CHAPTER

1

Cosmetic Analysis and Evaluation

Cosmetics

Cosmetics are substances or products used to enhance or alter the appearance of the face or fragrance and texture of the body. Many cosmetics are designed for use of applying to the face, hair and body. They are generally mixers of chemical compounds; some being derived from natural sources and some being synthetics or artificial.

Common makeup items include lipstick, mascara, eyeshadow, foundation. Whereas other common cosmetics can include skin cleansers and body lotions, shampoo and conditioner, hairstyling products perfume and cologne.

DETERMINATION OF PARAMETERS

ACID VALUE

- It is defined as number of mg of alkali (KOH , NaOH) required to completely neutralize the free fatty acids present in one gram of oil or fat substance.
- Acid value is an analytical tool used to determine the freshness of an oil. It works on simple acid base titration method, the free fatty acids which are present in an oil due to oxidative or hydrolytic process is titrated against a standard alkali using phenolphthalein as an indicator.
- The amount of alkali consumed represents the amount of fatty acid.

Calculate the acid value:

Result = (Mol. Wt. × V) × (N/W)

Mol. Wt = Molecular weight of potassium hydroxide, 56.11
V = volume (ml)
N = Normality of the potassium hydroxide solution or the sodium hydroxide solution
W = Weight of the sample taken (g)

- Therefore, oil with increasing acid number are unsafe for human being consumption.

Procedure

- Transfer an accurately weighed quantity 10 g of substance into 250 ml conical flask.

- Add 50 ml of a mixture of equal volumes of alcohol and ether (previously neutralized)
- If the test specimen does not dissolve in the cold solvent, connect the flask with a suitable condenser and warm slowly, with frequent shaking, until the specimen dissolves
- Add 1 ml of phenolphthalein and titrate with 0.1 N potassium hydroxide or 0.1 N sodium hydroxide until the solution remains faintly pink after shaking for 30 min.

Acid Value	**Sample Weight (g)**
0–1	20
1–4	10
4–15	2.5
15–74.9	0.5
$\geq$75.0	0.1

Applications

- Its measure of the free fatty acids present in the fat or oil.
- Used to determine the freshness of an oil/check the rancidity.

SAPONIFICATION VALUE

- The saponification value is the number of mg of potassium hydroxide required to neutralize the free acids and saponify the esters contained in 1.0 g of the fat or oil substance.

Procedure

- Transfer an accurately weighed quantity 1.5–2 g of substance
- Into 250 ml conical flask
- Add to it 25.0 ml of 0.5 N alcoholic potassium hydroxide
- Heat the flask on a steam bath, under a suitable condenser to maintain reflux for 30 min, frequently rotating the contents
- Then add 1 ml of phenolphthalein and titrate the excess KOH with 0.5 N hydrochloric acid.
- Perform a blank determination (without sample).

Calculate the Saponification Value:

Result = [M × (Vb – Vt) × N]/W

M = Mmolecular weight of potassium hydroxide, 56.11
Vb = Volume of 0.5 N hydrochloric acid consumed in the blank test (ml)
Vt = Volume of 0.5 N hydrochloric acid consumed in the actual test (ml)
N = Exact normality of the hydrochloric acid
W = Weight of the substance taken for the test (g)

Applications

- Saponification value determine the length of carbon chain of the acid present in oil or fat.

- It also determines the average molecular weight of the fat or oil.
- Higher the saponification value greater the percentage of the short chain acids.
- Higher the molecular weight of the fat, the smaller is its saponification value.

ESTER VALUE

- The Ester Value is the number of mg of potassium hydroxide required to saponify the esters in 1.0 g of the substance.
- If the saponification value and the acid value have been determined, the difference between these two represents the Ester Value.

Ester Value = Saponification Value – Acid Value

Procedure

- Place 1.5–2 g of accurately weighed substance, into a 250 ml flask, add 20–30 ml of neutralized alcohol and shake. Add 1 ml of phenolphthalein and titrate with 0.5 N alcoholic potassium hydroxide until the free acid is neutralized.
- Add 25.0 ml of 0.5 N alcoholic potassium hydroxide and proceed as directed in saponification value, beginning with "Heat the flask" and omitting the further addition of phenolphthalein and titrate with standardised HCl acid, calculate the Ester Value.

Result = [Mol wt × (Vb – Vt) × N]/W

Mol wt = Molecular weight of potassium hydroxide, 56.11
VB = Volume of 0.5 N hydrochloric acid consumed in the blank test (ml)
Vt = Volume of 0.5 N hydrochloric acid consumed in the actual test (ml)
N = Exact normality of the hydrochloric acid
W = Weight of the substance taken for the test (g)

IODINE VALUE

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

Analytical importance

- The most important application of the iodine value is to determine the amount of unsaturation contained in fatty acids.
- Iodine number is directly proportional to content of unsaturated fatty is used to analyze the degree of adulteration.
- This unsaturation is in the form of double bonds which react with iodine compounds.
- The higher the iodine value, the more unsaturated fatty acid bonds are present in a fat.

Procedure

- Weigh accurately an appropriate quantity of the dry oil/fat. into a 500 ml conical flask with glass stopper, to which 25 ml of carbon tetrachloride have been added.

- Mix the content well. Add 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.
- 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 standardized sodium thiosulphate solution, using starch as indicator at the end until the blue color 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 iodine solution as chloroform has a high coefficient of expansion.
- It is thus necessary that blanks, and determinations are made at the same time.

Calculation

$$\textbf{Iodine value} = (12.69(B - S) \times N)/W$$

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.

PEROXIDE VALUE

Definition

It is the number which expresses in milli equivalents of active oxygen that expresses the amount of peroxide containing 1000 gms (kg) of substances (mEq/kg).

- It is a measure of peroxides present in oil.
- A peroxide value is generally less than 10 mEq kg in fresh samples of oil.
- Due to temperature or storage, rancidity occurs causing increase in peroxide values.

Calculation

$$\textbf{Peroxide value} = T\text{-}B \times C/\text{wt of sample} \times 1000$$

Where,

T = Absorbance of test
B = Absorbance of blank
C = Concentration of HCl

RANCIDITY

- Rancidity is the natural process of decomposition of fats or oils by either hydrolysis or oxidation, or both.

- The process of degradation converts fatty acid esters of oils into free fatty acids.
- This gives rise to an unpleasant odour and taste in food.
- These lipids degrade to the point of becoming either unpalatable or unhealthy to ingest.

Types of Rancidity

There are three types/pathways of rancidity:

1. Oxidative Rancidity
2. Hydrolytic Rancidity
3. Microbial Rancidity

1. **Oxidative Rancidity**
   i. Known as auto-oxidation.
   ii. It is due to the auto-oxidation of PUFA present in triacylglycerols by the atmospheric O_2 on free radicals.
   iii. The end product is the formation of aldehyde epoxide and peroxide becoming either unpalatable or unhealthy to ingest.
2. **Hydrolytic Rancidity**
   i. Hydrolytic Rancidity also known as hydrolysis/enzymatic oxidation.
   ii. It is due to the contamination of fat by lipase leading to the formation of diacyl and triacylglycerols with free fatty acids.
   iii. The end product is the formation of aldehyde epoxide and peroxide.
3. **Microbial Rancidity**
   i. In which micro-organisms such bacteria, moulds and yeast use their enzymes to break down chemical structures in the oil, producing unwanted odors and flavors.
   ii. Water needs to be present for microbial growth to occur.
   iii. Can be prevented by sterilization

Factors Causing Rancidity

- Catalysts: Trace metal ions & inorganic salts
- Temperature
- Amount of PUFA
- Time
- Light
- Water

Determination of Rancidity

1. **Kries Test**
   Qualitative:
   - Shake 5 ml of the oil vigorously with 5 ml of 0.1% phloroglucinol solution in diethyl ether and add 5 ml of conc. hydrochloric acid.
   - A pink color indicates incipient rancidity.

2. **Colorimetric method**
   Quantitative
   i. Shake 5 ml of oil and 5 ml chloroform in a stoppered test tube.
   ii. Add 10 ml of a 30% solution of trichloroacetic acid in glacial acetic acid and 1 ml of 1 percent solution of phloroglucinol in glacial acetic acid.
   iii. Incubate the test tube at 45°C for 15 min.
   iv. After incubation, add 4 ml of ethanol and immediately measure the absorbance at 545 nm.
      - Absorbance values below 0.15 indicate no rancidity.
      - Absorbance values greater than 0.2 denote incipient rancidity, and absorbance values around 1.0 show that the sample is highly rancid.

MOISTURE

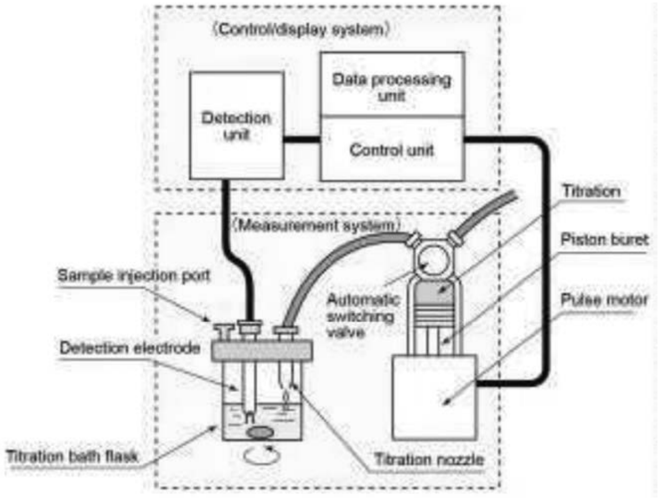
- Water content or moisture content is the quantity of water contained in a material.
- It can be given on a volumetric or mass (gravimetric) basis.
- Moisture content is determined using the Karl Fischer titration method.

Karl Fischer Titration

- The Karl Fischer method uses Karl Fischer reagent, which reacts quantitively and selectively with water, to measure moisture content. Karl Fischer reagent consists of iodine, sulfur dioxide, a base and a solvent, such as alcohol.
  $I2 + SO_2 + 3\ Base + ROH + H_2O\ 2Base + HI + Base + H_2SO_4R$
- During the titration, iodine is added to sample and the amount of iodine used to consume all the water contained in the sample is measured.

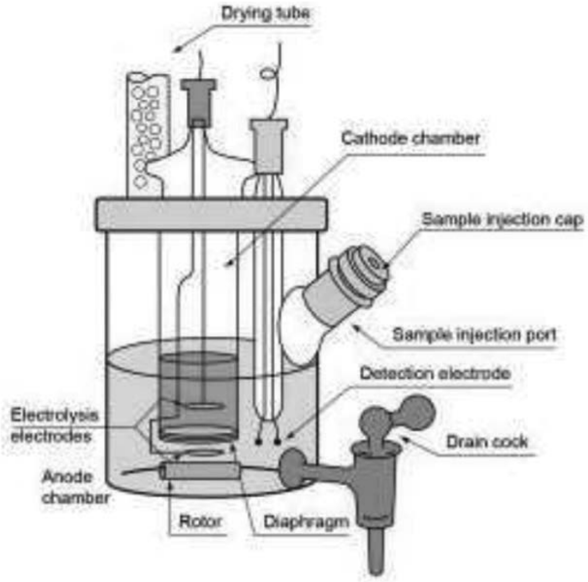
Volumetric Karl Fischer Titration

A solution with an exactly known concentration of iodine is added to sample by means of an electric burette. The amount of iodine added to the sample is calculated from the volume of iodine solution used.



Colorimetric Karl Fischer Titration

The iodine is electrolytically generated. The amount of iodine added to the sample is determined by measuring the current needed for the electrochemical generation of the iodine. When reacting with water, the brown iodine is reduced to the colorless iodide.



ASH CONTENT

- Ash is the inorganic residue remaining after the water and organic matter have been removed by heating in the presence of oxidizing agents, which provides a measure of the total amount of minerals with in a sample.
- The two main types of analytical procedure used to determine the ash content are: dry ashing and wet ashing.

Ashing of Sample

Dry ashing:

- It is high temperature muffle furnace capable of maintaining temperatures between 500 and 600ºC. Water and other volatile materials are vaporized andorganic substances are burned in the presence of the oxygen in air to CO_2, H_2O and N_2.
- The sample is weighed before and after ashing to determine the concentration of ash present.

Wet ashing: Sample is usually weighed into a flask containing strong acids and oxidizing agents and then heated. Heating is continued until the organic matter is completely digested. The temperature and time used depends on the type of acids and oxidizing agents used. Typically, a digestion takes from 10 mins to a few hours at temperature of about 350ºC.

VOLATILE MATTER

- Volatile matter content is total amount of all types of volatile matters combined in the sample. This depends upon the composition of the cosmetic product understudy for determination.
- It is usually carried out by using simple gravimetric LOD (loss on drying) method and sample do not require any preparations in this method and can be used assuch.
- **Determination of Volatile Content in Nail Lacquers and in raw materials (solvents) used in the formulation of Nail Lacquers:**
  – 10 ml of sample was taken in a petri dish and initial weigh were recorded. The dish was placed in the oven at 105ºC for 1hr, the petri dish was removed, cooled and weighed. The differences in the weights were recorded which contributes to the content of volatile matter present in sample. An average of triplicate readings was noted.

HEAVY METALS

- Generally heavy metals are those whose density is five times greater than the density of water.
- These includes antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium and zinc.
- Heavy metals are efficiently determined by using Atomic Absorption Spectroscopy.
- Nowadays, ICP-MS and ICP-OES are also used for heavy metal determination.

A large number of various chemicals and heavy metals are used in lipsticks, lip balm and anti ageing creams and in fairness creams. Some of these heavy metals are used as coloring agents, some of these are added as intentionally added ingredients while some are accidentally added from the environment which poses health risk to consumers. Hence cosmetic raw materials and finished products are evaluated for the presence of heavy metals.

Determination of heavy metals in lipsticks and in raw materials used in the formulation of lipsticks:

- All glass ware and plastic containers used were washed thoroughly with liquid soap and de-ionized water and soaked, in 10% v/v nitric 5 acid, for 24 hrs and cleaned thoroughly with de-ionized water and dried in such a manner as to ensure that any contaminants does not occur.
- The chemicals used were of analytical grade. Working standard solutions were prepared by step wise dilution of the stock solutions of the metals with de-ionized water

Procedure

- 1 gram of sample was weighed accurately and analyzed according to standardized procedure using wet digestion method. The wet digestion of the sample was done by using 65% nitric acid and 60% chloric acid in the ratio of 3:2 and was neutralized after each digestion using 4% hydrogen peroxide.

- The temperature of the reaction has to be maintained between 170– 200ºC aided with a microwave vessel as a heat source. The sample was heated until a white fume appears and after cooling, the solutions were filtered with Whatmann filter paper and transferred to a calibrated flask and madeup to mark (100 ml) with de-ionized water.
- The heavy metals were analyzed in the sample digest using flame atomica bsorption spectrophotometer using air-acetylene and nitrous oxide flame for heavy metals and the data was recorded according to obtained results.

FINENESS OF POWDERS

- Fineness of powders relate to size of particles of the raw materials of cosmetic products or the powders as such.
- The smaller is the particle size of powder; bulky becomes the powder and flow properties increases for that powder sample.
- The most common method for determining fineness of powder is Sieve Analysis method, which is used to determine the particle size distribution of a powder.
- This method is performed by passing the cosmetic raw materials powder or finished cosmetic products like face powders through a stack of wire mesh sieves, separating it into discrete size ranges.
- A sieve shaker is used to vibrate the sieve stack for a specific period of time.

Sr. No.	**Type**	**Passes through mesh aperture**	**Retianed on mesh aperture**
1.	Coarse	1700 microns	355 microns
2.	Moderately coarse	710 microns	250 microns
3.	Moderately fine	355 microns	180 microns
4.	Fine	180 microns	125 microns
5.	Very fine	125 microns	45 microns
6.	Microfine	45 microns	–

DENSITY

- Density is defined as its mass per unit volume and is measured in kg/m^3.
- The symbol most often used for density is ρ.
- Densities of samples are determined by diving their mass to the volume they occupy.

VISCOSITY

- The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress. For liquids, it corresponds to the informal concept of “thickness”.

- For example: Syrup has a higher viscosity than water. Units for viscosity are poise.
- Viscosity measurements are made by using various viscometers.
- Viscosity measurements of various cosmetic formulation raw materials and finished products like creams, lotions are carried out by 8 using viscometers such as Brookfield viscometer which can be used with a spindle 29 to determine the viscosity of different topical formulations.
- The tests are carried out at 21ºC. The spindle was rotated at 0, 0.5, 1, 2,2.5, 4, 5, 10, 20, 50 and 100 rpm values. All measurements were made in triplicate