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## Fertilizer

### INTRODUCTION

The fertilizers are the chemical substances which are directly respondent for the substantial growth of the plants (trees) or crops and being supply the nutrients in the form of nitrogen, phosphorus, potassium etc and keep the soils fertile.

Plants, like all other living things need food for their development and growth, and they require 16 essential elements. Hydrogen, carbon and oxygen are derived from the atmosphere and water soil. The remaining 13 essential elements (manganese, nitrogen, calcium, phosphorus, potassium, zinc, magnesium, sulfur, iron, copper, boron, molybdenum, and chlorine) are supplied either from soil minerals and soil organic matter or by inorganic or organic fertilizers. The microorganisms in bio-fertilizers restore the soil's natural nutrient cycle and build soil organic matter. Through the use of bio-fertilizers, healthy plants can be grown, while enhancing the sustainability and the health of the soil. Since they play several roles, a preferred scientific term for such beneficial bacteria is "plant-growth promoting rhizobacteria" . Therefore, they are extremely advantageous in enriching soil fertility and fulfilling plant nutrient requirements by supplying the organic nutrients through microorganism and their by products. Hence, bio-fertilizers do not contain any chemicals which are harmful to the living soil.

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### PLANT NUTRIENTS:

The essential plant nutrients include carbon, oxygen and hydrogen which are absorbed from the air, whereas other nutrients including nitrogen are typically obtained from the soil (exceptions include some parasitic or carnivorous plants).

There are 17 most important nutrients for plants. Plants must obtain the following mineral nutrients from their growing medium-

**1. Macronutrients:** nitrogen(N), phosphorus (P), potassium (K), calcium (Ca), sulfur (S), magnesium (Mg), carbon (C), oxygen(O), hydrogen (H).

**2 .Micronutrients** (or trace minerals) : iron(Fe), boron (B), chlorine (Cl), manganese (Mn), zinc (Zn), copper (Cu), molybdenum (Mo), nickel (Ni).

These elements stay beneath soil as salt. So plants consume these elements as ion. The macronutrients are consumed in larger quantities; hydrogen, oxygen, nitrogen and carbon contribute to over 95% of a plants' entire biomass on a dry matter weight basis. Micronutrients are present in plant tissue in quantities measured in parts per million, ranging from 0.1 to 200 ppm, or less than 0.02% dry weight.

### **1.1 NEED FOR FERTILIZERS IN INDIA**

Fertilizer is a substance to soil to improve plants' growth and yield. First used by ancient farmer's fertilizer technology developed significantly as the chemical needs of growing plants were discovered. Modern synthetic fertilizers are composed mainly of nitrogen, phosphorous and potassium compounds as the secondary nutrients added. The use of synthetic fertilizers has significantly improved the quality and quantity of the food available today but their long term use is debated by environmentalists. Following points show need for fertilizers in India:

(1) Its universally accepted that the use of chemical fertilizer is an integral part of the package of practice for raising the agricultural production to a higher place. Studies conducted by the Food and Agricultural Organization (FAO) of the United Nations have established beyond doubt that there is a close relationship between the crop yields and fertilizer consumption level. Moreover the nutritional requirement of different crops could not be fully met with the use of organic manures like FYM and other bulky organic manures like cake, neem, groundnut cake, castor, etc. for want of their availability in adequate quantities.

(2) Increasing agriculture production in India by area increasing process is no longer possible as cultivable and left over is only marginal. Further a considerable

cultivable land is being diverted year after year for housing and industrial etc. Hence self sufficiency in food lies in increasing the field per unit area per unit time through adoption of modern agricultural technology.

(3) Fertilizer have the advantages of smaller bulk easy transport relatively quick in an availability at plan- food constituents and the facility of their application in proportion suited to the actual requirements of crops and soils.

(4) There is need for an efficient use of fertilizers as major plant nutrient resource in enhancing the farm productivity.

(5) Other resource of plant nutrients like organic manures bio-fertilizers etc. Also should be integrated to get the maximum agriculture output term every kilogram of applied nutrient in the form of fertilizers.

(6) To improve our agriculture output India needs more fertilizers.

### **TYPES OF FERTILIZERS:**

There are two types of supplies for agriculture, specifically fertilizer and pesticide. It can be said that fertilizer is food, and pesticide is medicine for plants in conventional agriculture. Among the materials used in agriculture, fertilizer is the most widely used. Based on the production process, it can be roughly categorized into three types: *chemical, organic and biofertilizer*.

### **1 .CHEMICAL FERTILIZERS (Synthetic Fertilizer):**

Fertilizers play an important role in increasing crop production. The main macronutrients present in inorganic fertilizers are nitrogen, phosphorus, and potassium which influence vegetative and reproductive phase of plant growth.

#### **1. Nitrogen Fertilizers:**

Nitrogen fertilizers contain nitrogen necessary for the development of crops. Nitrogen is the main constituent of chlorophyll that maintains a balance in the process of photosynthesis. It is also a part of amino acids in plants and constitutes protein. Nitrogen fertilizers improve the production and quality of agricultural

products. . The sources of nitrogen used in fertilizers are many, including ammonia ( $\text{NH}_3$ ), diammonium phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ), ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ), calcium cyanamide ( $\text{CaCN}_2$ ), calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ), sodium nitrate ( $\text{NaNO}_3$ ), and urea ( $\text{N}_2\text{H}_4\text{CO}$ ).

## **2. Phosphorus Fertilizer:**

The main nutrient in a phosphorus fertilizer is phosphorus. The efficiency of fertilizer depends upon effective phosphorus content, methods of fertilizing, properties of soil and crop strains. Phosphate fertilizer is an essential fertilizer for the land. The need of this fertilizer is low in comparison to nitrogenous fertilizer. In the early age of plant this fertilizer is used for the health of green plants. There are three sub types of phosphate fertilizer viz: Water Soluble Phosphoric Acid, Citric Acid Soluble Phosphoric Acid and Insoluble in Water or Citric Acid. Super phosphate is the main example of water soluble phosphates acid. Di-calcium phosphate is the main example of citric acid soluble phosphoric acid. The main examples of insoluble phosphoric fertilizer in water are rock phosphate raw Bone meal, steamed bone meal and by product of basic slag. Phosphorus found in the protoplasm of the cell plays an important role in cell growth and proliferation. The phosphorus fertilizer is beneficial for the growth of roots of the plants.

### **Characteristics of Phosphate Fertilizer:**

- (i) Jointly use of nitrogenous and phosphate fertilizer increases the uptake capacity of the plant.
- (ii) Rock phosphate basic slag phosphates fertilizer is most suitable for application in acidic soils.
- (iii) Low paddy shorts considerable less response to phosphate fertilizers.
- (iv) The phosphate fertilizer like as super phosphate should be applied near the root zone of the crop or in soil layer.
- (v) The phosphate fertilizer namely super phosphate should be used in neutral to alkaline soil.

(vi) The phosphate fertilizer should be placed deep with deep cultivator in fruit trees like guava, citrus, apple etc.

### **Proportion of Nutrients and Elements of Phosphate Fertilizer:**

Common Single super phosphate, Triple calcium phosphate, Di-calcium phosphate, Ground phosphate rock, Phosphate Slag, Di-phosphoric phosphate are the phosphate fertilizer. Its main elements are  $\text{Ca}(\text{H}_2\text{PO}_4)\text{H}_2\text{O} + \text{H}_3\text{PO}_4 + \text{CaSO}_4$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)\text{H}_2\text{O} + \text{H}_3\text{PO}_4$ ,  $\text{CaHPO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Ca}_5\text{F}(\text{PO}_4)_3 \cdot 4\text{CaO} \cdot \text{P}_2\text{O}_5 + 5\text{CaO}$ ,  $\text{P}_2\text{O}_5 + \text{SiO}_2, 3\text{CaO} \cdot \text{P}_2\text{O}_5 + 3\text{CaO} \cdot \text{P}_2\text{O}_5$  respectively. And proportion of nutrients (in %) are respectively 14 to 21, 40 to 52, 27 to 40, 16 to 35, 14 to 20 and 20 to 38. It is seen that triple calcium phosphate fertilizer contains highest nutrients and it is 40 to 52% while phosphate slag contains the least nutrients and it is 14 to 20.9%.

### **3. Potassium fertilizers:**

Potassium sulphate is a potassium fertilizer. It is very essential for the healthy development of plants. With the help of potassium preparation of carbohydrate in the plants is possible. It increases resistance power of green plants. Classification of Potassium fertilizer is divided in two ways viz, potash and chloride from and potash in non-chloride form. Marinade of potash is the best example of potash in chloride form and sulphate of potash is the only example of potash in non-chloride nature. Potassium is used to build cellulose and aids in photosynthesis by the formation of a chlorophyll precursor.

**Main Elements:** Potassium chloride 50% to 62% KCl Mix potassium salt 30% to 42% KCl + NaCl Sulfuric of Potash 48% to 52%  $\text{K}_2\text{SO}_4$ . It is seen from the above table that out of all potassium fertilizer potassium chloride contains the highest nutrients and it is 50% to 62% mix potassium salt, the least nutrients and it is 30% to 42% sulphate of potash contains 48% to 52% nutrients. Potassium fertilizers are Potassium chloride [KCl], Potassium sulfate [ $\text{K}_2\text{SO}_4$ ], Potassium nitrate [ $\text{KNO}_3$ ], Potassium-magnesium sulfate [ $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$ ].

### **Characteristics of Potassium Fertilizer:**

(i) It can be used for all crops and for all types of soils.

(ii) In potassium fertilizer potassium sulphate is better than nitrate of potash for crops like tobacco, potatoes, fruit trees etc.

(iii) Now a days the application of potassium fertilizer namely potassium chloride or nitrate of potash as top dressing is considered good as nitrogenous fertilizer.

(iv) The potassium fertilizers are water soluble but not hygroscopic in nature and potassium is readily available to plants.

(v) On application of potassium fertilizer it dissociates to  $K^+$  ions and gets absorbed in the soil and absorbed by growing plants.

**4. Mixed Fertilizer:** In mixed fertilizer nitrogen, potash and phosphorus are included. All types of mixed fertilizer:

(i) **Open Formula Fertilizer Mixture:** The ingredients mixed in this type of fertilizer mixture in forms of kinds and quantity is disclosed by the manufacturer. This will be helpful for the cultivators to know the ingredients of fertilizer for the use of the same in particular crop in suitable amounts.

(ii) **Closed Formula Fertilizer Mixture:** The ingredients or straight fertilizer used in these fertilizer mixtures are not disclosed. It is called as a trade secret of the industry. So it is not possible for farmers to know the type and quantity of ingredients used in this fertilizer mixture. The farmer cannot select a correct mixture for their use in production of crops.

The elements like nitrogen, phosphorus and potash are the main chemical elements of mixed fertilizer and land receives most of nutrients from it and it is also seen that proportion of nitrogen is relatively higher than other chemical in the fertilizer. Only mixed fertilizer which does not consist nitrogen is magnesium ammonium phosphate. Phosphate is available in all mixed chemical fertilizers except potassium nitrate. Proportion of phosphate is relatively less than nitrogen. Potash is not available in mixed chemical fertilizer. Proportion of potash is as the proportion of nitrogen and phosphorus in some mixed fertilizer.

The mixed fertilizer like Ammonium Potassium Phosphate, Ammonium Potassium Nitrate, Urea Potassium Phosphate consist nitrogen, phosphorus and

Potash in equal proportion. Chemical fertilizer as like Ammoniated Super Phosphate, Ammonium Phosphate, Di- Ammonium Phosphate (DAP) and Ammonium Phosphate Nitrate did not contain Potash.

### **Advantages of Chemical Fertilizers:**

The advantages of fertilizers are mentioned below:

- They are easy to transport, store, and apply.
- For supplying a specific nutrient we can select a specific fertilizer due to its nutrient specific nature.
- They are water soluble and can easily dissolve in the soil. Hence, they are easily absorbed by the plants.
- They have a rapid effect on the crops.
- They increase the crop yield and provide enough food to feed the large population.
- They are predictable and reliable.

### **Disadvantages of Chemical Fertilizers**

Fertilizers have the following disadvantages:

- They are expensive.
- The ingredients in the fertilizers are toxic to the skin and respiratory system.
- Excessive use of fertilizers damages the plants and reduces soil fertility.
- Leaching occurs and the fertilizers reach the rivers causing eutrophication.
- Long term use reduces the microbial activity and disturbs the pH of the soil.

### **Importance of Chemical Fertilizers:**

It is very difficult to meet the demands of the increasing population with such less resources. Loss of soil fertility, pests, and lack of nutrients have resulted in a decrease in agricultural production. This has increased the importance of fertilizers in agriculture.

Fertilizers can be important to the plants in the following ways:

- Fertilizers increase plants' tolerance towards pests. This has reduced their reliance on insecticides and herbicides, thereby, producing healthier crops. Consequently, diseases have reduced providing aesthetic value to the crops.
- Fertilizers improve the water holding capacity of the plants and increase root depth.
- The potassium content present in the fertilizers strengthens the straws and stalks of the plants.
- The phosphorus present in the fertilizers helps in the faster development of roots and formation of seeds in the plants.
- Nitrogen in the fertilizers enhances the growth of the plants which can be characterized by the green colour of the plants.

Since the chemical fertilizers adversely affect soil fertility, bio-fertilizers were brought into use. These are substances that contain living or latent cells, and even micro-organisms. They provide the soil with the necessary nutrients and microbes for the growth of the plants. They help the soil to retain its fertility. They are environment-friendly. They also destroy pathogenic components responsible for causing disease in plants. Acetobacter and Rhizobium are two such widely used biofertilizers.

## **2 .ORGANIC FERTILIZERS:**

Organic fertilizer refers to materials used as fertilizer that occur regularly in nature, usually as a byproduct or end product of a naturally occurring process.

Like any fertilizer, organic fertilizers typically provide the three major macronutrients required by plants: nitrogen, phosphorus, and potassium. Organic

fertilizers include naturally occurring organic materials, (e.g. manure, worm castings, compost, seaweed), or naturally occurring mineral deposits.

## **2.1 Types of Organic Fertilizers**

### **(i) Animal manures:**

Animal manures are probably the most commonly available organic material used for their fertilizer value. Animal manure is essentially a complete fertilizer.

### **(ii) Sewage sludge:**

It is a recycled product of municipal sewage treatment plants. Forms commonly available are activated, composted and lime-stabilized

### **(iii) Plant substances**

They are often rich in specific nutrients, such as nitrogen.

### **(iv) Composts**

Although making compost from a variety of raw materials is possible, the finished products are remarkably similar in their final concentrations of nitrogen, phosphorus, and potassium.

### **Advantages of Organic Fertilizers:**

- Organic fertilizers are better sources of nutrient in balanced amounts than inorganic fertilizers where soil is deficient in both macro and micronutrients.
- Organic based fertilizer use is beneficial because it supplies micronutrients, and organic components that increase soil moisture retention and reduce leaching of nutrients.
- Organic fertilizers can be used on acid tolerant and those better suited to neutral or alkaline conditions.

- In addition to increasing yield and fertilizing plants directly, organic fertilizers can improve the biodiversity (soil life) and long-term productivity of soil, and may prove a large depository for excess carbon dioxide.
- Organic nutrients increase the abundance of soil organisms by providing organic matter and micronutrients for organisms such as fungal mycorrhiza.

### **Disadvantages of Organic Fertilizers:**

- Hard to get, Not sterile, Low nutrient content,
- Generally costs significantly more than synthetic fertilizer,
- Organic certification requires documentation and regular inspections,
- Organic fertilizers still release nutrients into their surroundings;
- These nutrients can find their way into local streams, rivers, and estuaries just as nutrients from synthetic sources do.

### **3. BIO-FERTILIZERS:**

Bio fertilizers are commonly called microbial inoculants which are capable of mobilizing important nutritional elements in the soil from non-usable to usable form through biological processes.

The term 'bio-fertilizer' include selective micro-organism like bacteria, fungi and algae which are capable of fixing atmospheric nitrogen or convert soluble phosphate and potash in the soil into forms available to the plants. Soil microorganisms play an important role in soil processes that determine plant productivity. Bacteria living in the soil are called free living and some bacteria support plant growth indirectly, by improving growth restricting conditions either via production of antagonistic substances or by inducing resistance against plant pathogens.

The interactions among the rhizosphere, the roots of higher plants and the soil borne microorganisms have a significant role in plant growth and development. The organic compounds, released by roots and bacteria, play an important role in the uptake of mineral nutrient. The hormones produced by the rhizosphere bacteria have direct effects on higher plants. Biofertilizer is most commonly

referred to the use of soil microorganisms to increase the availability and uptake of mineral nutrients for plants.

### **3.1 Advantages of Bio-fertilizers:**

Bio-fertilizers have definite advantage over chemical fertilizers.

- The use of bio-fertilizers effectively enrich the soil and cost less than chemical fertilizers, which harm the environment and deplete non-renewable energy sources..
- Chemical fertilizers supply over nitrogen whereas bio-fertilizers provide in addition to nitrogen certain growth promoting substances like hormones, vitamins , amino acids, etc.,.
- On the other hand bio-fertilizers supply the nitrogen continuously throughout the entire period of crop growth in the field under favorable conditions.
- Continuous use of chemical fertilizers adversely affect the soil structure whereas bio-fertilizers when applied to soil improve the soil structure.
- The effects of chemical fertilizers are that they are toxic at higher doses. Bio-fertilizers, however, have no toxic effects.

### **.3.2 Types of Bio-fertilizers:**

The following common types of bio-fertilizers are available to the farmers in various countries.

- (i) Nitrogen fixing bio-fertilizers eg. *Rhizobium*, *Brady rhizobium*, *Azospirillum* and *Azotobacter*.
- (ii) Phosphorous solubilising bio-fertilizers (PSB) eg. *Bacillus*, *Pseudomonas* and *Aspergillus*.
- (iii) Potassium mobilizing bio-fertilizer eg. *Frateuria aurentia*
- (iv) Plant growth promoting bio-fertilizers eg. *Pseudomonas*.

Sr. No	Name of the product	Classification	Role
<b>1.</b>	<b>Nitrogen fixer Biofertilizer</b>		
a.	<i>Azotobacter vinelindii</i>	Biofertiizer	N-fixer
b.	<i>Azotobacter chroococcum</i>	Biofertiizer	N-fixer
c.	<i>Azotospirillum lipoferum</i>	Biofertiizer	N-fixer
d.	<i>Acetobacter xylinum</i>	Biofertiizer	N-fixer
e.	<i>Rhizobium</i>	Biofertiizer	N-fixer
<b>2.</b>	<b>Phosphate solubilizer Biofertilizer</b>		
a.	<i>Pseudomonas putida</i>		
b.	<i>Bacillus megatherium</i>		
<b>3.</b>	<b>K-solubilizer</b>		
a.	<i>Frateuria Aurentia</i>		

The products in above table are some examples of bio fertilizers which provides N, P, K to the plant.

### 3.3 Action of bio-fertilizers:

- Bio-fertilizers fix atmospheric nitrogen in the soil and root nodules of legume crops and make it available to the plant.
- They solubilize the insoluble forms of phosphates like tricalcium, iron and aluminium phosphates into available forms.
- They scavenge phosphate from soil layers.

- They produce hormones and anti-metabolites which promote root growth.
- They decompose organic matter and help in mineralization in soil.
- When applied to seed or soil, bio-fertilizers increase the availability of nutrients and improve the yield by 10 to 25% without adversely affecting the soil and environment.

**Table No. 1.2 Type of Fertilizers Production in India**

<b>Type of fertilizers</b>	<b>Grade</b>
<b>1.Straight Nitrogenous</b>	
Ammonium Sulphate (SP)	20.6% N
Calcium Ammonium Nitrate (CAN)	25% N
Ammonium Chloride	25% N
Urea	46% N
<b>2.Straight Phosphatic</b>	
Single Super Phosphate (SSP)	16% P <sub>2</sub> O <sub>5</sub>
Triple Super Phosphate (TSP)	46%P <sub>2</sub> O <sub>5</sub>
<b>3.NP\NPK Complex Fertilizers</b>	
Urea Ammonium Phosphate	24-24-0
	28-28-0
	14-35-14
Ammonium Phosphate Sulphate	16-20-0
	20-20-0
Di-ammonium Phosphate (DAP)	18-46-0
Mono Ammonium Phosphate (MAP)	11-52-0
Nitro Phosphate	20-20-0
	23-23-0
Nitro Phosphate with Potash	15-15-15
NP\NPKs	17-17-17
	14-28-14
	19-19-19
	10-26-26
	12-32-16

Source: Department of Fertilizers Ministry of chemicals and fertilizers government of India (2012-2014).

## ANALYSIS OF N,P,K, FERTILIZER:

### 1. Analysis of total nitrogen in fertilizers:

#### *Estimation of Nitrogen by Kjeldahl method :*

**(1) Kjeldahl method:** This test method is applicable to fertilizers containing no nitrate nitrogen. Add sulfuric acid, potassium sulfate and copper (II) sulfate pentahydrate to an analytical sample, pretreated by Kjeldahl method to change total nitrogen (T-N) to ammonium ion, and add a sodium hydroxide solution to subject to steam distillation. Collect isolated ammonia with 0.25 mol/L sulfuric acid and measure surplus sulfuric acid by (neutralization) titration using a 0.1 mol/L – 0.2 mol/L sodium hydroxide solution to obtain the total nitrogen (T-N) in an analytical sample. Or collect isolated ammonia with a boric acid solution and measure ammonium ion by (neutralization) titration using 0.25 mol/L sulfuric acid to obtain the total nitrogen (T-N) in an analytical sample.

**(2) Reagents:** Reagents are as shown below:

**a) 0.1 mol/L - 0.2 mol/L sodium hydroxide solution :** Transfer about 30 mL of water to a polyethylene bottle, dissolve about 35 g of sodium hydroxide specified in JIS K 8576 by adding in small portions while cooling, seal tightly and leave at rest for 4-5 days. Transfer 5.5 mL -11 mL of the supernatant to a ground-in stoppered storage container, and add 1000 mL of water.

**Standardization:** Dry sulfamic acid reference material for volumetric analysis specified in JIS K 8005 by leaving at rest in a desiccator at no more than 2 kPa for about 48 hours, then transfer about 2.5 g to a weighing dish, and measure the mass to the order of 0.1 mg. Dissolve in a small amount of water, transfer to a 250-mL volumetric flask, and add water up to the marked line. Transfer a predetermined amount of the solution to a 200-mL - 300-mL Erlenmeyer flask, add a few drops of bromothymol blue solution (0.1 g/100 mL) as an indicator, and titrate with a 0.1 mol/L - 0.2 mol/L sodium hydroxide solution until the color of the solution becomes green.

Calculate the factor of a 0.1 mol/L - 0.2 mol/L sodium hydroxide solution by the following formula:

Factor of 0.1 mol/L - 0.2 mol/L sodium hydroxide solution (f1)

$$= (W1 \times A \times 0.01/97.095) \times (V1/V2) \times (1000/V3) \times (1/C1)$$

W1: Mass (g) of sulfamic acid sampled

A: Purity (% (mass fraction)) of sulfamic acid

V1: Volume (mL) of sulfamic acid solution transferred

V2: Constant volume (250 mL) of sulfamic acid solution

V3: Volume (mL) of 0.1 mol/L - 0.2 mol/L sodium hydroxide solution needed for titration

C1: Set concentration (mol/L) of 0.1 mol/L - 0.2 mol/L sodium hydroxide solution

**b) Sulfuric acid:** A JIS Guaranteed Reagent specified in JIS K 8951 or a reagent of equivalent quality.

**c) 0.25 mol/L sulfuric acid :** Add about 14 mL of sulfuric acid to a beaker containing 100 mL of water in advance, stir well, and add water to make 1000 mL.

**Standardization:** Transfer a predetermined amount of 0.25 mol/L sulfuric acid to a 200-mL - 300-mL Erlenmeyer flask, add a few drops of methyl red-methylene blue mixture solution, and titrate with a 0.1 mol/L -0.2 mol/L sodium hydroxide solution until the color of the solution becomes gray-green.

Calculate the volume of a 0.1 mol/L - 0.2 mol/L sodium hydroxide solution equivalent to 1 mL of 0.25 mol/L sulfuric acid by the following formula (1). Or, calculate the factor of 0.25 mol/L sulfuric acid by the following formula (2):

Volume (B) of 0.1 mol/L -0.2 mol/L sodium hydroxide solution equivalent to 1 mL of 0.25 mol/L sulfuric acid =  $V_4/V_5$  ..... (1)

Factor of 0.25 mol/L sulfuric acid (f2) =  $(f_1 \times C_1 \times V_4/V_5)/(C_2 \times 2)$  ..... (2)

V4: Volume (mL) of 0.1 mol/L -0.2 mol/L sodium hydroxide solution needed for titration

V5: Volume (mL) of 0.25 mol/L sulfuric acid subjected to standardization

C1: Set concentration (mol/L) of 0.1 mol/L - 0.2 mol/L sodium hydroxide solution

C2: Set concentration (0.25 mol/L) of 0.25 mol/L sulfuric acid

**d) Boric acid solution (40 g/L):** Dissolve 40 g of boric acid specified in JIS K 8863 in water to make 1000 mL.

**e) Catalyst :** Mix potassium sulfate specified in JIS K 8962 and copper (II) sulfate pentahydrate specified in JIS K 8983 in the ratio of 9 to 1.

**f) Sodium hydroxide solution (200 g/L - 500 g/L) :** Dissolve 100 g - 250 g of sodium hydroxide specified in JIS K 8576 in water to make 500 mL.

**g) Bromothymol blue solution (0.1 g/100 mL):** Dissolve 0.1 g of bromothymol blue specified in JIS K 8842 in 20 mL of ethanol (95) specified in JIS K 8102, and add water to make 100 mL.

**h) Methyl red solution (0.1 g/100 mL):** Dissolve 0.1 g of methyl red specified in JIS K 8896 in 100 mL of ethanol (95) specified in JIS K 8102.

**i) Methylene blue solution (0.1 g/100 mL):** Dissolve 0.1 g of methylene blue specified in JIS K 8897 in 100 mL of ethanol (95) specified in JIS K 8102.

**j) Methyl red - methylene blue mixture solution:** To 2 volumes of methyl red solution (0.1 g/100 mL), add 1 volume of methylene blue solution (0.1 g/100 mL).

**k) Bromocresol green solution (0.5 g/100 mL):** Dissolve 0.5 g of bromocresol green specified in JIS K 8840 in 100 mL of ethanol (95) specified in JIS K 8102.

**I) Methyl red - bromocresol green mixture solution:** To a methyl red solution (0.1 g/100 mL), add equal volume of bromocresol green solution (0.5 g/100 mL).

### **(3) Apparatus and instruments:**

Apparatus and instruments are as shown below.

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

### **(4) Test procedures :**

**Kjeldahl method:** Conduct digestion as shown below.

- a) Weigh 0.5 g - 5 g of an analytical sample to the order of 1 mg, and put it in a 300-mL - 500-mL digestion flask.
- b) Add 5 g - 10 g of catalyst, and further add 20 mL - 40 mL of sulfuric acid, shake to mix and heat gently.
- c) After bubbles cease to form, heat until white smoke of sulfuric acid evolves.
- d) Ignite until organic matters are completely digested .
- e) After standing to cool, add a small amount of water, mix well by shaking, transfer to a 250-mL - 500-mL volumetric flask with water , and further mix by shaking.

f) After standing to cool, add water up to the marked line to make the digestion solution.

### **(5) Measurement and Calculate:**

Conduct measurement as shown below. When 0.25 mol/L sulfuric acid is used in :

a) Titrate the distillate with 0.1 mol/L - 0.2 mol/L sodium hydroxide solution until the color of the solution becomes gray-green .

b) Calculate the total nitrogen (T-N) in the analytical sample by the following formula:

#### **Total nitrogen (T-N) (% (mass fraction)) in the analytical sample**

$$= (B \times V6 - V7) \times C1 \times f1 \times (V8/V9) \times (14.007/W3) \times (100/1000)$$

$$= (B \times V6 - V7) \times C1 \times f1 \times (V8/V9) \times (1.4007/W3)$$

B: Volume of 0.1 mol/L -0.2 mol/L sodium hydroxide solution equivalent to 1 mL of 0.25 mol/L sulfuric acid  
V6: Volume (mL) of 0.25 mol/L sulfuric acid transferred to the acceptor .

V7: Volume (mL) of 0.1 mol/L - 0.2 mol/L sodium hydroxide solution needed for titration

C1: Set concentration (mol/L) of 0.1 mol/L - 0.2 mol/L sodium hydroxide solution

f1: Factor of 0.1 mol/L - 0.2 mol/L sodium hydroxide solution

V8: Predetermined volume (mL) of the digestion solution

V9: Transferred amount (mL) of the digestion solution subjected to distillation

W3: Mass (g) of the analytical sample

## 2. Analysis of soluble phosphoric acid in fertilizers:

### Quinoline gravimetric analysis Method :

**(1) Principal:** This test method is applicable to fertilizers containing no phosphoric acid, etc. It is suitable for the fertilizers containing a relatively a high content of phosphoric acid. Extract by adding water to an analytical sample, then extract by adding an ammonium citric acid solution and combine respective pre-determined amounts of extract (equivalent volume). Heat after adding nitric acid and water, hydrolyze monorthophosphoric acid to orthophosphate ion and measure the mass of quinolium phosphomolybdate formed by the reaction with quinoline, molybdic acid and nitric acid to obtain ammonia alkaline ammonium citrate soluble phosphoric acid (soluble phosphoric acid (S-P<sub>2</sub>O<sub>5</sub>)) in an analytical sample.

**(2) Reagents:** Reagents are as shown below:

**a) Nitric acid:** Guaranteed Reagent (HNO<sub>3</sub> 60 % (mass fraction)) specified a reagent of equivalent quality.

**b) Ammonia solution:** Guaranteed Reagent (NH<sub>3</sub> 28 % (mass fraction)) specified a reagent of equivalent quality.

**c) Petermans citrate solution:** Dissolve 173 g of citric acid monohydrate specified by adding to water and add gradually an ammonia solution equivalent to 42 g of nitrogen while cooling. After standing to cool, add water to make 1000 ml. Additionally, check that the specific gravity of the solution is 1.082 -1.083 (15 °C) and the volume of nitrogen per 1 ml is 42 mg.

**d) Sodium molybdate solution:** Dissolve 70 g of sodium molybdate dihydrate in 150 ml of water.

**e) Quinoline solution:** Add 5 ml of quinoline specified in to the mixture solution of 35 ml of nitric acid and 100 ml of water.

**f) Quimosiac solution:** Add 60 g of citric acid monohydrate specified in to the mixture solution of 85 ml nitric acid and 150 ml of water to dissolve. Add gradually total volume of the sodium molybdate solution to mix them. Add gradually the total volume of the quinoline solution while mixing the solution. After leaving at rest overnight, filter the total volume with Type 3 filter paper. Add 280 ml of acetone specified and further add water to make 1000 ml.

**(3) Apparatus and instruments:** Apparatus and instruments are as follows:

**a) Water bath:** A water bath that can be adjusted to  $65\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$  or  $60\text{ }^{\circ}\text{C} - 65\text{ }^{\circ}\text{C}$ .

**b) Drying apparatus:** A drying apparatus that can be adjusted to  $220\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ .

**c) Crucible type glass filter:** A crucible type glass filter 1G4 specified in JIS R 3503. Let it stand to cool in a desiccator after heating at  $220\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$  in advance and measure the mass to the order of 1 mg.

**(4) Test procedures :**

**Extraction:** Conduct extraction as shown below.

a) Weigh 2.5 g of an analytical sample to the order of 1 mg, and put it in a small mortar.

b) Add about 20 ml - 25 ml of water, grind well and filter the supernatant with Type 6 filter paper into a 250-ml volumetric flask.

c) Further, after repeating 3 times the procedure in (b), transfer non-dissolved matter in the small mortar on a filter paper and wash with water until the filtrate becomes about 200 ml.

d) Add a small amount of nitric acid to the filtrate, and further add water up to the marked line to make the sample solution .

e) Transfer the non-dissolved matter on the filter paper together with the filter paper to another 250- ml volumetric flask, and add 100 ml of Petermans citrate solution and stopple. Then shake to mix until the filter paper breaks down.

f) Heat the volumetric flask in a water bath at  $65\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$  for 1 hour while shaking to mix every 15 minutes.

g) After standing to cool, add water up to the marked line.

h) Filter with Type 6 filter paper to make the sample solution.

#### **(5) Measurement:**

Conduct measurement as shown below.

a) Transfer a predetermined volume (the equivalents of 10 mg - 30 mg as  $\text{P}_2\text{O}_5$  and no more than the equivalents of 8 ml of Petermans citrate solution) (2) of sample solution (1) and sample solution (2) to a 300-ml tall beaker.

b) Add 5 mL of nitric acid and add water to make about 80 ml.

c) Cover with a watch glass. After boiling for about 3 minutes, wash the watch glass and the inside of the tall beaker with water and add water to make about 100 ml.

d) Immediately, add 50 ml of quimosiac solution, heat for about 15 minutes while sometimes mixing in a water bath at  $60\text{ }^{\circ}\text{C} - 65\text{ }^{\circ}\text{C}$  and produce the precipitate of quinolyum molybdate.

e) After standing to cool down to room temperature while sometimes mixing, filter under reduced pressure with a crucible type glass filter, wash the tall beaker

3 times with water and transfer the whole precipitate into a crucible type glass filter, further wash 7 - 8 times with water.

f) Transfer the precipitate together with the crucible type glass filter into a drying apparatus and heat at  $220\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$  for about 30 minutes.

g) As soon as heating is complete, move it into a desiccator and let it stand to cool.

h) After standing to cool, remove the crucible type glass filter from the desiccator and measure the mass to the order of 1 mg.

**Calculation:** Calculate soluble phosphoric acid ( $\text{S-P}_2\text{O}_5$ ) by the following formula.

Soluble phosphoric acid (% (mass fraction)) in an analytical sample

$$= A \times 0.03207 \times (V1/V2) \times (1/W) \times 100$$

A: Mass (g) of the precipitate in h)

W: Mass of an analytical sample (2.5 g)

V1: Predetermined volume (250 ml) of the sample solution

V2: Volume (ml) of the sample solution transferred in a

### 3 . Analysis of Water-soluble potassium in fertilizers:

#### Sodium tetra phenyl borate gravimetric analysis Method:

**(1) Principal:** This test method is applicable to fertilizers containing potassium salts. Extract by adding water to an analytical sample, mask co-existing ammonium and other salts with formaldehyde and ethylenediamine tetraacetate and measure the mass of potassium tetraphenylborate formed by the reaction with tetraphenylborate to obtain water-soluble potassium ( $W-K_2O$ ) in an analytical sample.

**(2) Reagents:** Reagents are as shown below:

**a) Hydrochloric acid:** A Guaranteed Reagent specified in a reagent of equivalent quality.

**b) Formaldehyde solution:** A Guaranteed Reagent specified in a reagent of equivalent quality.

**c) Sodium hydroxide solution (200 g/l):** Dissolve 200 g of sodium hydroxide specified in water to make 1000 ml.

**d) Aluminum chloride solution :** Dissolve 12 g of aluminum chloride (III) hexahydrate specified in water to make 100 ml.

**e) Tetraphenylborate solution:** Transfer 6.1 g of Sodium tetra phenyl borate to a 250-ml volumetric flask, dissolve by adding about 200 mL of water and add 10 ml of aluminum chloride solution. Add a methyl red solution (0.1 g/100 ml) as an indicator, and neutralize with a sodium hydroxide solution (200 g/l) until the color of the solution changes to yellow, and then add water up to the marked line. Filter with Type 3 filter paper and add sodium hydroxide solution (200 g/l) to the total filtrate. Filter with Type 3 filter paper in the case of usage.

**f) Tetraphenylborate washing solution** : Dilute 40 ml of tetraphenylborate solution with water to make 1000 ml.

**g) Ethylenediamine tetraacetate-sodium hydroxide solution** : Dissolve 10 g of ethylenediaminetetraacetic acid dihydrogen disodium dihydrate specified in and 8 gm of sodium hydroxide specified in a proper amount of water, add 6 ml - 10 ml of tetraphenylborate solution while mixing according to potassium content coexisting as impurity after standing to cool and then add water to make 100 ml. After leaving at rest for about 30 minutes while sometimes mixing, filter with Type 3 filter paper.

**h) Methyl red solution (0.1 g/100 ml)**: Dissolve 0.10 g of methyl red specified in 100 ml of ethanol (95) specified.

**(3) Apparatus and instruments:** Apparatus and instruments are as follows:

**a) Rotary shaker:** A rotary shaker that can rotate a 500-mL volumetric flask upside down at 30- 40 revolutions/min.

**b) Drying apparatus:** A drying apparatus that can be adjusted to  $120\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ .

**c) Crucible type glass filter:** A crucible type glass filter 1G4 specified into a drying apparatus Let it stand to cool in a desiccator after heating at  $120\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$  in advance and measure the mass to the order of 1 mg.

**d) Hot plate:** A hot plate whose surface temperature can be adjusted up to  $250\text{ }^{\circ}\text{C}$ .

**(4) Test procedures :**

**Extraction:** Conduct extraction as shown below.

***Mixed fertilizers containing potassium salts and magnesium potassium sulfate :***

a) Weigh 2.5 g of an analytical sample to the order of 1 mg, and transfer to a 300-ml tall beaker.

- b) Add about 200 ml of water, and cover with a watch glass and heat on a hot plate to boil for about 15 minutes.
- c) After standing to cool, transfer to a 250-ml volumetric flask with water.
- d) Add water up to the marked line.
- e) Filter with Type 3 filter paper to make the sample solution

**(5) Measurement:** Conduct measurement as shown below.

- a) Transfer a predetermined volume (the equivalents of 15 mg - 30 mg as  $K_2O$ ) of sample solution to a 100-mL tall beaker.
- b) Add water to the solution to reach 50 ml when the procedure in e) is complete.
- c) Add 2 mL of hydrochloric acid (1+9).
- d) Add 5 ml of formaldehyde solution, and then add 5 ml of ethylenediamine tetraacetate-sodium hydroxide solution.
- e) Add necessary volume (2) 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 supernatant with a crucible type glass filter, wash the vessel 5 times with 5 ml of tetraphenylborate washing solution and transfer the whole precipitate to the crucible type glass filter and further wash 2 times with 2 ml of water.
- h) Transfer the precipitate together with the crucible type glass filter into a drying apparatus adjusted to  $120\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$  and heat for 1 hour.
- i) After heating, move it quickly into a desiccator and let it stand to cool.
- j) After standing to cool, remove a ground-in stoppered weighing bottle from the desiccator and measure the mass to the order of 1 mg.

**Calculation:** Calculate water-soluble potassium (W-K<sub>2</sub>O) in the analytical sample by the following formula.

Water-soluble potassium (W-K<sub>2</sub>O) (% (mass fraction)) in an analytical sample

$$= A \times 0.1314 \times (V1/V2)/W \times 100$$

A: Mass (g) of precipitate

V1: Predetermined volume (ml) of the sample solution

V2: Volume (ml) of the sample solution transferred

W: Mass of an analytical sample (g)