Metrohm

Application Bulletin 204/2 e

Oxidation stability of oils and fats – Rancimat method

Branch

Food; pharmaceutical industry; cosmetics

Keywords

Oxidative stability; oxidation stability; rancidity; 892; oils; fats; cosmetics; sample preparation; extraction; branch 4; branch 7; branch 12

Summary

The Rancimat method is an accelerated aging test. Air is passing through the sample in the reaction vessel at constant elevated temperature. In this process fatty acids are oxidized. At the end of the test volatile, secondary reaction products are formed, which are transported into the measuring vessel by the air stream and absorbed in the measuring solution (deionized water). The continuously recorded electrical conductivity of the measuring solution is increasing 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.

This Application Bulletin provides a detailed description, above all of the requisite sample preparation steps.

Samples

Oils, fats, oil- and fat-containing products

Instruments

892 Professional Rancimat	2.892.0010
Set for the determination of the temperature correction	6.5616.100
Auxiliary instruments for sample preparation	
Laboratory balance (resolution ± 0.01 g)	

Reagents

- Deionized water

For sample preparation

- Petroleum ether, low boiling, boiling point 30 … 40 °C, puriss. p.a., CAS 101216-46-5

Sample preparation

Liquid oils

Liquid oils as a group of vegetable or animal fats that are liquid at room temperature can be measured directly. A disposable plastic Pasteur pipette is used to weigh the sample directly into the reaction vessel.

Solid fats

Solid fats as a group of vegetable or animal fats which are solid at room temperature and melt at elevated temperature can be measured directly. In case of problems weighing the sample into the bottom part of the reaction vessel, the sample can be previously melted on a water bath. Care has to be taken that the water bath temperature is not far beyond the melting point of the sample otherwise deterioration of the sample can be expected.

Water-containing fats

Water-containing fats (butter, margarine) can also be weighed in directly. The sample size has to be increased to compensate the sample loss caused by evaporation of the containing 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 has to be crushed and homogenized, e.g., by a mortar. Care has to 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., has to be extracted before the determination. This is preferably

done by cold extraction, since heating 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 approx. 10 g fat (sufficient for two measurements) is weighed into a conical flask. Approx. 3 times the sample volume of low boiling petroleum ether is added. The extraction is performed by stirring for at least 1 hour. The petroleum ether phase is then separated from the residues by either filtering in case of solid samples or by a separating 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.

Analysis

Preparation of the Rancimat

The heating block is heated up to the respective temperature.

Preparation of the measuring vessel

The measuring vessel is filled with 60 mL deionized water and placed on the Rancimat together with the measuring vessel cover. 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 taken into account. It has to be ensured that the electrode is immersed into the measuring solution at any time.

Preparation of the reaction vessel

For each determination, a new reaction vessel is used. To remove particles (e.g., from the cardboard box) the reaction vessel is air-cleaned inside and outside by a sharp stream of 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 3.0 ± 0.1 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. Ensure that the air inlet tube always immerses in the sample.

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.

The reaction vessel is closed with a reaction vessel cover assembled with an air inlet tube.

Determination

Before the determination can be started, the temperature of the heating block has to 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	Liquid samples: 3.0 ± 0.1 g Solid samples: 0.5 … 1 g
Measuring solution	60 mL
Temperature	80 … 160 °C
Gas flow	20 L/h
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 and 160 °C are appropriate. 50 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.

Typical results

Vegetable oils and fats

Sample	Temperature/°C	Induction time/h
Canola oil	130	12 … 17
Canola oil, hydro-genated	140	10 … 11
Citrus oil	90	approx. 0.5
Cocoa butter	120	9 … 15
Coconut oil	120	approx. 33
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

Sample	Temperature/°C	Induction time/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 fat	110	approx. 0.3
Tallow	120	3 … 8

Solid samples, direct determination

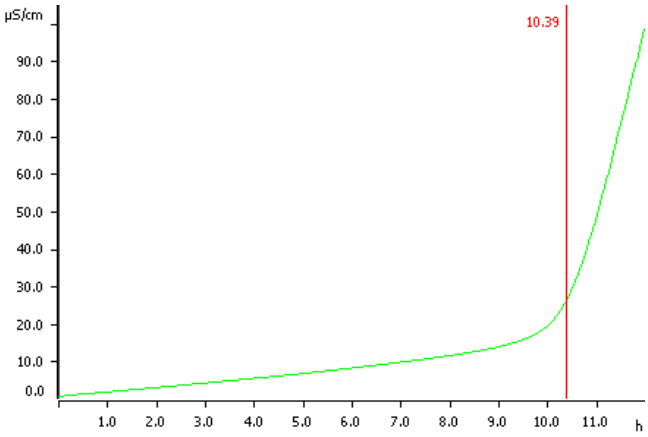
Sample	Temperature/°C	Induction time/h
Butter cookies	160	approx. 6
Coconut flakes	160	approx. 17
Hazelnuts	120	approx. 22
Instant noodles	120	15 … 30
Peanuts	110	approx. 10
Potato chips (crackers)	140	approx. 10

Solid samples after extraction

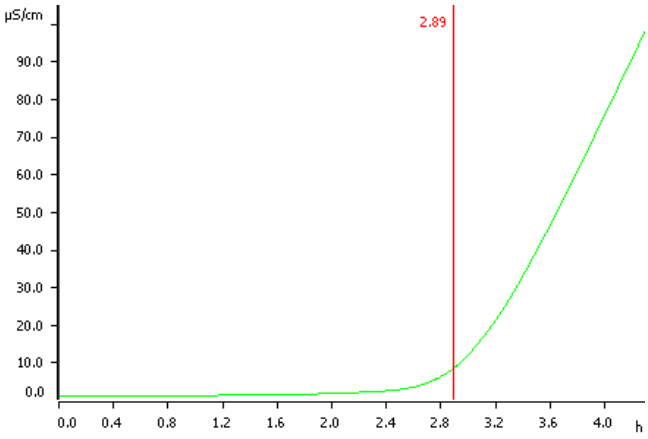
Sample	Temperature/°C	Induction time/h
Baby food	120	1 ….2
Hazelnuts	120	7 ….13
Mayonnaise	120	1 ….4
Peanuts	120	1 ….2
Potato chips (crackers)	140	approx. 2
Powdered milk	120	4 ….32
Salad dressing	120	approx. 2

Examples

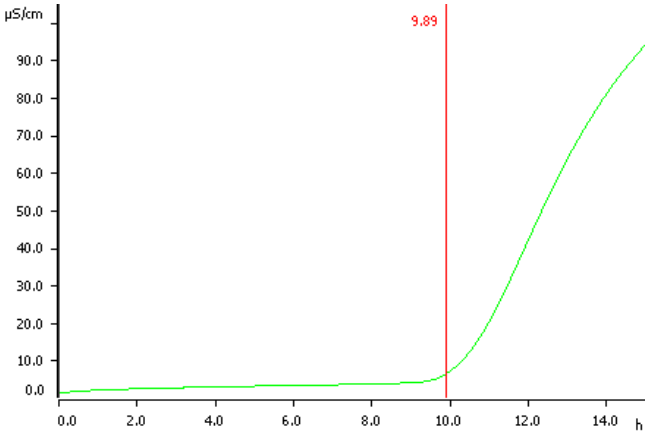
Olive oil , temperature 120 °C, induction time 10.39 h



Sunflower oil, temperature 120 °C, induction time 2.89 h



Peanuts (direct determination), temperature 110 °C, induction time 9.89 h



Comments

- Any kind of contamination, particles, or scratches in the glass can catalyze reactions and thereby affect the result. Contaminations 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 off particles by a sharp stream of nitrogen.
- The temperature is the most crucial parameter in the determination of the induction time. Especially if results from different instruments should be compared it is essential to determine the «temperature correction» value correctly. 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 a reliable transfer of the reaction products from the reaction vessel to the measuring vessel. Furthermore, it stirs the sample and thereby ensures a homogeneous temperature in the sample. Beyond that, there is no influence of the gas flow on the result as long as the cooling effect is compensated by the correct adjustment of the «temperature correction».
- For liquid samples and samples which melt at elevated temperature the sample size is no critical parameter. The lower limit for the volume is given by the air tube which has to immerse in the sample. The maximum volume to be used is approx. 12 mL. Above that a 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 the sample, no homogeneous temperature can be guaranteed in a larger volume. Hence a small sample size that just covers the bottom of the reaction vessel should be preferred.

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