Metrohm

Application Bulletin 141/4 e

Analysis of edible oils and fats

Branch

General analytical chemistry; food

Keywords

Titration; potentiometric titration; Karl Fischer titration; KFT; polarography; Rancimat; automation; DIS-Cover; oxidation stability; oxidative stability; iodine number; iodine value; peroxide number; peroxide value; saponification number; saponification value; acid number; acid value; free fatty acids; FFA; hydroxyl number; hydroxyl value; nickel traces; Ni; edible oil; edible fat; branch 1; branch 7

Summary

This Application Bulletin describes the following analytical methods for edible oils and fats:

- Water content according to Karl Fischer
- Oxidation stability – Rancimat method
- Iodine value
- Peroxide value
- Saponification value
- Acid value, free fatty acids (FFA)
- Hydroxyl value
- Nickel traces, using polarography

Special care was taken to avoid chlorinated solvents in these methods. Also as many methods as possible were automated.

Water content

Summary

The coulometric Karl Fischer method is preferred for this analysis because of the low water contents of pure oils and fats. For butter and margarines, which exhibit relatively high water contents, the volumetric Karl Fischer method should be used.

Instruments

- Coulometric KF titrator

  or
- Volumetric KF titrator

Electrodes

Double Pt-wire electrode for volumetry	6.0338.100
or	
Double Pt-wire electrode for coulometry	6.0341.100
Generator electrode with diaphragm	6.0344.100

Reagents

Coulometric

- Hydranal Coulomat Oil or equivalent
- Hydranal Coulomat CG or equivalent

Volumetric

- Hydranal Composite 5 or equivalent
- Methanol, dry, p.a.
- 1-Decanol, p.a.

Solutions

Solvent mixture	Methanol / 1-decanol, Φ(MeOH) = 66% (v/v)

Sample preparation

Hard fats should be melted before adding them into the titration vessel.

Butter and margarine should first be homogenized as their distribution of water is inhomogeneous. They should not be heated over 25 °C, otherwise phase separation may occur.

Analysis

Sample (Coulometric)

Add approximately 100 mL coulometric reagent to the titration vessel and condition it until a constant drift is achieved (< 10 µg/min is typical). Then fill a syringe 3 times with the sample and discard it. Fill again, and add approx. 0.5 g to 1 g sample to the titration vessel and titrate the water content.

Sample (Volumetric)

Add approximately 30 mL solvent mixture to the titration vessel and condition it until a constant drift of approximately 10–20 µL/min is reached. Fill the sample into a dry syringe (without needle). Add approx. 0.3 g sample to the titration vessel and titrate.

Parameters

Sample (Coulometric)

Mode	KFC
Start drift	20 µg/min
EP at	50 mV
Dynamics	70 mV
Min. rate	15 µg/min
Stop criterion	Rel. drift
Rel. stop drift	5 µg/min
Extraction time	0 s

Sample (Volumetric)

Mode	KFT Ipol
Start drift	20 µL/min
EP at	250.0 mV
Dynamics	100 mV
Stop criterion	Drift
Stop drift	20 µL/min
Extraction time	0 s

References

- DIN EN ISO 8534

  Animal and vegetable fats and oils – determination of water content – Karl Fischer method (pyridine free)

Oxidation stability

Summary

The Rancimat method is an accelerated aging test. Air is passing through the sample in the reaction vessel at a 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.

Instruments

- Rancimat
- Equipment for determining the temperature correction

Reagents

- Deionized water

Sample preparation

No sample preparation required.

Liquid oils can be weighed in directly. In case of problems weighing solid fat 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.

Analysis

Before the determination can be started, the temperature of the heating block has to be stable. Fill each measuring vessel with 60 mL deionized water and place it on the Rancimat together with the measuring vessel cover with the integrated conductivity cell. Use a new and clean reaction vessel. Weigh in 3 g of sample into the bottom part and close it with the reaction vessel cover with the air inlet tube attached. Connect the two tubing for the air supply, place the reaction vessel in the heating block and start the data recording immediately.

Parameters

Sample size	3 g
Measuring solution	60 mL deionized water
Temperature	80 – 160 °C
Gas flow	20 L/h
Evaluation	Induction time

Example determination

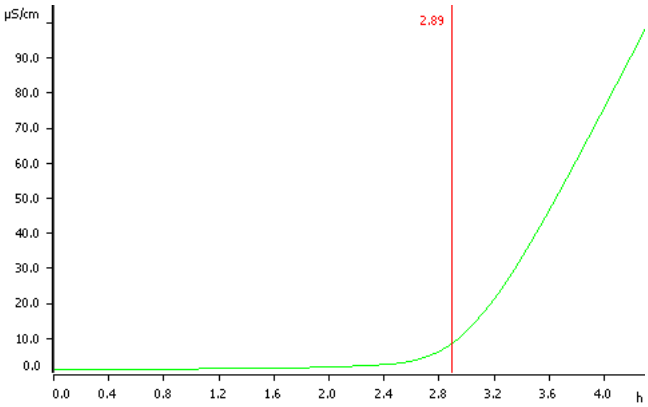

Fig. 1 Determination of oxidation stability of sunflower oil at a temperature of 120 °C, induction time 2.89 h.

Typical results

Sample	Temperature/°C	Induction time/h
Corn oil	120	approx. 5
Hazelnut fat	120	10 – 12
Hazelnut oil	120	7 – 11
Lard	100	1 – 3
Linseed oil	110	0.5 – 2
Margarine	120	2 –. 6
Olive oil	120	6 – 11
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
Tallow	120	3 – 8

Comments

- Temperature is the most critical parameter in this application. Therefore a temperature correction has to be included in the method settings to compensate for the cooling due to the gas flow. Tabled values are available for different temperatures and gas flow rates in the manual of the instrument software. But for best reproducibility of results it is recommended to determine the temperature correction using the optional equipment for determining the temperature correction. For more information see the instructions for use of the instrument.
- The induction time is usually determined at 120 °C. But the temperature can be chosen in a way that the induction time lies within 4 to 10 hours. As a rule of thumb the induction time decreases by a factor of 2 when the temperature is increased by 10 °C and vice versa.
- It is recommended to use a new reaction vessel for every determination to avoid side reactions due to contaminations. To remove particles (e.g., from the cardboard box) the reaction vessel is air-cleaned inside and outside by a sharp stream of nitrogen before the sample is weighed in.

References

- AOCS Cd 12b-92

  Sampling and analysis of commercial fats and oils – Oil Stability Index (OSI)
- DIN EN ISO 6886

  Animal and vegetable fats and oils – determination of oxidative stability (accelerated oxidation test)
- Metrohm Application Bulletin 204

  Oxidation stability of oils and fats – Rancimat method

Iodine value

Summary

The determination of the iodine value is based on the addition of iodine to the double bonds of unsaturated fatty acids. The result is given as g I_2 consumed by 100 g sample and is a measure for the unsaturation of an oil.

For the manual determination of the iodine value the beakers have to be placed in the dark after adding the reaction solution, magnesium acetate solution and glacial acetic acid. Before the titration the potassium iodide solution has to be added, all these steps are laborious and time consuming.

The automated determination is done with brown glass beakers and the Robotic DIS-Cover system. This method leads to good and reproducible results.

Instruments

- Sample changer with Swing Head and DIS-Cover
- Titrator with DET mode
- 2x Burette 20 mL (Glacial acetic acid, $Mg(CH_3COO)_2$)
- 4x Burette 50 mL (H_2SO_4, ICl, KI, $Na_2S_2O_3$)
- Propeller Stirrer

Electrodes

iPt Titrode	6.0471.300

Reagents

- Sulfuric acid, c(H_2SO_4) = 0.5 mol/L, volumetric solution
- Potassium iodate, KIO_3, p.a.
- Potassium iodide, KI, p.a.
- Sodium thiosulfate, c($Na_2S_2O_3$) = 0.1 mol/L, volumetric solution
- Magnesium acetate, $Mg(CH_3COO)_2$, purum
- Glacial acetic acid, p.a.
- Iodine chloride, Wijs-solution, c(ICl) = 0.1 mol/L, volumetric solution

Solutions

Titrant	c($Na_2S_2O_3$) = 0.1 mol/L If possible this solution should be bought from a supplier.
Potassium iodide solution	β(KI) = 100 g/L 50 g potassium iodide is weighed into a 500 mL volumetric flask and filled up with dist. water.
Magnesium acetate solution	w($Mg(CH_3COO)_2$) = 3% 15 g magnesium acetate is weighed into a 500 mL volumetric flask and filled up with dist. water.
Reaction solution	c(ICl) = 0.1 mol/L in glacial acetic acid If possible this solution should be bought from a supplier.

Standard

Iodate standard	Potassium iodate is dried in a drying oven for 2 h at 110 °C and allowed to cool down in a desiccator for at least 1 h.

Sample preparation

No sample preparation required.

Analysis

Titer

Approximately 70 mg potassium iodate is weighed into a 250 mL beaker and 80 mL dist. water is added to dissolve it. Afterwards 10 mL β(KI) = 100 g/L as well as 25 mL c(H_2SO_4) = 0.5 mol/L are given to the solution. The solution becomes dark brown and the originated iodine is titrated with c($Na_2S_2O_3$) = 0.1 mol/L up to the first end point.

Blank

20 mL glacial acetic acid, 25 mL c(ICl) = 0.1 mol/L and 10 mL w($Mg(CH_3COO)_2$) = 3% are given into a 250 mL brown glass beaker. The beaker is closed with the lid and left standing for five minutes. 15 mL β(KI) = 100 g/L is given to the solution and the originated iodine is titrated with c($Na_2S_2O_3$) = 0.1 mol/L until the first end point.

Sample

An appropriate sample amount is weighed into a 250 mL brown glass beaker (see table below) and placed onto the sample rack. 20 to 25 mL glacial acetic acid (see below), 25 mL c(ICl) = 0.1 mol/L and 10 mL w($Mg(CH_3COO)_2$) = 3%

are then added. Afterwards the beaker is closed with the lid and left standing for five minutes. 15 mL β(KI) = 100 g/L is given to the solution and the originated iodine is titrated with $c(Na_2S_2O_3)$ = 0.1 mol/L until the first end point.

Amount of sample and solvent

Expected IV / g / 100 g	Sample amount / g	Solvent volume / mL
< 1.5	15.00	25
1.5 – 2.5	10.00	25
2.5 – 5	3.00	20
5 – 20	1.00	20
20 – 50	0.40	20
50 – 100	0.20	20
100 – 150	0.13	20
150 – 200	0.10	20

Parameters

Titer

Mode	DET U
Pause	20 s
Signal drift	20 mV/min
Max. waiting time	38 s
Meas. point density	4
Min. increment	50 µL
Max. increment	off
EP criterion	5
EP recognition	greatest

Blank/Sample

Mode	DET U
Signal drift	20 mV/min
Max. waiting time	38 s
Meas. point density	4
Min. increment	10 µL
Max. increment	off
EP criterion	5
EP recognition	all

Calculation

Titer

$$\text{Titer} = \frac{m_s \times 6}{V_{EP1} \times c(Na_2S_2O_3) \times M_A}$$

Titer:	Titer of the selected titrant
m_s:	Mass of standard in mg
6:	Stoichiometric factor
V_{EP1}:	Titrant consumption until the first equivalence point in mL
$c(Na_2S_2O_3)$:	Concentration of the selected titrant in mol/L; here $c(Na_2S_2O_3)$ = 0.1 mol/L
M_A:	Molecular weight of the analyte; here 214.00 g/mol

Sample

$$IV = \frac{(V_{EP1} - V_{blank}) \times f \times c(Na_2S_2O_3) \times M_A}{10 \times m_S}$$

IV:	Iodine value of the sample in g iodine / 100 g
V_{EP1}:	Titrant consumption until the first equivalence point in mL
V_{blank}:	Blank value consumption for the used quantity of solvent in mL
$c(Na_2S_2O_3)$:	Concentration of the selected titrant in mol/L; here $c(Na_2S_2O_3)$ = 0.1 mol/L
f:	Correction factor («titer») without unit
M_A:	Molecular weight of the analyte; here 126.90 g/mol
m_s:	Sample size in g
10:	Conversion factor

Example determination

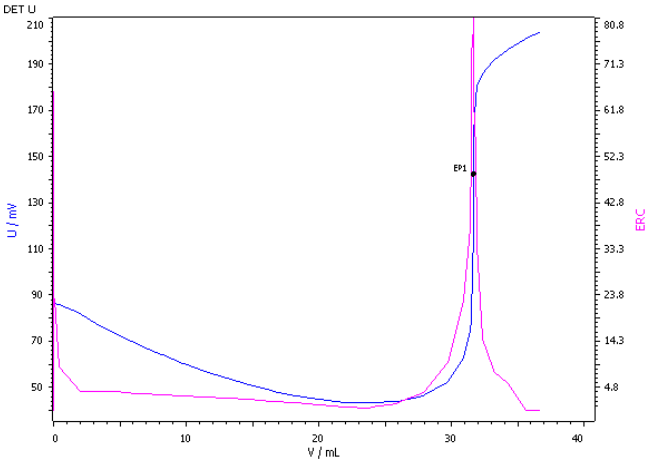

Fig. 2: Determination of the iodine value (blue = titration curve, pink = ERC)

Comments

- The method for determining the iodine value was adapted from the norm DIN EN ISO 3961. The following changes were made:
    - Magnesium acetate was used as catalyst, therefore shortening the reaction time from 1 - 2 h to 5 minutes.
    - Glacial acetic acid was used as solvent instead of a mixture of cyclohexane and glacial acetic acid.

References

- DIN 53241-1

  Determination of the iodine value – part 1: methods using Wijs solution
- DIN EN ISO 3961

  Animal and vegetable fats and oils – determination of iodine value

Peroxide value

Summary

The peroxide number gives information about the number of peroxide compounds in the oil and hence of the age and quality of the edible oil. The lower the peroxide numbers the better and/or newer the oil.

Instruments

- Sample changer with Swing Head and DIS-Cover
- Titrator with DET mode
- 1x Burette 5 mL
- 1x Burette 10 mL
- 3x Burette 20 mL
- 2x Burette 50 mL
- Propeller Stirrer

Electrodes

iPt Titrode	6.0471.300

Reagents

- Sulfuric acid, c(H_2SO_4) = 0.5 mol/L, volumetric solution
- Potassium iodate, KIO_3, p.a.
- Potassium iodide, KI, p.a.
- Sodium thiosulfate, c($Na_2S_2O_3$) = 0. 1 mol/L, volumetric solution
- Glacial acetic acid, p.a.
- 1-Decanol, p.a.

Solutions

Titrant	c($Na_2S_2O_3$) = 0.001 mol/L Prepared by dilution of the c($Na_2S_2O_3$) = 0.1 mol/L with dist. water.
Auxiliary solution	Saturated solution of KI:
Potassium iodide solution	w(KI) = 10% 50 g potassium iodide is weighed into a 500 mL volumetric flask and filled up with dist. water.
Solvent mixture	Glacial acetic acid / 1-decanol with approximately 20 mg I_2 / L Φ(1-decanol) = 40% (v/v)

Standard solution

Iodate standard	Potassium iodate is dried in a drying oven for 2 h at 110 °C and allowed to cool down in a desiccator for at least 1 h. Approximately 0.65 g is weighed into a 1 L volumetric flask and filled up to the mark with dist. water.

Sample preparation

No sample preparation required.

Analysis

Titer

0.75 to 1.25 mL potassium iodate standard solution is dosed into a 250 mL beaker. 80 mL dist. water, 10 mL w(KI) = 10% as well as 25 mL c(H_2SO_4) = 0.5 mol/L are added to the solution. The solution becomes dark brown and the originated iodine is titrated with c($Na_2S_2O_3$) = 0.001 mol/L up to the first end point.

Blank

20 mL solvent mixture and 0.2 mL auxiliary solution are dosed into a 250 mL brown glass beaker and closed with the DIS-cover. After one minute 80 mL dist. water is added and the solution is titrated with c($Na_2S_2O_3$) = 0.001 mol/L until the first end point.

Sample

5 or 10 g sample (depending on the expected value) is weighed into a 250 mL brown glass beaker and placed onto the sample rack. 20 mL solvent mixture and 0.2 mL auxiliary solution are added and the beaker is closed with the DIS-cover. After one minute 80 mL dist. water is added and the solution is titrated with c($Na_2S_2O_3$) = 0.001 mol/L until the first end point.

Parameters

Titer

Mode	DET U
Pause	20 s
Signal drift	20 mV/min
Max. waiting time	38 s
Meas. point density	4
Min. increment	50 µL
Max. increment	500 µL
EP criterion	5
EP recognition	all

Blank/Sample

Mode	DET U
Signal drift	5 mV/min
Min. waiting time	10 s
Max. waiting time	72 s
Meas. point density	4
Min. increment	10 µL
Max. increment	200 µL
EP criterion	20
EP recognition	greatest

Calculation

Titer

$$\text{Titer} = \frac{\beta(KIO_3) \times m_s \times 6}{V_{EP1} \times c(Na_2S_2O_3) \times M_A}$$

Titer:	Titer of the selected titrant
$\beta(KIO_3)$:	Exact mass concentration of the standard solution in mg/L
m_s:	Volume of the added standard solution in L
6:	Stoichiometric factor
V_{EP1}:	Titrant consumption until the first equivalence point in mL
$c(Na_2S_2O_3)$:	Concentration of the selected titrant in mol/L; here $c(Na_2S_2O_3)$ = 0.001 mol/L
M_A:	Molecular weight of the analyte; here 214.00 g/mol

Sample

$$PV = \frac{k \times (V_{EP1} - V_{blank}) \times f}{m_S}$$

PV:	Peroxide value of the sample in meq O_2 / kg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
V_{blank}:	Blank value consumption for the used quantity of solvent in mL
f:	Correction factor («titer») without unit
m_s:	Sample size in g
k:	Conversion factor, 1 for $c(Na_2S_2O_3)$ = 0.001 mol/L, 10 for $c(Na_2S_2O_3)$ = 0.01 mol/L

Example determination

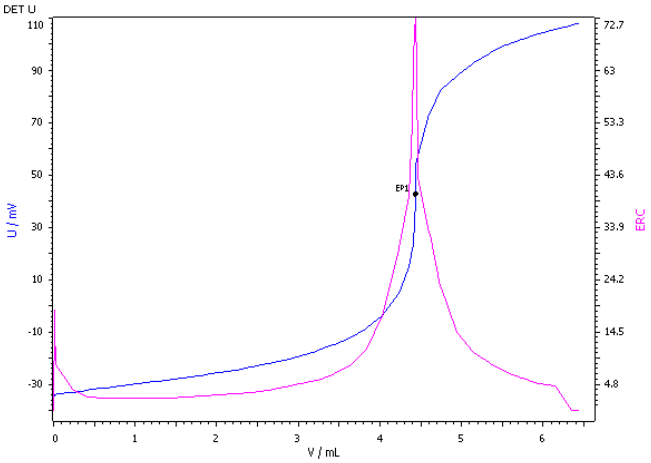

Fig. 3: Determination of the peroxide value (blue = titration curve, pink = ERC)

Comments

- The stirrer has to be set to a higher level (14) for the dissolving of the oil, than for the titration (10). Otherwise irreproducible results can occur.
- Before each determination series a preparation of all dosing units, especially of the solvent mixture has to be done. The solvent mixture contains iodine and the amount of iodine and therefore of the solvent mixture has to be the same during a series.
- As the peroxide value depends on the sample size the ISO/TC 34/SC 11 has decided to fix the sample size to 5 g for PV greater than 1, and at 10 g for PV less than or equal to 1.
- The method for determining the peroxide value was adapted from the norm DIN EN ISO 27107. The following changes were made:
  - H_2SO_4 was used in the titer determination instead of hydrochloric acid.
  - A mixture of 1-decanol and glacial acetic acid was used as solvent instead of a mixture of isooctane and glacial acetic acid.

References

- DIN EN ISO 27107

  Animal and vegetable fats and oils – determination of peroxide value – potentiometric end-point determination

Saponification value

Summary

The saponification value is expressed as the amount of potassium hydroxide in milligrams required to saponify 1 g of fat under the conditions specified. It contains the information of the average molecular weight of all fatty acids present.

Instruments

- Titrator with DET mode
- Burette 50 mL
- Stirrer
- Reflux condenser
- Heating device

Electrodes

Solvotrode easyClean	6.0229.020

Reagents

- Hydrochloric acid, c(HCl) = 0.5 mol/L, volumetric solution
- Potassium hydroxide, p.a.
- Ethanol, p.a.
- TRIS, p.a.

Solutions

Titrant	c(HCl) = 0.5 mol/L If possible this solution should be bought from a supplier.
Ethanolic potassium hydroxide solution	c(KOH) = 0.5 mol/L in ethanol If possible this solution should be bought from a supplier. The solution should be colorless or straw yellow. For the preparation of a stable colorless solution see paragraph 5.1 of ISO 3657.
Electrolyte	c(TEABR) = 0.4 mol/L in ethylene glycol Metrohm No. 6.2320.000

Standard

TRIS	TRIS is dried over night in a drying oven at 105 °C and allowed to cool down in a desiccator for at least 1 h.

Sample preparation

Weigh out an appropriate amount of the sample (see table below) in a round-bottomed flask. Add 25 mL ethanolic c(KOH) = 0.5 mol/L and a magnetic stirring bar. Attach the reflux cooler, heat up and boil gently for 60 minutes, tilting the flask back and forth now and then.

Amount of sample

Expected SV / mg KOH / g	Sample amount / g
150 – 200	2.2 – 1.8
200 – 250	1.7 – 1.4
250 – 300	1.3 – 1.2
> 300	1.1 – 1.0

Analysis

Titer

About 420 mg TRIS is weighed into a titration vessel. 20 mL deionized water and 50 mL ethanol are added. After a pause of 20 s the solution is titrated with c(HCl) = 0.5 mol/L until the first equivalence point. In between measurements the electrode membrane is rehydrated for 1 min in deionized water.

Blank

Perform a sample preparation without sample for the blank test. After cooling, dilute the flask contents sufficiently with ethanol, insert electrode and burette tip, then back-titrate the KOH excess with c(HCl) = 0.5 mol/L until the first equivalence point. In between measurements the electrode membrane is rehydrated for 1 min in deionized water.

Sample

After cooling, dilute the flask contents sufficiently with ethanol, insert electrode and burette tip, then back-titrate the KOH excess with c(HCl) = 0.5 mol/L until the first equivalence point. In between measurements the electrode membrane is rehydrated for 1 min in deionized water.

Parameters

Titer

Mode	DET U
Pause	20 s
Signal drift	20 mV/min
Max. waiting time	38 s
Meas. point density	4
Min. increment	50 µL
Max. increment	off
EP criterion	5
EP recognition	greatest

Blank/Sample

Mode	DET U
Pause	20 s
Signal drift	20 mV/min
Max. waiting time	38 s
Meas. point density	4
Min. increment	10 µL
Max. increment	off
EP criterion	5
EP recognition	greatest

Calculation

Titer

$$\text{Titer} = \frac{m_s}{V_{EP1} \times c(HCl) \times M_A}$$

Titer:	Titer of the selected titrant
m_s:	Mass of standard in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c(HCl):	Concentration of the selected titrant in mol/L; here c(HCl) = 0.5 mol/L
M_A:	Molecular weight of the analyte; here 121.14 g/mol

Sample

$$SV = \frac{(V_{blank} - V_{EP1}) \times f \times c(HCl) \times M_A}{m_S}$$

SV:	Saponification value of the sample in mg KOH / g
V_{EP1}:	Titrant consumption until the first equivalence point in mL
V_{blank}:	Blank value consumption for the used quantity of solvent in mL
c(HCl):	Concentration of the selected titrant in mol/L; here c(HCl) = 0.5 mol/L
f:	Correction factor («titer») without unit
M_A:	Molecular weight of KOH; 56.1056 g/mol
m_s:	Sample size in g

Example determination

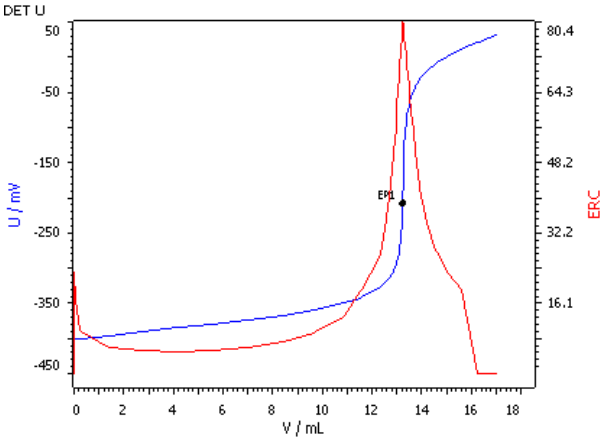

Fig. 4: Determination of the saponification value (blue = titration curve, red = ERC)

Comments

- Samples difficult to saponify should be boiled for 2 h.
- The potassium hydroxide solution should be colourless or straw yellow. A description for the preparation of a stable colourless solution can be found in the norm ISO 3657.
- For further information concerning the handling of the Solvotrode easyClean please study the leaflet sent with the electrode.

References

- DIN EN ISO 3657

  Animal and vegetable fats and oils – determination of saponification value

Acid value, free fatty acids

Summary

The acid value corresponds to the amount of carboxylic acid groups in fatty acids and is given in mg KOH per g sample. The older an oil is the higher the acid value as triglycerides are converted into fatty acids and glycerol upon aging.

Instruments

- Sample changer
- Titrator with DET mode
- Burette 20 mL
- Stirrer

Electrodes

Solvotrode easyClean	6.0229.020

Reagents

- Ethanol, p.a.
- Diethyl ether, peroxide-free, p.a.
- Phenolphthalein, p.a.

Solutions

Titrant	c(KOH) = 0.1 mol/L in ethanol or methanol If possible this solution should be bought from a supplier.
Solvent mixture	Ethanol / diethyl ether, Φ(EtOH) = 50% (v/v) Neutralized, just before use, with KOH in presence of 0.3 mL phenolphthalein solution per 100 mL solvent mixture.
Phenolphthalein solution	Phenolphthalein in ethanol, β(phenolphthalein) = 1 g / 100 mL.

Standard

Benzoic acid	Benzoic acid is dried in a desiccator over night.

Sample preparation

No sample preparation required.

Analysis

Titer

100 – 120 mg benzoic acid is weighed into the titration vessel and dissolved in 50 mL ethanol. The solution is then titrated using c(KOH) = 0.1 mol/L until after the first equivalence point.

Sample

An appropriate sample amount is weighed into a 150 mL beaker (see table below). 50 to 100 mL solvent mixture is added and the sample dissolved. After a pause of 30 s the solution is titrated until the first equivalence point using alcoholic c(KOH) = 0.1 mol/L.

Amount of sample

Expected AV / mg KOH / g	Sample amount / g	Accuracy / g
0 – 1	20	0.05
1 – 4	10	0.02
4 – 15	2.5	0.01
15 - 75	0.5	0.001
> 75	0.2	0.001

Parameters

Titer

Mode	DET U
Signal drift	50 mV/min
Max. waiting time	26 s
Meas. point density	4
Min. increment	10 µL
Max. increment	off
EP criterion	5
EP recognition	all

Sample

Mode	DET U
Signal drift	20 mV/min
Max. waiting time	38 s
Meas. point density	4
Min. increment	10 µL
Max. increment	off
EP criterion	5
EP recognition	all

Calculation

Titer

$$\text{Titer} = \frac{m_s}{V_{EP1} \times c(KOH) \times M_A}$$

Titer:	Titer of the selected titrant
m_s:	Mass of standard in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c(KOH):	Concentration of the selected titrant in mol/L; here c(KOH) = 0.1 mol/L
M_A:	Molecular weight of the analyte; here 122.12 g/mol

Acid value

$$AV = \frac{V_{EP1} \times f \times c(KOH) \times M_A}{m_S}$$

AV:	Acid value of the sample in mg KOH / g
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c(KOH):	Concentration of the selected titrant in mol/L; here c(KOH) = 0.1 mol/L
f:	Correction factor («titer») without unit
M_A:	Molecular weight of KOH; 56.1056 g/mol
m_s:	Sample size in g

Free fatty acids

$$FFA = \frac{V_{EP1} \times f \times c(KOH) \times M_A}{10 \times m_S}$$

FFA:	Acid value of the sample in %
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c(KOH):	Concentration of the selected titrant in mol/L; here c(KOH) = 0.1 mol/L
f:	Correction factor («titer») without unit
M_A:	Molecular weight of the acid chosen for the expression of the result in g/mol according to the fat type (see table below)
m_s:	Sample size in g

Choice of fatty acids for the free fatty acid content

Type of fat	Expressed as	Molar mass / g/mol
Coconut oil, Palm kernel oil and similar oils	Lauric acid	200
Palm oil	Palmitic acid	256
Oils from certain cruciferae	Erucic acid	338
All other fats	Oleic acid	282

Example determination

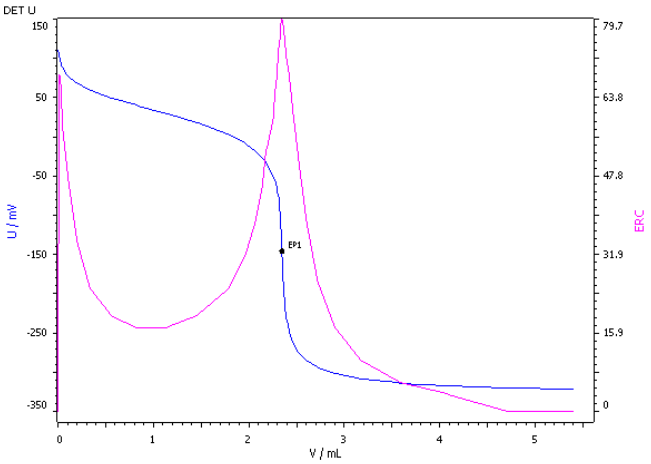

Fig. 5: Determination of the acid value (blue = titration curve, pink = ERC)

Comments

- For hard or animal fats, a solvent mixture of one volume ethanol and three volumes *tert*-butyl methyl ether or toluene is recommended.

  This mixture should also be neutralized.
- In the case of rapeseed oil having a maximum of erucic acid content of 5%, the acidity shall be expressed as oleic acid.
- If the results of the free fatty acids are simply reported as acidity, without further definition, this is by convention, expressed as oleic acid. If the sample contains mineral acids, these are, by convention, determined as fatty acids.
- For the determination of the free fatty acids with Titrotherm see Application Bulletin 315
- For further information concerning the handling of the Solvotrode easyClean please study the leaflet sent with the electrode.

References

- DIN EN ISO 660
  Animal and vegetable fats and oils – determination of acid value and acidity
- Application Bulletin 315
  Determination of free fatty acids (FFA) in edible oils with 859 Titrotherm

Hydroxyl value (ASTM E1899-08)

Summary

The hydroxyl value is given in mg KOH per g sample and gives information about the degree of esterification within the sample.

Instruments

- Sample changer
- Titrator with DET mode
- 1x Burette 50 mL (acetonitrile)
- 2x Burette 20 mL (reaction solution, titrant)
- 1x Burette 2 mL (dist. H_2O)
- Magnetic stirrer for sample changer
- DIS-Cover

Electrodes

Solvotrode easyClean	6.0229.010

Reagents

- Acetonitrile, HPLC quality
- Toluene-4-sulfonyl-isocyanate, purum (TSI)
- Ethanol, purity >99.8%
- Potassium hydrogen phthalate, KHP, p.a.

Solutions

Titrant	Tetrabutyl ammonium hydroxide, c(TBAOH) = 0.1 mol/L in isopropanol/methanol, Φ(MeOH) = 50% (v/v) If possible, this solution should be bought from a supplier.
TSI solution	The solution reacts vigorous with water, it is therefore recommended to work in a fume hood and under protective gas. Approximately 250 mL acetonitrile is given into a 500 mL volumetric flask and 20 mL TSI is added. The flask is filled up to the mark with acetonitrile and mixed. The reaction solution is stable for approximately 1 month.

Standard

KHP	KHP is dried in a drying oven for 2 h at 120 °C and allowed to cool down in a desiccator for at least 1 h.

Sample preparation

No sample preparation required.

Analysis

Titer

To approximately 180 mg KHP 60 mL dist. H_2O is added and the suspension stirred for about a minute in order to dissolve the KHP. The solution is then titrated until the first equivalence point using c(TBAOH) = 0.1 mol/L.

Sample

An appropriate amount of sample (see calculation below) is weighed into the titration vessel and dissolved in 10 mL acetonitrile. The beakers are covered and the solution is stirred for 30 s (stirring rate 8). 10.0 mL TSI solution are added and the sample is covered again and the mixture stirred (stirring rate 4). After 5 minutes 0.5 mL dist. H_2O is added, the lid is again closed and the solution stirred for another 60 s (stirring rate 4). 40 mL acetonitrile is added and the solution is titrated until after the second end point with c(TBAOH) = 0.1 mol/L.

After each titration, the burette and vessel are rinsed first with ethanol, then with dist. H_2O and the electrode is then conditioned for 1 min in dist. H_2O.

$$m_s = \frac{40}{OHV_{expected}}$$

m_s: Sample amount in g
$OHV_{expected}$: Expected hydroxyl value

Parameters

Titer

Mode	DET U
Pause	30 s
Signal drift	50 mV/min
Max. waiting time	26 s
Meas. point density	4
Min. increment	10 µL
Max. increment	off
EP criterion	5
EP recognition	greatest

Sample

Mode	DET U
Pause	30 s
Signal drift	50 mV/min
Max. waiting time	26 s
Meas. point density	4
Min. increment	10 µL
Max. increment	off
EP criterion	5
EP recognition	all

Calculation

Titer

$$\text{Titer} = \frac{m_s}{V_{EP1} \times c(\text{TBAOH}) \times M_A}$$

Titer:	Titer of the selected titrant
m_s:	Mass of standard in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c(TBAOH):	Concentration of the selected titrant in mol/L; here c(TBAOH) = 0.1 mol/L
M_A:	Molecular weight of the analyte; here 204.22 g/mol

Sample

$$\text{OHV} = \frac{(V_{EP2} - V_{EP1}) \times f \times c(\text{TBAOH}) \times M_A}{m_S}$$

OHV:	Hydroxyl value of the sample in mg / g KOH
V_{EP1}:	Titrant consumption until the first equivalence point in mL
V_{EP2}:	Titrant consumption until the second equivalence point in mL
c(TBAOH):	Concentration of the selected titrant in mol/L; here c(TBAOH) = 0.1 mol/L
f:	Correction factor («titer») without unit
M_A:	Molecular weight of the analyte; here 56.1 g/mol
m_s:	Sample size in g

Example determination

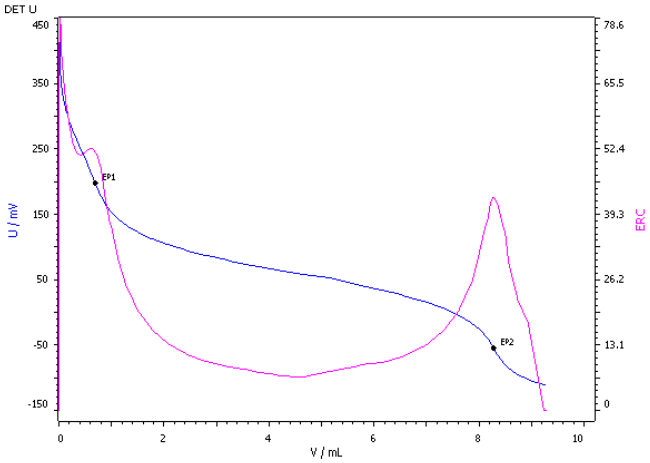

Fig. 6: Determination of the hydroxyl value (blue = titration curve, pink = ERC)

Comments

- The ASTM method is presented here, as it is faster (12 min) than the DIN 53240-2 method (40 min). For information about the automated determination of the hydroxyl value according to the DIN method see Metrohm Application Bulletin No. 322.
- For further information concerning the handling of the Solvotrode easyClean please study the leaflet sent with the electrode.

References

- ASTM E1899-08

  Standard test method for hydroxyl groups using reaction with p-toluene sulfonyl isocyante (TSI) and potentiometric titration with tetrabutyl ammonium hydroxide

Nickel traces

Summary

The production of margarine often involves the hardening of liquid oils by a catalytic hydrogenation of the fatty acids. A catalyst used for this process is nickel. Polarography can be used to determine traces of nickel impurities in the final product.

Instruments

- VA instrument
  capable of operating a mercury electrode and supporting DP mode

Electrodes

WE	Multi-Mode Electrode pro (MME pro)	6.1246.120
	Mercury drop capillary	6.1226.030
AE	Separate Pt rod electrode	6.0343.000
RE	Ag/AgCl reference electrode c(KCl) = 3 mol/L	6.0728.020
	Electrolyte vessel filled with c(KCl) = 3 mol/L	6.1245.010

Reagents

- Hydrochloric acid, w(HCl) = 30%, for trace analysis*, CAS 7647-01-0
- Ammonium hydroxide solution, w(NH_3) = 25 %, for trace analysis*, CAS 1336-21-6
- Dimethylglyoxim disodium salt octahydrate, Na_2DMG, for analysis, CAS 75006-64-3
- Ni standard stock solution, β(Cu^{2+}) = 1 g/L, commercially available
- Nitric acid, w(HNO_3) = 65 %, for trace analysis* CAS 7697-37-2
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

* e.g. Merck suprapur®, Sigma-Aldrich TraceSelect® or equivalent

Solutions

DMG solution	c(Na_2DMG) = 0.1 mol/L Dissolve 0.304 g Na_2DMG in 10 mL ultrapure water. This solution needs to be prepared daily.

Standard solution

Ni standard	β(Ni^{2+}) = 10 mg/L 0.5 mL Ni standard stock solution (1 g/L) and 0.05 mL nitric acid (65%) are made up to 50 mL with ultrapure water.

Sample preparation

Weigh out accurately 2.5 g sample in a round-bottomed flask. Add 2.5 mL w(HCl) = 30%, attach a reflux condenser, heat up the solution and keep boiling for 15 minutes. Rinse out the warm solution with a small quantity of ultrapure water into a separating funnel. Separate and collect the aqueous phase. Extract the round-bottomed flask and the fatty phase another three times with hot ultrapure water. Filter the combined aqueous extracts through a paper filter (e.g «White Ribbon Filter» grade 589/2) into a 100 mL volumetric flask, add 5 mL w(NH_3) = 25% and make up to the mark with ultrapure water.

Analysis

Measuring solution

20 mL sample extract (after sample preparation)

0.1 mL DMG solution

Pipette 20 mL of the prepared sample solution (corresponding to a 0.5 g portion of the original sample) into the polarography vessel and add 0.1 mL DMG solution. The pH of the measuring solution has to be 9.5 ± 0.1.

The concentration of Ni is quantified by two additions of Ni standard solution β(Ni^{2+}) = 10 mg/L.

Parameters

Volumes

Sample amount	0.5 g
Cell volume	20.1 mL

Voltammetric

Electrode	DME
Mode	DP – Differential pulse
Initial purge time	300 s
Hydrodynamic measurement	No
Sweep	
Start potential	-0.8 V
End potential	-1.4 V

Pulse amplitude	0.05 V
Pulse time	0.04 s
Voltage step	0.006 V
Voltage step time	0.6 s
Sweep rate	0.01 V/s

Substance and calibration

Name	Nickel
Peak potential	-1.0 V
Tolerance	0.05 V
Calibration method	Standard addition

Example determination

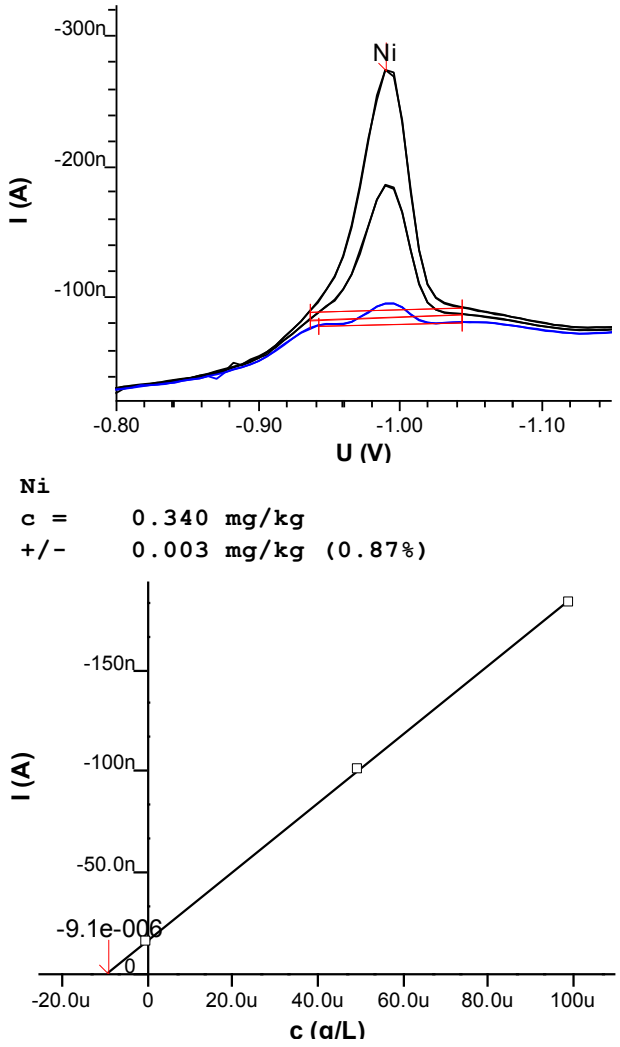

Fig. 7: Voltammogram and calibration curve of a determination of Ni in margarine (2.7 g sample extracted into 100 mL)

Comments

- Combustion as decomposition is unsuitable because volatile nickel carbonyl is lost in process.
- To determine the reagent blank the sample preparation procedure is carried like described just without the sample. The blank concentration is determined with the same parameters as for the sample. The blank concentration is then subtracted from the sample concentration.

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