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Oxidation stability in solid food products – Rancimat method

Industry sector

Food & beverage

Keywords

Stability; oxidation stability; antioxidant content; stability index; SI; rancidity; antioxidants; Rancimat; 892 Professional Rancimat; PEG; polyethylene glycol; sample preparation; oxidative stability; oil; fat; extraction; petroleum products; lard; pure lard; butter cookies; muffins; potato chips; potato crackers; peanut curls; almonds; peanuts; instant noodles; soup pearls; hazelnuts; Kitsune Udon noodles; Yakisoba noodles; breadcrumbs; cookies; wheat; wheat flour; coconut; cereals; instant drink powder; polenta; corn; 2.892.0010; 6.5616.100; 6.0913.130; 6.6068.202; AOCS Cd 12b-92; EN ISO 6886; JOCS 2.5.1.2-1996; S07; S070; S071; S072; S073; S076; S077; S078; S079

Summary

The Rancimat method, also called oxidation stability index (OSI), is an accelerated aging test. Air passes through a sample in the reaction vessel at constant elevated temperature. Fatty acids are oxidized in this process. At the end of the accelerated oxidation test, volatile secondary reaction products are formed, transported into the measuring vessel via the air stream, and absorbed in the measuring solution (deionized water). The continuously recorded electrical conductivity of the measuring solution increases due to the absorption of the reaction products. Thus, their appearance can be detected. The time until secondary reaction products are detected is called the induction time. It characterizes the oxidation stability of oils and fats.

The determination of the oxidation stability of solid food is important for quality control in the corresponding industry. The oxidation stability of fats and oils in solid foodstuffs is directly measured if possible, or by using the isolated fat after cold extraction with petroleum ether if the samples cannot be measured directly.

In addition to direct measurement, the PEG (polyethylene glycol) method has proven to be an additional reliable way to test OSI with a Rancimat. The method is especially well-suited for products with a complex matrix or when time-consuming sample preparation should be avoided. This approach does not directly measure the oxidative stability of the sample; rather, it measures its influence on the oxidative stability of the PEG.

Another established method is the determination of the stability index (SI), which is a measure of the antioxidant capacity of a product. Here, the sample is mixed with a reference of antioxidant-free fat (e.g., pure lard), and the induction time is then compared with the reference alone as a control. It is evident that, owing to its inherent properties, the product exerts a retarding effect on the oxidation of the reference. The lard method is no longer widely used because pure lard is not available in all countries and is not offered in a standardized form. Conversely, the aforementioned method using PEG has demonstrated a high degree of reliability and ease of standardization.

This Application Bulletin contains a comprehensive description of all the Rancimat test methods mentioned, as well as the requisite steps for sample preparation.

The 892 Professional Rancimat is an analysis system that has been developed for the simple and reliable determination of the oxidation stability of solid food using the proven Rancimat method. The apparatus is equipped with eight measuring positions which are distributed across two heating blocks. Its integrated display provides a visual representation of the device's status and the status of each individual measuring position. Initiation of measurements is facilitated by buttons designated for each measuring position, thereby enabling the commencement of the measurement process directly on the device. The cleaning effort required can be minimized by utilizing practical disposable reaction vessels and dishwasher-safe accessories. This approach has been shown to foster significant gains in terms of time and cost efficiency while enhancing the accuracy and reproducibility of the process.

Please note that all the accessories needed for the aforementioned determinations are included within the scope of delivery. The StabNet software is required for the control of devices, the acquisition and evaluation of data, and the storage of data.

Oxidation stability of fats and oils in solid food products

Instruments and accessories

- 892 Professional Rancimat
- Equipment for the determination of the temperature correction
- Measuring vessels for stability measurements
- Reaction vessels for stability measurements
- Auxiliary instruments for sample preparation

Electrode

Measuring vessel cover with built-in conductometric measuring cell	6.0913.130

Reagents

- Deionized water
- Polyethylene glycol, PEG, Mean molecular weight 3000 g/mol
- Petroleum ether, low boiling, bp 30–40 °C, puriss. p.a.

Sample preparation

Fat-containing solids – Direct measurement

Solids with a high amount of fat, such as nuts and oil seeds (e.g., hazelnuts, almonds, sunflower seeds, sesame seeds, etc.), can be measured directly. Before the sample is weighed in, it must be crushed and homogenized, e.g., by a mortar. Care must be taken so that the sample is not overheated nor contaminated by traces of transition metals.

Fat-containing solids – Cold extraction

Fat from samples with a complex matrix (e.g., foodstuffs like mayonnaise, powdered milk, chocolate, biscuits, etc.) could be extracted before the determination. This is preferably done by cold extraction since heating alters the fat. Before extraction, the sample must be crushed if it is not already liquid or powdered. Enough sample to extract approximately 10 g fat (sufficient for two measurements) is weighed into a conical flask. Approximately three times the sample volume of low-boiling petroleum ether is added. The extraction is performed by stirring for at least one hour. The petroleum ether phase is then separated from the residues by either filtering (for solid samples) or by a separating funnel (for liquid samples) and transferred into a round bottom flask. The petroleum ether is distilled off at 20–30 °C under vacuum, e.g., with a rotary evaporator.

Fat-containing solids – PEG Method

When measuring stability with the Rancimat, the PEG method has proven to be the most effective method in addition to direct measurement. It is particularly suitable for products with a difficult matrix or when time-consuming sample preparation should be avoided.

The principle is based on the ability of the sample's own antioxidants to stabilize the induction time of the PEG. The induction time can therefore be used directly in connection with the oxidation stability of the sample.

Typically, 3 g of PEG is used as a carrier and depending on the antioxidant content, a few milligrams to 1 g of sample is added. Liquid or creamy samples do not require any sample preparation, while solid samples should be crushed if possible.

Analysis

Preparation of the Rancimat

The heating block is heated up to the respective temperature.

Before the first analysis is started, it is recommended to perform a temperature correction for each 892 Professional Rancimat heating block for each air flow. The temperature correction is automatically stored in the software and should be repeated every few months as required.

Preparation of the measuring vessel

A volume of 60 mL deionized water was added to each measuring vessel, and each vessel was placed on the 892 Professional Rancimat together with the measuring vessel cover. The displayed conductivity must not exceed 10 µS/cm. For long analysis times (>72 h), it is recommended to increase the volume to compensate for evaporation loss. An evaporation rate of 5–10 mL water per day must be considered. Ensure that the electrode is immersed into the measuring solution at all times.

Preparation of the reaction vessel

For each determination, a new reaction vessel is used. Particles (e.g., from the cardboard box) are removed from inside and outside the reaction vessel by blowing them away with a sharp stream of pressurized nitrogen gas. Then the sample is weighed directly into the reaction vessel.

A sample size of 3.00 g ± 0.10 g is used for extracted fat, liquid samples, and samples that melt at elevated temperatures. For samples with significant water content (>5%)

the sample size must be increased to compensate for the decrease in volume when the water evaporates.

Solid samples which do not melt should only cover the bottom of the reaction vessel. In this case, 0.5–1 g of the powdered sample is weighed into the reaction vessel.

For measurement of samples with PEG as carrier material, 3.00 g ± 0.10 g polyethylene glycol and a suitable amount of sample (depending on antioxidant content) is weighed into the reaction vessel.

The reaction vessel is closed with a reaction vessel cover which is assembled with an air inlet tube. Ensure that the air inlet tube is always immersed in the sample.

Determination

Before the determination can be started, the temperature of the heating block must be stable. The two tubings between Rancimat and reaction vessel and between reaction vessel and measuring vessel are connected. Then the reaction vessel is placed in the heating block and the measurement is started immediately.

Parameters

Sample size	Extracted fat: 3.00 g ± 0.10 g Solid samples (direct measurement): 0.50–1.00 g Samples with PEG: 3.00 g ± 0.10 g PEG and 0.05–1.00 g sample
Measuring solution	60 mL
Temperature	80–160 °C
Temperature correction	auto
Gas flow (air)	20.0 L/h
Conductivity	400 µS/cm
Endpoint(s)	yes
Stop once all the criteria have been fulfilled	yes
Evaluation	Induction time
Evaluation sensitivity	1.0

The measuring temperature depends on the oxidation stability of the sample. For the sample types described in this document, usually temperatures between 80 °C and 160 °C are appropriate. Temperatures of 50 °C to 220 °C are possible. Most tests are carried out at 120 °C (lower stability – lower temperature). The rule of thumb is a temperature increase of 10 °C lowers the induction time by a factor of two.

Results

Solid samples, direct determination

Table 1. Typical results for the oxidation stability of solid samples by direct determination.

Sample	Temperature in °C	Induction time in h
Butter cookies	120	approx. 24
Butter cookies	160	approx. 6
Muffins (Magdalenas)	120	approx. 10
Coconut flakes	160	approx. 17
Hazelnuts	120	approx. 22
Instant noodles	120	15–30
Kitsune Udon noodles	120	approx. 15
Yakisoba noodles	120	approx. 21
Peanuts	120	approx. 3
Peanut curls	120	approx. 8
Almonds	120	approx. 8
Potato chips (crackers)	120	approx. 29
Potato chips (crackers)	140	approx. 10
Soup pearls	120	approx. 8

Solid samples after cold extraction

Table 2. Typical results for the oxidation stability of solid samples after cold extraction.

Sample	Temperature in °C	Induction time in h
Baby food	120	1–2
Hazelnuts	120	7–13
Butter cookies	120	approx. 28
Peanuts	120	1–2
Potato chips (crackers)	140	approx. 2
Powdered milk	120	4–32
Popcorn grains	120	approx. 4
Olive paste	120	approx. 20
Sausage	120	4–6

Solid samples, PEG method

Table 3. Typical results for the oxidation stability of solid samples by PEG method.

Sample	Temperature in °C	Induction time in h
Fish food	120	2–4
Sausages	120	1–3
Dog treats	110	1 –2
Green tea	130	4–12
Coffee (powder)	120	2–12
Chocolate	120	1–4
Rosemary (chopped)	120	8–9
Black pepper (ground)	120	1–3

Example

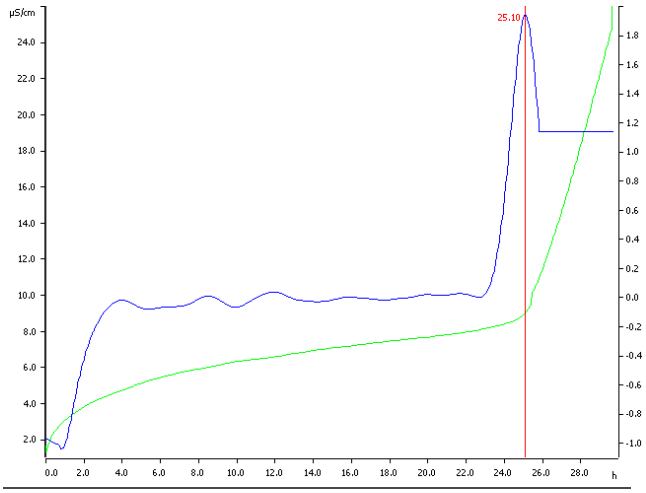

Figure 1. Determination of the oxidation stability of butter cookies at 120 °C (direct determination).

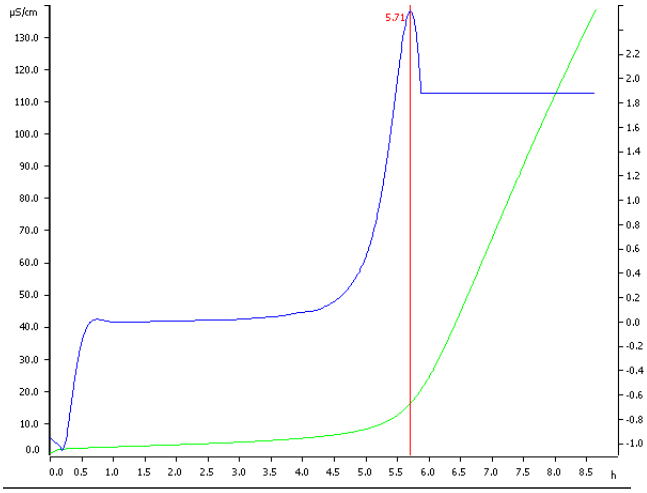

Figure 2. Determination of the oxidation stability of sausage at 120 °C after cold extraction.

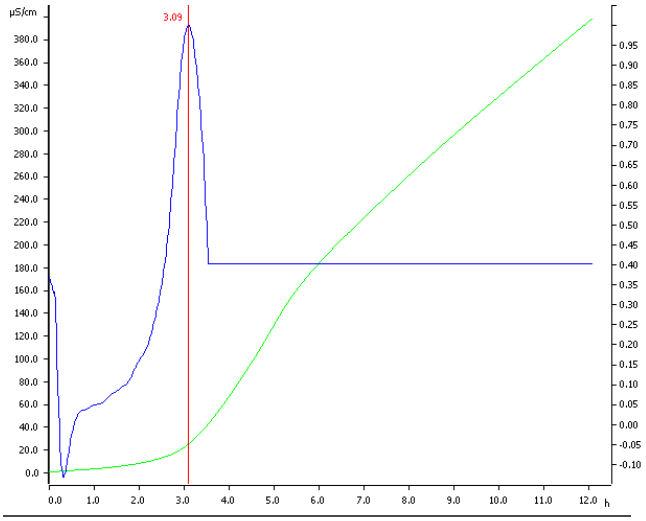

Figure 3. Determination of the oxidation stability of black pepper at 120 °C with PEG as carrier material.

Comments

Any kind of contamination, particles, or even scratches in the glass can catalyze reactions and thereby affect the result. Sample contamination may deteriorate the reproducibility of the results or cause incorrect results. Therefore, it is recommended to use a new reaction vessel and air tube for each determination, and remove particles by using a sharp stream of N_2 gas.

The temperature is the most crucial parameter in the determination of the induction time. It is essential to determine the «temperature correction» value correctly, especially if results from different instruments must be compared. For more information about the «temperature correction» and its determination, see the StabNet software tutorial and the 892 Professional Rancimat instrument manual.

The gas flow is relevant for the application to guarantee a sufficient supply of oxygen for the oxidation of the fatty acids and to reliably transfer the reaction products from the reaction vessel to the measuring vessel. Furthermore, the gas flow mixes the sample and thereby ensuring a homogeneous sample temperature. Beyond that, there is no influence of the gas flow on the result if the cooling effect is compensated for by the correct adjustment of the «temperature correction».

The analysis of samples can be conducted through two primary methodologies: direct measurement and cold extraction. It is important to note that the results obtained from direct measurement and cold extraction differ due to the influence of the sample matrix on the oxidation reaction.

Sample size can be a critical parameter for the direct determination of solid samples. Since the air stream cannot mix the sample, no homogeneous temperature can be guaranteed in larger volumes. Hence, a small sample size that just covers the bottom of the reaction vessel is preferred.

Polyethylene glycol (PEG) 3000 is suitable as a carrier material for oxidation stability for many reasons. It is non-toxic, inert, storage stable, cheap, and easily available. At room temperature, it is solid and therefore easy to handle (for example, for weighing). The melting point is approximately 55 °C. Therefore, PEG 3000 is liquid when used as a carrier material in the Rancimat (enclosing the sample and conducting the temperature quickly and optimally). The ignition temperature is 420 °C, so there are no dangers for the user. Additionally, PEG 3000 can be disposed of as household waste.

Stability index (SI) of solid food products

Instruments and accessories

- 892 Professional Rancimat
- Equipment for the determination of the temperature correction
- Measuring vessels for stability measurements
- Reaction vessels for stability measurements
- Auxiliary instruments for sample preparation

Electrode

Measuring vessel cover with built-in conductometric measuring cell	6.0913.130

Reagents

- Deionized water
- Pure lard (control sample)

Sample preparation

Samples that were grainy were used immediately. Samples like butter cookies, hazelnut cookies, and breakfast cereals were crushed with a mortar and pestle to make them less than 1 mm in diameter.

Pure lard is heated to 50 °C in a closed flask in a thermostatic bath for 30 minutes to melt. The lard was melted so that it could be mixed with the sample in the measuring vessel. The same process was used for the control group.

Analysis

Preparation of the Rancimat

The heating block is heated up to the respective temperature.

Before the first analysis is started, it is recommended to perform a temperature correction for each 892 Professional Rancimat heating block for each air flow. The temperature correction is automatically stored in the software and should be repeated every few months as required.

Preparation of the measuring vessel

A volume of 60 mL deionized water was added to each measuring vessel, and each vessel was placed on the 892 Professional Rancimat together with the measuring vessel cover. The displayed conductivity must not exceed 10 µS/cm. For long analysis times (>72 h), it is recommended to increase the volume to compensate for evaporation loss. An evaporation rate of 5–10 mL water per day must be considered. Ensure that the electrode is immersed into the measuring solution at all times.

Preparation of the reaction vessel

A new reaction vessel is used for each determination. Particles (e.g., from the cardboard box) are removed from inside and outside the reaction vessel by blowing them away with a sharp stream of pressurized nitrogen gas. The sample is then weighed directly into the reaction vessel.

For the control, 3.00 g ± 0.10 g of melted pure lard were used. For the samples, 0.50 ± 0.05 g of sample and 2.50 ± 0.10 g of melted lard were used. When adding the sample, make sure it doesn't stick to the side walls.

The reaction vessel is closed with a reaction vessel cover assembled with an air inlet tube. Ensure that the air inlet tube is always immersed in the sample.

Determination

Before the determination can be started, the temperature of the heating block must be stable. The two tubings between Rancimat and reaction vessel and between reaction vessel and measuring vessel are connected. Then the reaction vessel is placed in the heating block and the measurement is started immediately.

Parameters

Sample size	Control sample: 3.00 g ± 0.10 g Solid samples: 0.50 ± 0.05 g of sample and 2.50 ± 0.10 g of melted lard
Measuring solution	60 mL
Temperature	110 °C
Temperature correction	auto
Gas flow (air)	20.0 L/h
Conductivity	100 µS/cm
Endpoint(s)	yes
Stop once all the criteria have been fulfilled	yes
Evaluation	Induction time
Evaluation sensitivity	1.0

Calculations

Stability Index (SI)

$$SI = \frac{\text{Induction time of sample/lard mixture}}{\text{Induction time of pure lard}}$$

SI: Stability Index without unit
Induction time: Induction time in h

Results

Table 4. Typical results for the induction time for the stability index (SI) of solid samples when mixed with pure lard (control sample).

Sample	Induction time in h	Stability index (SI)
Control sample	1.96	N/A
Breadcrumbs	2.16	1.10
Instant malt dairy drink powder	2.37	1.21
Breakfast cereal I	2.55	1.30
Polenta	2.87	1.47
Durum wheat semolina	2.98	1.52
Grated dried coconut	3.17	1.62
Wheat flour	3.38	1.73
Chocolate sprinkles	3.46	1.77
Breakfast cereal II	4.05	2.07
Butter cookies	4.33	2.21
Hazelnut cookies	4.52	2.31

Example

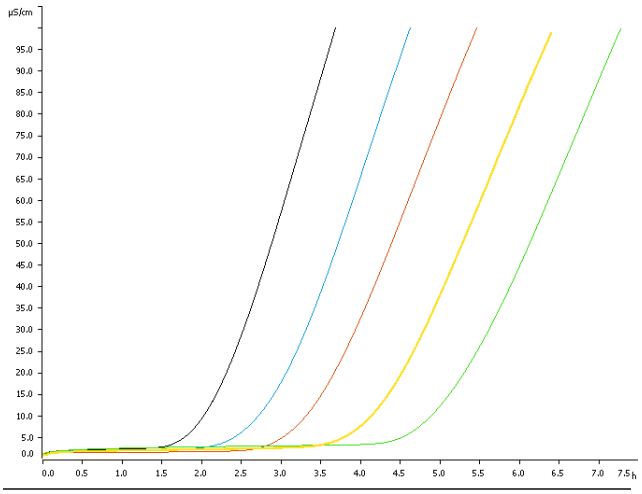

Figure 4. Comparison of the oxidation stability for the stability index (SI) of control sample (black) when mixed with pure lard, polenta (blue), wheat flour (red), breakfast cereal II (yellow), and butter cookies (green).

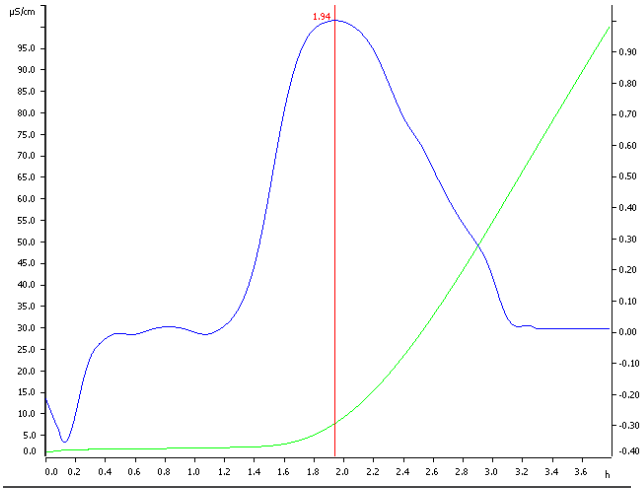

Figure 5. Determination of the oxidation stability of pure lard (control sample) at 110 °C.

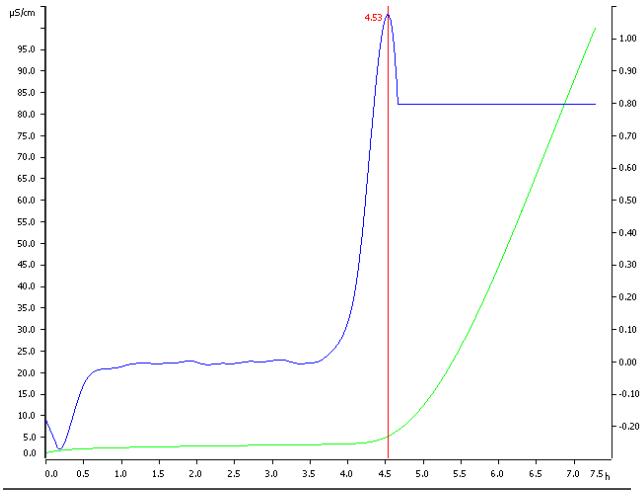

Figure 6. Determination of the oxidation stability of butter cookies in pure lard at 110 °C.

Comments

Any kind of contamination, particles, or even scratches in the glass can catalyze reactions and thereby affect the result. Sample contamination may deteriorate the reproducibility of the results or cause incorrect results. Therefore, it is recommended to use a new reaction vessel and air tube for each determination and blow away particles with a sharp stream of N_2 gas.

The temperature is the most crucial parameter in the determination of the induction time. It is essential to determine the «temperature correction» value correctly, especially if results from different instruments must be compared. For more information about the «temperature correction» and its determination, see the StabNet software tutorial and the 892 Professional Rancimat instrument manual.

The gas flow is relevant for the application to guarantee a sufficient supply of oxygen for the oxidation of the fatty acids and to reliably transfer the reaction products from the reaction vessel to the measuring vessel. Furthermore, it mixes the sample and thereby ensures a homogeneous sample temperature. Beyond that, there is no influence of the gas flow on the result if the cooling effect is compensated for by the proper adjustment of the «temperature correction».

The induction time of the control sample (pure lard) should be determined frequently, i.e., once per week. Also, care must be taken to ensure that the lard in the sample/lard mixture is from the same batch (or package) as the pure lard reference, since the induction time may differ between lard batches.

Pure lard should always be used fresh and stored in a refrigerator at approximately 5 °C.

The melting of lard has no effect on its induction time. This was tested with pure lard that was not heated before the measurement. Without melting, pure lard had an induction time of 2.55 h with SD(abs) = 0.08 h (n = 4), which was not significantly higher than the values derived when melted, i.e., 2.49 h with SD(abs) = 0.06 h (n = 4).

It is also possible to melt lard in a closed bottle within a heated oven. In this instance, 20 g of pure lard are measured and transferred into a glass bottle that has been meticulously cleaned. The bottle is then sealed with a screw cap. The glass bottle is then placed in a heated oven set at 50 °C for a duration of 30 minutes. Subsequently, the lard assumes a transparent liquid form, rendering it readily miscible with the product. It has been demonstrated that this melting procedure does not have an impact on the induction time. It has been established that 30 minutes represents the maximum time necessary for lard to be liquefied at 50 °C. It has been shown that with increased treatment duration or elevated melting temperatures, the induction time is reduced in comparison to the untreated reference sample.

References

AOCS Cd 12b-92
Oil Stability Index – Commercial Fats and Oil

DIN EN ISO 6886
Animal and vegetable fats and oils – Determination of oxidative stability (accelerated oxidation test)

2.5.1.2-1996
(JOCS – Japan Oil Chemists' Society): Fat stability – CDM Conductometric Determination Method

Pokhrel, K.; Kouřimská, L.; Rudolf, O.; Tilami, S. K. Oxidative Stability of Crude Oils Relative to Tocol Content from

Eight Oat Cultivars: Comparing the Schaal Oven and Rancimat Tests. *Journal of Food Composition and Analysis* **2024**, *126*, 105918. https://doi.org/10.1016/j.jfca.2023.105918.

Läubli M. W., Bruttel P. A.: Determination of the oxidative stability of fats and oils: Comparison between the active oxygen method (AOCS Cd 12-57) and the Rancimat method, JAOCS 63 (1986) 792-795.

Läubli M. W., Bruttel P. A., Schalch E.: A modern method of determining the oxidative stability of fats and oils, Int. Food Marketing & Technology 1 (1988) 16-18.

Warner K., Frankel E.N., Mounts T.L.: Flavor and oxidative stability of soybean, sunflower and low erucic acid rapeseed oils, JAOCS 66 (1989) 558-564.

Brochure: 892 Professional Rancimat, 8.892.5001

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