of bound and free fatty acids, the number of double bonds, existing antioxidants and existing pro-oxidants at elevated temperatures. This gives an overall picture of the quality of an oil and how it will behave over time.

The extraction method used plays a decisive role, particularly in situations where natural oils contain a high proportion of unsaturated fatty acids. In this case the Rancimat method offers a clear basis for deciding which method is most suitable. A natural oil that is rancid cannot be reversed. However, if it is known that the natural oil will become rancid in the near future, this process can be slowed or even prevented by adding natural antioxidants (e.g., rosemary extract, tea extract, or vitamin E) in advance.

Therefore, measuring induction time on the Rancimat allows manufacturers to get as much value from the oil as possible by determining the shelf life and deciding if further actions are needed to extend it prior to sale.

References

[1] ISO/TR 18811:2018 Cosmetics – Guidelines on the stability testing of cosmetic products
https://www.iso.org/standard/63465.html

[2] ISO 16128-1:2016 Guidelines on technical definitions and criteria for natural and organic cosmetic ingredients and products — Part 1: Definitions for ingredients
https://www.iso.org/standard/62503.html

[3] ISO 16128-2:2017 Cosmetics — Guidelines on technical definitions and criteria for natural and organic cosmetic ingredients — Part 2: Criteria for ingredients and products
https://www.iso.org/standard/65197.html

[4] Stability Application Note **R-029**: Oxidation stability of cosmetic raw materials
https://www.metrohm.com/en/applications/AN-R-029

[5] Oxidation in foods and beverages and antioxidant applications Volume 2: Management in different industry sectors **ISBN 978-0-08-101457-8**

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