Core Course 12: Food Chemistry – I

UNIT 3: Lipids (part - b)

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Introduction

In continuation with the first part, let us learn about the physical and chemical properties of lipids in this unit. In earlier unit, you learnt about the definition of lipids, followed by classification. You learnt how lipids are named, based on their common name, systemic or Geneva name, or omega system.

Lipid plays a major role in foods. In addition to their nutritional importance lipids are also used in foods because of their characteristic physicochemical properties. They are also used as heat transfer agents during the preparation of other foods. In order to make changes in lipid composition while ensuring the production of high quality foods, a fundamental understanding of the chemical and physical properties of lipids is critical. It is important to know analytical techniques that can be used to characterize the physicochemical properties of lipids. Therefore, this chapter focuses on the chemical and physical properties of lipids.

Thorough study of this unit will be able to understand:

- ✓ Physical properties -melting point, softening point, specific gravity, refractive index, smoke, flash and fire point, turbidity point.
- ✓ Chemical properties-reichert meissel value, polenske value, iodine value, peroxide value, saponification value.

1. Physical properties:

1.1. Melting Point

When a pure chemical compound is heated, it undergoes a phase transition from solid to liquid at a sharply defined temperature. *The melting point is an index of the force of attraction between molecules. The greater the attractive forces between molecules, the more easily they will associate to form a solid. It is harder to separate*

them when they are in the crystalline form and convert them to a liquid. A lot of energy in the form of heat must be put in to convert a solid to a liquid. Therefore, melting point will be high for particular fat. In other words, a high melting point indicates a strong attractive force between molecules. A strong attractive force indicates a good degree of fit between the molecules. Molecules that do not fit together well do not have strong attractive forces holding them together. Therefore, they have low melting points.

A fat or oil, which is a mixture of several triglycerides, has a lower melting point and a broader melting range. The melting range is dependent on the fatty acids of the component triglycerides. Fats also may be plastic at room temperature, containing some triglycerides that are liquid and some that are solid. Oils, liquid at room temperature tend to be more unsaturated, have shorter chains, and have lower melting points. Fats, which are plastic or solid, with long chains and high melting points at room temperature.

As mentioned, the melting point of a fat or oil is actually a range, not a sharply defined temperature. Each fat or oil contains triglycerides that melt at different temperatures, depending on their component fatty acids. Some fats have a wide melting range, whereas others, such as butter or chocolate, have a narrow melting range. Chocolate has a narrow melting range that is close to body temperature. This accounts for its characteristic melt-in-mouth property.

The melting points of individual fatty acids depend on chain length, number of double bonds (degree of saturation), and isomeric configuration. All these factors affect the degree of fit and the force of attraction between fatty acid molecules.

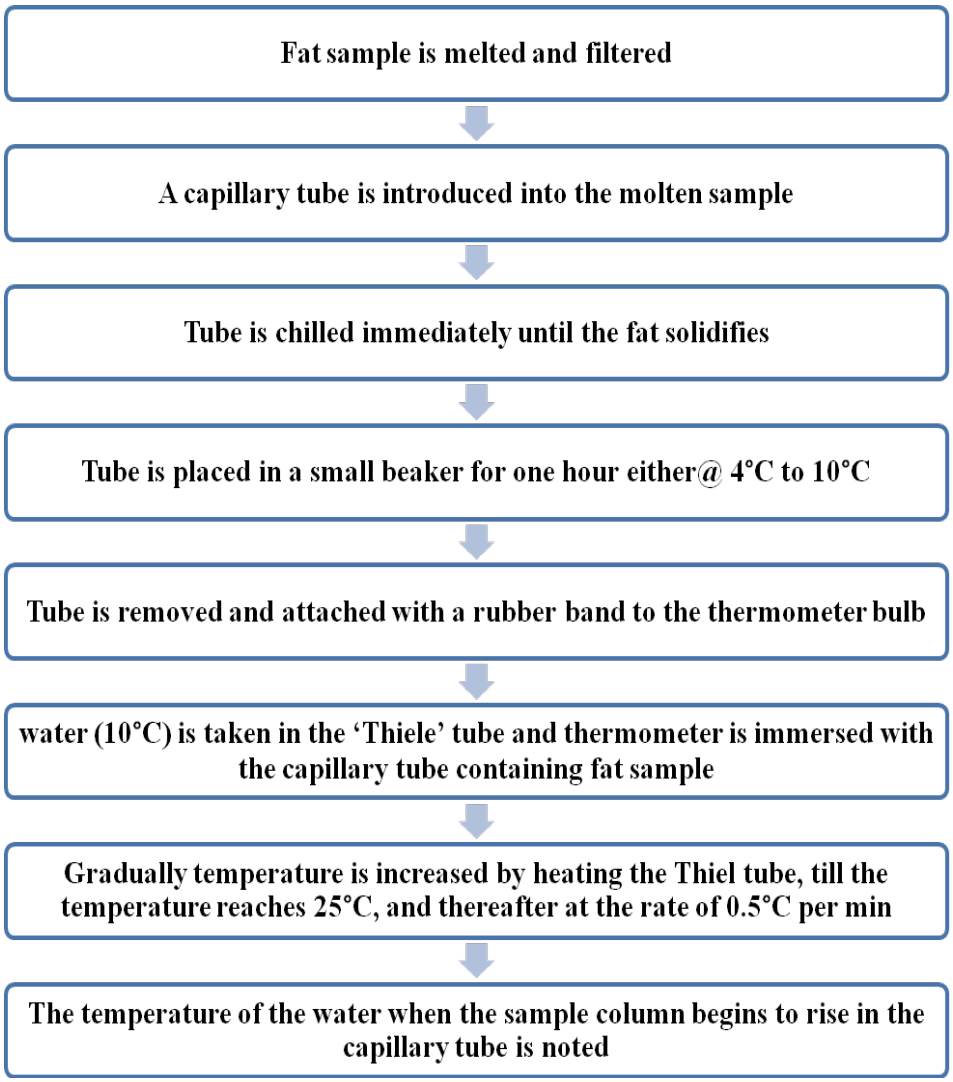
1.1.1. Chain length: Long-chain fatty acids have a higher melting point than short chain fatty acids. Potential for attraction is more between long chains than there is between short chains. For example, butyric acid (4:0) has a melting point of −7.9°C, whereas stearic acid (18:0) has a higher melting point of 69.6°C. Stearic acid is a crystalline solid and butyric acid is a liquid at room temperature.

1.1.2. Number of double bonds: As the number of double bonds increases, the melting point decreases. Double bonds introduce kinks into the chain and it is harder for molecules to fit together to form crystals. Thus, the attractive forces between the molecules are weaker. This is demonstrated by comparing the melting points of stearic, oleic, linoleic, and linolenic acids in **Table 1**.

1.1.3. Isomeric configuration: Geometric isomers have different melting points. Cis double bond configuration introduces a much bigger kink into the molecule than does the trans configuration. Consequently, the cis isomer has a lower melting point than the trans isomer.

1.1.4. Determination of melting point:

Melting point is determined by Open-tube capillary-slip method. The principle in this method is the temperature at which the oil or fat softens or becomes sufficiently fluid to slip or run as determined by the open-tube capillary-slip method **(Figure 1)**. The procedure for estimation of melting point of fats is shown below.



1.2. Softening point

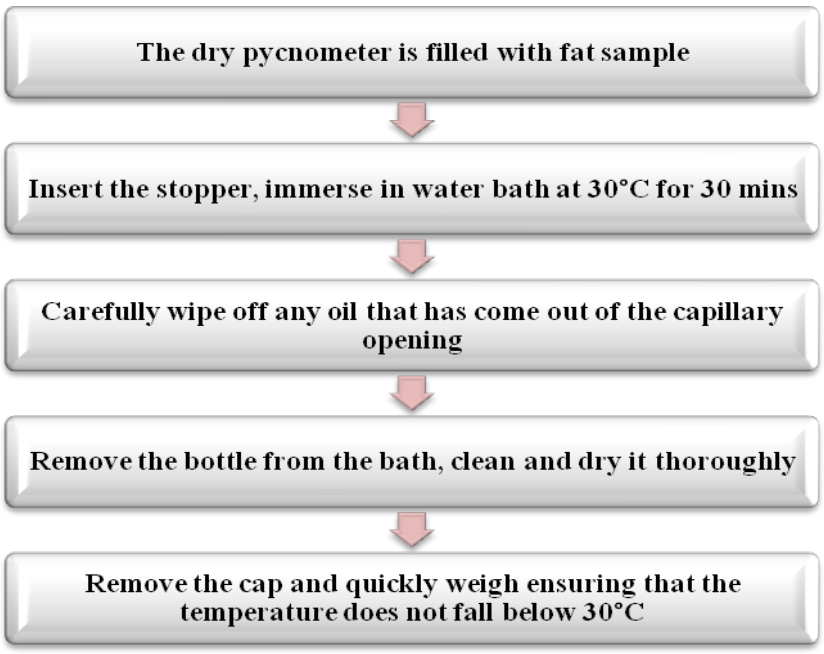
Fats do not melt immediately, but soften over a range of temperatures. This property is called softening of fats, and gives each fat its unique character. A plastic

fat is moldable because it contains both liquid oil and solid crystals of triglycerides. If liquid triglycerides are more, fats will be softer. If solid triglycerides are more, fats will be harder. A plastic fat is a two-phase system, containing solid fat crystals surrounded by liquid oil. The liquid phase acts as a lubricant, enabling the solid crystals to slide past one another. Therefore, fat can be pressed and moulded into shapes without breakage. A fat that contains only solid triglycerides is brittle and cannot be molded. In these, the crystals cannot move past each other.

1.2.1. Determination of Softening point: The principle for determination of softening point and melting point is same. In melting point estimation, open capillary tube is followed, where as in estimation of softening point, closed capillary tube method is followed. The endpoint is the physical movement of the fat column under a standardized hydrostatic pressure.

1.3. Specific gravity:

The term specific gravity is used to denote the ratio between the weight of a substance and the weight of an equal volume of water. The weights are compared at the same temperature. The specific gravity of the fats is less than 1 (about 0.86) and, therefore, they float on water surface. Solid fats are lighter than the liquid fats. Oils spread on water to form thin layers. The procedure for the estimation of specific gravity using pycnometer **(Figure 2)** is shown below.



Specific gravity at 30°C / 30°C = $\frac{A - B}{}$

C – B

Where,

A = weight in gm of specific gravity bottle with oil at 30°C

B = weight in gm of specific gravity bottle at 30°C

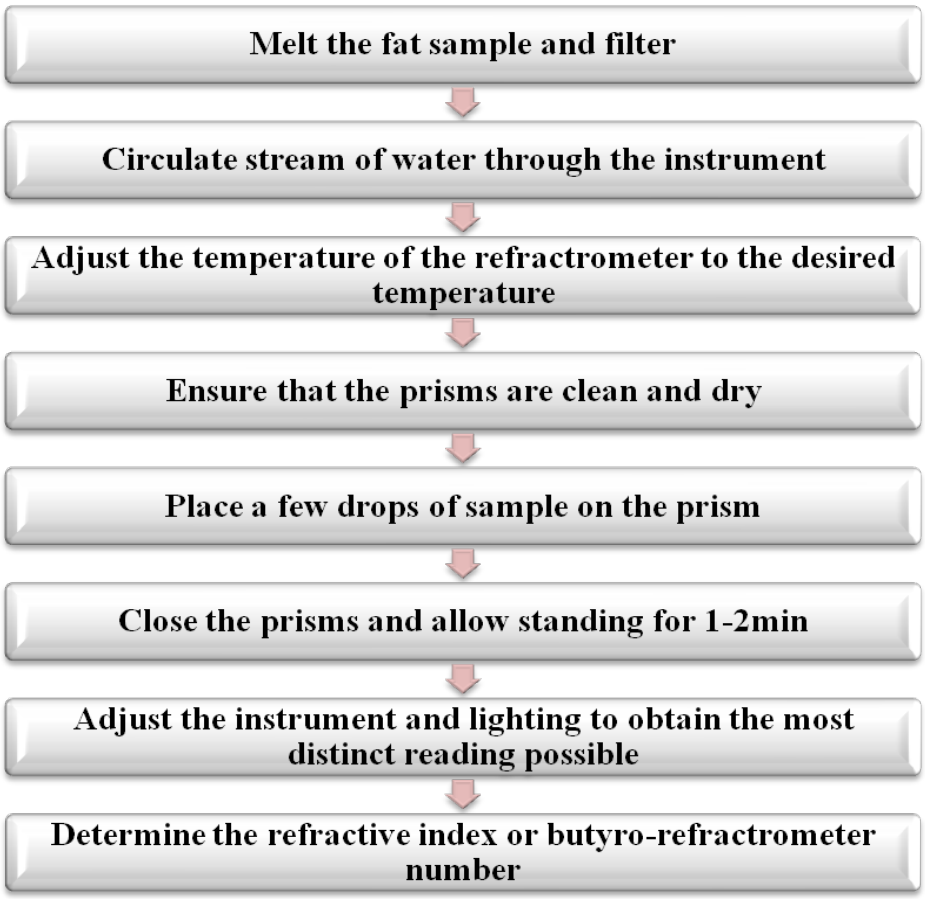
C = weight in gm of specific gravity bottle with water at 30°C

If the specific gravity of an oil is given as 0.919 at 25°/25°C. It means that the weight of the oil at 25°C is compared with the weight of an equal volume of water at 25°C. The average specific gravity of some edible fats and oils are.

- Butter: not <0.905 at 40°/40°C
- Cottonseed oil: 0.917-0.918 at 25°/25°C
- Corn oil: 0.919-0.921 at 25°/25°C
- Lard: 0.931-0.932 at 15°/15°C
- Olive oil: 0.916-0.918

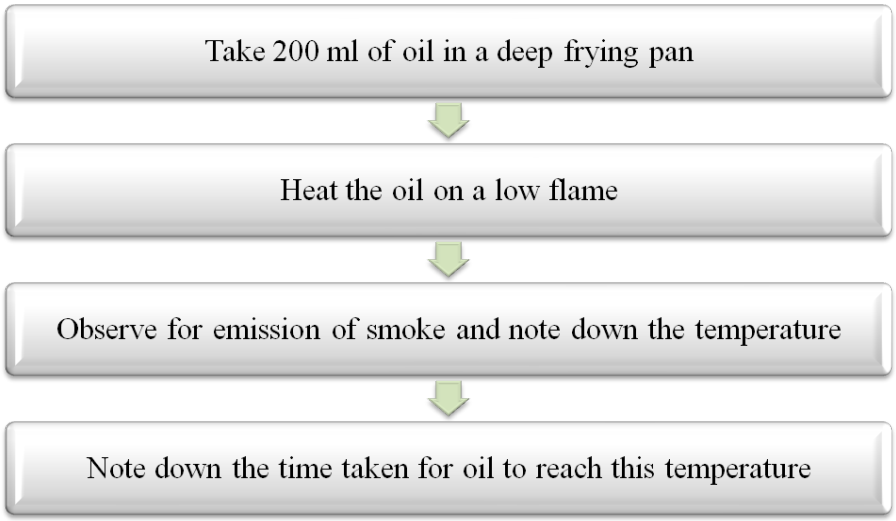
1.4. Refractive Index

Refractive Index is the ratio of velocity of light in vacuum to the velocity of light in the oil or fat. It expresses the ratio between the sine of angle of incidence to the sine of angle of refraction when a ray of light of known wave length passes from air into the oil or fat. Refractive index varies with temperature and wavelength. Measurement of the refractive index of the sample is carried out by means of a suitable refractrometer **(Figure 3)**. The procedure for measuring refractive index is shown below.



1.5. Smoke Point

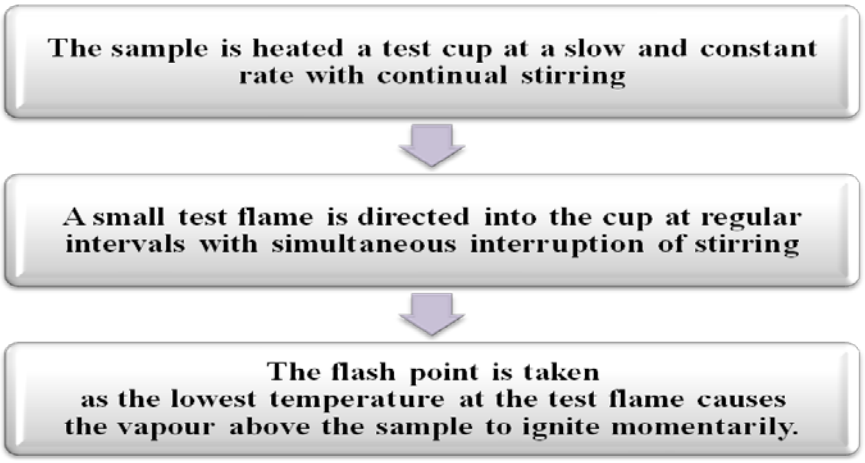
The smoke point is the temperature at which fat gets heated before continuous puffs of blue smoke come from the surface of the fat under controlled conditions. The presence of smoke indicates that free glycerol has hydrolyzed to yield acrolein. Acrolein is a mucous membrane irritant. Monoglycerides in hydrogenated shortenings and diglycerides are hydrolyzed more easily than triglycerides. Monoglycerides and diglycerides tend to have a low smoke point. There are many factors which affect the smoking point **(Table 2).** Smoking point is measured by using the following AOCS Method.



Smoking temperature is important for fats used for frying. Fats with low smoke point **(Table 3)** are not suitable for frying because of the odour and irritating effect of the fumes. The decomposition products may give an unpleasant flavour to the food. Hence it is preferable to use fats with relatively high smoking temperatures for frying.

1.6. Flash Point:

The flash point is the temperature at which the volatile products generated by the lipid are being produced at a rate where they can be temporarily ignited by application of a flame, but cannot sustain combustion. Flash point is determined by Pensky Marten (Closed Cup) Method **(Figure 4)**. The following method helps to determines the temperature at which the sample will flash when a test flame is applied.

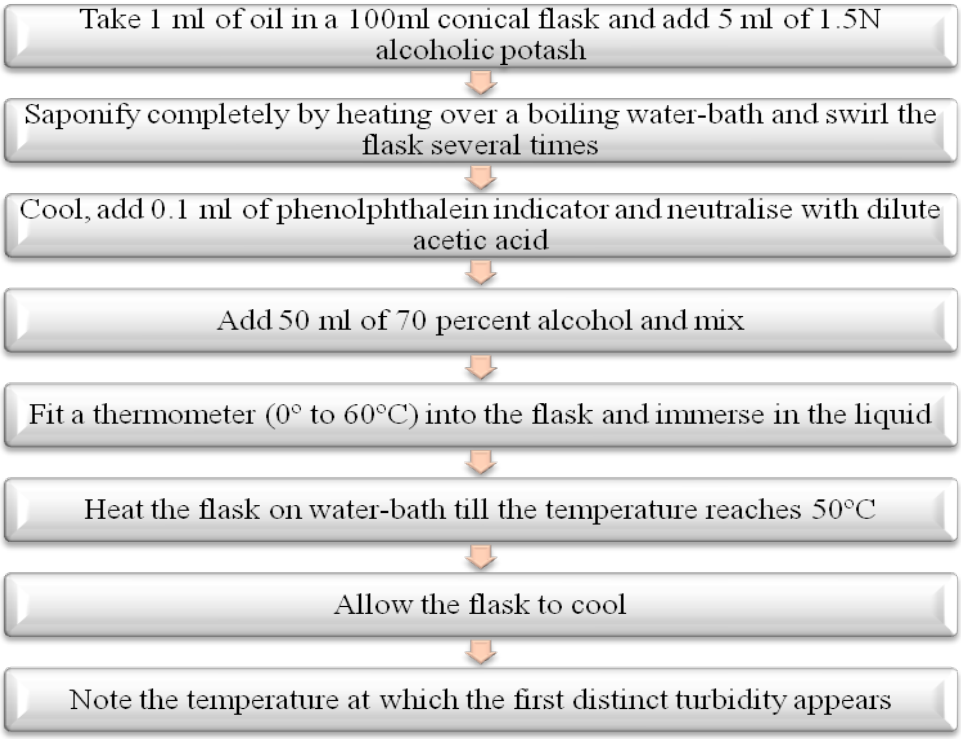


1.7. Fire Point:

The fire point is the temperature at which the volatile products will support continued combustion with application of a flame **(Figure 5)**. Measurements of these temperatures are particularly important when selecting lipids that are going to be used at high temperatures (e.g., during baking or frying).

1.8. Turbidity Temperature:

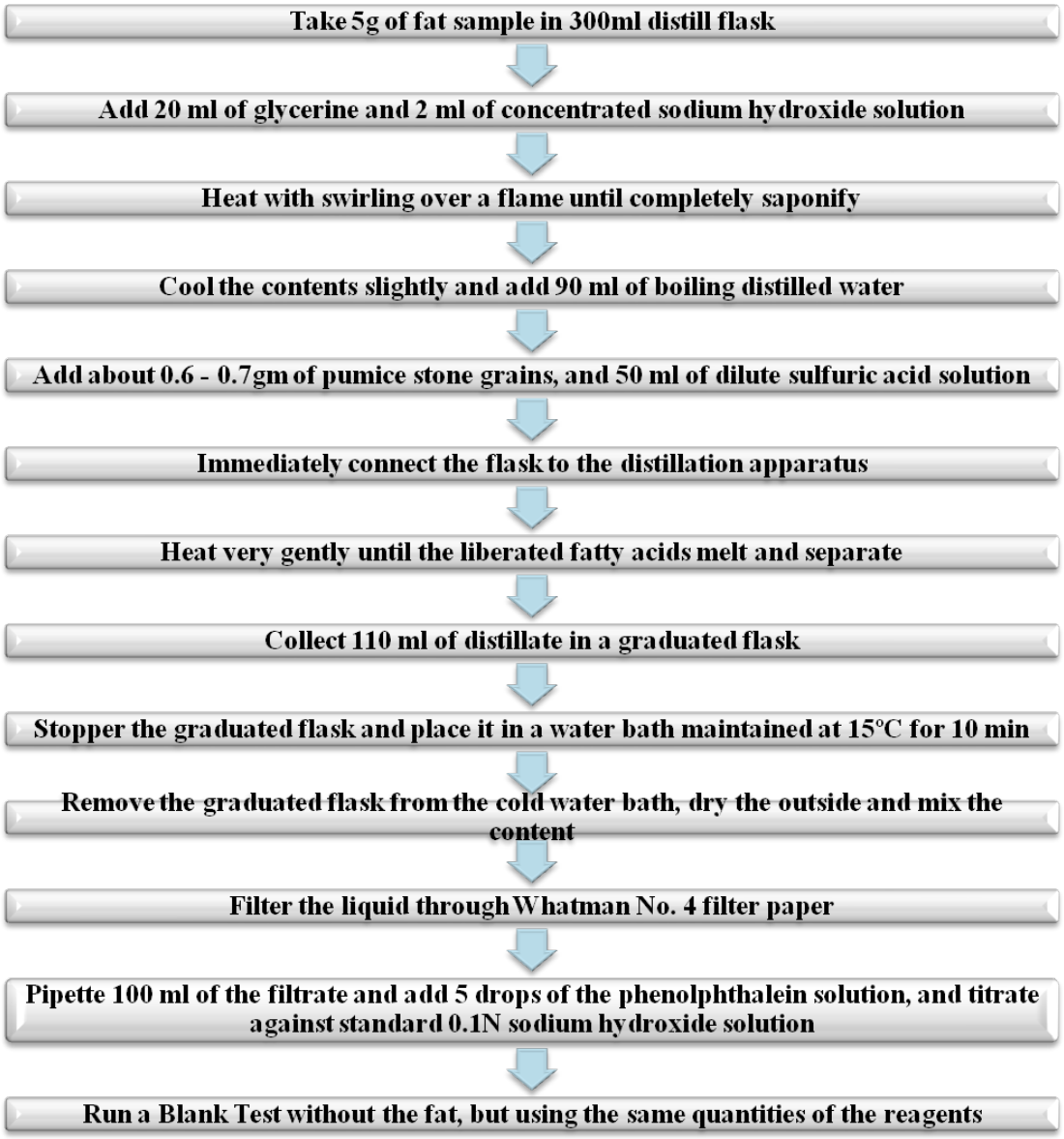
Oils containing long chain saturated fatty acids give a precipitate at a particular temperature. This temperature is specific for the oil when their alcoholic soap solution is treated with dilute acetic acid solution and 70% ethyl alcohol. Turbidity temperature is measured by using following Bellier Test using Acetic Acid.



2. Chemical properties

2.1 Reichert-Meissl value and Polenske value:

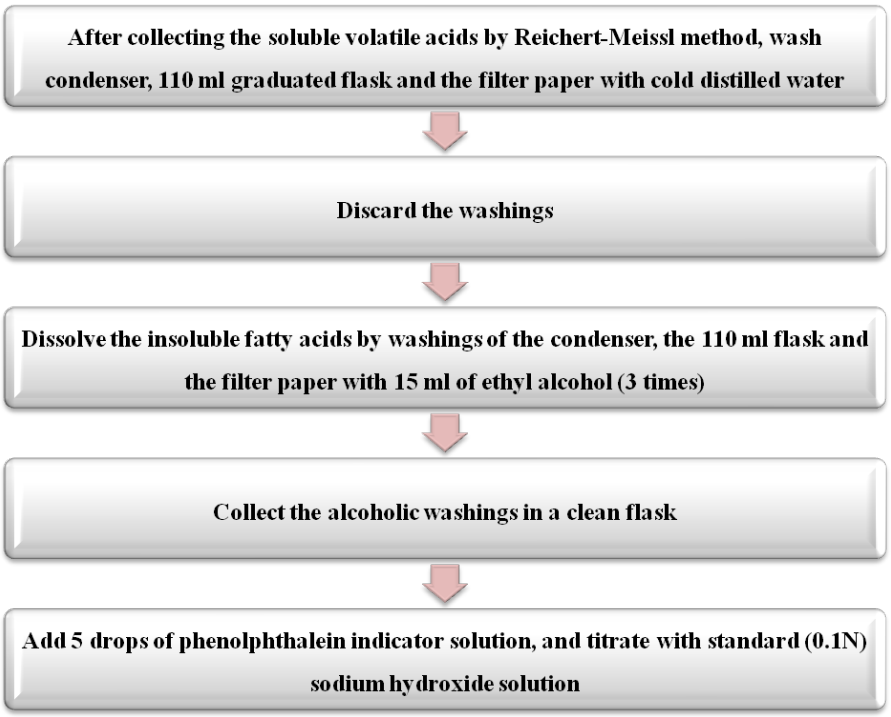
The Reichert-Meissl value is the number of milliliters of 0.1N aqueous sodium hydroxide solution required to neutralize steam volatile water-soluble fatty acids distilled from 5g of an oil/fat under the prescribed conditions **(Figure 6A)**. It is a measure of water-soluble steam volatile fatty acids chiefly butyric and caproic acids present in oil or fat by the following method.



Reichert-Meissl Value = (A – B) x N x 11

where,
A = Volume in ml of standard sodium hydroxide solution required for the test
B = Volume in ml in standard sodium hydroxide solution required for the blank
N = Normality of standard sodium hydroxide solution.

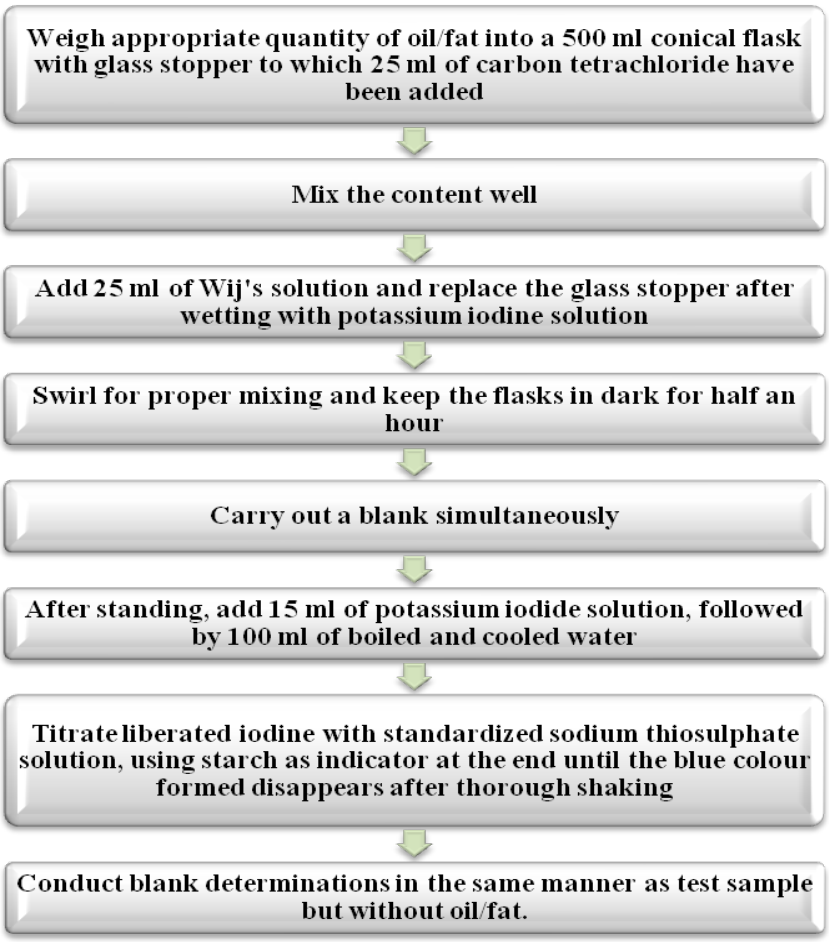
The Polenske value is the number of millilitres of 0.1N aqueous KOH required to neutralize steam volatile water insoluble fatty acids distilled from 5 gm of fat/oil under the prescribed conditions **(Figure 6B)**. It is a measure of the steam volatile and water insoluble fatty acids, chiefly caprylic, capric and lauric acids present in oil or fat by the following method.



The Reichert-Meissl number, measures the quantity of short chain fatty acids (up to C 10 inclusive) in the fat molecule. The Reichert-Meissl numbers of coconut and palm oils range between 5 and 8. Butterfat is exceptional in having a high Reichert-Meissl number, ranging from 17-35. This high value makes possible the detection of any foreign fats which are, sometimes, adulterated in the manufacture of butter. Coconut and palm kernel oil contain appreciable quantities of caprylic and capric and lauric acid glycerides. These fatty acids are steam volatile but not soluble in water, and hence give high Polenske value.

2.2 Iodine value

The iodine value is defined as the percentage of iodine absorbed by an oil, fat or wax. The iodine value is a simple and rapidly determined chemical constant for a fat or oil. It is a valuable characteristic in fat analysis that measures unsaturation but does not define the specific fatty acids. Iodine-value analyses are very accurate and provide nearly theoretical values. Iodine value is a useful tool for process control and product specification. Iodine value is a measure of the unsaturation of fats and oils and is expressed as the iodine absorbed per 100 parts by weight of fat. The following method is used to measure iodine value of fat sample.



Iodine value = $\frac{12.69\ (B - S)\ N}{W}$

Where,

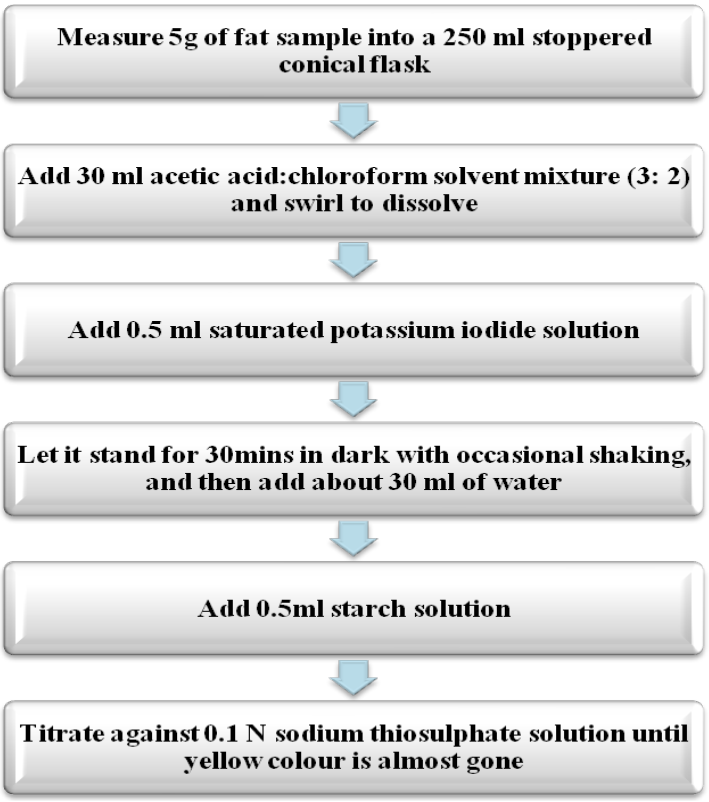
B = volume in ml of standard sodium thiosulphate solution required for the blank
S = volume in ml of standard sodium thiosulphate solution required for the sample
N = normality of the standard sodium thiosulphate solution
W = weight in g of the sample

The iodine-value procedure must be performed very precisely and timed carefully. Oils like soybean, corn and cottonseed have higher iodine numbers (133, 127 and 109, respectively) than the solid fats such as beef fat or tallow (42). Because they contain more unsaturated fatty acids in the fat molecule.

2.3. Peroxide Value

Oxidation of lipids is a major cause of their deterioration. Hydroperoxides formed by the reaction between oxygen and the unsaturated fatty acids are the primary products of this reaction. Hydroperoxides have no flavor or odor but break

down rapidly to form aldehydes, which have a strong, disagreeable flavor and odor. The peroxide concentration, usually expressed as peroxide value, is a measure of oxidation or rancidity in its early stages. *Peroxide value (PV) measures the concentration of substances (in terms of milliequivalents of peroxide per 1000 grams of sample) that oxidize potassium iodide to iodine.* Peroxide value is one of the most widely used chemical tests for the determination of fats and oils quality. PV shows good correlation with organoleptic flavor scores. The method for estimation of PV is shown below.



Peroxide value expressed as milli equivalent of peroxide oxygen per kg sample (meq/kg):

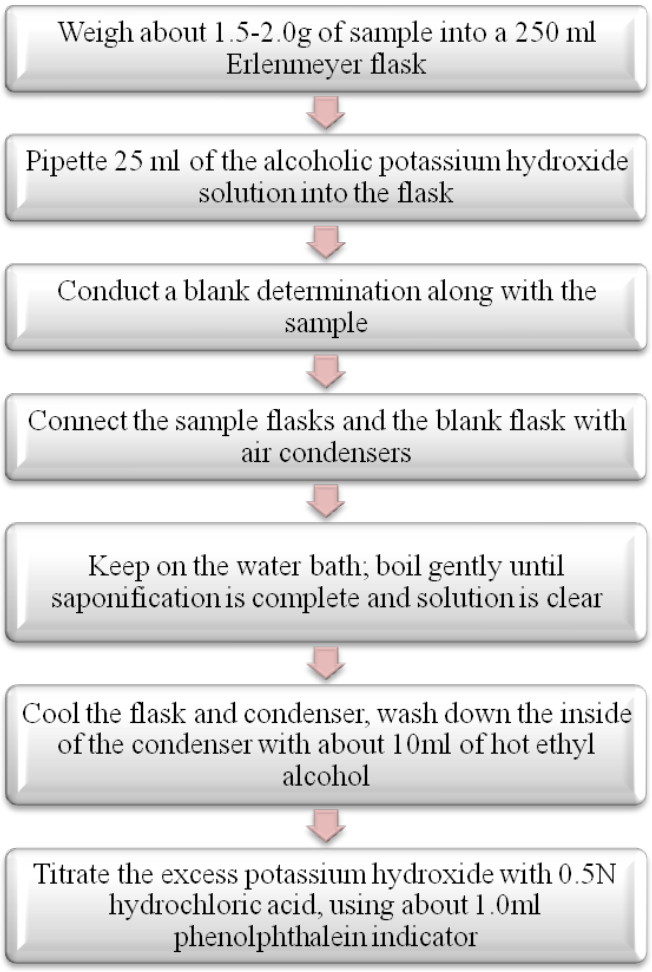
$$\text{Peroxide value} = \frac{\text{Titre X N X 100}}{\text{Weight of the sample}}$$

Where,
Titre = ml of Sodium Thiosulphate used (blank)
N = Normality of sodium thiosulphate solution.

2.4. Saponification Value:

The saponification value is defined as the number of mg of potassium hydroxide required to saponify 1 gram of oil/fat. Saponification value is a measure of

the alkali-reactive groups in fats and oils and is useful in predicting the type of glycerides in a sample. Glycerides containing short-chain fatty acids have higher saponification values than those with longer chain fatty acids. The saponification value, along with the iodine value determination, have been useful screening tests both for quality control and for characterizing types of fats and oils. The method for estimation of saponification value is shown below.



$$\text{Saponification Value} = \frac{56.1\,(B-S)N}{W}$$

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

3. Conclusion:

Lipid plays a major role in foods. Analytical techniques followed for estimation of physical and chemical properties is required for making changes in lipid composition. The methods that are used for the analysis of physical properties are melting point, softening point, specific gravity, refractive index, smoke, flash and fire point, turbidity point. Analysis of chemical properties includes, reichert meissel value, polenske value, iodine value, peroxide value and saponification value. Melting point is determined by open-tube capillary-slip, while softening point by closed-tube capillary-slip method. Melting points of individual fatty acids depend on chain length, number of double bonds, and isomeric configuration. Specific gravity is measured using pycnometer and the specific gravity of the fats is less than 1. Refractive index varies with temperature and wavelength and is estimated using butyro refractrometer. The smoke, flash and fire points of a fatty material are standard measures of its thermal stability when heated in contact with air. Oils containing fatty acids of low molecular weight have lower smoke, flash, and fire points. Reichert-Meissl helps to estimate volatile water-soluble fatty acids, while Polenske value estimates volatile water insoluble fatty acids. Peroxide value helps in determination of oxidation of lipids. Saponification value and iodine value, have been useful screening tests for quality control and for characterizing types of fats and oils.

Table 1: Melting point of different fatty acids

Systematic Name	Common Name	No. of Carbons	Melting Point (°C)
Ethanoic	Acetic	2	
Butanoic	Butyric	4	-7.9
Hexanoic	Caproic	6	-3.4
Octanoic	Caprylic	8	16.7
Decanoic	Capric	10	31.6
Dodecanoic	Lauric	12	44.2
Tetradecanoic	Myristic	14	54.4
Hexadecanoic	Palmitic	16	62.9
Octadecanoic	Stearic	18	69.6
Eicosanoic	Arachidic	20	75.4
Docosanoic	Behenic	22	80
9-Octadecenoic	Oleic	18-1	16.3
9,12-Octadecadienoic	Linoleic omega-6	18-2	-6.5
9,12,15-Octadecatrienoic	Linolenic omega-3	18-3	-12.8

Table 2: Factors affecting Smoking Point

Factor	Effect
Hydrolysis of fat	Smoking point decreases
Repeated use	Decrease in smoking point
Suspended particles	Lowering of smoking point
Greater surface area	Lower smoking point
Shallow wide pans with sloping sides	Lower the smoking point
Vertical sides and small pans	Higher smoking point

Table 3: Smoking points of some fats and oils

Fat / oil	**Temperature of smoking (°C)**
Coconut oil	138
Groundnut oil	149-162
Crude olive oil	176
Lard	194
Butter	208
Hydrogenated fat	221-232
Cottonseed oil	230
Soyabean oil	230
Refined olive oil	234
Shortenings (monoglycerides as emulsifiers)	176 and then 190-193*

* This happens as the emulsifier gives off smoke first at a lower temperature and later the smoking point rises to 190-193°C

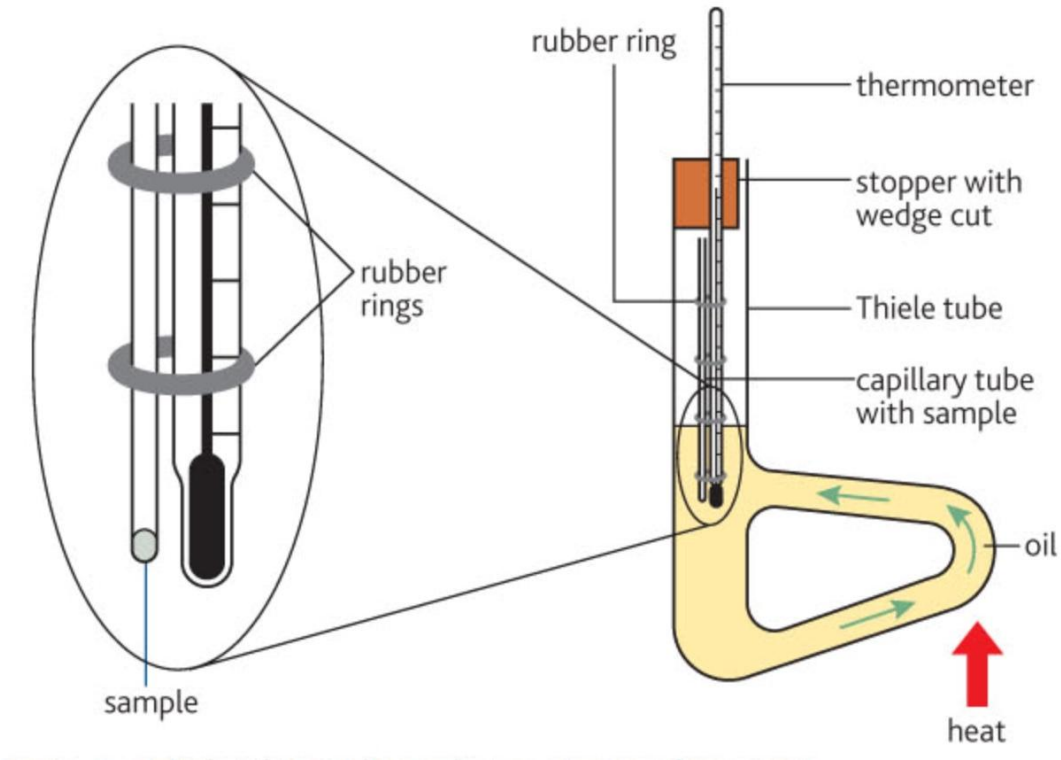
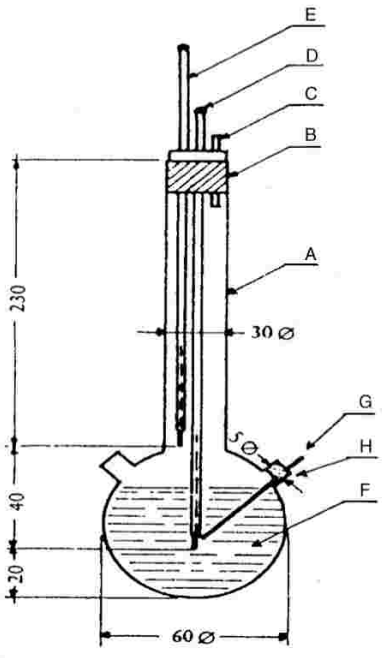


Figure 1: Open-tube capillary-slip method for Estimation of Melting Point



A: Measurement vessel
B: Stopper
C: Vent
D: Thermometer
E: Auxiliary thermometer
F: Bath liquid
G: Capillary tube made of glass, 80 to 100 mm in length, 1,0 ± 0,2 mm inner diameter, 0,2 to 0,3 mm wall thickness
H: Side tube

Figure 2: Estimation of Specific Gravity using Pycnometer

Figure 3: Butyro-Refractrometer for Estimation of Refractive Index

Figure 4: Estimation of Flash Point using Pensky Marten Method

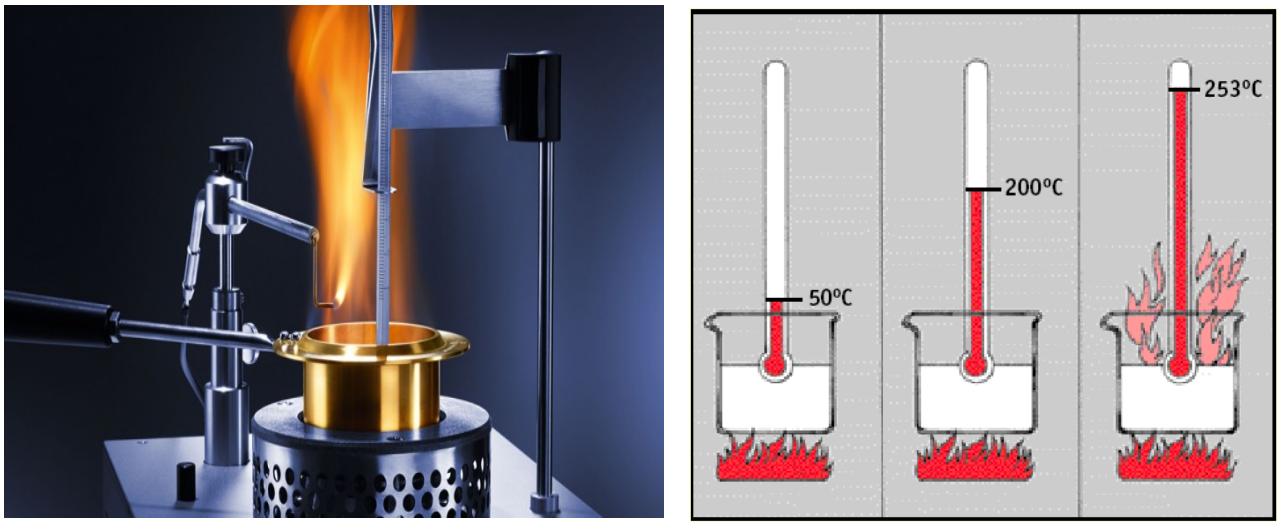


Figure 5: Estimation of Fire Point

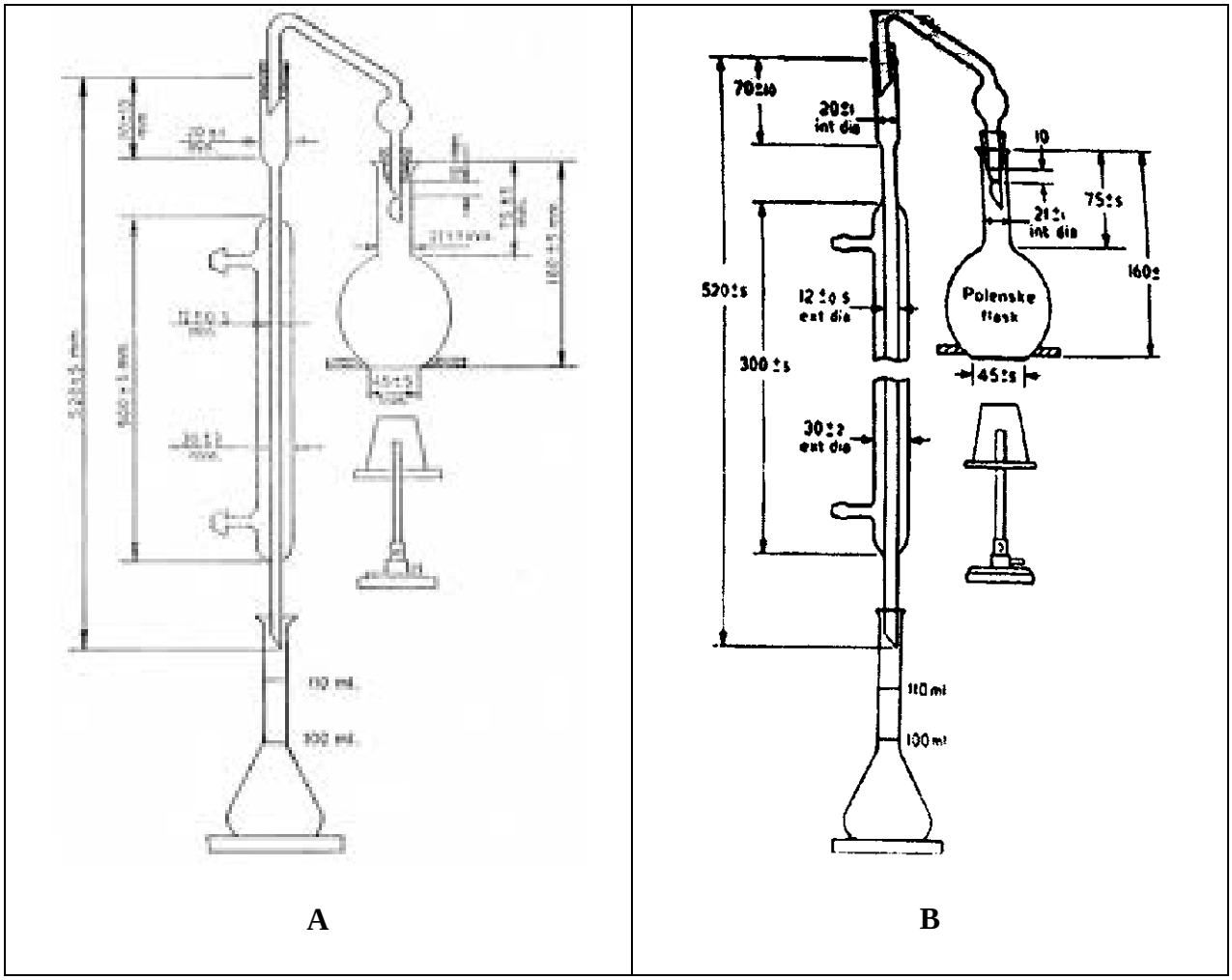


Figure 6: A. Reichert-Meissl; B. Polenske value Apparatus design