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Oxidation stability of oils and fats – Rancimat method

Industry sector

Pharmaceuticals; petroleum & petrochemicals; polymers & plastics; food & beverage; personal care & cosmetics

Keywords

Stability; oxidation stability; antioxidant content; rancidity; antioxidants; Rancimat; 892 Professional Rancimat; PEG; polyethylene glycol; sample preparation; oxidative stability; oil; fat; cosmetics; extraction; petroleum products; 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; S04; S040; S043; S044; S05; S050; S051; S06; S060; S07; S070; S071; S072; S073; S076; S077; S078; S079; S12; S120; S122; S123

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 and are 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 induction time. It characterizes the oxidation stability of oils and fats.

The determination of the oxidation stability of fats and oils is important for quality control in the food industry. Not only can liquid samples be measured by the Rancimat analysis, but also solid foodstuffs. 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.

Furthermore, when OSI testing with the Rancimat, the new PEG (polyethylene glycol) method has proven to be the most effective method aside from direct measurement. It is particularly suitable for products with difficult matrices or when time-consuming sample preparation should be avoided.

This Application Bulletin provides a detailed description of all the mentioned Rancimat test methods and the requisite sample preparation steps.

The 892 Professional Rancimat is an analysis system for the simple and safe determination of the oxidation stability of natural fats and oils with the well-established Rancimat method. The instrument has eight measuring positions in two heating blocks. Its built-in display shows the status of the instrument and each individual measuring position. Start buttons for every measuring position enable simple analysis. Cleaning effort can be minimized by using practical disposable reaction vessels and dishwasher-safe accessories. This saves time and costs and significantly improves accuracy and reproducibility.

All accessories necessary for carrying out determinations are included in the scope of delivery. The StabNet software is required for instrument control, data recording and evaluation, and for data storage.

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

Liquid oils

Liquid oils are a group of vegetable or animal fats that are liquid at room temperature (e.g., extra virgin olive oil, canola oil, sunflower oil, palm oil) and can be measured

directly. A disposable plastic Pasteur pipette is used to weigh the sample directly into the reaction vessel.

Solid fats

Solid fats are a group of vegetable or animal fats which are solid at room temperature and melt at elevated temperature (e.g., coconut oil, chicken fat, or lard) and can be measured directly. In case of difficulty weighing the sample into the bottom part of the reaction vessel, the sample can be melted first with a water bath. Care must be taken that the water bath temperature is not much higher than the melting point of the sample, otherwise sample deterioration can be expected.

Water-containing fats

Water-containing fats (e.g., butter, margarine) can also be weighed in directly. The sample size must be increased to compensate the sample loss caused by evaporation of the contained water.

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 that the sample is not overheated and not 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.) can be extracted before the determination. This is preferably done by cold extraction since heating the sample would alter the fat. Before the extraction, the sample has to 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 triple 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 in case of solid samples, or via separation funnel in case of 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.

All samples – PEG method

When measuring stability with the Rancimat, the PEG method has proven to be the most effective method aside from 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 set directly in connection with the oxidation stability of the sample.

Typically, 3 g of PEG is used as a carrier and a few milligrams to 1 g of sample is added, depending on the antioxidant content. Liquid or creamy samples do not require any sample preparation, although 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 time 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

60 mL deionized water is added to each measuring vessel before placement 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 evaporation loss. An evaporation rate of 5–10 mL water per day has to 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) were removed from inside and outside of the reaction vessel by blowing them away with a focused stream of pressurized nitrogen. Then sample is weighed directly into the reaction vessel.

For liquid samples and for samples that melt at elevated temperatures, a sample size of 3.00 g ± 0.10 g is used. For samples with significant water content (>5%), the sample size has to be increased to compensate 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 in the reaction vessel.

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 the Rancimat and reaction vessel and between the 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	Liquid samples: 3.00 g ± 0.10 g Solid samples: 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 from 50 °C to 220 °C are possible. Most tests are carried out at 120 °C (lower stability – lower temperature). The rule of thumb is that a temperature increase of 10 °C lowers the induction time by a factor of two.

Results

Vegetable oils and fats

Table 1. Typical results for the oxidation stability of vegetable oils and fats.

Sample	Temperature in °C	Induction time in h
Canola oil	130	12–17
Canola oil, hydrogenated	140	10–11
Citrus oil	90	approx. 0.5
Cocoa butter	120	9–15
Coconut oil	160	approx. 3
Coffee oil	110	approx. 0.25
Corn oil	120	approx. 5
Cottonseed oil	120	2–3
Hazelnut fat	120	10–12
Hazelnut oil	120	7–11
Linseed oil	110	0.5–2
Margarine	120	2–6
Olive oil	120	6–11
Orange oil	90	approx. 2
Palm oil	120	7–12
Peanut fat	120	9–10
Peanut oil	120	3–15
Pumpkin seed oil	120	approx. 7
Rapeseed oil	120	3–5
Safflower oil	120	1–2
Sesame oil	120	approx. 5
Soybean oil	120	1–7
Sunflower oil	120	1–4

Sweet almond oil	120	approx. 4
Walnut oil	120	approx. 2

Animal oils and fats, direct determination

Table 2. Typical results for the oxidation stability of animal oils and fats by direct determination.

Sample	Temperature in °C	Induction time in h
Butter	120	3–6
Chicken fat	110	approx. 0.5
Fish oil	80	approx. 0.25
Kidney fat	110	3–4
Lard	100	1–3
Pigeon (squab) fat	110	approx. 0.3
Tallow	120	3–8

Solid samples, direct determination

Table 3. Typical results for the oxidation stability of solid samples by direct determination.

Sample	Temperature in °C	Induction time in h
Butter cookies	160	approx. 6
Coconut flakes	160	approx. 17
Hazelnuts	120	approx. 22
Instant noodles	120	15–30
Peanuts	110	approx. 10
Potato chips (crackers)	140	approx. 10

Solid samples after cold extraction

Table 4. Typical results for the oxidation stability of solid samples after cold extraction with petroleum ether.

Sample	Temperature in °C	Induction time in h
Baby food	120	1–2
Hazelnuts	120	7–13
Mayonnaise	120	1–4
Peanuts	120	1–2
Potato chips (crackers)	140	approx. 2
Powdered milk	120	4–32
Salad dressing	120	approx. 2

Samples, PEG method

Table 5. Typical results for the oxidation stability of samples by the PEG method.

Sample	Temperature in °C	Induction time in h
Moisturizing cream	120	0.5–2
Sausages	120	1–3
Liquors	120	1–3
Green tea	130	4–12
Coffee	120	2–12
Chocolate	120	1–4
Tobacco	120	1–2

Examples

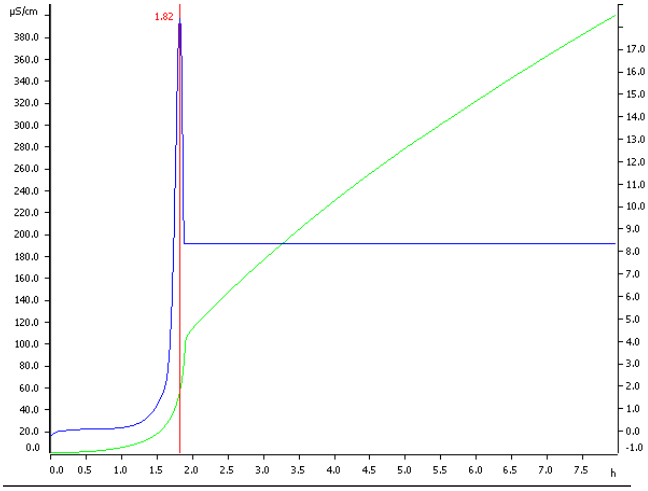

Figure 1. Determination of the oxidation stability of sausage at 120 °C with PEG as carrier material.

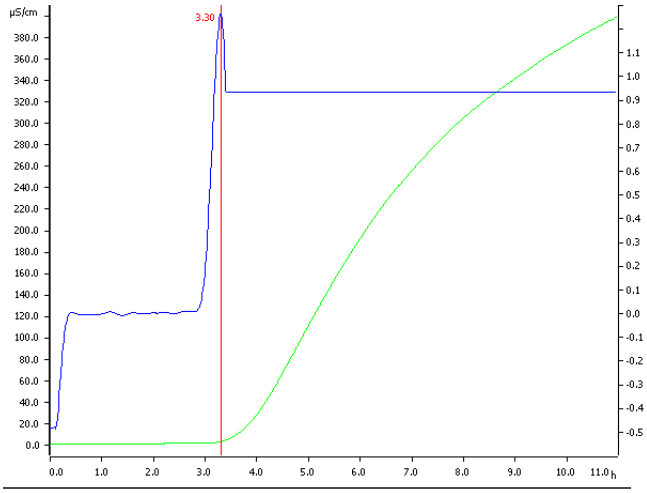

Figure 2. Determination of the oxidation stability of coconut oil at 160 °C.

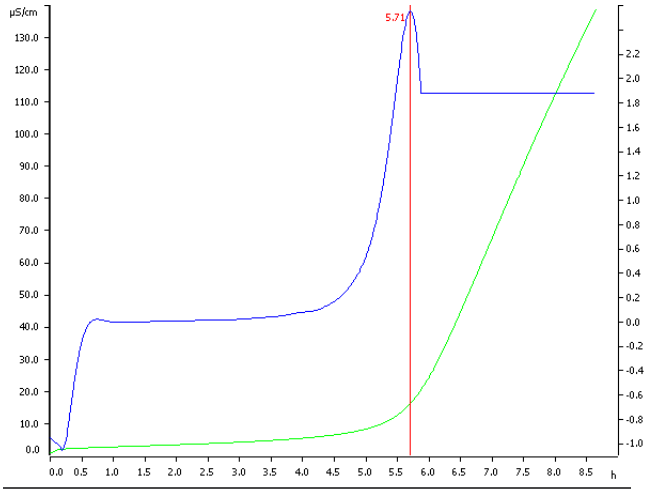

Figure 3. Determination of the oxidation stability of sausage at 120 °C after cold extraction with petroleum ether.

Comments

Any kind of contamination, particles, or even scratches in the glass can catalyze reactions and thereby affect the result. Contaminations may impact 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 to eliminate any particles with a focused stream of nitrogen.

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 should 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 an adequate supply of oxygen to oxidize the fatty acids and 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 by the proper adjustment of the «temperature correction».

For liquid samples and samples that melt at elevated temperatures, the sample size is no critical parameter. The lower limit for the volume is given by the air tube which must be immersed in the sample. The maximum volume to be used is approximately 12 mL. Above that value, proper heating of the sample cannot be ensured.

The sample size can be a critical parameter for the direct determination of solid samples. Since the air stream cannot mix these samples, no homogeneous temperature can be guaranteed in a larger volume. Therefore, 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, chemically inert, storage stable, cheap, and easily available. At room temperature, it is solid and therefore easy to handle (e.g., for weighing). Its 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.

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