Stability Measuring Instruments

743 Rancimat

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Overview

Rancidity
Principle of Rancimat method
Evaluation
Influences on the determination
Temperature Extrapolation
GLP - Validation of the instrument
The 743 Rancimat
Applications Rancimat
Rancidity

hydrolytic rancidity
oxidative rancidity
Hydrolytic Rancidity

\[
\text{triglyceride} + H_2O \xrightarrow{\text{enzymes}} \text{diglyceride} + \text{CH}_3(\text{CH}_2)_n\text{COOH}
\]

fatty acid
Hydrolytic Rancidity

use only dry air for Rancimat measurements
Oxidative Rancidity

Radical chain reaction:

Initiation
- RH → R·

Propagation
- R· + O₂ → RO₂·
- ROO· + RH → R-OOH + R·

Termination
- R· + R· → R-R
- ROO· + R· → R-OO-R
Oxidative Rancidity

Primary reaction products:
- Peroxides (R-OO-R)
- Hydroperoxides (R-OOH)

Secondary reaction products:
- Aldehydes
- Alcohols
- Carbonic acids
Factors Accelerating Oxidation

Oxygen

Heavy metal ions (e.g. Fe, Cu)
  - catalyse chain initiation

UV light
Stability

Antioxidants

Chain breaking substances
- E.g. phenolic compounds
- Examples
  - natural compounds
  - synthetic antioxidants: BHA, BHT, TBHQ, ...
  - Tocopherol

Complexing agents
- citric acid, phosphoric acid, ascorbic acid, ...

UV deactivators
- phenyl salicylate, hydroxybenzophenone
Limitations for measurement of antioxidant activity

Volatile antioxidants

Antioxidants unstable at high temperatures
Principle of Rancimat Method
Quality Assessment of Fats/Oils

Rancimat test = accelerated oxidation test
- at elevated temperature
- under exposure of air
faster autoxidation in a few hours instead of weeks/months
Principle of Rancimat Method

Fatty acids are oxidised by oxygen from air. Low molecular organic acids are formed and stripped out of the oil by air flow.
Principle of Rancimat Method

- Air inlet
- Reaction vessel
- Oil sample
- Heating block (e.g. 120°C)
- Measuring vessel
- Conductivity cell
- Absorption solution (water)
**Rancimat Curve**

*Induction period:*
- oxidation of fatty acids $\rightarrow$ peroxide formation
- slow reaction
- no formation of volatile carboxylic acids

- accelerated fast reaction
- oxidation of fatty acids $\rightarrow$ formation of volatile carboxylic acids
Evaluation
Rancimat Curve

induction time: 10.53 h
stability time: 10.78 h

µS/cm vs. time (h)
Evaluation of Induction Time

$2^{nd}$ derivative of measured curve → shows maximum
= induction time
Evaluation of Stability Time

Absolute increase in conductivity in the absorption solution

$\Delta \kappa = 50 \, \mu S/cm$
Reevaluation

Automatic result can be modified
Tangent method (only manual)
Influences on the determination
Temperature Extrapolation

Temperature
Gas flow
Sample weight
Influences on the results

Temperature:
- 10°C increase → 50% induction time
- max. deviation of temperature: 0.3°C
- stability of temperature <0.1°C
- exact temperature adjustment important

Gas flow:
- small influence
- no changes within ±10% flow change

Sample weight:
- small influence
- cooling effect depending on the sample weight
Temperature Calibration

Necessary equipment:
- GLP set
- with certified temperature sensor

Control of the accuracy of the heating block
Determination of the temperature correction
- for each temperature
- for each heating block
- each gas flow
Temperature Dependency

Sample at different temperatures
Temperature Extrapolation

evaluation of dependency:
temperature vs. induction time

\[ T = f(t) \]

\[ t = A \cdot e^{(B \cdot T)} \]
Extrapolation

Standard factor = temperature coefficient:
change of induction time per 10°C

estimated shelf life time

theoretical value = 2
Stability

The 743 Rancimat
The new PC controlled Rancimat

8 samples
2 temperatures
up to 4 Rancimats/Thermomats per PC
Single Button - Single Connection

optional: calibrated external Temperature Sensor
Stability

Internal or external Air Supply

only Rancimat
Operation

Disposable reaction vessels and gas inlet tubes
   → no time-consuming cleaning
no fragile and expensive glassware
One-piece measuring vessel cover and conductivity cell
Conductivity Cell

Cell constant:
1.1 cm⁻¹ (± 0.1)
Features

743 Rancimat is controlled by PC
(Windows™ 95/98/NT/2000/XP)

8 samples per Rancimat in 2 independent heating blocks (2
temperatures per Rancimat)

up to 4 Rancimat units may be attached to 1 PC (32 Samples)
every channel may be handled independently

Temperature range: 50 ... 220 °C

Stability of temperature: < 0.1 °C
Features

Live curve
Automatic determination of results acc. to AOCS Cd 12b-92, AOM or other standard formats
Database functions
Reprocessing of single runs
Determination of the temperature coefficient
Disposable glassware
Hardware validation / GLP Function --> improved result accuracy.
Instrument Operation
Main Screen

Stability

Method settings
Start/Stop heating
Start/Stop determination
Live display
Parameters

For oils and fats 100 – 140°C

Tabled value (see manual)

→ Determine with external temperature sensor

See tab Evaluation
Evaluation

Induction time = maximum of 2nd derivative

Δκ absolute increase in conductivity
Standards

Extrapolation function

Theoretical factor 2

Free

Fixed to 110°C (AOCS)
97.8°C (AOM)
Preparing determination

Select method and modify parameters if necessary

Start heating

- 45 min to 120°C
- 60 min to 220°C

Prepare measuring vessel

- Low conductivity of the distilled water (< 5 µS/cm)
- Check conductivity cells (cell constant 1.0 – 1.2)
- Replace plastic beakers (10 – 20 determinations)

Prepare reaction vessel

- Remove particles (cardboard box, cullet, ...)
- Position of the air inlet tube
When temperature is reached

Place measuring vessel
Connect tubings
Insert reaction vessel
Start determination immediately
Stability

Results
GLP
Validation of the instrument
GLP – Hardware Validation

Automatic Monitoring:
- Temperature
- Conductivity
- Gas flow

GLP Status Information

<table>
<thead>
<tr>
<th>Test type</th>
<th>Next test due date</th>
<th>Due in</th>
<th>Last test result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Mittwoch, 3. März 1999</td>
<td>DUE NOW!</td>
<td>No test yet</td>
</tr>
<tr>
<td>Conductivity</td>
<td>Mittwoch, 3. März 1999</td>
<td>DUE NOW!</td>
<td>No test yet</td>
</tr>
<tr>
<td>Gas flow</td>
<td>Mittwoch, 3. März 1999</td>
<td>DUE NOW!</td>
<td>No test yet</td>
</tr>
</tbody>
</table>
GLP Test Temperature

TEST PARAMETERS
Select at least one channel per block!

Channels used for test

Block A
- Channel 1
- Channel 2
- Channel 3
- Channel 4

Block B
- Channel 1
- Channel 2
- Channel 3
- Channel 4

Test duration per channel: 10 min
GLP Test Conductivity

PREPARATION OF TEST

- Use test resistor
- Use standard solution

Test with resistor:
- Resistance: 10000 Ohms

Test with standard solution:
- Enter approx. 60 mL of a standard solution into the vessel of each measuring channel.
- Make sure the electrode covers are inserted properly!
- Conductivity of standard solution: 133 uS/cm
Applications Rancimat
Applications Rancimat

Oxidative stability of pure edible fats and oils from plants or animals

Oxidative stability of natural fats and oils from food or cosmetics after extraction with petrol ether

Antioxidant research

Oxidative stability of FAME (fatty acid methyl ester, biodiesel)

Oxidation stability of light heating oil with Cu catalyst
Rancimat Applications 1
Oxidation Stability of Edible Fats and Oils

Animal fats/oils:
- Butter, fish oil, lard, etc.

Vegetable fats/oils:
- soybean, sunflower, coconut, peanut, palm

Fat/oil containing products
- direct measurements: margarine
- after extraction of the fat: meat, nuts, etc.

Antioxidant research
Sesame Oil

4 temperatures: 100°C, 110°C, 120°C, 130°C
Sesame Oil

4 temperatures: 100°C, 110°C, 120°C, 130°C

estimated life time at 20°C: 1.2 years
Olive Oil

4 temperatures: 100°C, 110°C, 120°C, 130°C
Olive Oil

4 temperatures: 100°C, 110°C, 120°C, 130°C

estimated life time at 20°C: 0.7 years
Standards

ISO 6886
- Animal and vegetable fats and oils – Determination of oxidation stability

AOCS Cd 12b-92
- Sampling and analysis of commercial fats and oils: Oil Stability Index

AOM - Active oxygen method

2.4.28.4-93
- Fat stability test on Autoxidation. CDM, Japan
Stability

Information on Applications

Application Bulletins
- 204, 141, 232, 237

Application Notes
- R-1, R-3, R-4, R-5, R-6, R-7

Reprint
- A modern method of determining the oxidative stability of fats and oils (679)
- Comparison AOM - Rancimat
AOM – Rancimat method

Comparison Rancimat - AOM

Induction time Rancimat [h]

Induction time AOM [h]
The oxidative stability is, in addition to other quantities, an important criterion for evaluating the quality of oils and fats; this has recently been extended to cover fatty acid methyl esters (biodiesel). Today, the Rancimat method developed by Hadorn and Zürcher 1974 [1] for the determination of the oxidative stability has to a large extent replaced the arduous and time-consuming AOM or SWIFT methods. Apart from the comfortable and fully automatic determination of the induction time, it also allows considerably more determinations to be carried out in less time. This means that it is now possible to make new statements with respect to human health (oxidative stress in the human body) [3].

Important and well-known antioxidants are tert-butylhydroxyanisole BHA (2- or 3-tert-butyl-4-methoxyphenol) and butylhydroxytoluene BHT (2,6-di-tert.-butyl-4-methylphenol) which are legally permitted food additives, vitamin C (ascorbic acid) or the more lipophilic ascorbyl palmitate and vitamin E (tocopherol). Multi-functional antioxidants are obtained from extracts, e.g. carnosic acid from rosemary or sesamin from sesame extract. These highly effective substances are used in the food industry.

Table 1: Total tocopherol concentration (tocopherols and tocotrienol oils) of various oils and fats (in mg/kg)

<table>
<thead>
<tr>
<th>Oil Type</th>
<th>Tocopherol Concentration (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat germ</td>
<td>2443</td>
</tr>
<tr>
<td>Corn</td>
<td>1006</td>
</tr>
<tr>
<td>Soybean</td>
<td>937</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>654</td>
</tr>
<tr>
<td>Sunflower</td>
<td>625</td>
</tr>
<tr>
<td>Olive</td>
<td>133</td>
</tr>
<tr>
<td>Cocoa butter</td>
<td>56</td>
</tr>
<tr>
<td>Hog’s lard</td>
<td>17</td>
</tr>
<tr>
<td>Butterfat</td>
<td>36</td>
</tr>
</tbody>
</table>
Rancimat Applications 2
Oxidation Stability of FAME / Biodiesel

*FAME = fatty acid methyl ester*

replaces mineral oil based fuels (i.e. diesel) produced

- from vegetable oils (e.g. canola oil, soybean oil)
- by transesterification

subsidized by government in some countries

quality control (oxidative stability) by Rancimat method

⇒ *EN 14112*
Production of FAME

A triglyceride reacts with methanol in the presence of a catalyst to produce fatty acid methyl ester (FAME) and glycerol.
FAME: Temperature Dependency

temperatures from 60° - 130°C
FAME: Temperature Dependency

Resultate:

Formel: $t = A \times e^{(B \times T)}$

$A = 16780.033711789$
$B = -0.0688698524198639$
$r^2 = 0.997902425192587$

Zeit = 12,740 h

Jahre = 1.45

Zieltemperatur = 4 °C

Anzahl Bestimmungen = 16

Normfaktor = 1.991
Information on Applications

Application Note R-9
Standard EN 14112

- Fatty Acid Methyl Esters (FAME) – Determination of oxidation stability (Accelerated oxidation test)
Rancimat Applications 3
Oxidative stability of light heating oil with Cu catalyst

Heating oil and heating oil with additive
Application Information

Application Works

- D7-078-0700
- D7-082-0201