Oleochemistry

Analyses in Oleochemistry

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The student should be able to understand and applied:

- The basic principles of analyses in Oleochemistry
- Method to determine some of the main properties of oleochemicals

Analysis in Oleochemistry

- Acid value (AV) / Free fatty acids (FFA)
- Saponification value (SV)
- Colour
- Moisture content
- Unsaponinifiable matter
- Iodine value (IV)
- Fatty acid composition analysis (GC)
- Lipid classes (HPTLC/ HPLC)
- Slip melting point (SMP)
- Peroxide value
- Insoluble impurities
- Heating and cooling profile using DSC

Acid value

Definition:

The acid value is the number of milligrams of potassium hydroxide necessary to neutralize the free acids in 1 gram of sample.

Number of mgs of KOH required to neutralize the Free Fatty Acids in 1 g of fat.

$$AV = \frac{\text{ml of KOH x N x 56}}{\text{Weight of Sample}} = \text{mg of KOH}$$

Acid value

In chemistry, acid value (or "neutralization number" or "acid number" or "acidity") is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound, such as a fatty acid, or in a mixture of compounds. In a typical procedure, a known amount of sample dissolved in organic solvent (often isopropanol), is titrated with a solution of potassium hydroxide with known concentration and with phenolphthalein as a color indicator.

Saponification value

Saponification value represents the number of milligrams of potassium hydroxide required to saponify 1g of fat under the conditions specified. It is a measure of the average molecular weight (or chain length) of all the fatty acids present. As most of the mass of a fat/triester is in the 3 fatty acids, it allows for comparison of the average fatty acid chain length. The long chain fatty acids found in fats have a low saponification value because they have a relatively fewer number of carboxylic functional groups per unit mass of the fat as compared to short chain fatty acids

$$\text{Saponification value} = \frac{56.1\ M\ (vb\text{-}vs)}{w}$$

Calculation:

i.	Weight of oils and fats that are used	=	w
ii.	Volume (mL) of needed hydrochloric acid for the sample	=	vs
iii.	Volume (mL) of needed hydrochloric acid for the blank	=	vb
iv.	Molarity of hydrochloric acid	=	M

Saponification value determination

Saponification # --mgs of KOH required to saponify 1 g of fat.

1. 5 g in 250 ml Erlenmeyer.
2. 50 ml KOH in Erlenmeyer.
3. Boil for saponification.
4. Titrate with HCl using phenolphthalein.
5. Conduct blank determination.

$$SP\# = \frac{56.1(B - S) \times N \text{ of HCl}}{\text{Gram of Sample}}$$

B - ml of HCl required by Blank.

S - ml of HCl required by Sample.

Saponification Value of Fats and Oils

Fat	Saponification #
Milk Fat	210-233
Coconut Oil	250-264
Cotton Seed Oil	189-198
Soybean Oil	189-195
Lard	190-202

Moisture content

Common method

1. Distillation method (moisture only)
2. Hot plate method (moisture &volatile matter)
3. Air oven method (moisture &volatile matter)
4. Vacuum oven method (moisture &volatile matter)
5. Modified Karl Fisher method
6. Modified Moisture ad volatiles matters method

1. Distillation method

(AOCS Official Method C2a045)

- Determine the moisture by distillation with an immiscible solvent
- Applicable to all normal fats and oils, including emulsion for the determination of moisture only.
- Not applicable to samples containing water miscible volatile substances or to samples containing added MAG

2. Hot plate method

(AOCS Official method Ca 2b-38)

- Determine the moisture and any other material volatile under the conditions of the test
- Applicable to all ordinary fats and oils including emulsions such as butter, oleomargarine & high-acid coconut oil
- Not applicable to certain abnormal samples such as solvent-extracted fats and oils which may contain residue from solvents with fairly high boiling points or to samples containing added MAG

3. Air oven method

(AOCS Official method Ca 2c-25)

- Determine the moisture and any other material volatile under the conditions of the test

- Applicable to animal and vegetable fats, but not to drying or semi-drying oils or oils of the coconut group

- Also not applicable to fats containing added MAG

4. Vacuum oven method

(AOCS Official method Ca 2d-25)

- Determine the moisture and any other material volatile under the conditions of the test

- Applicable to all normal fats and oils, except those of the coconut oil group containing 1% or more of FFA.

- Also not applicable to fats containing added MAG

5. Modified Karl Fisher Method

(AOCS Official method Ca 2e-84)

- Determine the actual water content of the fats and oils by titration with Fischer reagent which reacts quantitatively with water

- Applicable to fats and oils that do not react with and are soluble in the reagents and that do not contain impurities leading to 2nd reactions.

- Such impurities includes alkaline compounds and peroxides which react with the reagent and therefore show high results.

6. Modified Moisture ad volatiles matters method

(AOCS Official method Ca 2f-93)

- Determine moisture and volatile matter in fats and oils by addition of acetone to the fat or oil, followed by heating at 100°C
- Moisture and volatile matter are removed during evaporation of the acetone & are determine by the loss in weight of the original sample
- Applicable to crude fats and oil.
- Can be completed within an hour without the use of elaborated equipment
- Permitting a rapid determination of the commercial value of crude fats and oils.

Unsaponifiable matter (USm)

- Weight 5g±0.1mg sample in erlenmeyer flask.
- Add ethyl alcohol (30ml) & 50% KOH solution (5ml)
- Boil gently but reflux for 1 hour.
- Transfer to extraction cylinder and wash with 95% ethyl alcohol (40ml)
- Top up to 80ml with warm and cold distilled water.
- Wash with petroleum ether (5ml) & transfer into the cylinder; cool to RT
- Add petroleum ether (50ml) and shake vigorously.
- Allow for phase separation
- Upper layer (pet ether) is transferred into separation funnel
- Repeat at least 6 x.
- Remove solvent using rotary evaporators.
- Purge with N2 stream.
- Place in desiccators & weigh

Unsaponinifiable matter (USm)

$$\text{Unsaponifiable matter, \%} = \frac{A - (B+C) \times 100}{\text{Mass of sample, g}}$$

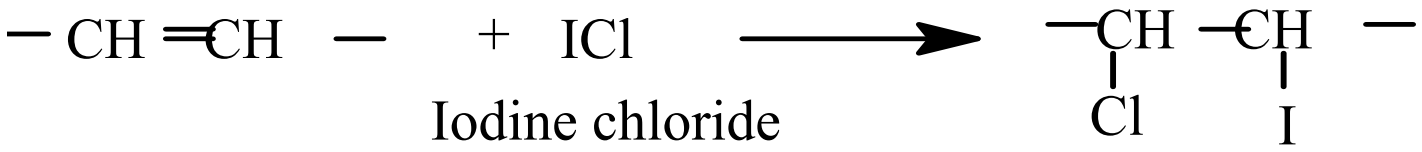
Where

A = mass of residue, g
B = mass of fatty acids, g
C = mass of blank, g

Cholesterol-Lowering by Rice Bran and Rice Bran Oil Unsaponifiable Matter in Hamsters

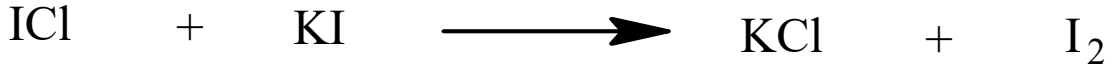
Iodine value (IV)

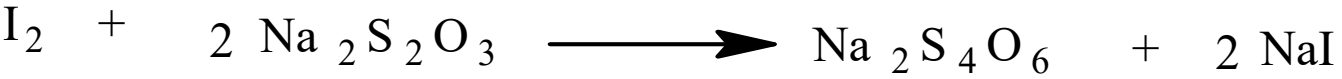
- the number of halogen (g) that has absorbed in the 100g fat and labeled as weight of iodine.



Principle of Iodine Value

- Iodine monochloride solution in acetic acid and carbon tetrachloride is added into the fat sample.
- After a certain fixed time, the amount of excess halogen is determined.
- This is carried on by changing the excess of iodine monochloride into the free iodine molecule through the addition of potassium iodide solution.
- The amount of free iodine is determined by titration with sodium thiosulphate, which is already standardized.





Iodine value (IV)

Table1: weigh the wanted fat mass depends on the iodine value prediction.

Prediction of iodine value	Fat mass is needed (g)
<5	3.00
5-20	1.00
21-60	0.34
61-80	0.25
81-130	0.15
>130	0.10

Iodine value (IV)

$$\text{Iodine value} = \frac{12.69N\,(vb-vs)}{w}$$

Calculation:

i. The mass (g) oil and fat is used = w

ii. The volume (mL) thiosulphate solution is needed for sample titration = vs

iii. The volume (mL) thiosulphate solution is needed for blank = vb

iv. The concentrate of sodium thiosulphate solution is needed = N

Fatty acid composition (FAC) analysis using Gas Chromatography (GC)

FAC analysis in a fats/oils samples generally can be divided into steps below:

a) Derivatization of lipid samples

b) Extraction of fatty acid methyl esters (FAMEs)

c) Sample preparation into GC vials

d) Injection into GC-FID

e) Determine peak areas of fatty acid

- Fatty acid are identified by retention time as compared to standards

Fatty acid composition (FAC) analysis using Gas Chromatography (GC)

2 generally used derivatization methods:

a) Acid-catalyzed esterification

(e.g. Boron trifluoride/methanol anhydrous)

b) Base-catalyzed transesterification

(e.g. sodium/potassium methoxide)

Conclusion

- The quality of oleochemicals can be determined by several methods.

Chapter description

All pictures/photographs/diagrams/figures used in this chapter is subjected to common creative that for education purposes