WEL-COME

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Analysis of Fertilizers

Introduction:

- A fertilizer is any material of natural or synthetic origin that is applied to soil or to plant tissues to supply one or more plant nutrients essential to the growth of plants.

- Fertilizers enhance the growth of plants. This goal is met in two ways, the traditional one being additives that provide nutrients.

- The second mode by which some fertilizers act is to enhance the effectiveness of the soil by modifying its water retention and aeration.

- Plants are made up of four main elements **Hydrogen, Oxygen, Carbon and Nitrogen.** Carbon, hydrogen and oxygen are widely available as water and carbon dioxide. Although nitrogen makes up most of the atmosphere, it is in a form that is unavailable to plants.

The Nutrients are required for the healthy plant life are classified into,

I. **Macronutrients: N, P, K**

II. **Micronutrients: Cu, Fe, Mn, Zn, B etc**

Three main macronutrients:

The macro-nutrients are consumed in larger quantities and are present in plant tissue in quantities from 0.15% to 6.0% on a dry matter(DM).

- **Nitrogen (N)**: leaf growth
- **Phosphorus (P)**: Development of roots, flowers, seeds, fruit;
- **Potassium (K)**: Strong stem growth, movement of water in plants, promotion of flowering and fruiting

Nitrogen is the most important fertilizer since nitrogen is present in proteins, DNA, and other components (e.g., chlorophyll). To be nutritious to plants, nitrogen must be made available in a "fixed" form. Only some bacteria and their host plants (notably legumes) can fix atmospheric nitrogen (N_2) by converting it to ammonium Phosphate is required for the production of DNA and ATP, the main energy carrier in cells, as well as certain lipids.

Three secondary Macronutrients:

- Calcium (Ca)
- Magnesium (Mg)
- Sulfur (S)

Micronutrients:

- Copper(Cu)
- Iron (Fe)
- Manganese (Mn)
- Molybdenum (Mo)
- Zinc (Zn)
- Boron (B)

The nutrients are required for healthy plant life are classified according to the elements, but the direct elements are not used as fertilizers so that the elements containing compounds are used as fertilizer.

Classification of Fertilizer

Fertilizers are classified according to whether they provide a single nutrient (e.g., K, P, or N) or provide two or more nutrients in which case they are classified as

- ❖ straight fertilizers: they provide a single nutrient (e.g., K, P, or N)
- ❖ Multinutrient fertilizers : provide two or more nutrients
- ❖ Inorganic Fertilizer: fertilizer excluding C- containing fertilizer
- ❖ Organic Fertilizer: Usually they are Plant or animal derived matter which is recycled

Straight fertilizers: The fertilizer which can provide a single nutrient to the plant.

- The main nitrogen-based straight fertilizer is ammonia or its solutions. Ammonium Nitrate (NH_4NO_3) is also widely used.

- Urea is another popular source of nitrogen, having the advantage that it is solid and non-explosive, unlike ammonia and ammonium nitrate, respectively.

- A few percent of the nitrogen fertilizer market (4% in 2007)has been met by Calcium Ammonium Nitrate ($Ca(NO_3)_2 \bullet NH_4 \bullet 10H_2O$).

- The main straight phosphate fertilizers are the superphosphates. **Single superphosphate** (SSP) consists of 14–18% P_2O_5, again in the form of $Ca(H_2PO_4)_2$, but also phosphogypsum ($CaSO_4 \bullet 2H_2O$).

- **Triple superphosphate** (TSP) typically consists of 44-48% of P_2O_5 and no gypsum.

- A mixture of single superphosphate and triple superphosphate is called **double superphosphate**. More than 90% of a typical superphosphate fertilizer is water-soluble.

- The main **potassium-based straight fertilizer** is Muriate of Potash (MOP). Muriate of Potash consists of 95-99% KCl, and is typically available as 0-0-60 or 0-0-62 fertilizer.

Multinutrient fertilizers:

These fertilizers are common. They consist of two or more nutrient components.

i) Binary (NP, NK, PK) fertilizers:

Major two-component fertilizers provide both nitrogen and phosphorus to the plants. These are called NP fertilizers. The main NP fertilizers are monoammonium phosphate (MAP) and diammonium phosphate (DAP).

ii) NPK fertilizers:

NPK fertilizers are three-component fertilizers providing nitrogen, phosphorus, and potassium.

Estimation of Macronutrients:

1) Estimation of Nitrogen (N): Distillation Method
2) Estimation of Phosphorus (P): Gravimetric Analysis
3) Estimation of Potassium (K): Gravimetric Analysis

***Estimation of Nitrogen from fertilizer sample*:**

Distillation method: The testing method is applicable to fertilizers containing nitrate nitrogen.

❖ ***Reagents:***

1) 0.1 mol/L - 0.2 mol/L sodium hydroxide (NaOH) solution
2) 0.25 mol/L sulfuric acid (H_2SO_4)
3) 4% Boric acid solution (Dissolve 40 g of boric acid in water to make 1000 mL)
4) 0.32% $KMnO_4$
5) Mixed Indicator: Methyl red - bromocresol green mixture solution to a methyl red solution (0.1 g/100 mL) add an equal volume of bromocresol green solution (0.5 g/100 mL).

❖ ***Instruments:*** Instruments are as shown below:

a) Steam distillation apparatus

b) Distillation flask: A Kjeldahl flask or a round bottom flask that can be connected to a steam distillation apparatus.

❖ ***Test procedures:***

1) Weigh 0.25 g - 1 g of an analytical sample and put it in a 300-mL - 500-mL distillation flask

2) Add about 25 mL of water to make the sample solution.

Distillation:

1) Transfer a predetermined amount of fertilizer sample in distillation tube and load this tube in distillation unit.

2) On the other end of distillation unit keep 20 ml of 4% Boric acid with mixed indicator in conical flask.

3) 25 ml 0.32% $KMnO_4$ and 0.1 mol/L - 0.2 mol/L NaOH solution was automatically added in distillation Unit.
4) Send steam to the distillation flask to heat the solution in the distillation flask and distill at a distillation rate of 5 mL/min - 7 mL/min.
5) The ammonia is librated during the distillation is absorbed in a 20 ml of boric acid containing mixed indicator.
6) With absorption of ammonia , the pinkish colored solution turns to green.
7) The green colored distillate is titrated against 0.25 mol/L sulfuric acid and end point is light red color.
8) Note down the blank and sample reading and calculate the Nitrogen Content in fertilizer sample.

Reactions:

$$2KMnO_4 + H_2O \xrightarrow{\text{Alkaline medium}} 2MnO_4 + 2KOH + 3O^{-}$$

Nascent Oxygen

$$\text{R- CH-NH}_2\text{-COOH} + O^{-} \xrightarrow{\text{Oxidation}} \text{R-CO-COOH} + NH_3$$

Organic N- fraction

$$NH_3 + H_2O \xrightarrow{\text{Distillation}} NH_4OH$$

$$3NH_4OH + H_3BO_3 \longrightarrow (NH_4)_3BO_3 + 3H_2O$$

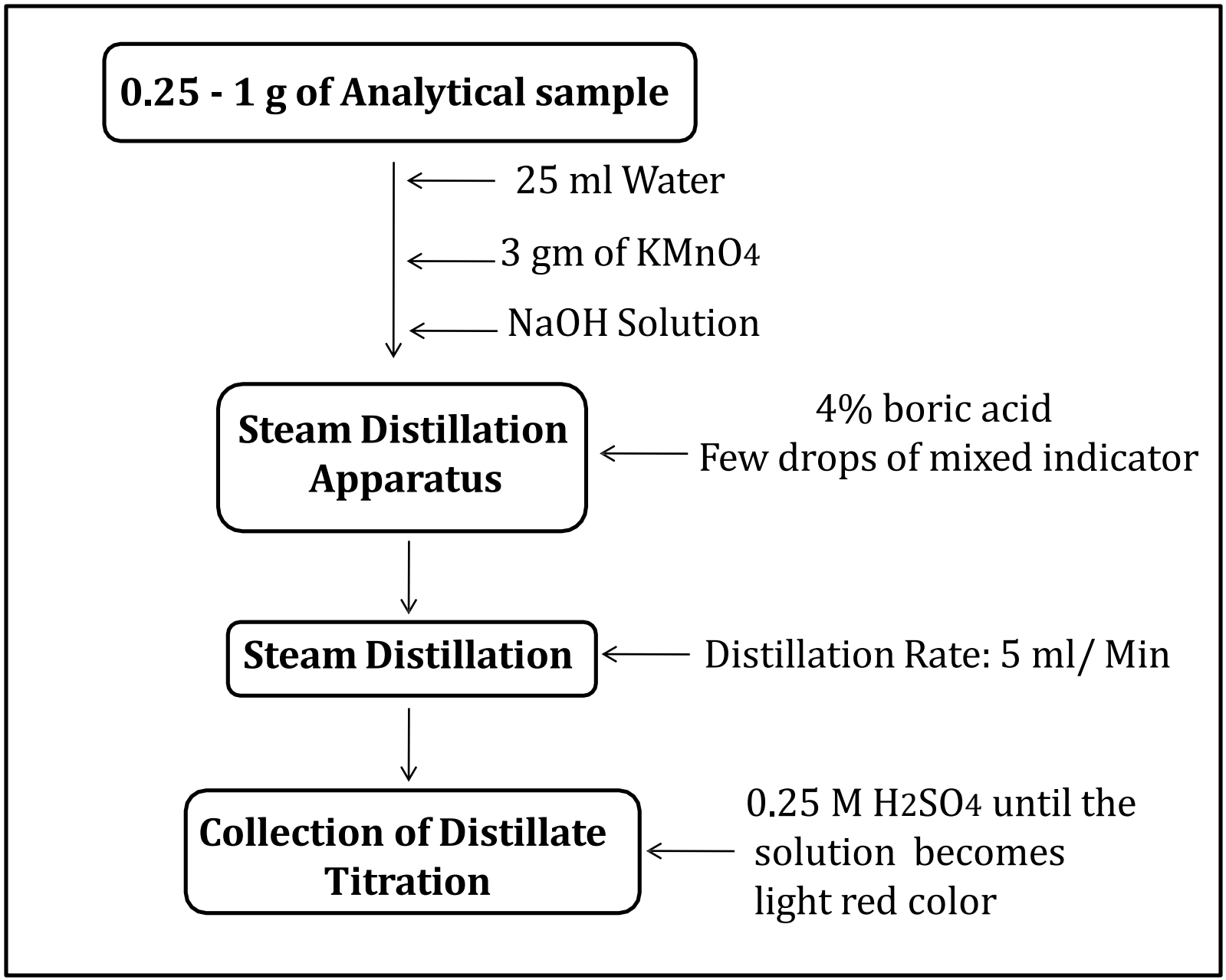
In Titration

$$(NH_4)_3BO_3 + 3H_2SO_4 \longrightarrow 2(NH_4)_3SO_4 + 2H_3BO_3$$

Calculations:

$$\text{Available Nitrogen} = \frac{(\text{Sample reading} - \text{Blank reading}) \times \text{Normality of acid} \times \text{At. Wt. Of Nitrogen}}{\text{Sample Weigh} \times 1000}$$

Flow Chart:


0.25 - 1 g of Analytical sample
25 ml Water
3 gm of KMnO4
NaOH Solution
Steam Distillation Apparatus
4% boric acid
Few drops of mixed indicator
Steam Distillation
Distillation Rate: 5 ml/ Min
Collection of Distillate Titration
0.25 M H2SO4 until the solution becomes light red color

Estimation of Potassium from fertilizer sample:

Gravimetric Analysis: This test method is applicable to the fertilizers containing potassium

1) Reagents:

i) Hydrochloric acid (HCl)

ii) Formaldehyde solution (CH2O)

iii) Sodium hydroxide solution (NaOH): Dissolve 200 g of sodium hydroxide in water to make 1000 mL.

iv) Tetraphenylborate solution

vi) Ethylene diamine tetraacetate - Sodium hydroxide solution

2) ***Instruments:*** Instruments are as shown below

a) Electric furnace: An electric furnace that can be adjusted to 550 ºC ± 5 ºC.

b) Drying apparatus: A drying apparatus that can be adjusted to 120 ºC ± 2 ºC.

c) Crucible: A crucible type glass filter into a drying apparatus. Let it stand to cool in a desicator after heating at 120ºC

d) Hot plate or sand bath: A hot plate whose surface temperature can be adjusted up to 250 ºC.

3) Test procedures:

1. **Extraction:** Conduct extraction as follows

a) Weigh 5 g of an analytical sample and put it in a 200- mL - 300-mL beaker

b) Put the beaker in an electric furnace, and heat gently.

c) Ignite at 550 ºC ± 5 ºC for no less than 4 hours to incinerate.

d) After standing to cool, moisten the residue with a small amount of water, add gradually about 10 mL of hydrochloric acid, and further add water to make 20 mL.

e) Cover the tall beaker with a watch glass, and heat on a hot plate or a sand bath to boil for about 5 minutes.

f) After standing to cool, transfer to a 500-mL volumetric flask and dilute up to the mark.

3.2 Measurement: Conduct measurement as shown below.

a) Transfer a 25 ml predetermined volume of sample solution to a 100-mL beaker.

b) Add water to the solution to reach 50 mL

c) Add hydrochloric acid, so that the hydrochloric acid becomes equivalent to 0.2 mL.

d) Add 5 mL of formaldehyde solution, and then add 5 mL of ethylenediamine tetraacetate - sodium hydroxide solution.

e) Add necessary volume of tetraphenylborate solution at the rate of one or two drop(s) per second while mixing, and further add 4 mL of the same solution in the same manner.

f) Leave at rest for about 30 minutes while sometimes mixing to form the precipitate of potassium tetraphenylborate.

g) Filter the solution in a crucible , wash it and heat at 120 ºC ± 2 ºC for 1 hour.

h) After heating, move it quickly into a desicator and let it stand to cool.

i) Calculate the total potassium from the weight of precipitate.

Calculation:

$$\% \text{ of Potassium} = \frac{\text{Weight of Potassium precipitate}}{\text{Weight of Fertilizer}} \times 100$$

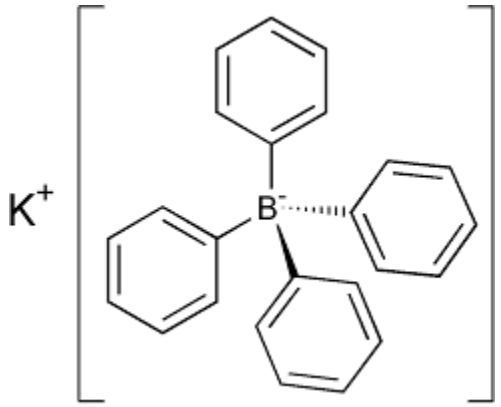
Reactions:

a) Pretreat an analytical sample by incineration and hydrochloric acid to convert the total potassium into potassium ion.

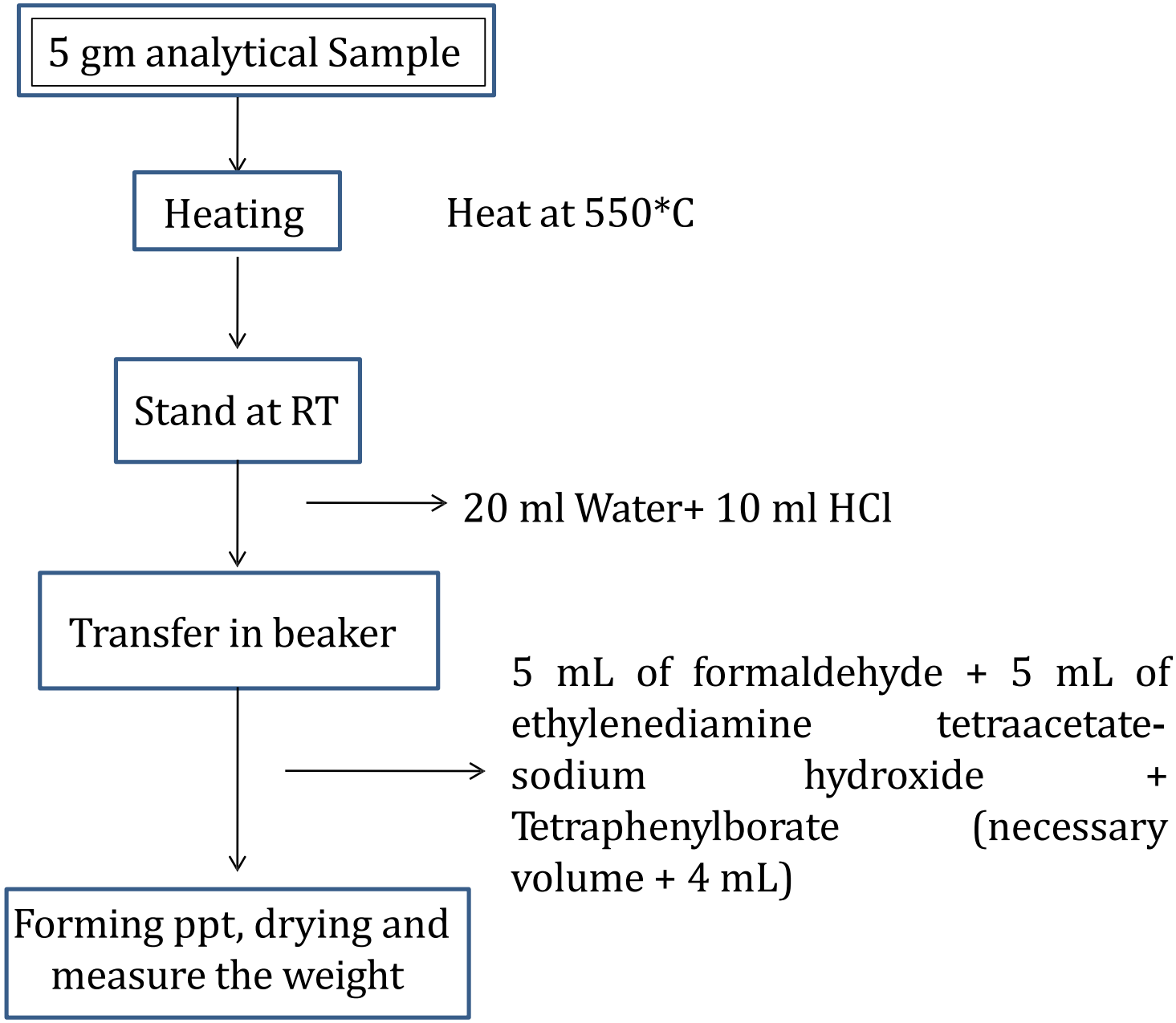
b) Mask the co-existing potassium ion with formaldehyde and ethylenediamine tetraacetate.

c) Then the potassium ion reacts with traphenylborate to form potassium tetraphenylborate.

$$K^+ + NaB(Ph)_4 \rightarrow KB(Ph)_4 + Na^+$$



Flow chart :


5 gm analytical Sample
Heating
Heat at 550*C
Stand at RT
20 ml Water+ 10 ml HCl
Transfer in beaker
5 mL of formaldehyde + 5 mL of ethylenediamine tetraacetate-sodium hydroxide + Tetraphenylborate (necessary volume + 4 mL)
Forming ppt, drying and measure the weight

***Estimation of Phosphorus from fertilizer sample*:**

Gravimetric Analysis:

1) **Reagents:**

a) 0.4 M Magnesium sulphate solution ($MgSO_4$)

b) 3% Aqueous Ammonia

Test Procedure:

a) Weight accurately about 3 gm of fertilizer sample

b) Dissolve it in 50 ml water.

c) Stir the mixture for few min. until most of the fertilizer sample has dissolved

d) Filter the solution to remove undissolved material

e) Then add 50 ml 0.4 M $MgSO_4$ solution .

f) Add ammonia to get a precipitate

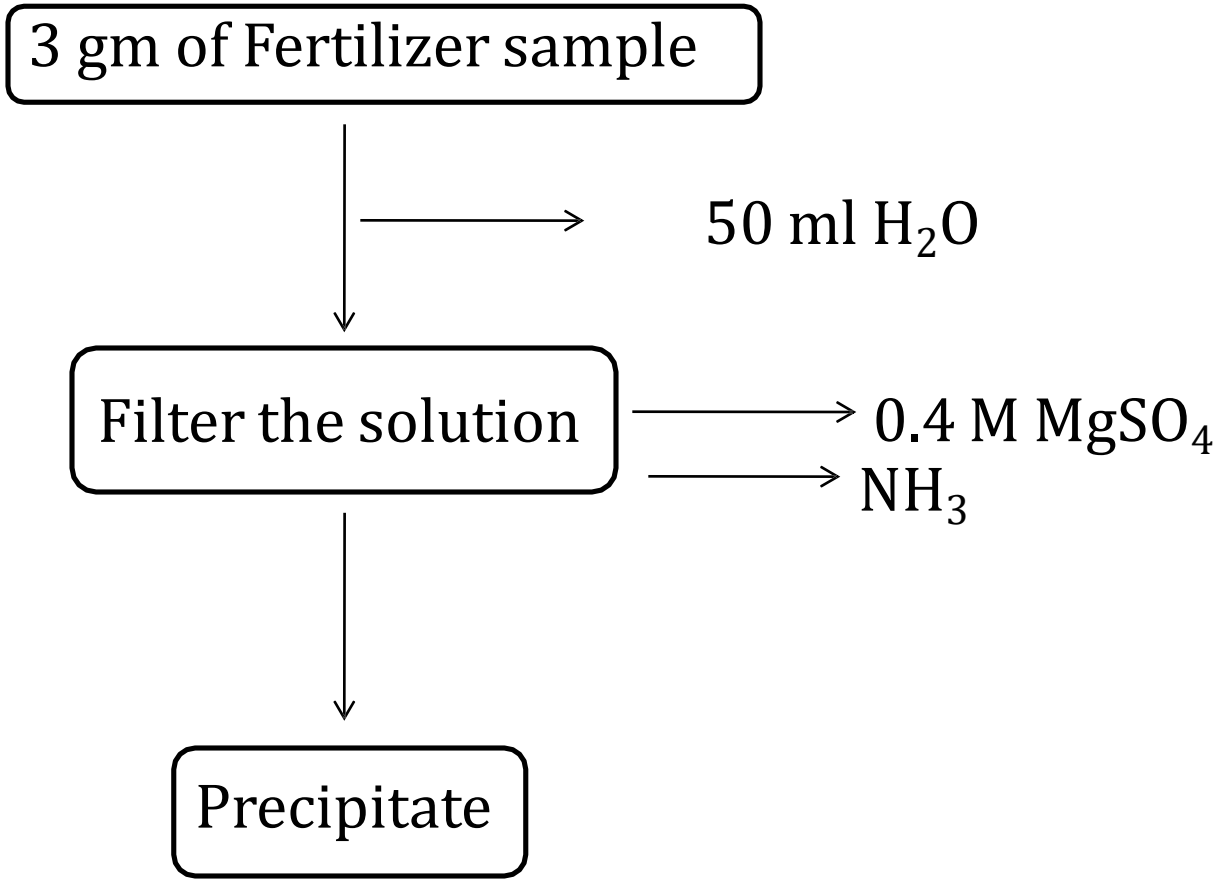
Calculation:

$$\% \text{ of Phosphorus} = \frac{\text{Weight of Phosphorus precipitate}}{\text{Weight of Fertilizer}} \times 100$$

Reactions:

$$HPO_{4}^{2-} + Mg^{2+} + NH_3(aq.) + 6H_2O \longrightarrow MgNH_4PO_4.6H_2O$$

Flow Chart:


3 gm of Fertilizer sample
50 ml H_2O
Filter the solution
0.4 M $MgSO_4$
NH_3
Precipitate


Thank You!