Fats: Triesters of long chain of saturated fatty acids with glycerol, e.g. wool fat
Oils: Triesters of long chain of unsaturated fatty acids with glycerol, e.g. oleive oil

Physical properties of oils and fats

The analysis of the physical properties of oils and fats allows us to understand the behavior and characteristics of these elements, as well as their differences. For this, the crystallization, the melting point, the viscosity, the refractive index, the density, the solubility, the plasticity and the emulsifying capacity will be analyzed. Here we provide more detail on each of these.

Crystallization

Fats differ from oils in their degree of solidification at room temperature, since in these conditions the oils are in a liquid state (not crystallized) while the fats are in the solid (crystallized) state.

The proportion of crystals in fats have great importance in determining the physical properties of a product. Fats are considered solid when they have at least 10% of their crystallized components.

The fat crystals have a size between 0.1 and 0.5 μm and can occasionally reach up to 100 μm. The crystals are maintained by Van der Waalls forces forming a three-dimensional network that provides rigidity to the product.

An important feature of fat is its crystalline polymorphism since mono-di and triglyceride crystallize in different crystalline forms (α, β, β')

- **Form α (vitreous state):**
  - appears when the fat solidifies by a quick method.
  - the crystals formed are of the hexagonal type and are organized randomly in space.
- **Form β:**
  - it occurs when the cooling is slow or if the tempering is carried out at a temperature slightly below the melting point, this form being the most stable of all.
  - in the β form, tricyclic crystals are formed oriented in the same direction.
  - the β form is typical of palm oil, peanut, corn, coconut, sunflower, olive and lard.
- **Form β':**
  - it is produced from the tempering above the melting point of the α form.
  - in the β-form, orthorhombic crystals are formed which are oriented in opposite directions.
  - the β'form is typical of modified partial cottonseed oil, fats, fats and modified lard.

Both α, β and β'form have a melting point, an X-ray diffusion pattern and a refractive index. The more double bond there is, the crystallization with which it tends to be liquid is hindered.

Melting point

The melting point of a fat corresponds to the melting point of the β form which is the most stable polymorphic form and is the temperature at which all the solids melt.

When short chain or unsaturated acids are present, the melting point is reduced.

The melting point is of great importance in the processing of animal fats.

The melting points of pure fats are very precise, but since fats or oils are made up of a mixture of lipids with different melting points we have to refer to the melting zone which is defined as the melting point of the fat component. the fat that melts at a higher temperature.

Viscosity

The viscosity of a fat is due to the internal friction between the lipids that constitute it. It is generally high due to the high number of molecules that make up a fat.

By increasing the degree of unsaturation the viscosity decreases and when the length of the chain increases the fatty acids components also increases the viscosity.

Refractive index

The refractive index of a substance is defined as the ratio between the speed of light in air and in matter (oil or fat) that is analyzed.

Increasing the degree of unsaturation increases the refractive index and when the length of the chain increases, the refractive index also increases and that is why it is used to control the hydrogenation process.

As the temperature increases, the refractive index decreases.

The refractive index is characteristic of each oil and fat, which helps us to perform a quality control on them.

Density

This physical property is of great importance when it comes to designing equipment to process grease.

Density decreases when fats dilate when going from solid to liquid

When the fats melt, their volume increases and therefore the density decreases.

For the control of percentages of solid and liquid in commercial fat, dilatometric curves are used.

Solubility

Solubility has great relevance in the processing of fats.

Fats are fully soluble apolar solvents (benzene, hexane …).

Except for phospholipids, they are completely insoluble in polar solvents (water, acetonitrile). They are partially soluble in solvents of intermediate polarity (alcohol, acetone)

The solubility of fats in organic solvents decreases with increasing chain length and degree of saturation.

Phospholipids can interact with water because the phosphoric acid and the alcohols that compose them have hydrophilic groups.

Generally the surface tension increases with the length of the chain and decreases with temperature. Surface tension and interfacial tension decrease with ease with the use of surfactant agents such as monoglycerides and phospholipids.

Plasticity

It is the property that has a body to preserve its shape by resisting a certain pressure.

The plasticity of a fat is caused by the presence of a three-dimensional network of crystals inside which liquid fat is immobilized.

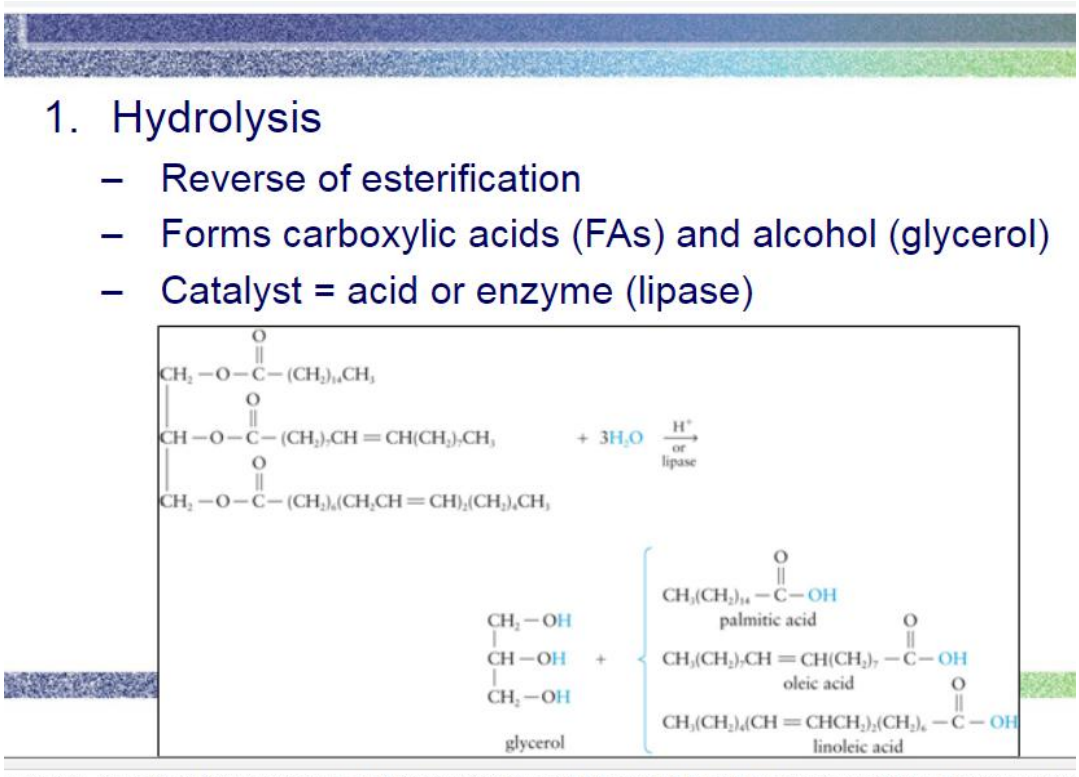
For a grease to be plastic and extensible there must be a ratio between the solid and liquid part (20 - 40% solid state fat), the nets must not be tight and their crystals must be in α form.

The plastic fats act as a solid until the deforming forces that are applied break the crystal lattice and the grease passes to behave like a viscous liquid and therefore can be smeared.

Emulsifying capacity

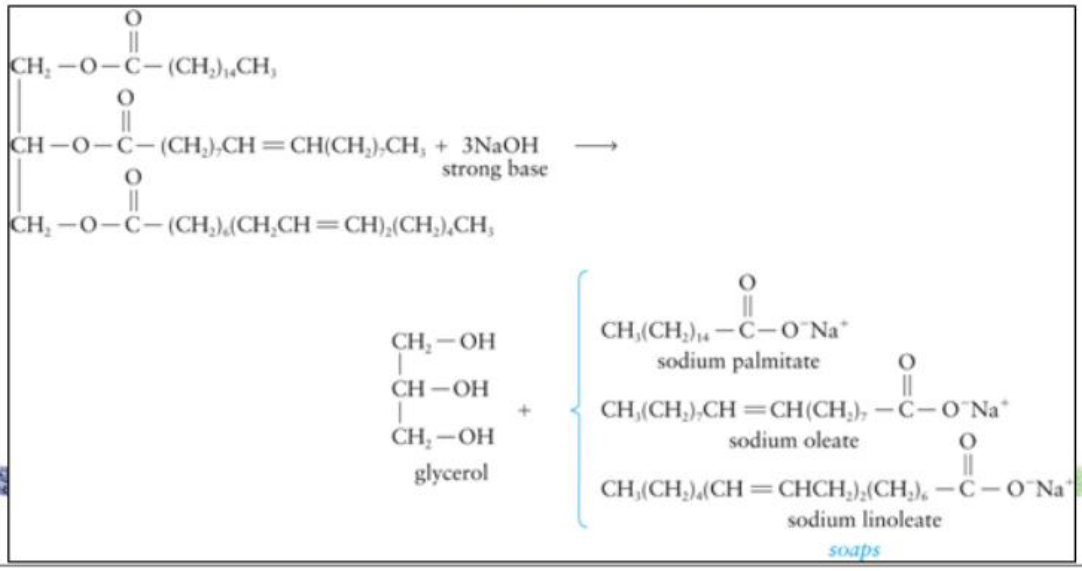
The emulsifying capacity is the capacity in the water / oil interface allowing the formation of emulsion.

Chemical properties of oils and fats



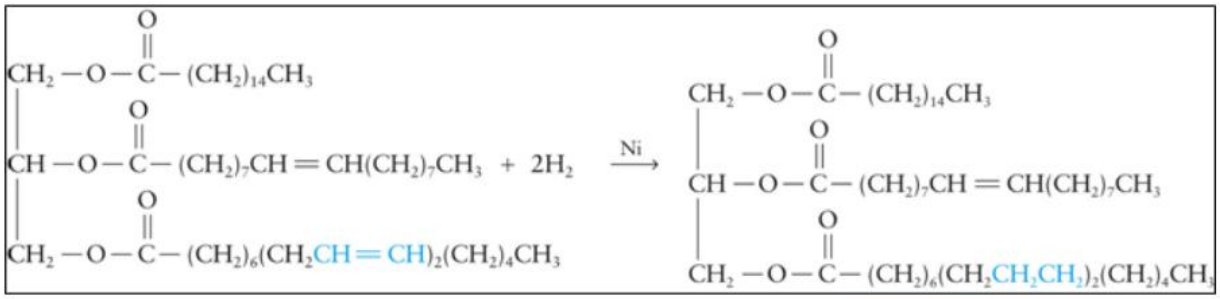
2. Saponification (hydrolysis in base)

- Forms carboxylic acid salts (soaps)
- Na^+ = hard soap; K^+ = liquid soap



3. Hydrogenation

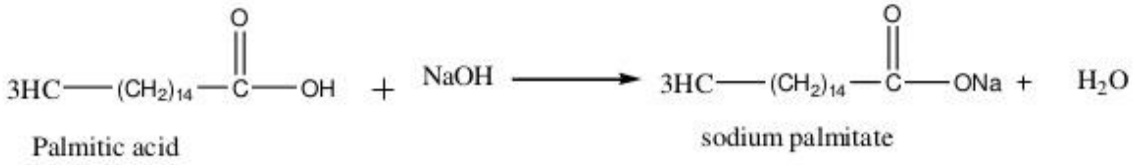
- Unsaturated chains add H_2 (become "hydrogenated")
- Increase the melting point (become semi-solid)



- Side effect = production of trans fats

Chemical reaction:

1.Salt formation: Fatty acid reacts with base to form salt or soap.

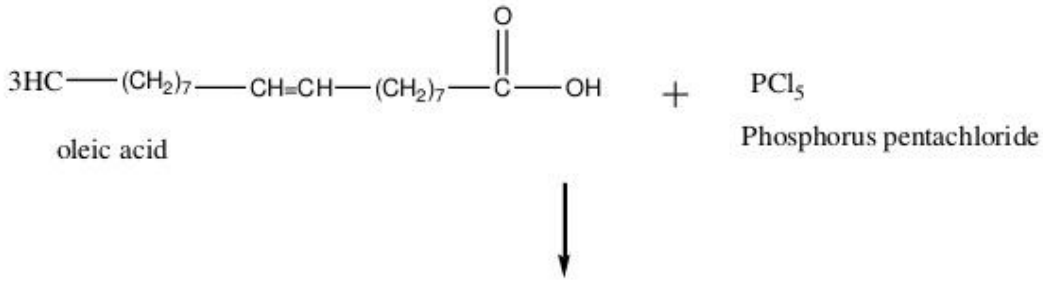


Palmitic acid

sodium palmitate

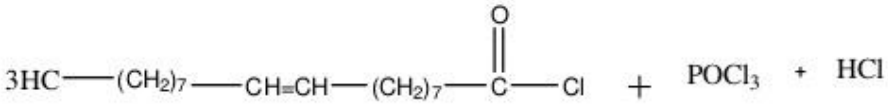
2. Formation of halides:

Fatty acids react with phosphorus halides to form acyl halides.



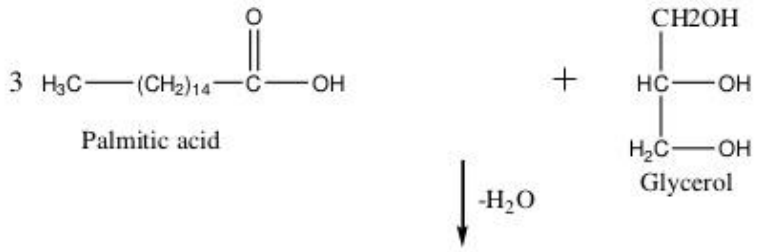
oleic acid

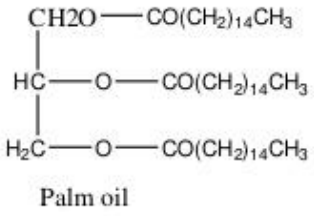
Phosphorus pentachloride



3. Formation of esters:

Fatty acids reacts with alcohol in the presence of a strong acid to form ester(triglycerides)



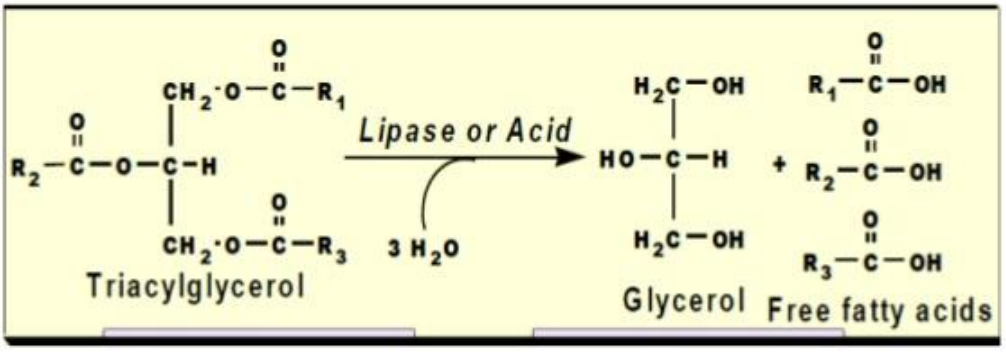


Palm oil

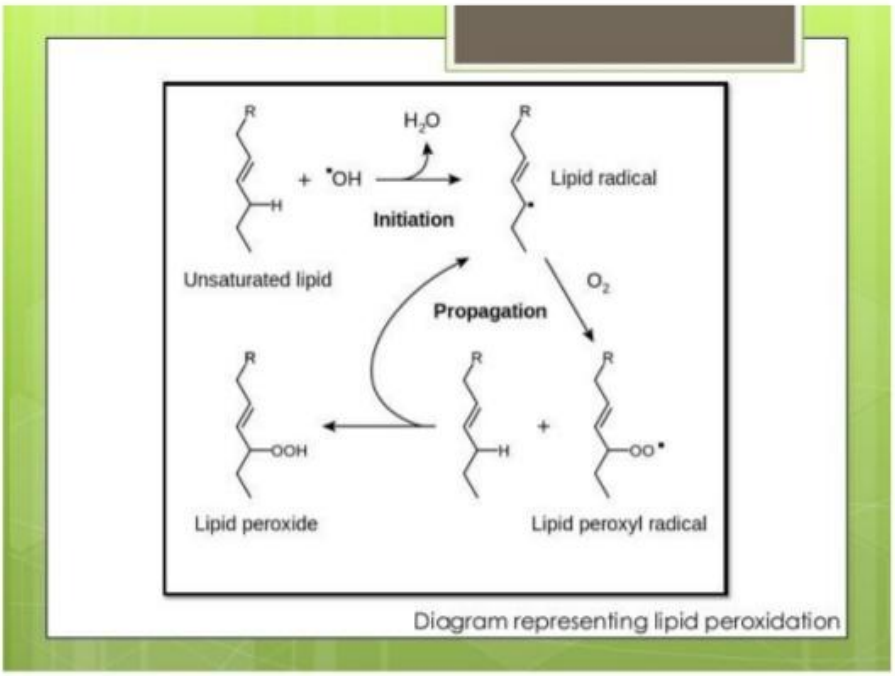
5. Rancidity

The term rancid is applied to any fat or oil that develops a disagreeable odour when left exposed to warm, moist air for any length of time.
Rancidity is by hydrolysis of the ester links and oxidation of double bonds of the triglycerides. The lower molecular weight acids that are produced are volatile and impart an offensive odour to fat or oil.

Hydrolytic rancidity



Oxidative rancidity: lipid perioxidation



Identification of fats and oils

Lipid index	Details	Significance
Saponification number	Number of mg of KOH required to saponify the free and combined fatty acids in 1G. of a given fat	Indicates molecular weight and is inversely proportional to it.
Iodine number	Number of grams of iodine absorbed by 100 gm of fat	It is a measure of degree of unsaturation of a fat
Acid number	Number of mg of KOH required to neutralize the fatty acids in a gram of a fat	Indicates the degree of rancidity of a fat

Identification of fats and oils(Contd.)

Lipid index	Details	Significance
Polenske number	Number of ml of 0.1 normal KOH required to neutralize the insoluble fatty acids from 5 gram of fat	Indicates the presence of non volatile fatty acids in a given fat
Reichert-Meissl Number	Number of ml of 0.1 N alkali required to neutralize the soluble fatty acids distilled from 5 G of fat	Measures the amount of volatile soluble fatty acids.
Acetyl Number	Number of mg of KOH required to neutralize the acetic acid obtained by saponification of 1G.of fat after it has been acetylated.	Measures the number of –OH groups present in a fatty acid

Determination of Saponification Value

Definition:

The saponification value is the number of mg of potassium hydroxide required to saponify 1 gram of oil/fat.

Principle:

The oil sample is saponified by refluxing with a known excess of alcoholic potassium hydroxide solution. The alkali required for saponification is determined by titration of the excess potassium hydroxide with standard hydrochloric acid.

Apparatus:

a.250 ml capacity conical flask with ground glass joints.

b.1 m long air condenser, or reflux condenser (65 cm minimum in length) to fit the flask (a).

c.Hot water bath or electric hot plate fitted with thermostat.

Reagents:

(i) Alcoholic potassium hydroxide solution - Reflux 1.2 litre alcohol 30 minutes with 10 gm KOH and 6 gm granulated Aluminium or Al foil. Distill and collect 1 litre after discarding first 50 ml. Dissolve 40 g of potassium hydroxide in this 1 litre alcohol keeping temperature below 15 0 Cwhile dissolving

alkali. Allow to stand overnight, decant the clear liquid and keep in a bottle closed tightly with a cork or rubber stopper.

ii) Phenolphthalein indicator solution - Dissolve 1.0 g of phenolphthalein in 100 ml rectified spirit.

iii) Standard hydrochloric acid: approximately 0.5N

Procedure:

Melt the sample if it is not already liquid and filter through a filter paper to remove any impurities and the last traces of moisture. Make sure that the sample is completely dry. Mix the sample thoroughly and weigh about 1.5 to 2.0 g of dry sample into a 250 ml Erlenmeyer flask.

Pipette 25 ml of the alcoholic potassium hydroxide solution into the flask. Conduct a blank determination along with the sample. Connect the sample flasks and the blank flask with air condensers, keep on the water bath, boil gently but steadily until saponification is complete, as indicated by absence of any oily matter and appearance of clear solution. Clarity may be achieved within one hour of boiling. After the flask and condenser have cooled somewhat wash down the inside of the condenser with about 10 ml of hot ethyl alcohol neutral to phenolphthalein. Titrate the excess potassium hydroxide with 0.5N hydrochloric acid, using about 1.0 ml phenolphthalein indicator.

Calculation:

Saponification Value = 56.1 (B-S)N / W

Where,

B = Volume in ml of standard hydrochloric acid required for the blank.

S = Volume in ml of standard hydrochloric acid required for the sample

N = Normality of the standard hydrochloric acid and

W = Weight in gm of the oil/fat taken for the test.

Determination of Acid Value

Definition:

The acid value is defined as the number of milligrams of potassium hydroxide required to neutralize the free fatty acids present in one gram of fat. It is a relative measure of rancidity as free fatty acids are normally formed during decomposition of oil glycerides. The value is also expressed as per cent of free fatty acids calculated as oleic acid.

Principle:

The acid value is determined by directly titrating the oil/fat in an alcoholic medium against standard potassium hydroxide/sodium hydroxide solution.

Apparatus:

250 ml conical flasks.

Reagents:

a) Ethyl alcohol :- Ninety-five per cent alcohol or rectified spirit neutral to phenolphthalein indicator.

b)Phenolphthalein indicator solution :- Dissolve one gram of phenolphthalein in 100 ml of ethyl alcohol.

c)Standard aqueous potassium hydroxide or sodium hydroxide solution 0.1 or 0.5 N.The solution should be colorless and stored in a brown glass bottle.

Procedure:

Mix the oil or melted fat thoroughly before weighing. Weigh accurately about 5 to 10 g of cooled oil sample in a 250 ml conical flask and add 50 ml to 100 ml of freshly neutralised hot ethyl alcohol and about one ml of phenolphthalein indicator solution. Boil the mixture for about five minutes and titrate while hot against alkali solution shaking vigorously during the titration. The weight of the oil/fat taken for the estimation and the strength of the alkali used for titration shall be such that the volume of alkali required for the titration does not exceed 10 ml.

Calculation:

Acid value = 56.1VN/ W

Where V = Volume in ml of standard potassium hydroxide or sodium hydroxide used

N = Normality of the potassium hydroxide solution or Sodium hydroxide solution; and

W = Weight in g of the sample

The acidity is frequently expressed as free fatty acid for which calculation shall be

Free fatty acids as oleic acid = $\frac{28.2\ VN}{W}$ per cent by weight

Acid value = Percent fatty acid (as oleic) x 1.99

Determination of Iodine Value

Definition:

The iodine value of an oil/fat is the number of grams of iodine absorbed by 100g of the oil/fat, when determined by using Wijs solution.

Principle:

The oil/fat sample taken in carbon-tetrachloride is treated with a known exces of iodine monochloride solution in s acetic (Wijs solution). The excess of iodine monochloride is treated with potassium iodide and the liberated iodine estimated by titration with sodium thiosulfate solution.

Apparatus:

500 ml Erlenmeyer flask.

Reagents:

i)Potassium dichromate AR
ii) Concentrated hydrochloric acid AR
iii) Glacial acetic acid, free from ethanol
iv) Carbon tetrachloride, analytical reagent grade
v) Iodine mono-chloride (ICl)
vi)Potassium iodide (free from potassium iodate) - 10% solution prepared fresh
vii)Starch solution - Mix 5 g of starch and 0.01 g of the mercuric iodide with 30 ml of cold water and slowly pour it with stirring into one litre of boiling water.

Boil for three minutes. Allow to cool and decant off the supernatant clear liquid.

viii) Wij's Iodine monochloride solution - Dissolve 10 ml of iodine monochloride in about 1800 ml of glacial acetic acid and shake vigorously. Pipette 5 ml of Wij's solution, add 10 ml of potassium iodide solution and titrate with 0.1N standard sodium thiosulphate solution using starch as indicator. Adjust the volume of the solution till it is approximately 0.2 N

Iodine Content – Pipette 5 ml Wij Solution into 500 ml Erlenmeyer flask containing 150 ml saturated Cl – water and some glass beads. Shake , heat to boiling point and boil briskly 10 minutes. Cool, add 30 ml H_2SO_4 (1 + 49) and 15 ml 15 % KI solution and titrate immediately with 0.1 N $Na_2S_2O_3$.

Total Halogen content – Pipette 20 ml Wij's solution into 500 erlenmeyer flask containing 150 ml recently boiled and cooled water and 15 ml 15 % KI solution. Titrate immediately with 0.1 N $Na_2S_2O_3$. I / Cl = 2 X / (3B – 2 X) where X = ml of 0.1 $Na_2S_2O_3$ required for I content and B = ml required for total halogen content. I / Cl ratio must be 1.10 0.1

ix) Standard sodium thiosulphate solution (0.1N)- Dissolve approximately 24.8 g of sodium thiosulphate crystals ($Na_2S_2O_3.5H_2O$) **in distilled water** and make up to 1000 ml.

Procedure:

Oil / fat may be weighed accurately following the Table given below:

Expected Iodine Value	Weight to be taken for estimation (g)	
	Maximum	Minimum
5	6.3460	5.0770
10	3.1730	2.5384
50	0.6612	0.5288
100	0.3173	0.2538
150	0.2125	0.1700
200	0.1586	0.1269

Weigh accurately an appropriate quantity of the dry oil/fat as indicated in the Table above, into a 500 ml conical flask with glass stopper, to which 25 ml of carbon tetrachloride have been added. Mix the content well. The weight of the sample shall be such that there is an excess of 50 to 60 percent of Wij's solution over that actually needed. Pipette 25 ml of Wij's solution and replace the glass stopper after wetting with potassium iodine solution.

Swirl for proper mixing and keep the flasks in dark for half an hour for non-drying and semi-drying oils and one hour for drying oils. Carry out a blank simultaneously. After standing, add 15 ml of potassium iodide solution, followed by 100 ml of recently boiled and cooled water, rinsing in the stopper also. Titrate liberated iodine with standardised sodium thiosulphate solution, using starch as indicator at the end until the blue colour formed disappears after thorough shaking with the stopper on.

Conduct blank determinations in the same manner as test sample but without oil/fat. Slight variations in temperature appreciably affect titre of I 2 solution as chloroform has a high coefficient of expansion. It is thus necessary that blanks and determinations are made at the same time

12.3.5 Calculation:

Iodine value = 12.69 (B – S) N/ W

Where, B = volume in ml of standard sodium thiosulphate solution required for the blank.

S= volume in ml of standard sodium thiosulphate solution required for the sample.

N = normality of the standard sodium thiosulphate solution. W = weight in g of the sample.

Reichert-Meissl number:

- The amount of free water soluble, volatile fatty acids butyric - C to capric - C 10) present in a fat or oil is expressed in terms of *Réichert-Meissl umber.*
- *It is defined as the Number of millilitres of 0-1 M potassium hydroxide solution required* to neutralise 5 grams of fat. Reichert-Meissl Number of a fat is determined by treating a known weight of it with ethanolic alkali and distilling the volatile acids. These are titrated against M/10 potassium hydroxide and Reichert-Meissl Number calculated.

Principle:

In this method, milk fat is saponified using glycerol- alkali solution, diluted with water and acidified by sulphuric acid to liberate free fatty acids. Thereafter, the liberated fatty acids are steam distilled in a glass apparatus under specified conditions and the steam volatile fatty acids are collected (as condensate). The cooled condensate of the steam volatile fatty acids is filtered for separation of water soluble and water insoluble fatty acids. The water soluble fatty acids which pass through the filter paper are estimated by **titration with alkali to give RM value, while the water - insoluble fatty acids collected on the filter paper are dissolved in alcohol and titrated to give the polenske value.**