Identification / Analysis of Oil/Fats

- It usually involves determination of physical constants like melting point, refractive index, specific gravity and viscosity, etc. and chemical constants (often referred to as fat constant) like acid value, saponification value, iodine value, acetyl value, ester value and Rm value (Reichert Miessel value).

1. Acid Value

- It is defined as **"the no. of milligrams of KOH (potassium Hydroxide) required to neutralise the free carboxylic acid present in 1g of fat/oil"**.
- The acid value is determined by dissolving a weighed quantity of fat/oil in neutral alcohol and titrating the solution against standard KOH solution using phenolphthalein as an indicator.
- The acid value gives an idea of the amount of free acids present in a fat/oil.
- Higher acids value indicates a rancid oil/fat stored under improper condition.

Procedure:

i. Mix the oil/fat (melted) thoroughly before weighing. The mass of the test sample shall be taken based on the colour and expected acid value.

Expected acid value	Mass of test portion (g)	Accuracy of weighing test portion (g)
< 1	20	0.05
1-4	10	0.02
4-15	2.5	0.01
15-75	0.5	0.001
>75	0.1	0.0002

ii. Weigh accurately amount of the cooled oil sample in a 250 ml conical flask and add 50 to 100 ml of neutralised ethyl alcohol and about 1 ml of phenolphthalein indicator solution.

iii. Boil the mixture for about 5 min and titrate against standard alkali solution shaking vigorously during the titration.

iv. The weight of the oil/fat taken for estimation and the strength of the alkali used for titration shall be such that the volume of alkali required for titration does not exceed 10 ml.

Calculation:

Acid value = 56.1 x V x N / w

where v= volume in ml of standard KOH / NaOH used

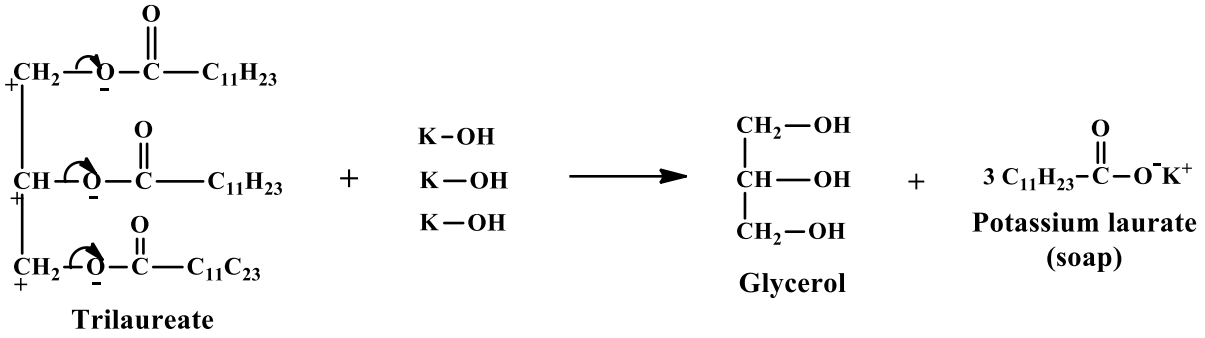
N= Normality of KOH solution or NaOH Solution

w= weight in gram of sample

2. Saponification Value

- The alkaline hydrolysis of fat/oil is called saponification because one of the product of hydrolysis is soap (Na^+/K^+ salt of fatty acids).

- This hydrolysis provides a method for determination of a constant called saponification number or value, which is defined as **" the number of milligrams of KOH required to completely saponify 1g of oil /fat, that is, to neutralise the fatty acids resulting from the complete hydrolysis of 1g of oil/ fat".**



Saponification value / no. of Trilaureate

= 3 molecules of KOH x 1000 / 1 molecule of oil/fat

= 56 x 3 x 1000/638

= 263.3

Saponification no. = 1,68,000 / M

where M = Mol. wt of fat/oil

Therefore, saponification value/no. $\propto$ 1 / M

- Higher the molecular wt. of fat, the smaller is its saponification value.
- saponification value of a fat gives an idea about its overage molecular wt.
- It also indicates the length of C chain of acid moiety of oil/fat.

Procedure:

i. Melt the sample if it is not already liquid and filter through a filter paper to remove any impurities and dry it, make sure that the sample is completely dry.

ii. Mix the sample thoroughly and weigh about 1.5-2 g of dry sample into a 250ml flask.

iii. Pipette 25ml of alcoholic potassium hydroxide solution into the flask. Conduct a blank determination along with sample.

iv. Connect the sample flask and blank flask with air condenser, keep on water bath, boil until saponification in complete as indicated by absence of any oily matter and appearance of clear solution.

v. Clarity may be achieved with in 1 hour of boiling. After the flask and condenser have pulled somewhat wash down the inside of condenser with about 10ml of hot ethyl alcohol neutral to phenolphthalein.

vi. Titrate the excess KOH with 0.5 N HCl, using about 1ml of phenolphthalein indicator.

3. Iodine Value /Number:

- The degree of unsaturation of a fat/oil is measured by its iodine value.
- The degree of absorption of halogen by a fat/oil is proportional to the no. of double bond in fatty acid moiety. Therefore, this addition reaction can be used as an index of degree of unsaturation in fat/oil.

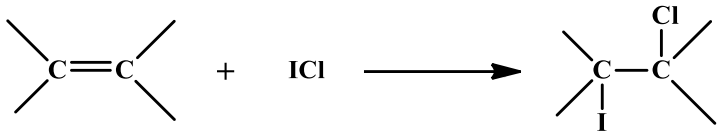
The index value is called iodine value/ number and is defined as **"the no. of grams of iodine (or its equivalent like ICl) that will add to 100gm of fat/oil"**.

- A known weight of fat /oil is dissolved in chloroform **Wij's solution** (Iodine monochloride ICl dissolved in acetic acid solution) is then added. ICl add across the C=C double bond. Excess ICl is then treated with KI solution to liberate the equivalent amount of Iodine and this is back titrated against standard hypo or sodium thiosulphate or sodium hyposulphite ($Na_2S_2O_3$) solution using starch as indicator, ICl (or an equivalent amount of I) that had added across the double bond is thus determined and the iodine value of fat/oil can be calculated as-

Iodine value = (V1-V2) x N x 12.7 / w

where V1= Vol. of hypo used for blank

ii) V2= Vol. of hypo used by unreacted iodine in back titration
iii) N = Normality of hypo solution
iv) w = Wt. of sample (fat/oil)



$$ICl + KI \rightarrow KCl + I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

Therefore, greater the no. of double bonds (unsaturation) an oil/fat, the greater is its iodine value.

4. Reichert-Meissl Value:

It is the **"no. of millilitres of 0.1 N KOH solution requires to neutralise the volatile water soluble acid obtained by hydrolysis of 5 g of fat."**

Rm Value = (A-B) x N X 11

Where- A = Volume in ml ofstandard NaOH solution required for test
B = Volume in ml of standard NaOH solution required for blank.
N = Normality of standard NaOH solution.

5. Acetyl Value:

Acetyl value is **" no. of milligrams of KOH required to neutralise the acetic acid produced hydrolysis of one gram of acetylated substance"**.

Acetyl Value= (Vol. of N/10 KOH used to neutralise acid) x (5.61) / Wt. of acetylated product taken

6. Ester Value:

The ester Value is **"the no. of milligrams of KOH required to saponify the esters in 1g of substance"**.

If the saponification value and acid value have been determined, the difference between these two represent the ester value i.e.,

Ester value = Saponification value - Acid value

Procedure:

i. Take 1.5 – 2.0 g substance, accurately weigh in250 ml of flask, add 20-30ml of neutralised alcohol and shake well.

ii. Add 1 ml of phenolphthalein and titrate with 0.5 N alcoholic KOH until the free acid is neutralised.

iii. Add 25 ml of 0.5 N alcoholic KOH.

iv. Collect the sample flask and blank flask with air condenser. Keep on water bath, boil until saponification is complete as indicated by absence of oily matter and appearance of clear solution.

v. Clarity may be achieved within 1 hr. of boiling. After the flask and condenser have pulled somewhat wash down the inside of condenser with about 10ml of hot ethyl alcohol neutral to phenolphthalein.

vi. Titrate the excess KOH with 0.5 N HCl, using about 1ml of phenolphthalein.

vii. Calculate the ester value.

$$\text{Ester value} = [\text{Mol. wt.} \times (V_B - V_T) \times N] / w$$

where- mol. wt. = Mol. Wt. of KOH (56.1)

V_B = Vol. of 0.5 N HCl consumed in the blank test (ml)

V_T = Vol. of 0.5 N HCl consumed in actual test (ml)

N = Normality of HCl

W = Wt. of substance taken for the test (g)