

Fertilizer Manual

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भारत सरकार कृषि अनुसंधान और शिक्षा विभाग एवं भारतीय कृषि अनुसंधान परिषद कृषि मंत्रालय, कृषि भवन, नई दिल्ली 110 001

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FOREWORD



India being a tropical country, the reserve of organic carbon in soils is very low. The deficiency of N is universal in India. Most of the Indian soils are low to medium in P. With passage of time, K deficiency has also become widespread. The deficiency of S is increasing. Apart from macro elements, the increasing deficiency of micronutrients is becoming a cause of concern. Among the micronutrients, deficiency of Zn is the most acute, followed by B and Mo. With this background, chemical fertilisers have played a significant role in increasing this production in India. Now India is second only to China in fertiliser consumption which is projected to reach 41.6 million tonnes in 2020. Fertilisers are becoming indispensable for the crop production systems of modern agriculture. Efficient application of the correct types with right quality and amounts of fertilizers at right time for the supply of the nutrients is an important part of achieving profitable and sustainable yields. The manual will help ensure that proper account is taken of mineral fertilizers and suite to the need of students, teachers and practitioners. Using this manual, farmers and land managers will have better assess the fertilizer required for the range of crops they plan to grow, by suggesting what level of nutrients are required to provide the best return with highest use efficiency. I commend the author of the manual for this contribution.

(S. Ayyappan)



Preface

The proper feeding of the rapidly growing populations in countries like India is the most important challenge for us. Presently, about 200 million people in India are suffering from chronic malnutrition due to shortage of suitable foods. The successful production of crops requires a farmer to make maximum use of all available resources. One of the most important and necessary resources is fertilizer, which provides the nutrients needed by plants to grow properly and yield a quality product. The use of fertilizers has become an essential and routine part of many crop production systems. Farmers do not use fertilizers just to grow big crops or to increase the nutrient content of their soils. They do so to make a living. As a result, any fertilizer practice must be technically correct to ensure it gives a fair economic return to the farmers. When fertilizers are applied to crops care must be taken to ensure that the fertilizers are placed near enough to the roots for absorption. Further, concentrations of fertilizers in the root zone must not be high enough to cause injury to the roots. The three general methods used for fertilizer application are broadcast, placement and foliar. Efficiency of fertilizer use by crops is of major agronomic interest. There is growing concern that fertilizers be used as efficiently as possible to minimize losses and environmental pollution. Nutrients are lost to the environment through crop removal, leaching, denitrification, volatilization and erosion. The inefficient use of fertilizers can also result in environmental pollution. The ways through which pollution occur are eutrophication, high nitrate levels in water, soil acidification and greenhouse gas emissions. Fertilizers pose little danger to the environment particularly groundwater once stored and applied properly. The storage, quality control and handling of fertilizers is also a serious issue that needs due attention for efficiency and sustainability point of view. I am confident that this manual is useful for students in undergraduate and post graduate level as well as the extension of fertilizer usage to a large number of farmers for improvement of crop yield and other benefits, while minimizing impairments on the resource base.

Amitava Rakshit

Acknowledgments

Prima facea, I am grateful to the God for the good health and wellbeing that were necessary to complete this manual. This manual is written for academics, researcher, technicians and extension workers who are involved in fertilizer research, production and application. I would like to thank the Indian Council of Agriculture Research for the sponsorship. The publication of the manual would not be possible without the efforts and assistance of our supporting staff in the Department of Soil Science & Agricultural Chemistry. I am grateful to all the faculty members of Soil Science & Agricultural Chemistry for their cooperation. Thanks are also extended to my undergraduate and post graduate students for sharing their requirements and inputs. Special thanks to Prof. R. P. Singh, Director, Institute of Agricultural Sciences, BHU for his advice on the publication of the manual. I would like to thank colleagues and organizations for sharing their resources that have been utilized to write this manual. The organizations whose resources I have used in writing this manual are: IFDC—An International Center for Soil Fertility and Agricultural Development, P.O. Box 2040, Muscle Shoals, AL 35662 (U.S.A.); Yara Fertiliser Industry, Norway; Central Fertilizer Quality Control & Training Institute, Faridabad, India and IFA, 28, rue Marbeuf, 75008 Paris, France. Finally, I would thank my family, immediate and extended for their untiring effort, unconditional support, unflagging love in putting everything together and inspiration to complete the manual. I welcome any suggestions for improvements in the content of the manual, as well as notification of any errors.

Introduction

1. The Fertilizer Manual

The successful production of crops requires a farmer to make maximum use of all available resources. One of the most important and necessary resource is fertilizer, which provides the nutrients needed by plants to grow properly and yield a quality product. Fertilizers account for one-third or more of crop yields. Inadequate fertility starves plants. Excess fertility is wasted and can cause physical injury and death to plants as well as pollution to the environment. It is necessary therefore to supply plants with precise and balanced amounts of nutrients needed for their optimal growth and development but avoiding excessive amounts that can be eventually lost to the environment. This manual has the following chapters: 1) Introduction, 2), 3), 4), and 5), from advanced basic information to practical methods in each participating country. We try to write as easy as possible for scientists and technicians involved in biofertilizers in India. However, we admit that this manual may be quite difficult for farmers. It is our hope that scientists and technicians will translate some part of this manual into the respective mother language in some brochures or pamphlets for farmers. The basic concepts related to fertilizer use, types of fertilizers, methods of application, efficient use of fertilizers, storage, handling and environmental hazards are given prominence.

PLANT NUTRIENTS

Some soils are naturally low in nutrients whilst others become depleted due to continuous cropping. Farmers are generally aware when this condition arises. They usually refer to their soils in this state as being 'run down'. Farmers invariably use fertilizers and manures to correct this problem. A fertilizer is a material that provides one or more elements (nutrients or plant food) for the growth and development of plant. The use of fertilizers has become an essential and routine part of many crop production systems. Farmers do not use fertilizers just to grow big crops or to increase the nutrient content of their soils. They do so to make a living. As a result, any fertilizer practice must be technically correct to ensure it gives a fair economic return to the farmers.

Plant nutrients are chemical elements that are essential for the growth and development of plants.

Classification

There are 17 nutrients that are required for the growth and development of plants (Table 1). Additionally, some nutrients such as silicon (Si) are also necessary for successful rice production.

Classification Elements

Table 1: Classification of Elements Essentials for Plant Growth

Table I. Diassification of Elementa Essentials for Figure of Owth				
Classification		Elements		
Macronutrients	Available from air or water	Carbon, Hydrogen, Oxygen		
	Primary Nutrients	Nitrogen, Phosphorus, Potassium		
	Secondary Nutrients	Calcium, Magnesium, Sulphur		
Micronutrients		Boron, Cobalt, Chlorine, Copper,		
		Iron, Manganese, Molybdenum,		

	l <u> </u>
	1 7.
	l Zinc
	I ZIIIG

Nine plant nutrients are required in relatively large amounts. These are referred to as the major elements or macronutrients. Of these, carbon, hydrogen and oxygen, (make up 90-95% of the dry matter of plants) are obtained from carbon dioxide and water. These nutrients are therefore not regarded as components of fertilizers. The other major elements are divided into primary nutrients (nitrogen, potassium and phosphorus) and secondary nutrients (calcium, magnesium and surplus). The remaining eight plant nutrients are required in much smaller quantities are known as micronutrients or minor elements.

Roles and functions of plant nutrients

Plant nutrients obtained from the soil are essential for the growth of healthy plants. Sixteen plant food nutrients are essential for proper crop development. Each is equally important to the plant, yet each is required in vastly different amounts. These differences have led to the grouping of these essential elements into three categories; primary (macro) nutrients, secondary nutrients, and micronutrients. Rrequirements of these diversified nutrients is essential for a plant to complete its life cycle and are utilized by plants during the basic metabolic processes which are absolutely essential for the continued life of all plants. For plants to utilize these nutrients efficiently, light, heat, and water must be adequately supplied. Cultural practices and control of diseases and insects also play important roles in crop production. Each type of plant is unique and has an optimum nutrient range as well as a minimum requirement level. Below this minimum level, plants start to show nutrient deficiency symptoms. Excessive nutrient uptake can also cause poor growth because of toxicity. Adequate provision of nutrients impacts greatly on plant growth and as such is of crucial importance in the context of agriculture.

Plant concentrations of essential elements may exceed the critical concentrations, the minimum concentrations required for growth, and may vary somewhat from species to species (Table 2). Nonetheless, the following table gives the general requirements of plants:

Table 2: Typical concentrations sufficient for plant growth (After E. Epstein. 1965. "Mineral metabolism" pp. 438-466. in: Plant Biochemistry (J.Bonner and J.E. Varner, eds.) Academic Press, London.)

Element	Criteria of essentiality	Symbol	mg/kg	Percent	Relative number of atoms
Nitrogen	Theodore de Sassure(1804)	N	15,000	1.5	1,000,000
Potassium	Sprengel(1839)	K	10,000	1.0	250,000
Calcium	Sprengel(1839)	Ca	5,000	0.5	125,000
Magnesium	Sprengel(1839)	Mg	2,000	0.2	80,000
Phosphorus	Sprengel(1839)	Р	2,000	0.2	60,000
Sulfur	Salm-Horstman(1851)	2	1,000	0.1	30,000
Chlorine	Broyer et al(1954)	Cl	100		3,000
Iron	Gris(1943)	Fe	100		2,000
Boron	Warington(1923)	В	20		2,000
Manganese	Mcttargne(1922)	Мп	50		1,000
Zinc	Sommer & Lipman(1931)	Zn	20		300
Copper	Sommer & Lipman(1931	Си	6		100
Molybdenum	Arnon & Stout(1939)	Mo	0.1		1
Nickel	Brown et al(1987)	Ni	0.1		

PRIMARY (MACRO) NUTRIENTS

Primary (macro) nutrients are nitrogen, phosphorus, and potassium. They are the most frequently required in a crop fertilization program. Also, they are need in the greatest total quantity by plants as fertilizer.

NITROGEN

- · Necessary for formation of amino acids, the building blocks of protein
- · Essential for plant cell division, vital for plant growth
- · Directly involved in photosynthesis
- · Necessary component of vitamins
- · Aids in production and use of carbohydrates
- · Affects energy reactions in the plant

PHOSPHORUS

- \cdot Involved in photosynthesis, respiration, energy storage and transfer, cell division, and enlargement
- · Promotes early root formation and growth
- · Improves quality of fruits, vegetables, and grains
- · Vital to seed formation
- · Helps plants survive harsh winter conditions
- · Increases water-use efficiency
- · Hastens maturity

POTASSIUM

- · Carbohydrate metabolism and the break down and translocation of starches
- · Increases photosynthesis
- · Increases water-use efficiency
- · Essential to protein synthesis
- · Important in fruit formation
- · Activates enzymes and controls their reaction rates
- · Improves quality of seeds and fruit
- · Improves winter hardiness
- · Increases disease resistance

SECONDARY NUTRIENTS

The secondary nutrients are calcium, magnesium, and sulphur. For most crops, these three are needed in lesser amounts that the primary nutrients. They are growing in importance in crop fertilization programs due to more stringent clean air standards and efforts to improve the environment.

CALCIUM

- · Utilized for Continuous cell division and formation
- · Involved in nitrogen metabolism
- · Reduces plant respiration
- · Aids translocation of photosynthesis from leaves to fruiting organs
- · Increases fruit set
- · Essential for nut development in peanuts
- · Stimulates microbial activity

MAGNESIUM

- · Key element of chlorophyll production
- · Improves utilization and mobility of phosphorus
- · Activator and component of many plant enzymes
- · Directly related to grass tetany
- · Increases iron utilization in plants
- · Influences earliness and uniformity of maturity

SULPHUR

- · Integral part of amino acids
- · Helps develop enzymes and vitamins
- · Promotes nodule formation on legumes
- · Aids in seed production
- Necessary in chlorophyll formation (though it isn't one of the constituents)

MICRONUTRIENTS

The micronutrients are boron, chlorine, cooper, iron, manganese, molybdenum, and zinc. These plant food elements are used in very small amounts, but they are just as important to plant development and profitable crop production as the major nutrients. Especially, they work "behind the scene" as activators of many plant functions.

BORON

- · Essential of germination of pollon grains and growth of pollen tubes
- · Essential for seed and cell wall formation
- · Promotes maturity
- · Necessary for sugar translocation
- · Affects nitrogen and carbohydrate

CHLORINE

- · Not much information about its functions
- · Interferes with P uptake
- · Enhances maturity of small grains on some soils

COPPER

- · Catalyzes several plant processes
- · Major function in photosynthesis
- · Major function in reproductive stages
- · Indirect role in chlorophyll production
- · Increases sugar content
- \cdot Intensifies color
- · Improves flavor of fruits and vegetables

IRON

- · Promotes formation of chlorophyll
- · Acts as an oxygen carrier
- · Reactions involving cell division and growth

MAGANESE

- · Functions as a part of certain enzyme systems
- · Aids in chlorophyll synthesis
- · Increases the availability of P and CA

MOLYBDENUM

- \cdot Required to form the enzyme "nitrate reductas" which reduces nitrates to ammonium in plant
- · Aids in the formation of legume nodules
- · Needed to convert inorganic phosphates to organic forms in the plant

ZINC

- · Aids plant growth hormones and enzyme system
- · Necessary for chlorophyll production
- · Necessary for carbohydrate formation
- · Necessary for starch formation
- · Aids in seed formation

In addition to the 13 nutrients listed above, plants require carbon, hydrogen, and oxygen, which are extracted from air and water to make up the bulk of plant weight.

Visual nutrient deficiency symptoms can be a very powerful diagnostic tool for evaluating the nutrient status of plants. One should keep in mind, however, that a given individual visual symptom is seldom sufficient to make a definitive diagnosis of a plant's nutrient status. Many of the classic deficiency symptoms such as tip burn, chlorosis and necrosis are characteristically associated with more than one mineral deficiency and also with other stresses that by themselves are not diagnostic for any specific nutrient stress. However, their detection is extremely useful in making an evaluation of nutrient status. In the following table (Table 3 and 4) deficiency symptoms and probable cause have been presented for macro and micro nutrients which can be used to evaluate the qualitative status of plant nutrient status with a relatively high degree of confidence.

Table 3: Primary and secondary nutrient deficiency symptoms, the cause and method of correction

Element	General deficiency symptoms	Probable cause of deficiency	Method of correction
Nitrogen (N)	yellow leaves, stunted growth lower leaves turn brown, leaves abort	low soil N, leaching from the soil, inadequate N applied	apply N fertilizer
Phosphorus (P)	small plants, reddish-purple leaves, slow growth, loss of plant vigor	low soil P; cool, wet soils, inadequate P applied	apply P fertilizer
Potassium (K)	small plants, brown margins on lower leaves, small stems, lodging of plants, poor yield and quality	Low soil K, leaching from the apply K fertilizer ,weak soil, inadequate K applied	apply K fertilizer
Calcium (Ca)	small plants, deformed buds distorted leaves, failure to grow poor fruit development	low soil pH, leaching from the soil, inadequate lime applied	apply lime or, Ca fertilizer
Magnesium (Mg)	lower leaves—in severe cases entire plants—turn yellow with green interveinal areas	low soil pH, leaching from the soil, no Mg applied fertilizer	apply dolomitic lime or Mg fertilizer
Sulfur (S)	yellow plants, slow growth low vigor .no response to applied nitrogen ,low crop yield and quality	low soil S, leaching from soil, low organic matter content ,no S fertilizer applied	apply S fertilizer

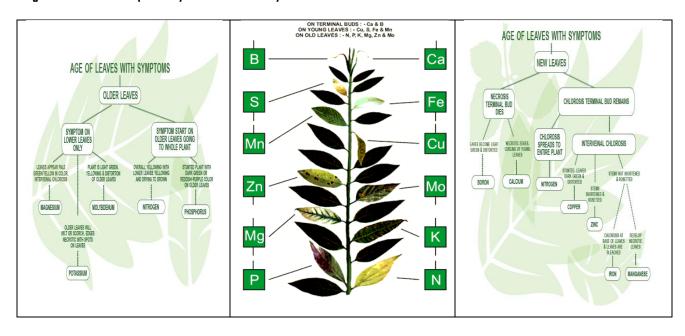
Table 4: Micronutrient deficiency symptoms, the probable cause and method of correction

Element	General deficiency symptoms	Probable cause of deficiency	Method of correction
,	interveinal chlorosis of leaves, stunted plants, yellow cast over due to over liming spray, reduced yield & quality	low soil Mn, high soil pH lower	apply foliar or add Mn to
Manganese(Mn)		soil pH	soil deficient areas

Zinc (Zn)	chlorotic leaves, slow growth reduced vigor, white streaks parallel to leaf blade	low Zn in soil, high soil pH, lower soil pH high soil P	apply foliar spray or add Zn to soil
Copper (Cu)	reduced growth, leaf-tip dies back, leaf tip breaks down leaves ragged	low soil Cu, high organic matter	apply foliar spray or add Cu to soil
Boron (B)	terminal bud dies, multiple lateral branches (rosette with short internodes, older leaves thick and leathery, petioles short, twisted, and ruptured), hollow heart (in vegetables), small deformed fruit (in grapes), cork spot (in apples)	low soil B, esp. on sandy	apply foliar spray or add B soils to soil
Malybdenum(Ma)	reduced growth; pale green color; necrotic areas adjacent to midrib between veins and along leaf edges; twisted stems	low soil pH, low Mo content	apply in soil foliar spray, or add Mo to soil, inoculate seed with Mo
Chlorine (CI)	reduced growth; stubby roots; interveinal chlorosis; nonsucculent tissue (in leafy vegetables)	low soil Cl, esp. in soils subject to leaching	apply Cl-containing fertilizer

Nutrient deficiencies can be identified in field through visual observations(Fig 1). However, additional analysis, either plant or soil testing is often necessary to confirm nutrient stress. The following is a quick-reference flow chart that can be used in field to identify potential nutrient deficiencies. Each nutrient has unique deficiency symptoms. Deficiencies will appear in many ways. It can be confused with other plant problems like pathogens or spray damage. But nutrient deficiencies can often be recognized because they tend to form symmetrical patterns, where both sides of leaf or plant parts show the same pattern.

Fig 1: A visual aid to help identify nutrient deficiency



History of Fertilizers

When humans began to make stone tools, grow their food, and live in permanent communities from then onwards they probably used fertilizers. Over time, fertilizer technology became more refined. New substances that improved the growth of plants were discovered. The Egyptians are known to have added ashes from burned weeds to soil. Ancient Greek and Roman writings indicate that various animal excrements were used, depending on the type of soil or plant grown. It was also known by this time that growing leguminous plants on plots prior to growing wheat was beneficial. Other types of materials added include sea-shells, clay, vegetable waste, waste from different manufacturing processes, and other assorted trash. But the history of modern chemical fertilizers begins in 18th century when first fertilizer produced by chemical processes was ordinary superphosphate, made early in the 19th century by treating bones with sulfuric acid. Coprolites and phosphate rock soon replaced bones as the P source. The K fertilizer industry started in Germany in 1861. In North America the K industry started during World War I and expanded with development of the New Mexico deposits in 1931 and the Saskatchewan deposits in 1958. Modern K fertilizers are more the product of physical than of chemical processes. The first synthetic N fertilizer was calcium nitrate, made in 1903 from nitric acid produced by the electric arc process. The availability of synthetic ammonia after 1913 led to manynew N fertilizers, but physical quality was poor.

The major contributions were those of Liebig, Lawes, Haber, Bosch, Wohler, Johansen and Frasch(Fig 2). Foundations of the fertilizer industry were laid primarily in Europe and part of America. In the 1730s, Viscount Charles Townshend (1674–1738) first studied the improving effects of the four crop rotation system that he had observed in use in Holland. He noticed that the farms where this was employed was more fertile than what it would be with a single crop. He started to research soil nutrition cycles. Johann Friedrich Mayer (1719-1798) was the first to present to the public a series of experiments upon it the relation of gypsum to agriculture, and many chemists have followed him in the 19th century.

Chemist Justus von Liebig (1803–1883) contributed greatly to the advancement in the understanding of plant nutrition. His influential works first denounced the vitalist theory of humus – which claimed that inorganic chemicals had no part in creating or sustaining plant life – arguing first the importance of ammonia, and later the importance of inorganic minerals. He is known as the "father of the fertilizer industry" for his discovery of nitrogen as an essential plant nutrient, and his formulation of the Law of the Minimum which described the effect of individual nutrients on crops. The Law of the Minimum states that growth is controlled not by the total of resources available, but by the scarcest resource. This concept was originally applied to plant or crop growth, where it was found that increasing the amount of plentiful nutrients did not increase plant growth. Only by increasing the amount of the limiting nutrient was the growth of a plant or crop improved. Primarily his work succeeded in setting out questions for agricultural science to address over the next 50 years. In England he attempted to implement his theories commercially through a fertilizer created by treating phosphate of lime in bone meal with sulfuric acid. Although it was much less expensive than the guano (bird droppings) that was used at the time, it failed because it was not able to be properly absorbed by crops. At that time in England, Sir John Bennet Lawes (1814–1900) was experimenting with crops and manures at his farm at Harpenden (in the county of Hertfordshire) and was able to produce a practical superphosphate in 1842 from the phosphates in rock and coprolites. Lawes had begun to interest himself in growing various medicinal plants on the Rothamsted estates, which he inherited on his father's death in 1822. About 1837 he began to experiment on the effects of various manures on plants growing in pots, and a year or two later the experiments were extended to crops in the field. One

immediate consequence was that in 1842 he patented a manure formed by treating phosphates with sulphuric acid, and thus initiated the artificial manure industry. Encouraged, he employed Sir Joseph Henry Gilbert, who had studied under Liebig at the University of Giessen, as director of research. To this day, the Rothamsted research station that they founded still investigates the impact of inorganic and organic fertilizers on crop yields.

Fig2: Major contributors in Fertilizer



In France, Jean Baptiste Boussingault (1802–1887) was instrumental in understanding the importance of Nitrogen fixing on plants. A chemist, who started out in the mining industry, he was appointed to the chair of agricultural and analytical chemistry at the Conservatoire des Arts et Metiers in Paris in 1839 and then he devoted himself mainly to agricultural chemistry and animal and vegetable physiology, with occasional excursions into mineral chemistry. The breakthrough came in 1828 when Friedrich Wohler (1800-1882) of Germany wanted to make ammonium cyanate by mixing ammonium chloride with silver cyanate. And like many major discoveries in science, it was accidental which yield urea. It was not the first organic compound to be made in the lab. In fact Wohler himself had made oxalic acid from an inorganic compound called cyanogens. In the early decades of the 20th Century, Nobel prize-winning chemists Carl Bosch of IG Farben and Fritz Haber developed the process that enabled nitrogen to be cheaply synthesized into ammonia, for subsequent oxidization into nitrates and nitrites. Both scientists were working for the German company BASF. This was an extremely important development as until then, there was no method to synthesize Nitrogen to a form that plants could take in. However this discovery was first used in manufacture of explosives and chemical weapons for World War I (1914-1919). Agriculture was not given much importance at that time. Post war (after 1920), this development enabled industrial production of Nitrogen fertilizers. It is now widely believed that this process enabled an increase in food production which in turn has caused the World's population to go from 1.6 billion in

1948 to the current 6 billion. The earliest fertilizer companies were established in England in the early 1800s and processed naturally available sources such as fossilized bones to obtain fertilizers – primarily phosphate fertilizers. By the end of the century, this had become a major industry on the east coast of England. As the industry grew, so did the variety of fertilizers. Colonization mean access to natural resources from around the world which enabled supply of different sources. After World War I these businesses came under financial pressure through new competition from guano (bird excreta), primarily found on the Pacific islands, as their extraction and distribution had become economically attractive. The inter-war period (1919-1938), with the application of the Haber-Bosch process, saw innovative competition from Imperial Chemical Industries (ICI) who developed synthetic ammonium sulfate in 1923, Nitro-chalk in 1927, and a more concentrated and economical fertilizer called CCF based on ammonium phosphate in 1931. In 1927 Erling Johnson developed an industrial method for producing nitrophosphate, also known as the Odda process after his Odda Smelteverk of Norway. Among the advocators of fertilizer the contribution of Borlaug cannot be overlooked. The late Nobel Laureate Dr. Norman Borlaug, often called the "father of the Green Revolution," has called improved seeds the "catalysts that ignited the Green Revolution" and mineral fertilizer the "fuel" that powers it.

Mineral and Organic Fertilizer

Plants need adequate supplies of nutrients for good growth and high yields. When the soil itself cannot supply the quantities of nutrients needed by the plant, best yields would not be obtained unless the shortage of plant nutrients is made up by applying the missing substances as fertilizers. A fertilizer is a material of natural or synthetic origin, the main function of which is to provide plant nutrients. By legal definition, the term fertilizer refers to a soil amendment that guarantees the minimum percentages of nutrients (at least the minimum percentage of nitrogen, phosphate, and potash).

An organic fertilizer refers to a soil amendment derived from natural sources that guarantees the minimum percentages of nitrogen, phosphate, and potash. The term soil amendment refers to any material mixed into a soil. Mulch refers to a material placed on the soil surface. By legal definition, soil amendments make no legal claims about nutrient content or other helpful (or harmful) effects they will have on the soil and plant growth.

The purpose of fertilizer use, especially for higher yields, is identical in temperate and tropical climates:

- to supplement the natural soil nutrient supply and build up soil fertility in order to satisfy the demand of crops with
 a high yield potential;
- to compensate for the nutrients exported by the harvested products or lost by unavoidable leakages to the
 environment in order to maintain good soil conditions for cropping.

Kinds of Fertilizers

Fertilizers are classified into two categories — inorganic and organic. The inorganic (mineral) fertilizer is a substance in which the declared nutrients are in the form of inorganic salts obtained by extraction and/or by physical and/or chemical industrial processes. Organic fertilizers are carbonaceous materials mainly of vegetable and/or animal origin added to the soil specifically for the nutrition of plants.

Fertilizer can be classified based on the number of plant nutrients they supply to the soil.

Straight fertilizers: Straight fertilizers are those which supply only one primary plant nutrient, namely nitrogen or phosphorus or potassium. E.g. Urea, ammonium sulphate, potassium chloride and potassium sulphate.

Complex fertilizers: Complex fertilizers contain two or three primary plant nutrients of which two primary nutrients are in chemical combination. These fertilizers are usually produced in granular form e.g. Diammonium phosphate, nitrophosphates and ammonium phosphate.

Mixed fertilizers: Physical mixtures are straight fertilizers. They contain two or three primary plant nutrients. Mixed fertilizers are made by thoroughly mixing the ingredients either mechanically or manually.

Fertilizers can also be classified based on physical form: Solid fertilisers and liquid fertiliser.

Solid fertilizers are in several forms:

- Powder (single superphosphate)
- Crystals (ammonium sulphate)
- Prills (urea, diammonium phosphate, superphosphate),
- Granules (Holland granules)
- Supergranules (urea supergranules)
- Briquettes (urea briquettes).

Liquid form fertilizers are applied with irrigation water or for application. Ease of handling, less labour requirement and possibility of mixing with herbicides has made the liquid fertilizers more acceptable to farmers.

Nitrogenous fertilizers

More than 80 per cent of the fertilizers used in this country are made up of nitrogenous fertilizers (Fig 3), particularly urea.

Ammoniacal: Ammoniacal fertilizers contain the nutrient nitrogen in the form of ammonium or ammonia. Except rice, all crops absorb nitrogen in nitrate form. These fertilizers are resistant to leaching loss, as the ammonium ions get readily absorbed on the colloidal complex of the soil. Example: Ammoniumm Sulphate, Ammonium chloride, Anhydrous ammonia

Nitrate: Nitrate fertilizers contain the nitrogen in the form of NO₃. These ions are easily lost by leaching because of the greater mobility of nitrate ions in the soil. Continuous use of these fertilizers may reduce the soil acidity as these nitrogenous fertilizers are basic in their residual effect on soils. Example: Sodium Nitrate, Calcium Nitrate, Potassium Nitrate

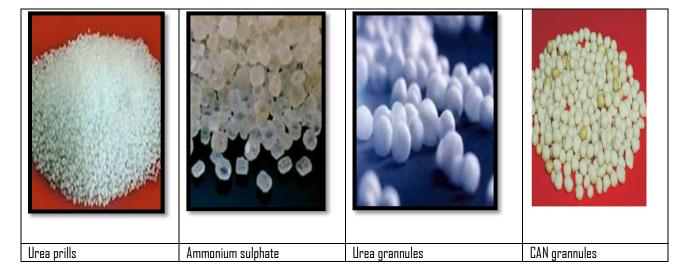


Fig3: Nitrogenous fertilizers

Ammoniacal and Nitrate: These fertilizers contain nitrogen in both ammonium and nitrate forms. The nitrates are useful for rapid utilization by crops and the ammonical is gradually available. Example: Ammonium Nitrate, Calcium Ammonium Nitrate, Ammonium Sulphate Nitrate

Amide: Amide fertilizers are readily soluble in water and easily decomposable in the soil. Example: Urea, Calcium Cynamide

Phosphatic fertilizers

Phosphatic fertilizers(Fig 4) are chemical substances that contain the nutrient phosphorus in absorbable form (Phosphate anions) or that yield after conversion in the soil.



Fig4: Nitrogenous fertilizers

Potassic fertilizers

There are a limited number of fertilizer materials (Fig 5) that can be used to supply K when needed. Example: Potassium chloride, Potassium-magnesium sulfate , Potassium nitrate, Potassium sulfate.

Common fertilizer sources of K

Material	Chemical formula	K₂O content
Potassium chloride	KCI	60
Potassium-magnesium sulfate	K ₂ SO ₄ -2MgSO ₄	20
Potassium nitrate	KNO ₃	44
Potassium sulfate	K_2SO_4	50



Fig 5:Potassic fertilizers

Multinutrient Fertilizers

Fertilizers having a declarable content of at least two of the primary plant nutrients (NP, NPK, PK, or NK) are classified as multinutrient fertilizers (Fig 6). They can also often contain one or more of the secondary nutrients and/or micronutrients. Multinutrient fertilizers, also often referred to as compound fertilizers, are available in an almost infinite number of grades. Multinutrient Fertilizers are produced by either physical blending or by one of several different chemical processes and are mostly in granular form. The chemical formula depends on raw materials used and grade produced; numerous grades are available.

Fig 6:Multinutrient Fertilizers



Secondary major-nutrient fertilizers

Magnesium fertilizers: These are chemical substances containing the nutrient magnesium in the form of magnesium cations (Mg^{2*}) . Example: Magnesium Sulphate $(MgSO_4)$. The utilization rate of magnesium fertilizers decreases with increasing potassium supplies.

Calcium fertilizers: These are the chemical substances containing the nutrient calcium in absorbable calcium cations ('Ca2+) form. The raw material of calcium fertilizers is lime found in nature.

Sulphate Fertilizers:These are chemical substances containing the nutrient sulphur in the form of absorbable sulphate anions (SD_4^{2-}) . The sulphur requirements of plants are about two third of their phosphorus requirements. Substantial sulphur supplies occur as minor constituents of various N, P and K fertilizers.

Micronutrient Fertilizers

The importance of fertilization of crops with micro-nutrients is increasing mainly because of greater removal from the soil, intensive liming of soil, intensive drainage of soil, higher use of nitrogenous, phosphatic and potassic fertilizers etc.

- a. There are seven essential micronutrients required by plants.
- b. These are iron, manganese, zinc, copper, chlorine, boron and molybdenum.

Fig 7: Secondary and micro nutrient fertilizers



Fertiliser can also be classified based on the residual effect (Table 5) it exterts on soil. There are three types of fertilizers i.e., Physiological acidic fertilizer, Physiological basic fertilizer and Physiological neutral fertilizer.

Equivalent Acidity: The amount of $CaCO_3$ required to neutralise the acid residues caused by acidic fertilizers in the soil e.g. 100 kg (NH₄)₂SO₄ produces acidity which needs 110 kg of $CaCO_3$ to neutralise it. Therefore equivalent acidity of (NH₄)₂SO₄ is 110; Anhydrous NH₃ has more equivalent acidity than other fertilizers.

Equivalent Basicity: Residual basicity caused by application of basic fertilizers, expressed in terms of $CaCO_3$ equivalent of basic residues left by a fertilizer material (in kg/100 kg of fertilizer salt).

Table 5: Residual effect of Fertilizer

S. No.	Fertilizer	Equivalent Acidity	Equivalent Basicity	Physiological neutral
1.	CaCN	-	63	
2.	$NaNO_3$	-	29	
3.	KNO ₃	-	29	
4.	$Ca(NO_3)_2$	-	21	
5.	Nitrate of Soda Potash	-	26	
6.	Anhydrous Ammonia	148	-	
7.	NH ₄ CI	128	-	
8.	$(NH_4)_2SD_4$	110	-	
9.	$(NH4)_2SD_4.NH_4ND_3$	93	-	
10.	Urea	80-84	-	
11.	DAP	77	-	
12.	Ammonium Nitrate	60	-	
13.	Mono-ammonium Phosphate	55		
14.	Calcium Ammonium Nitrate			0

Fertilisers can also be classified as natural fertilisers and synthetic fertilisers. Natural fertilisers are products that have been extracted from living things or from the earth. On the other hand synthetic fertilizers are those composed of the synthesized chemicals of nitrogen, phosphorus and potassium. In general, natural fertilizers contain lesser amounts of N-P-K than their synthesized counterparts, so one need to use more of them to supply the plant with the required amount of nitrogen, phosphorus or potassium.

Fertiliser can be also be classified based on physical condition. They are solid (crystalline, powdered, prilled or granular) of various size ranges; liquid (solutions and suspensions) and gaseous (liquid under pressure, e.q. ammonia).

Liquid fertilizers

Liquid form fertilizers are applied with irrigation water or for application. Liquid chemical fertilizers have a number of benefits for soil, plants and users. Ease of handling, less labour requirement and possibility of mixing with herbicides has made the liquid fertilizers

more acceptable to farmers. These products are easy to apply and provide quick results. More than just bottles of specified plant food, liquid fertilizers also balance the chemicals that naturally occur in soil and create an ideal growing environment for plants. Liquid fertilizers are easy to apply at varied stages of plant growth. They can encourage seeds to sprout and take root and later help the development of fruit and flowers. If a plant needs to be transplanted, liquid fertilizer can be appled directly to the root to encourage the plant to settle into its new home. When using irrigation solutions like in a drip system, liquid fertilizer is an ideal companion. Drip irrigation relies on specialized hoses that allow water to seep out into the soil at the base of a plant, where it is most needed. By adding the liquid fertilizers at the source of the water supply, each plant receives equal fertilization. Once the fertilizer is used up, the container can be removed from the supply until it is time to fertilize again.

Liquid fertilizers comprise anhydrous ammonia, aqueous solutions of ammonia, aqueous solutions of ammonium nitrate and or urea. These concentrated products may be diluted with water to form a concentrated liquid fertilizer (e.g. UAN).

Based on nutrient release it can be grouped as quick-acting (water-soluble and immediately available); slow-acting (transformation into soluble form required, e.g. direct application of phosphate rock); controlled-release by coating and stabilized by inhibitors.

Physical Properties of Fertilizer

Physical properties of fertilizers are important in processing, handling, transportation, bagging, storage, and application. The physical properties of fertilizers (Table 6) are critical relative humidity, moisture absorption-penetration characteristics, flowability, caking tendency, size analysis, angle of repose, bulk density, apparent density, true density of solids and liquids viscocity, granule crusning strength, abrasion resistance, impact resistance, handling strength, sphericity, conditioner adherence, dustiness, surface area, disintegration rate, and porosity.

Critical Relative Humidity

Critical relative humidity (CRH) is that humidity of the atmosphere above which a material will absorb a significant amount of moisture and below which it will not. For each fertilizer compound or mixture, there is a maximum relative humidity to which the fertilizer can be exposed without absorbing moisture from the air. Determination of this value is necessary when controlled-humidity storage areas are being designed for a material. Tile value is of interest also as an indication of the degree of protection that is likely to be required during handling. In the case of mixtures, determination of CRH is one check on compatibility; some mixtures have an intolerably low CRH, much lower than the CRH of either component alone. The procedure for determination of CRH involves exposure of small fertilizer samples to progressively higher relative humidities in a variable-humidity chamber. The lowest homidity that initiates significant absorption of moisture is determined by frequent weighings of the sample; this is taken to be the CRH

Table 6: Physical properties of different fertilizer

Fertiliser	Critical Relative Humidity at 30°C	Flowability (Minutes at 30°C and 90% RH) 75% non flowable	Angle of repose (°)	Bulk density (gcc ⁻¹)	Apparent density (gcc ⁻¹)	Granule crushing strength (kg/granule)
Prilled urea	70-75	15	28	0.76	1.32	1.0
Ammonium sulfate	70-75	280	38	0.78	1.59	2.5
Ammonium nitrate	60-65	16	32	0.83	1.67	1.7
Diammonium phosphate	70-75	180	37	1.00	1.65	3.9
Monoammonium phosphate	70-80	190	37	1.00	1.72	2.5
Potassium chloride	70-80		37	1.02	1.95	4.0
Potassium sulfate	80-85		41	1.04	1.99	3.0

Flowability

Flowability is the ability of a material to remain flowable under humid conditions. Flowability is important when considering the movement of material in conveyor systems and fertilizer applicators.

Caking Tendency

Caking tendency is the tendency of a fertilizer to agglomerate or lump in either bulk or bag storage and is affected by one or more of the following: (1)moisture content. (2) particle size. (3) particle hardness. (4) presence of conditioners. (5) storage temperature. (6) storage pressure. (7) storage time. (8)curing time, and (9)material composition. Excessive caking can cause problems in handling and field application.

Bulk Density

Bulk density is the weight per unit volume of a material, including voids between particles and is a measure of the density of the material, its porosity, and the voids between the particles of the material. Loose-pour bulk density represents the minimum density (greatest volume occupancy) that would be expected from a given material. Bulk density is of interest in bag sizing, in calibration of volumetric feeders calibration of volumetric feeders, and when considering capacity of storage bins and transport vehicles. For the fertilizer dealer, bulk density is of interest in bag sizing and when considering the capacity of storage spaces and transport vehicles. Less dense materials such as urea will require a larger bag than more dense materials like potassium chloride. Additionally, you can get more of a denser material in a given storage space than a less dense material.

Size Analysis (Sieve Method)

Particle size of fertilizer products and/or fertilizer raw materials is defined as the particle diameter ranges of the test material. Particle size affects agronomic response; granulation techniques; and storage, handling, and blending properties. These procedures can be used to determine size distributions of materials ranging in size from 25.0 mm to 38 pm.

Anale of Repose

The angle of repose is the angle at the base of the cone of fertilizer obtained by allowing a sample to fall onto a horizontal base plate or dropped into a pile from a fixed overhead point. It is of interest when considering storage capacity and the design of hoppers, chutes, conveyors, and sloped roofs of bulk-storage buildings. Knowing the angle of repose of a fertilizer material is essential when determining the capacity of a bulk storage building or bin. The angle of repose of fertilizers is influenced mostly by particle shape, size, and surface texture. Angle of repose values for fertilizers normally range from about 25° to about 40°. Spherical products, such as prilled urea, usually have lower angle of repose values (<30°). Irregularly shaped products, such as granular potassium chloride, usually have higher angle of repose values (>35°).

Apparent Density

Apparent density is the weight per unit volume of a material, excluding voids between particles. The apparent density of individual granules often is of interest in connection with development of new fertilizer processes; for a given product, variations in granule density can result in variations in hardness, moisture-holding capacity, and storage properties. Determinations of granule density are made in a special apparatus by measuring the volume of mercury that is displaced by submerging a known weight of granules.

Granule Crushing Strength

Crushing strength is a measure of the resistance of granules to deformation or fracture under pressure. Crushing strength is of interest in estimating the expected handling and storage properties of agranular material and determining the pressure limits applied during bag and bulk storage. This mechanical strength, of a fertilizer particle is influenced by its chemical composition, method of production, particle porosity, particle shape, surface crystals, and moisture content. Fertilizers should be strong enough to withstand normal handling and storage without significant fracturing of particles and creation of excessive dust. A fertilizer particle can be subjected to static and/or dynamic mechanical stresses. Static stress results from pressures exerted on particles at the bottom of a

bulk pile or stack of bags. Dynamic stress results from abrasion (creation of dusts and fines) or fracturing of particles as a result of particle-to-particle and particle-to equipment contact during handling. A "finger test" is a reasonably good, simple field method for evaluating the mechanical strength of fertilizer particles. In this test, a particle/granule that can be crushed between the thumb and forefinger can be classified as "soft/weak." If it is not classified as soft/ weak, but can be crushed between the forefinger and a hard surface, it can be regarded as being of "medium hardness." If it remains intact when subjected to pressure by the forefinger against a hard surface, it can be classified as "hard/strong.

Dustiness

This can be a problem with some fertilizers. Excessive dust can result in significant losses during handling, resulting in lost revenue. It can also possibly create environmental problems as well as expose employees to unhealthy levels of dust.

Protocols for Physical Parameters Estimation

1. Moisture

Two important forms of water present in fertilizers are: (i) absorbed/adsorbed water; and (ii) free water. They are interchangeable depending on the degree of moisture saturation and temperature. Some fertilizers also contain water as an integral part of their composition, which is referred to as water of crystallization, as in the case of ZnSO4.7H2O and CuSO4.5H2O. As fertilizers are

generally hygroscopic in nature, they tend to absorb moisture from the atmosphere (depending on the relative humidity and their packing and storage conditions).

Excessive moisture may damage the granular structure of fertilizers, affect their quality and influence their nutrient content by increasing the weight of fertilizers in a given container.

Therefore, moisture estimation is critical to determining the quality of a fertilizer. The method used depends on the type of fertilizer and the nature of moisture held by it. Some common methods are:

i. gravimetric method;

- ii. vacuum desiccator method:
- iii. Karl Fischer titration method.

Gravimetric method

With the gravimetric or oven-drying method, the loss of water on heating fertilizer samples at a certain temperature is estimated. This method is suitable for fertilizers such as ammonium sulphate, sodium nitrate, superphosphates, muriate of potash (MOP) and sulphate of potash (SOP). It is not suitable for fertilizers that yield volatile substances (such as NH₄) other than moisture on drying at a specified temperature, e.g. calcium ammonium nitrate and di-ammonium phosphate (DAP).

Moisture is estimated by the gravimetric method where the loss in weight at a constant temperature of $100 \, ^{\circ}\text{C} \pm 1 \, ^{\circ}\text{C}$ for 5 hours is measured, e.g. zinc sulphate, and copper sulphate. In the case of sodium nitrate, superphosphates, ammonium sulphate, SOP and MOP, the heating is at $130 \, ^{\circ}\text{C} \pm 1 \, ^{\circ}\text{C}$. For urea and urea-based fertilizers, the heating is at $70 \, ^{\circ}\text{C}$. However, heating at $70 \, ^{\circ}\text{C}$ does not reflect full moisture content. Therefore, another method such as the Karl Fischer method is preferred.

The apparatus required consists of: a glass weighing bottle;an electronic balance; a temperature-controlled oven.

The procedure:

- 1. Weigh 2.0 g of fertilizer sample in a pre-weighed glass weighing bottle.
- 2. Heat in a temperature-controlled oven for about 5 hours at the specified temperature, as given above for different types of fertilizers.
- 3. Cool in a desiccator, and weigh.

The relevant calculation is: Moisture % by weight=(B-C)/(B-A)*100

where:

A = weight in grams of the empty sample bottle; B = weight in grams of the bottle plus material before drying and C = weight in grams of the bottle plus material after drying.

Vacuum desiccator method

With the vacuum desiccator method, the free moisture present in the fertilizer is absorbed by the desiccant (sulphuric acid), and the loss in weight is reported as moisture. This method is suitable for fertilizers such as calcium ammonium nitrate, DAP, and NPK complexes.

In this method, the sample is kept in a vacuum desiccator over sulphuric acid. Free moisture present in fertilizers is absorbed by the acid, and the loss in weight of the sample is recorded as the moisture content in the sample.

The apparatus required consists of: a vacuum desiccator; a porcelain dish; a balance.

The procedure is:

- 1. Weigh (accurately) 5 g of sample in a porcelain dish, and keep it in a desiccator for 24 hours.
- 2. Take the weight again after 24 hours. The loss in weight is equal to moisture content in the sample.

The relevant calculation is:

% moisture=(B-C)/(B-A)*100

where: A = weight in grams of the porcelain dish; B = weight in grams of the porcelain dish plus the fertilizer sample and C = weight in grams of the porcelain dish plus the fertilizer sample after desiccation for 24 hours.

Karl Fischer method

The Karl Fischer titration method is suitable for fertilizers such as nitrophosphates, urea, and urea-based fertilizers, which do not withstand high temperatures.

The apparatus required consists of: a Karl Fischer titrator; a balance; a beaker or flask and a graduated cylinder.



Fig 8: Components of Karl Fischer Titrator (Source: http://en.wikipedia.org/wiki/Karl Fischer titration)

The reagents required are:

Karl Fischer reagent (pyridine-free). Disodium tartrate dihydrate ($Na_2C_4O_62H_2O$) – AR-grade, Methanol – Karl Fischer grade / spectroscopy grade containing less than 0.05 % water.

The procedure is:

- 1. Standardization of Karl Fischer reagent: Set up the instrument. Add about 25 ml of methanol to the titration vessel until the electrodes are dipped, and titrate with Karl Fischer reagent to a pre-set end point that persists for 30 seconds. Add 100 mg of the disodium tartrate dihydrate to the titration vessel carefully, and titrate with Karl Fischer reagent to a pre-set end point (the end point should persist for 30 seconds). Note the volume (ml) of Karl Fischer reagent used as VI.
- 2. Weigh accurately about 1 g of the prepared sample, transfer it carefully to the titration vessel, and stir until dispersed.
- 3. Titrate with Karl Fischer reagent to the same pre-set end point as above, and note the volume (ml) of Karl Fischer reagent used as V2.

The relevant calculation is:

Moisture % in sample=FXV2/Wt of sample* $100(for\%)/1000(for\ mg\ to\ g)$ where: Disodium tartrate dihydrate contains 0.1566 % moisture.

2. Particle size

Fertilizers are manufactured with varying degrees of particle size. This property of fertilizer has a bearing on its efficiency when used in various types of soil for crop production. The size and strength of the particle determine its dissolution time when applied in soil. Most fertilizers are highly water soluble; hence, they dissolve quickly when they come into contact with soil moisture.

Fertilizers can be crystalline or granular. With a view to reducing losses caused by rapid dissolution, fertilizers with large granules are also being manufactured, e.g. granular urea and super granular urea. Granular fertilizers are considered superior for machine application, for preparing bulk blends with greater homogeneity and uniformity, and they are also less vulnerable to adulteration.

Therefore, particle size estimation is an important aspect in determining the fertilizer quality. Most granular fertilizers range between 1 and 4 mm, with a specific particle size for a specific fertilizer. The apparatus required for particle size estimation consists of sieves of various sizes. The procedure consists of sieving through a given sieve size. The material is passed through a sieve with a mesh equal to the maximum particle size prescribed for a given fertilizer. The material so sieved is retained on a sieve with a mesh equal to the minimum particle size prescribed for that fertilizer.

For example, a fertilizer is sieved through a 4 mm sieve and is retained on a 1 mm sieve, kept below the 4 mm sieve. The material retained on the 4 mm sieve is larger than 4 mm in size and that passed through the 1 mm sieve is less than 1.0 mm in size. The material retained on the 1 mm sieve is that with a particle size of between 1 and 4 mm. Generally, 250 g of the fertilizer is taken and sieved as per the requirement. Sieving can be done mechanically or manually.

Chemical Analysis of Mineral and Organic Fertilizer

The main objective in analysing fertilizers is to assess their quality. The analysis examines both their physical and chemical composition. The quality of fertilizers is stated by the manufacturers and, in most countries, it is statutorily notified. Hence, analysis is carried out to determine whether the stated quality meets the statutorily notified standards or not. Fertilizer quality is notified in terms of physical and chemical characteristics. The chemical parameters refer to the amount and form of nutrients, and to various impurities that may be toxic to plants above a critical limit, e.g. biuret in urea. The efficiency of a fertilizer depends on its form of nutrient content. A phosphatic fertilizer may have water-soluble, citrate-soluble, water-insoluble or citrate-insoluble forms of phosphate. A nitrogenous fertilizer may contain ammoniacal, nitrate and amide forms of N in various proportions.

Therefore, in fertilizer analysis, in addition to estimating total nutrient content, it is necessary to estimate the forms of nutrients and other associated compounds in order to assess their quality properly.

For organic fertilizers, the C content and the total content of nutrients are considered relevant and not their forms as they are low-analysis materials. The analytical methods for fertilizers as described are applicable to most common fertilizers and the forms of nutrient content in them. The procedures as applicable to a particular nutrient could be applicable to any fertilizer with the nutrient in that particular form.

Sample preparation for analysis

The sample received for analysis is recorded in the laboratory with adequate details, and a laboratory code number is assigned in order to identify the sample and to keep its identity confidential.

About half of the sample is ground, sieved through a 1 mm sieve, and stored in a sample bottle for analysis. The remaining half is kept unground for particle size estimation. The samples are stored in an airtight glass bottle or taken for analysis in a moisture-free room (fitted with a dehumidifier) as most fertilizers are hygroscopic in nature.

Generally, the term fertilizer refers to mineral fertilizers, which are manufactured chemical products of standard composition, while the term organic fertilizers refers to organic manures, compost, agro-industrial wastes, etc. The compositions of organic fertilizers, unlike mineral fertilizers, are quite variable and, thus, difficult to regulate precisely.

Chemical Parameters

Estimation oF pH

25g fertiliser was mixed with 50ml of distilled water and kept on rotary shaker for 2 hours. Filtrate was obtained through Whatman filter paper under vacuum using a funnel. pH of filtrate is determined using pH meter.

Estimation of electric conductivity

Fresh sample of fertilizer was passed through a 2-4 mm sieve.20gm of the sample is added to 100ml of distilled water to it to give a ratio of 1:5.Stirring is done for about an hour at regular intervals. Calibrate the conductivity meter by using 0.01 potassium chloride solution (of AR grade). Using conductivity meter conductivity of the fertilizer suspension was measured.

Nitrogen

Nitrogen in fertilizers may be present in various forms such as NH_4 -N, NO_3 -N, urea-N (amide) and organic N. The estimations are carried out for total N and its forms. For urea fertilizer, the total N estimation method is followed. The principle of N estimation is based on the Kjeldahl method. For including or excluding a particular form of N in total N estimation, specific chemicals/catalysts are used.

For example, in nitrate-containing fertilizers, 2 g of salicylic acid and 5 g of sodium thiosulphate are added in the digestion mixture. This helps to bind the ND_3 -N in the form of nitrosalicylic acid, and it is converted eventually into NH_4 -N in the presence of H_2SD_4 and is estimated along with other forms of N present in the sample. Devarda's alloy (2-3 g per sample) can also be used instead of salicylic acid and thiosulphate.

Total nitrogen by the Kjeldahl method

The method and procedure are the also used for estimation of total N in soil. The fertilizer sample size may vary between 0.2 and 0.5 g depending on the N content of the sample. A smaller amount of sample may be taken for high-analysis fertilizers (e.g. urea) and a larger amount for low analysis fertilizer (e.g. ammonium sulphate).

The apparatus required consists of: a Kjeldahl distillation unit(Fig 9); some flasks, beakers and pipettes; a burette.

The reagents required are: Freshly ignited carbonate-free MgO, Standard acid (O.IM HCI), Standard alkali (O.IM NaOH), NaOH (40 %) for distillation and Methyl red indicator.

The procedure is:

- 1. Put $0.5\,\mathrm{g}$ of the sample in a $600\,\mathrm{ml}$ distillation flask with about $250\,\mathrm{ml}$ of water.
- 2. Add 2 g of freshly ignited carbonate-free MgD or 5 ml of NaDH solution (40 %) by tilting the flask and through the side of the flask so that the contents do not mix at once.
- 3. Connect the flask to a condenser by a Kjeldahl connecting bulb and connecting tube.
- 4. Start heating, and distil about 100 ml of liquid into a measured quantity of standard acid (0.1M HCl).
- 5. Titrate the distillate with standard NaOH (0.1M) to determine the remaining amount of unused acid, using methyl red indicator. The acid used to neutralize ammonia is equivalent to the N content in the sample.
- 6. Carry out a blank.

The relevant calculation is: Percent $NH_4-N=[(A-C)-B]/W*0.0014*100$

where: A = ml of standard acid (0.1M HCl) taken to receive ammonia; B = ml of standard alkali (0.1M NaOH) used in titration; W = weight of the sample taken; C = ml of standard alkali used in the blank and 1 ml 0.1M HCl = 0.0014 g N

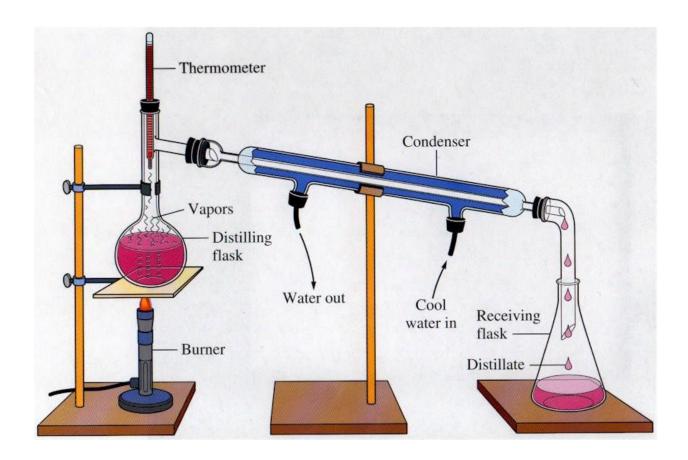


Fig 9: Nitrogen estimation by the distillation method

Ammoniacal plus nitrate-nitrogen by the distillation method

Devarda's alloy (50 % Cu+45 % Al+5 %Zn) reduces NO_3 to NH_4 in an alkaline condition. The method is same as for NH_4 -N estimation (above), except that 2-3 g of Devarda's alloy is added before distillation in order to take into account the NO_3 by reducing it to ammonia form.

Nitrate-nitrogen

In fertilizers containing both NH₄ and NO₃-N, first ammoniacal nitrogen is estimated followed by NH₄ plus NO₃ estimation. From the combined value of NH4 and NO₃, the value of ammoniacal N is subtracted to obtain the nitrate-N content.

Urea nitrogen

The urea form of N can be estimated together with total N by digestion with sulphuric acid. For example, total N is estimated for urea fertilizer. However, for some NPK complexes, urea N has to be estimated separately. In such cases, it is done by the urease method. The apparatus required for the urease method consists of: some beakers; some flasks; a Gooch crucible; some filter paper.

The reagents required are: Neutral urease solution(Shake 1 g of jack bean meal with 100 ml of water for 5 minutes. Transfer 10 ml of the solution to a 250 ml Erlenmeyer flask, dilute with 50 ml water, and add 4 drops of methyl purple indicator. Titrate with 0.1M HCl to reddish purple, then back titrate to green colour with 0.1M NaOH. From the difference in volume used, calculate the amount of 0.1M HCl required to neutralize 10 ml of solution. Based on the calculated acid required, add 0.1M HCl to the remaining 90 ml of solution (about 2.5 ml of acid is required per 100 ml of solution), and shake well.),HCl (0.1M)(Dilute 100 ml of concentrated HCl to 1 litre, and titrate with the standard alkali to establish the exact strength of the acid.), NaOH (0.1M)(Dissolve 4 g of NaOH in 900 ml of water in a 1-litre volumetric flask, make the volume up, and standardize with the standard acid.),Sodium carbonate (10 %) and Barium hydroxide (saturated).

The procedure is:

- 1. Weigh 10 ± 0.01 g of the sample and transfer it to 15 cm No. 12 fluted filter paper.
- 2. Leach with about 300 ml of water into a 500 ml volumetric flask.
- 3. Add 75–100 ml of saturated barium hydroxide solution to precipitate phosphates.
- 4. Let it settle, and test for complete precipitation with a few drops of saturated barium hydroxide solution.
- 5. Add 20 ml of 10 % sodium carbonate solution to precipitate excess barium and any soluble Ca salts.
- 6. Let it settle, and test for complete precipitation (when the addition of a few more drops of sodium carbonate does not show further precipitation).
- 7. Dilute to volume, mix, and filter through 15 cm No. 12 fluted paper.
- 8. Transfer 50 ml of aliquot (equivalent to 1 g of sample) to a 200 or 250 ml Erlenmeyer flask, and add 1–2 drops of methyl purple indicator.
- 9. Acidify solution with 0.1M HCl, and add 2-3 drops in excess (after colour change is noticed).
- 10. Neutralize (titrate) solution with 0.1M NaOH to the first change in colour of the indicator.
- 11. Add 20 ml of neutral urease solution, close flask with rubber stopper, and let it stand for 1 hour at 20-25 °C.
- 12. Cool the flask in ice water slurry, and titrate at once with 0.1M HCl to full purple colour, then add about 5 ml in excess.
- 13. Record total volume added; back titrate excess HCl with 0.1M NaOH to neutral end point.

The relevant calculation is:

% Urea-N=(ml 0.1M HCl-ml 0.1M NaOH)X0.0014X100/Wt of sample(1g contained in 50 ml aliquot)

Biuret

Biuret ($C_2O_2N_3H_5$) is a chemical compound formed by the combination of two molecules of urea with a release of a molecule of ammonia when the temperature during the urea manufacturing process exceeds the controlled level. Fertilizer grade urea contains biuret, which usually varies between 0.3 and 1.5 %.

Biuret is toxic to plants particularly when applied through foliar spray.

The apparatus required for estimating biuret consists of: a water-bath shaker; a spectrophotometer; some beakers and flasks; a burette.

The reagents required are: Alkaline tartrate solution(Dissolve 40 g NaOH in 50 ml of cold water and 50 g of NaKC $_4$ H $_4$ O $_6$.4H $_4$ O $_6$

The procedure is:

1. Preparation of the standard curve:

Transfer a series of aliquots, 2-50 ml of standard biuret solution, to a 10ml volumetric flask. Adjust the volume to about 50 ml with CO_2 -free water. Add one drop of methyl red, and neutralize with 0.1M H_2SO_4 to a pink colour. Add, with swirling, 20 ml of alkaline tartrate solution and then 20 ml of $CuSO_4$ solution. Dilute to volume. Shake for 10 seconds, and place in a water-bath for 15 minutes at 30 °C \pm 5 °C. Also prepare a reagent blank. Determine absorbance of each solution against the blank at 555 nm on the spectrophotometer with a 2.4 cm cell, and plot the standard curve.

- 2. Stir continuously 5 g of the sample in 100 ml of water for 30 minutes.
- 3. Filter and wash in 250 ml volumetric flask and dilute to volume.
- 4. Transfer 25 ml of aliquot to 100 ml volumetric flask and proceed as given under preparation of standard curve.

Phosphorus

Phosphate (P_2O_5) in fertilizers may be present in different forms: (i) water soluble; (ii) neutral ammonium citrate soluble or insoluble; (iii) citric acid soluble or insoluble; and (iv) acid soluble.

Phosphate is generally present as bound with Ca as monocalcium phosphate, dicalcium phosphate and tricalcium phosphate.

Monocalcium phosphate is in water soluble form, is considered available, while dicalcium phosphate becomes available in slightly acidic situations. Tricalcium phosphate is in an unavailable form and can be available only in acidic situations. Similarly, the aluminium and iron phosphates are also in plant-unavailable forms. Neutral ammonium citrate soluble form is also considered as available, which includes both monocalcium phosphate and dicalcium phosphate. In view of the variability in availability to plants, the estimation of different forms of phosphate is critical.

For the so-called "available" forms of P, appropriate extractants have been designed to extract P from fertilizers under a set of well-defined sampling conditions: extractant ratio, temperature, time of extraction, shaking period, etc.

The form of P as a fraction of the total P is extracted by a particular method.

Estimation of the extracted P utilizes various testing methods: (i) gravimetric; (ii) volumetric; and (iii) colorimetric.

The following methods are used for P estimation in fertilizers: gravimetric ammonium phosphomolybdate; gravimetric quinolinium phosphomolybdate; volumetric quinolinium phosphomolybdate and spectrophotometric vanadium phosphomolybdate.

All the methods are used in various laboratories. For total phosphate estimation, the gravimetric quinolinium phosphomolybdate method is generally preferred because of the minimal interference of other ions and its accuracy and simplicity. Another common method providing acceptable accuracy and simplicity is volumetric ammonium phosphomolybdate.

Gravimetric quinolinium phosphomolybdate method

Various forms of P present in fertilizers are first converted into orthophosphate through chemical treatments. On reaction with quimociac reagent, the orthophosphate precipitates as quinolinium phosphomolybdate $[(C_9H_7N)_3H_3PO_4.12\ MoO_3]$ in a boiling medium. The precipitate is weighed gravimetrically, which gives the P content of the sample.

In the gravimetric method, Ca, Fe, Mg, alkali metals and citrates do not affect the analysis. The citrate in the reagent complexes the ammonium ions, thus preventing interference from precipitation of ammonium phosphomolybdate by the ammonium salts usually present in mixed fertilizers. The citrates also reduce interference from soluble silica.

The apparatus required consists of: a volumetric flask; some beakers; a Gooch crucible (Fig 10); some filter paper; an analytical balance.

The reagents required are: Concentrated nitric acid, Concentrated hydrochloric acid, Magnesium nitrate solution (9 %): Dissolve 90 g of P-free $Mg(NO_3)_2$ in water, and dilute to 1 litre, Acetone, Citric acid, Sodium molybdate dehydrate, Quinoline and Quimociac reagent: Dissolve 60 g of citric acid in a mixture of 85 ml of HNO_3 and 150 ml of water, and cool. Dissolve 70 g of sodium molybdate dihydrate in 150 ml of water. Gradually add the sodium molybdate solution to the citric acid — nitric acid mixture, with stirring. Dissolve 5 ml of synthetic quinoline in a mixture of 35 ml of HNO_3 and 100 ml of water. Gradually add this solution to the molybdate citric-nitric acid solution, mix, let it stand for 24 hours, and filter. Add 280 ml of acetone, dilute to 1 litre with water, and mix well. Store in a polyethylene bottle.



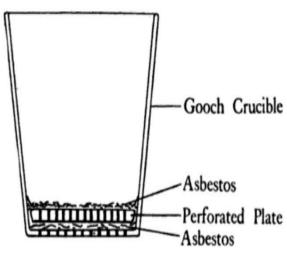


Fig 10: A Gooch crucible

According to the nature of the fertilizer, the sample solution should be prepared using one of the following methods:

For materials and fertilizer mixtures with a high OM content: Put 1 g of the sample in an evaporation dish. Add 5 ml of $Mg(NO_3)_2$ solution, and evaporate to dryness. Ignite to destroy the OM, and dissolve in 10 ml of HCl.

For materials with a low OM content: Put 1 g of the sample in a 50 ml beaker. Add 30 ml of HNO $_3$ and 5 ml of HCl, and boil gently until the OM is destroyed and red-brown fumes cease to appear.

For basic slag and fertilizers containing iron or aluminium phosphate: Treat 1 g of the sample with 30 ml of HCl and 10 ml of HNO3, and boil gently until red-brown fumes disappear.

Cool the solution, prepared by any of the above three methods, dilute to 250 ml, mix, and filter through a dry filter, if required (may contain some insoluble material).

The procedure is:

- 1. Pipette 5–25 ml of aliquot (sample solution) depending on the P content (containing not more than 25 mg P_2O_5 in the aliquot) into a 250 ml beaker, and dilute to 100 ml with distilled water.
- 2. Add 50 ml of quimociac reagent, cover with a watch glass, place on a hotplate, and boil for 1 minute.
- 3. Cool the material to room temperature, swirl carefully 3-4 times during cooling.
- 4. Filter the precipitate with fiberglass filter paper (or Gooch crucible G4) previously dried at 250 °C and weighed. Wash 4–5 times with 25 ml portions of water. Dry the crucible/filter paper and contents for 30 minutes at 250 °C. Cool in a desiccator to a constant weight.
- 5. Run a reagent blank with each batch. Subtract the weight of the blank from the weight of the sample precipitate.

The relevant calculation is:

Total phosphate (as P_2O_5)%=3.207(S-B)/IOO*df*IOO/W=3.207(S-B)/W*df

where: S = weight of sample precipitate in grams; B = weight of blank precipitate in grams and df = dilution factor for aliquot taken: Suppose volume of the aliquot (solution) taken for estimation = 5 ml, and total volume of fertilizer solution prepared = 250 ml; W = weight of sample taken in grams and df=Total volume of fertilizer solution/Aliquot taken=250/5=50

For percentage=100/W

Factor 3.207 = the quinolinium phosphomolybdate precipitate contains $3.207 \% P_2 D_5$ on weight basis.

In cases where MoO_3 . Na_2MoO_4 . ZH_2O (quinoline) is not of standard quality, the exact volume of quimociac reagent to be added for precipitation should be calculated by running a series of known standards and observing the phosphate recovery in them.

Volumetric ammonium phosphomolybdate method

Phosphorus is precipitated from the acidic solution as ammonium phosphomolybdate [(NH₄)₃PO₄.12MoO₃] by adding ammonium molybdate solution. The precipitate is dissolved in a measured excess of the standard alkali after filtration and washing until free of the acid.

The apparatus required consists of: some volumetric flasks / beakers; a burette; a shaker; a water-bath; some No. 44 filter paper.

The reagents required are: Magnesium nitrate solution (9%): Dissolve 90 g of P-free Mg(NO₃)₂ in water, and dilute to 1 litre. Concentrated nitric acid, Concentrated hydrochloric acid, Ammonium molybdate solution (3%): Dissolve 30 g of ammonium molybdate in hot distilled water, and make the volume up to 1 litre, Standard NaOH solution (D.IM) (Dissolve 4 g of NaOH in 1 litre of water, and standardize against standard acid.), Standard H_2SO_4 solution (D.IM)(Take 5.6 ml of concentrated H_2SO_4 and make the volume up to 1 litre. Standardize against a primary standard alkali such as Na₂CO₃.), Sodium nitrate (2%): Dissolve 20 g of AR-grade sodium nitrate in 1 litre of distilled water, Phenolphthalein indicator (1%): Dissolve 1 g of phenolphthalein in 100 ml of 95.5% ethanol, Ammonium nitrate (AR-grade) and Sodium carbonate (AR-grade). The sample solution should be prepared using one of the methods indicated for the gravimetric quinolinium phosphomolybdate method.

The procedure is:

1. Pipette 5–25 ml of aliquot (sample solution) depending on the P content (containing not more than 25 mg P_2O_5 in the aliquot) in a 250 ml beaker, and dilute to 100 ml with distilled water.

- 2. Add about 5-10 ml of concentrated HNO_3 and about 10 g of ammonium nitrate.
- 3. Heat this mixture on a water-bath at 55-60 °C for 10 minutes.
- 4. Add 3 % ammonium molybdate solution in the beaker drop by drop with the help of a burette. Continue stirring with a glass rod until about 50 ml of molybdate solution is added. Stir for another few minutes until the yellow precipitate appears to become granular.
- 5. Cover the beaker with glass and allow it to settle for some time. Decant the clear solution through No. 44 filter paper, and wash the precipitate with 2 % sodium nitrate solution, agitate thoroughly, and allow the precipitate to settle. Transfer the precipitate to the filter paper, and wash with NaNO3 solution until free from acid (by test with a litmus paper).
- 6. Transfer the precipitate and filter paper to a beaker, and add 10 ml of 0.1M NaOH at a time by pipette until the precipitate becomes soluble.
- 7. Add I-2 drops of 1 % phenolphthalein, and titrate the excess of alkali against 0.1M sulphuric acid.
- 8. Run a reagent blank with each batch.

The relevant calculation is:

Total phosphate (as P_2O_5) per cent= $F^*(V_1M_1-V_2M_2)^*df=0.0031^*(40^*0.1-10^*0.1)^*250/5^*100/1=46.5$ where: F= factor for P_2O_5 corresponding to 1 ml of IM alkali (NaOH).

The calculation is as follows: 23 g equivalent of NaOH = 31 g P = 71 g P_2O_5 (P × 2.29 = P_2O_5)

1 equivalent of NaOH or 1000ml of 1M NaoH=71/23 g P_2O_5

1 ml of 1M NaOH=71/23*1/1000g P₂O₅₌0.0031 g P₂O₅

M = volume of 0.1M NaOH required to dissolve the precipitate (e.g. 40 ml);

V2 = volume of 0.1M H₂SO₄ used for titration to neutralize excess alkali (e.g. 10 ml);

M = molarity of the standard alkali (NaOH);

M2 = molarity of the standard acid (H_2SO_4);

df = dilution factor for aliquot taken:

Suppose, volume of the aliquot (solution) taken for estimation = 5 ml; total volume of fertilizer solution prepared = 250 ml.

 $df{=}Total\ volume\ of\ fertilizer\ solution/Aliquot\ taken{=}250/5{=}50$

For percentage=100/W

Water-soluble phosphate (P_2O_5)

The water-soluble phosphate is obtained from the sample by dissolving it in distilled water or by washing the sample successively with distilled water. As a procedure, put 1 g of the sample on a filter paper fitted on a 12 cm funnel. Wash with small portions of water at a time to collect about 250 ml of filtrate and make up the exact volume.

Pour water into the funnel only when the earlier portion has drained fully.

Otherwise, filtration and complete washing may be prolonged (which should be completed in 1 hour). The filtrate so obtained is used for estimation of phosphate by the gravimetric quinolinium phosphomolybdate method or volumetric ammonium phosphomolybdate method as described above.

The residue remaining on the filter paper contains the water-insoluble portion of P in the sample.

Available phosphate (neutral ammonium citrate-soluble P_2O_5)

For estimating available phosphate, an indirect method is followed whereby total, water-soluble and ammonium citrate-insoluble fractions are estimated. By subtracting citrate-insoluble P from total P, estimates are made for the available P.

The apparatus required for estimation of citrate-insoluble P consists of: a volumetric flask / beaker; a burette; a water-bath-cumshaker; a Buchner funnel.

The reagents required are: Concentrated HNO_3 , Concentrated HCl, Concentrated H_2SO_4 , Ammonium hydroxide, Ammonium nitrate (5%), Quimociac reagent (same as described in total P_2O_5 estimation), Filter paper and Neutral ammonium citrate solution (Dissolve 370 g of pure citric acid in 1500 ml of distilled water. Add about 345 ml of 28–29% ammonium hydroxide so that the acid is neutralized. After neutralization, the solution must attain a pH of 7.0; if it does not, adjust the pH by adding NH₄OH or citric acid solution.)

The procedure is:

- 1. Follow the procedure as described above for the preparation of a sample solution for estimation of water-soluble phosphate. Within 1 hour, transfer the filter paper and residue to a 250 ml conical flask containing 100 ml of ammonium citrate solution previously heated to $65\,^{\circ}$ C.
- 2. Close the flask tightly with a smooth rubber stopper, shake vigorously until the filter paper is transformed to pulp, and release pressure by removing stopper occasionally.
- 3. Agitate continuously the contents of the stoppered flask in a controlled temperature (65 $^{\circ}$ C ± 0.5 $^{\circ}$ C) water-bath-cum-shaker for 1 hour.
- 4. Exactly 1 hour after adding the filter paper and residue, remove the flask from the shaker, and filter immediately by suction as rapidly as possible through No. 5 filter paper or equivalent, using a Buchner or ordinary funnel.
- 5. Wash with distilled water at 65 $^{\circ}$ C until the volume of filtrate is about 350 ml, allowing time for thorough draining before adding more water. If the material is such that it will yield a cloudy filtrate, wash with 5 % NH₄NO₃ solution.
- 6. Determine the P2O5 in the citrate-insoluble residue (remainder on filter paper) after digestion by one of the following methods:
- Transfer the dry filter paper and contents to a crucible, ignite until all OM is destroyed. Digest with 10-15 ml of HCl until phosphates are dissolved. Transfer the filter paper and residue to a 250 ml Kjeldahl flask, boil for 30-45 minutes with 30 ml of HNO_3 and 10 ml of HCl. Boil very gently until it is colourless and white dense fumes appear in the flask.
- 7. Dilute the solution to 250 ml, mix well, and filter through dry filter paper if required. Pipette out 25 ml of aliquot containing not more than 25 mg of P_2O_5 into a 500 ml Erlenmeyer flask, and proceed as described for estimation of total P_2O_5 using quimociac reagent (above).

The relevant calculation is:

Citrate insoluble $P_2O_5\%=3.207(S-B)/100*df*100/W$

where: S = weight of sample precipitate in grams; B = weight of blank precipitate in grams and W = weight of sample in grams; df=Total volume of fertilizer solution/Aliquot taken=250/5=50

For percentage=100/W

Percent available (citrate-soluble) $P_2O_5 = \%$ total $P_2O_5 - \%$ citrate-insoluble P_2O_5

The procedure for total P_2O_5 estimation is described above.

Potassium

In all potassic fertilizers, K is generally present in water-soluble form. Therefore, it is estimated directly in fertilizer solution either gravimetrically, volumetrically or flame photometrically. In manures and organic fertilizers, wet digestion with acid is required prior to determination of K in order to bring the element into solution by digestion.

The methods used for K determination in fertilizers and manures are:

- gravimetric perchloric acid method;
- gravimetric chloroplatinate method;
- gravimetric and volumetric cobaltinitrite method;
- gravimetric and volumetric sodium tetraphenyl boron (STPB) method.

The ADAC-based STPB volumetric method is commonly used in laboratories because of its accuracy and simplicity.

STPB method

Potassium from the fertilizer sample is first extracted with water or ammonium oxalate. The K in extracted solution is precipitated with an excess of STPB as potassium tetraphenyl boron. The excess of STPB is backtitrated with benzalkonium chloride (BAC) or quaternary ammonium chloride using Clayton yellow as indicator:

 $Na[B(C_6H_5)_4]+K \longrightarrow K[B(C_6H_5)_4]+Na^+$

Interference of NH4 + takes place during K precipitation. It is avoided by complexing NH4+ with formaldehyde under slightly alkaline conditions before precipitation of K. The chlorides and sulphates do not interfere in the titration.

The apparatus required consists of: some volumetric flasks and beakers; a burette / semi-microburette; some filter paper.

The reagents required are: 20% Sodium hydroxide solution (Dissolve 20 g of NaOH in 100 ml of distilled water),37% Formaldehyde (HCHO) solution, 1.2%STPB solution (Dissolve 12 g of STPB in about 800 ml of water. Add 20–25 g of Al(OH)3, stir for 5 minutes, and filter through No. 42 filter paper (or equivalent) into a 1 litre volumetric flask. Rinse the beaker sparingly with water and add to the filtrate. Collect the entire filtrate, add 2 ml of 20 % NaOH solution, dilute to volume (1 litre) with water, and mix).

Let it stand for 48 hours, and then standardize (as described below). Adjust (by using K salt of known composition for prior standardization by trial and error) so that 1 ml of STPB = $1 \% K_2O$. Store at room temperature.

0.625% BAC or quaternary ammonium chloride solution (Dilute 50 ml of 12.8 % BAC to 1 litre with water, mix and standardize (as described below). If a different concentration is used, adjust the volume accordingly :BAC of 0.625 % strength is required so the dilution can be done according to the concentration available). 0.04% Clayton yellow indicator(Dissolve 40 mg of Clayton yellow powder in 100 ml of water.),4% Ammonium oxalate solution [(NH4)2 C204] (Dissolve 40 g of ammonium oxalate in 1 litre of distilled water.)

The procedures for standardizing the solutions are:

BAC solution: Put 1 ml of STPB solution in a 250 ml Erlenmeyer flask; add 20–25 ml of water, 1 ml of 20 % NaOH, 2.2 ml of HCHO, 1.5 ml of 4 % ammonium oxalate, and 6–8 drops of Clayton yellow indicator. Titrate to pink end point with BAC solution, using a 10 ml semimicroburette. Adjust by increasing or decreasing the strength of the BAC solution so that 2 ml = 1 ml of STPB solution (keeping 1 ml STPB = 1 % k_2 D).

STPB solution: Dissolve 2.5 g of KH_2PO_4 in about 150 ml of water in a 250 ml volumetric flask, add 50 ml of 4 percent ammonium oxalate solution, dilute to volume with water, and mix. Transfer 15 ml of aliquot (51.92 mg of K20 or 43.10 mg of K) to a 100 ml volumetric flask, add 2 ml of 20 percent NaOH, 5 ml of HCHO and 43 ml of STPB solution. Dilute to volume (100 ml) with water, and mix thoroughly. Let it stand for 5–10 minutes, and then pass through dry No. 42 filter paper. Transfer 50 ml of aliquot of filtrate to a 250 ml Erlenmeyer flask, add 6–8 drops of Clayton yellow indicator, and titrate excess STPB with BAC solution to pink end point.

Calculate factor (f) by: $f = percent K_2D/ml$ of STPB solution = 34.61/(43-ml of BAC used for standardization) where, $34.61 = \% K_2D$ present in standard KH₂PO₄.

The procedure is:

- 1. K extraction/preparation of sample solution: Dissolve a known weight (2.5 g) of straight K fertilizer (MOP, SOP, potassium magnesium sulphate) in 200 ml of distilled water, and make the volume up to 250 ml for estimation. For NPK complex fertilizers or NPK fertilizer mixtures, dissolve the sample in 125 ml of water, add 50 ml of 4 % ammonium oxalate solution, and boil for 30 minutes; after cooling, filter through dry No. 12 filter paper, and make the volume up to 250 ml for further estimation.
- 2. Transfer 15 ml of aliquot of sample solution to a 100 ml volumetric flask and add 2 ml of 20 % NaOH and 5 ml of HCHO.
- 3. Add 1 ml of standard STPB solution for each 1 % of K_2D expected in the sample plus an additional 8 ml in excess in order to ensure complete precipitation.

- 4. Dilute to volume (100 ml) with water, mix thoroughly, let it stand for 5–10 minutes, and pass it through No. 12 filter paper (or equivalent).
- 5. Transfer 50 ml of filtrate to a 250 ml Erlenmeyer flask, add 6–8 drops of Clayton yellow indicator, and titrate excess STPB with standard BAC solution to pink end point.

The relevant calculation is:

where, f = % K20/ml of STPB solution. This factor applies to all fertilizers where 2.5 g of sample is diluted to 250 ml, and 15 ml of aliquot is taken for analysis. To express the results as K rather than K20, substitute 28.73 for 34.61 in calculating the value of f.

Organic fertilizers

In the case of organic fertilizers, the C content and the total content of nutrients are considered relevant and not their forms as they are low-analysis materials.

The methods for estimation of total N, P and K in organic fertilizers are the same as described above for mineral fertilizers. With organic fertilizers, the sample always needs to be prepared using the wet-digestion method. The sample size should be 1.0 g (to be weighed exactly).

Wet Oxidation Method for the Determination of Total Organic Carbon.

Wet chemistry techniques can be divided into two phases, namely, sample extraction and sample quantification. The extraction technique employed is essentially the same for all methods in the literature with variations existing only in the strength and combination of reagents used during extraction. Quantification techniques associated with the wet chemistry determination of TOC either rely on titration (volumietric) (manual or automated), calorimetric, or gravimetric techniques.

Volumetric method

Sample Extraction - The standard wet chemistry technique for the sample extraction involves the rapid dichromate oxidation of organic matter. The Walkley-Black procedure is the best known wet digestion method. In this procedure, potassium dichromate ($K_2Cr_2O_2$) and concentrated H_2SO_4 are added to 1.0 g of the organic fertilizer material. The solution is swirled and allowed to cool (note: the sample must be cooled as a result of the exothermic reaction when the potassium dichromate and sulfuric acids are mixed) prior to adding water to halt the reaction. Orthophosphate H_3PO_4 is added to the digestive mix after the sample has cooled to eliminate interferences from the ferric (Fe $^{3+}$) iron that may be present in the sample.

The chemistry of this extraction procedure is as follows:

 $2Cr_2O_7 2-+3 CO + 16H+ = 4Cr^{3+} + 3CO_2 + 8H_2O.$ (3)

The Walkley-Black procedure is widely used because it is simple, rapid, and has minimal equipment needs. However, this procedure has been shown to lead to the incomplete oxidation of organic C. Studies have shown that the recovery of organic C using the Walkley-Black procedure range from 60 to 86% with a mean recovery being 77%. As a result of the incomplete oxidation and in the absence of a site-specific correction factor, a correction factor of 1.33 is commonly applied to the results to adjust the organic C recovery.

To overcome the concern of incomplete digestion of the organic matter, the Walkley-Black procedure was modified to include extensive heating of the sample during sample digestion. In this variation of the method, the sample and extraction solutions are gently boiled at 150°C for 30 minutes, allowed to cool, and then water is added to halt the reaction. The addition of heat to the system leads to a complete digestion of the organic C in the sample; therefore, no correction factor is needed. The temperature of this method must be strictly controlled because the acid dichromate solution decomposes at temperatures above 150°C (Charles and Simmons, 1986).

Sample Quantification Upon completion of the sample extraction phase, the quantity of organic carbon present in the fertilizer material can be determined through a variety of different techniques. These techniques include: manual titration, automated titration using potentiometric determination, calorimetry, gravimetric determination, or volumetric/manometric measurement.

Upon examination of the equation above, the three measurable products of the acid dichromate digestion process are the excess/unused dichromate (Cr2O7), chromate (Cr3+) and CO2. Both the Cr2O72-and Cr3+ will remain in solution and can be measured titrimetrically (volumetrically) or calorimetrically while the evolved CO2, in its gaseous state, can be measured gravimetrically or manometrically.

To perform manual titrimetric quantification, an indicator solution is added to the digestate. The most common indicators used are ortho-phenanthroline ferrous complex (commercially available as "Ferroin"), barium diphenylamine sulfonate, and N-phenylanlhranilic acid. The excess Cr2072- is titrated with ferrous ammonium sulfate [Fe(NH4)2(SO4)2*6H2O] or ferrous sulfate (FeSO4) until color change occurs in the sample. Color changes associated with these indicators are: (1) green to reddish brown for the orthophenanthroline ferrous complex, (2) purple/blue to green for the barium diphenylamine sulfonate, and (3) dark violet-green to light green for the N-phenylan-thranilic acid. The primary concern with the manual titration technique is the low visibility or

subtlety of color changes during titration. Color changes may also be obscured by naturally-occurring high organic fertilizer materials.

The use of an automated titrator eliminates the need for indicators to be added to the digestate. Similar to manual titrimetric quantification, excess Cr2072- is titrated with ferrous ammonium sulfate or ferrous sulfate. However, the endpoint is not a color change but is determined potentiometrically. In this technique, a simple calomel electrode or platinum electrode is placed in the digestate, and the titer is added until a fixed electrical potential endpoint is reached. The endpoint is dependent upon the type of electrode used. Once the endpoint is reached, the titration is stopped and the TOC content calculated. The automated titration technique has the distinct advantage over manual titration since the endpoint is not dependent upon operator optical determination of exactly when the color changed. The only disadvantage of the automated technique is the necessity to purchase (i.e., cost) an automated titrator and suitable electrodes.

The apparatus required for the volumetric method (Walkley and Black, 1934) consists of:

- _ a conical flask (500 ml);
- _ some pipettes (2, 10 and 20 ml);
- a burette (50 ml).

The reagents required are: Phosphoric acid -85%, Sodium fluoride solution -2%, Sulphuric acid -96%containing 1.25 % of Ag₂SO₄. Standard 0.1667M K₂Cr₂O₇: Dissolve 49.04 g of K2Cr₂O₇ in water and dilute to 1 litre. , Standard 0.5M FeSO₄ solution: Dissolve 140 g of ferrous sulphate or 196.1 g of FeSO₄.(NH₄)₂.6H₂O in 800 ml of water, add 20 ml of concentrated H₂SO₄ and make the volume up to 1 litre, Diphenylamine indicator: Dissolve 0.5 g of reagent-grade diphenylamine in 20 ml of water and 100 ml of concentrated H₂SO₄.

The procedure is:

- 1. Weigh 1.0 g of the prepared soil sample in a 500-ml conical flask.
- 2. Add 10 ml of 0.1667M $K_2Cr_2O_7solution$ and 20 ml of concentrated H_2SO_4 containing Ag_2SO_4 .
- 3. Mix thoroughly and allow the reaction to complete for 30 minutes.
- 4. Dilute the reaction mixture with 200 ml of water and 10 ml of H_3PO_4 .
- 5. Add 10 ml of NaF solution and 2 ml of diphenylamine indicator.
- 6. Titrate the solution with standard 0.5M FeSO4 solution to a brilliant green colour.
- 7. Run a blank without sample simultaneously.

The percentage of organic C is given by: 10(S-T)*0.003/S*100/Wt of soil

As 1 g of soil is used, this equation simplifies to: 3(S-T)/S

where: S = millilitres of FeSO₄ solution required for blank; T = millilitres of FeSO₄ solution required for soil sample; 0.003 = weight of C (1 000 ml 0.1667M K₂Cr₂O₇ = 3 g C. Thus, 1 ml 0.1667M K₂Cr₂O₇ = 0.003 g C).

Organic C recovery is estimated to be about 77%. Therefore, the actual amount of organic C will be:

Percent value of organic carbon obtained*100/77 Or: percentage value of organic C \times 1.3.

Colorimetric method

Colorimetric quantification of TOC is performed through the measurement of the color change that results from the presence of Cr3+ in solution. After sample digestion, the digestate is centrifuged or filtered to remove any suspended particles and then placed in a calorimeter set to measure the light absorbance at a wavelength of 660 nM. Quantification is performed by comparison of the results against a standard curve. The calorimetric technique has the same advantages (i.e., a measurable fixed endpoint with no human interpretation) and disadvantages (i.e., primarily initial cost) as the automated titration technique.

The apparatus required for the colorimetric method consists of: a spectrophotometer; some conical flasks (100 ml); some pipettes (2, 5 and 10 ml).

The reagents required are: Standard potassium dichromate 0.1667M., Concentrated sulphuric acid containing 1.25 % of Ag₂SO₄, Sucrose (AR-grade).

The procedure is:

Preparation of standard curve: Sucrose is used as a primary standard C source. Place different quantities of sucrose (1–20 mg) in 100-ml flasks. Add 10 ml of standard K2Cr2O7 and 20 ml of concentrated H2SO4 in each flask. Swirl the flasks, and leave for 30 minutes. Prepare a blank in the same way without adding sucrose. A green colour develops, which is read on spectrophotometer at 660 nm, after adjusting the blank to zero. Plot the reading so obtained against milligrams of sucrose as C source (C = weight of sucrose × 0.42 – because the C content of sucrose is 42 %) or against milligrams of C directly.

Standard curve for organic carbon on spectrophotometer

- 2. Place 1 g of soil in a 100-ml conical flask.
- 3. Add 10 ml of 0.1667M $K_2Cr_2O_7$ and 20 ml of concentrated H_2SO_4 containing 1.25 % of Aq_2SO_4 .
- 4. Stir the reaction mixture and allow it to stand for 30 minutes.
- 5. The green colour of chromium sulphate so developed is read on a spectrophotometer at 660 nm after setting the blank, prepared in the similar manner, at zero.

The C content of the sample is found from the standard curve, which shows the C content (milligrams of C vs spectrophotometer readings as absorbance): Percent C = M = milligrams of C observed \times 100 / 1 000 (observed reading is for 1 g soil, expressed as milligrams).

Total nitrogen

Total N includes all forms of inorganic N, such as NH_4 , ND_3 and NH_2 (urea), and the organic N compounds such as proteins, amino acids and other derivatives.

Depending on the form of N present in a particular sample, a specific method is to be adopted for determining the total N value. While organic N materials can be converted into simple inorganic ammoniacal salt by digestion with sulphuric acid, for reducing nitrates into ammoniacal form, the modified Kjeldahl method is adopted with the use of salicylic acid or Devarda's alloy. At the end of digestion, all organic and inorganic salts are converted into ammonium form, which is distilled and estimated by using standard acid.

As the precision of the method depends on complete conversion of organic N into NH4-N, the digestion temperature and time, the solid-acid ratio and the type of catalyst used have an important bearing on the method. The ideal temperature for digestion is 320–370 °C. At a lower temperature, the digestion may not be complete, while above 410 °C, loss of NH3 may occur. The salt-acid (weight-volume) ratio should not be less than 1:1 at the end of digestion. Commonly used catalysts to accelerate the digestion process are CuSO4 and mercury (Hg).

Potassium sulphate is added to raise the boiling point of the acid so that loss of acid by volatilization is prevented.

The apparatus required for this method consists of: a Kjeldahl digestion and distillation unit; some conical flasks; some burettes; some pipettes.

The reagents required are: Sulphuric acid (93–98 %), Copper sulphate (CuSO₄.H₂O) (AR-grade), Potassium sulphate or anhydrous sodium sulphate (AR-grade), 35% sodium hydroxide solution(Dissolve 35O g of solid NaOH in water and dilute to 1 litre.); O.IM NaOH(Prepare O.IM NaOH by dissolving 4.O g of NaOH in water and make the volume up to 1 litre. Standardize against O.IM potassium hydrogen phthalate or standard H_2SO_4 .), O.IM HCl or 0.05M H_2SO_4 (Prepare approximately the standard acid solution and standardize against O.IM sodium carbonate.), Methyl red indicator, Salicylic acid for reducing NO_3 to NH_4 , if present in the sample and NO_3 to NH_4 , if present in the sample.

The procedure is

- 1. Weigh 1 g of soil sample. Place in a Kieldahl flask.
- 2. Add 0.7 g of copper sulphate, 1.5 g of K2SO4 and 30 ml of H2SO4.
- 3. Heat gently until frothing ceases. If necessary, add a small amount of paraffin or glass beads to reduce frothing.
- 4. Boil briskly until the solution is clear and then continue digestion for at least 30 minutes.
- 5. Remove the flask from the heater and cool, add 50 ml of water, and transfer to a distilling flask.
- 6. Place accurately 20-25 ml of standard acid (0.1M HCl or 0.05M H2SO4) in the receiving conical flask so that there will be an excess of at least 5 ml of the acid. Add 2-3 drops of methyl red indicator. Add enough water to cover the end of the condenser outlet tubes.
- 7. Run tap-water through the condenser.
- 8. Add 30 ml of 35% NaOH in the distilling flask in such a way that the contents do not mix.
- 9. Heat the contents to distil the ammonia for about 30-40 minutes.
- 10. Remove the receiving flask and rinse the outlet tube into the receiving flask with a small amount of distilled water.
- 11. Titrate excess acid in the distillate with O.1M NaOH.
- 12. Determine blank on reagents using the same quantity of standard acid in a receiving conical flask.

The calculation is:

Percent $N=1.401[(V_1M_1-V_2M_2)-(V_3M_1-V_4M_2)]/w*df$

where: \mathcal{U} – millilitres of standard acid put in receiving flask for samples; \mathcal{U} – millilitres of standard NaOH used i titration; \mathcal{U} 3 – millilitres of standard acid put in receiving flask for blank; \mathcal{U} 4 – millilitres of standard NaOH used in titrating blank; \mathcal{U} 6 – molarity of

standard acid; MZ – molarity of standard NaOH; W – weight of sample taken (1 g); df – dilution factor of sample (if 1 g was taken for estimation, the dilution factor will be 100).

Note: 1 000 ml of 0.1M HCl or 0.05M H2SO4 corresponds to 1.401 g of N.

The following precautions should be observed:

- _The material should not solidify after digestion.
- _ No NH4 should be lost during distillation.
- _lf the indicator changes colour during distillation, determination must be repeated using either a smaller sample weight or a larger volume of standard acid.

Estimation of heavy metal atomic absorption spectroscopy

- 1. Sampling- Approximately 50 gm of sample was taken. Then the samples were air dried for a period to remove excess moisture. Air dried sample are then passed through 0.5mm sieve. The sample passing through the sieve is mixed and used to obtain the analytical sample.
- 2. Sample treatment for total element determination- About 1gm of the sieved sample was accurately weight and it was transfer to a 100 ml beaker. From a measuring cylinder about 20 ml of 1:1 nitric acid and is boiled gently on a

hot plate until the volume of nitric acid is reduced to about 5ml. Addition of about 20 ml of deionized water in the sample and boil gently again until the volume is approximately 10 ml. The suspension is cooled and filtered through a

whatman filter paper, then the beaker and filter paper is washed with small portion of de-ionized water until a volume of about 25 ml is obtained. The filtrate is then transferred to a 50 ml graduated flask and make up to the mark with deionized water.

What is Customized Fertilizer?

The Central Fertilizer Committee has included customized fertilizers in the Fertilizer (Control) Order 1985, as a new category of fertilizers that are area/soil/crop specific. Customized fertilizers are multi- nutrient carriers facilitating the application of the complete range of plant nutrients in right proportion to suit the specific requirements of a crop during its stages of growth. Soil fertility status, climate, and cropping pattern in a region pave the way for the development of customized fertilizer formulations. Customized fertilizers are unique and ready to use granulated fertilizers, formulated on sound scientific plant nutrition principles integrated with soil information, extensive laboratory studies and evaluated through field research. Customized fertilizers development process is complex but, the end very promising. It optimizes the nutrient use for quality produce, high farm productivity and profitability. The farmer will have choice for customized fertilizers on account of crop and area specificity and the advantage of ready to use fertilizer material available to them. It can maximize nutrient use efficiency and ultimately programmed to improve soil fertility hence, are environmental friendly as well. Of late, FCO recognizes these fertilizers and are defined as: Multi-nutrient carriers designed to contain macro, secondary and/or micro-nutrient both from inorganic sources and/or organic sources, manufactured through a systematic process of granulation, satisfying the crop's nutritional needs, specific to its site, soil and stage validated by a scientific crop model, capability developed by an accredited fertilizer manufacturing /marketing company.

Concept

Customized fertilizer is more than simply a fertilizer- it is the concept around the plant nutrition. Such fertilizers are backed by sound scientific plant nutrition principles research. For the development of customized fertilizer, a team of dedicated scientists focusing on specifics of crop and soil condition is required. These specialists know how to get the best out of a plant, to ensure that the plant realizes its natural growth potential and yield attributes. To put it quite simply, customized fertilizer provide the best nutritional package for premium quality plant growth. The customized fertilizer is designed to contain nutrients (both macro and micro) forms, contents, and their proportions, which are highly area and crop specific. In other words customized fertilizers are multi-nutrient carriers precisely tailored to meet specific basal nutritional need of crop. The technology used in manufacture of such fertilizers make them high quality so that all granules fertilizers are highly uniform in physical form and chemical composition. For ensuring homogeneous supply of all plant it is necessary that these fertilizers are band placed at the time of sowing/planting.

Advantages

The main objective of customized fertilizers is to promote site-specific nutrient management in order to achieve the maximum fertilizer use efficiency of applied nutrients in a cost effective manner. The customized fertilizers may include the combination of nutrients through various sources based on soil test information and requirement of crop and the formulation may be of primary, secondary, and /or micronutrient. It may include 100% water soluble fertilizer grades as customized combination products required in various stages of crop growth based on research findings. In a nutshell following benefits can be obtained using customized fertilizer:

It supplies the plant available nutrient in adequate amount and in proper proportion.

Customized fertilizer is a soil-crop-climate based fertilizer and is less influenced by soil, plant and climatic condition that lead to more uptakes of nutrients and less loss of nutrient.

Customized fertilizer supplies not only primary nutrients but also secondary and micronutrients.

Customized fertilizer reduces the cost of fertilizer application that ultimately reduces cost of cultivation.

Customized fertilizer is a major component of Site Specific Nutrient Management and Precision Agriculture, which promotes maximum fertilizer use efficiency of the applied nutrients in a cost-effective manner.

Soil health can be improved by developing site and crop specific fertilizers.

The farmers will have preference for customized fertilizers on account of the following points:

- For better crop quality and productivity.
- Maximize nutrient use efficiency.
- Specific to crop and area based on soil fertility.
- Developed using scientific data base.
- Available in ready to use form in a balanced way.
- Improves soil fertility and is environment friendly.
- Adaptable to varied field applications.
- . Checks distribution of spurious fertilizers such as micro-nutrients

Approaches for Development of Customized Fertilizers

India has diverse and numerous agro-ecological bones and production environment. Most of the farmers are in small and marginal category with variable investment capacity. This grossly influence input usage and increase variability in soil condition. Therefore defining the scale of a region for developing customized fertilizer is a point of debate. Isolated successful stories of site specific nutrient management research may not be adoptable due to its limitation in operational application.

Government Policy Interventions

Considering the recommendation of Task Force, Government of India (GDI) has created separate category of fertilizers named as "Customized Fertilizers". Subsequently, customized fertilizer was included in the Gazette in 2006 under clause 20 B of FCO 1985. Later customized fertilizer policy quidelines were issued on 2008 by GOI.

Preparedness of Farmers and Trade

As we see the customized fertilizers are knowledge driven. We have to prepare farmers for adoption of new nutrient package and its application technology. This is only way to assure the country 'Ever Green Revolution, Food and Nutritional Security'. Some of the general approaches to promote concept of customized fertilizers are listed below:

- > Sensitization of the concept of customized fertilizer
- Large scale trials through ICAR and agricultural farms
- > Farmers and dealers training
- > Development of soil health and INM services
- Development of fertilizer metering and placement devices
- > Demonstration at farmer's fields

Development of Protocol

The research on customized fertilizers aims at developing and perfecting the scientific protocol to arrive at a crop and region specific grade. Conventional approach adopted by soil scientist/agronomist might not be appropriate in handling multi-nutrient deficiency and inter-nutrients interaction. Crop and soil-process modeller also has limitation of integrating these phenomena in the mechanistic growth models. Most of the dynamic models in the globe deal with one nutrient at a time. The basic framework of logistic evolution of customized fertilizer grades, as a currently under development have three primary components:

- 1. Defining fertility management zones
- 2. Using empirical models like QUEFTS/STCR
- 3. Use secondary research data and experiential learning's

Defining Fertility Management Zones

For soil fertility tracking the geo-referenced sampling of soil, crop and water samples is done by a qualified team of crop specialist. The geo-referenced sampling is a rigorous process which is done in a two months time available after *Rabi* and *Kharif* season (after *Rabi* season (June) and after *Kharif* season (October and November). Crop specialist use hand held

GPS (Global Positioning System) and record latitude, longitude and altitude value of the field from where they take sample. Soil, crop and water samples are analyzed for nutrients to build database for deciding the management zones.

Use of Empirical Models like QUEFTS/STCR (for N,P and K Optimization to Attain Target Yield)

QUEFTS needs to be calibrated for 'a' and 'd' values for N, P and K; which basically refers to the nutrient uptake efficiency under adequate and limited grown conditions. For this purpose, the database from secondary literature as well from crop cutting trials were collected for the test crop to develop customized fertilizer basal grade. The soil supplying capacity was computed on the basis of soil test. The mechanistic model of QUEFTS was run for optimizing N, P and K requirement for a targeted crop yield by using the 'a' and 'd' values and the model class soil test values for N, P and K. On the basis of the general availability of the micronutrient, common representative dose of these specific nutrients were decided. Soil Test Crop Response (STCR) approach was also applied in optimization of N, P and K for the same target yield of the crop.

Use of Secondary Research Data and Experiential Learning

Value of N, P and K requirement from both the approaches were compared and evaluated. The final decision making was however based on secondary research data and experiential learning.

Validation of Formulation Grade

Multi-location trials were conducted on the farmers' fields and KVK farms using prevalent recommended varieties of the test crop. In all these tests, RBD design was used with 4 replications.

Eligibility Criteria for Manufacture and Sale of Customized Fertilizers

Permission for manufacture and sale of customized fertilizers shall be granted to only such manufacturing companies whose annual turnover is Rs.500 crores and above. Manufacturing companies should have soil testing facility with an annual analyzing capacity of 10,000 samples per annum for NPK, secondary and micro nutrients. Such laboratory must possess the requisite instrument viz., Atomic Absorption Spectrophotometer, Flame Photometer, pH meter Conductivity Bridge, Kjeldhal Distillation etc. The grades of customized fertilizers, which company will manufacture, must be based on scientific data obtained from area-specific, soil-specific and crop-specific and soil testing results. Prospective manufacturers or marketers are expected to use the software tools like Decision Support System like DSSAT, crop models, etc. to determine the optimal grades of customized fertilizers. The manufacturing companies, in association with agricultural universities/KVKs concerned, should also conduct agronomy tests of the proposed grade to establish its agronomic efficacy. Such manufacturing companies should generate multi-location trials (not on farm demonstrations) on different crops for minimum one season. Such manufacturing companies must draw these soil samples from within its operational areas and should also ensure that minimum one sample is necessarily, drawn from University/State government may also be used to prepare soil fertility map and for determination of required soil, area, and crop specific grades for existing and potential marketing areas.

Grant of Permission

Subject to fulfillment of eligibility criteria referred above, the permission for manufacture and sale of customized fertilizers is granted by Department of Agriculture & Cooperation, Ministry of Agriculture, GOI. Such permission, for manufacture and sale of particular customized fertilizers grade is granted only for the specific area and for a period not exceeding three years. For grant of permission to produce and sell such customized fertilizers, the concerned manufacturing companies should necessarily apply for permission, to the Ministry of Agriculture under intimation to the State Government, in the prescribed proforma. The competent authority shall expedite the requisite permission/authorization or otherwise within 45 days of the receipt of such applications. Such manufacturing companies are to required start their manufacturing and sales process within a period of six month from the date of grant of such permission.

Renewal and Revision of Customized Fertilizer Grades

On completion of three years or earlier, manufacturing company of customized fertilizers shall submit a renewal/revision application for varied customized fertilizers manufactured by it. In case, no change in the already approved composition of

customized fertilizers is required, the same shall also be declared by the manufacturer. The competent authority, shall, thereon, accord its approval within a period of 45 days from the date of receipt of such applications, failing which the duly acknowledge copy of such application shall be treated as official approval.

Manufacturing methodologies

Fertilizers industry is a form of secondary chemical production. There are basically three options (FAI-NR, 2011) from the simplest to the more complex i.e.,

Bulk Blending Compound Granulation/Steam Granulation and Complex/Chemical Granulation

Bulk Blending

It is the simplest and cheapest option which involves pure mixing of solid fertilizers in a ratio required to get the desired nutrient ratio. It only requires warehouse, weighing and mixing equipment. It has the advantage of smaller capacities of decentralized production uniquely suited to give the customer exactly the NPK ratio he requires. The option is mostly widely practiced in USA and is now getting popular in Europe too. The physical standard should be such that the shape and size of all fertilizers, raw materials, which are to be used in bulk blends, are similar. For example, if granular urea is allowed in bulk blends then its size and shape need to be equal to DAP. But the problem lies in its storage and application due to the segregation of different sizes and forms of raw material resulting in settlement of heavier particle at the bottom of the sack. Secondly, because of the stringent specification on raw material size and shape, the cost of raw material become very high and the overall cost of fertilizer increases. In India, such fertilizers are not available and due to cost factor, importing such fertilizers in bulk with the above physical specification will be unviable. Thus, bulk blends route seems to be a remote option for making customized fertilizers in India.

Compound Granulation or Stem Granulation

In this process of manufacturing, all the raw materials are in its solid form. Granulation is formed purely by agglomeration process and formed by the use of water, steam and heat in the dryer. These types of fertilizers are, popularly called 'compound granulation' or 'steam granulation' or 'physical granulation'. Incidentally it is wrong to call them 'mixtures', a term many people still use. One could call bulk blends as mixture, but not compound NPK granulation. This option of fertilizer production somewhere in between the option of chemical route and bulk blending. While it does not have the tremendous flexibility offered by the bulk blends, it offers far great flexibility in producing various types of fertilizer grades than that by chemical granulation. Its investment costs are much higher than that required for bulk blend but are much cheaper than chemical granulation plants. The main reason is that no cost is involved in creating infrastructure for storage and handling of chemicals involved. Change of grade is easy and takes a change over time of about 3 to 4 hours. As control over quality is assured, this option is the ideal option for manufacturing customized fertilizers of different grades and more so in our country where large sector players are coming in this field. In fact, almost all Asian countries are following the route to steam/physical granulation for NPK production. The compound granulation route is the most effective way for India for the promotion of customized fertilizer availability.

Chemical Granulation

Chemical granulation is also called 'slurry granulation' or 'complex granulation'. NPK's are produced primarily by a chemical reaction between ammonia and acid to form an ammonium sulphate or ammonium nitrate salt and then granulated with the addition of discrete K_2D either in solid form or even in some plants in a liquid form. The process of granule formation is by accretion plus agglomeration method. The limitations of this technology are:

It needs a large capacity plant and cost of creating infrastructure for storage and handling of acid and ammonia is huge. Ideally it has to be located near the sea shore to conveniently unload liquids like phosphoric acid and even in some cases ammonia.

Since it is a large capacity plant, it loses its flexibility to produce a variety of grades. At best two grades can be manufactured by this type of plants. The process option is not convenient when many customized NPK grades are to be produced.

Customized Fertilizer Formulations

A better yield starts with a better mix. The system returns a formula using the most economical mix of available ingredients and an application rate minimized to cost per acreage. Example of these formulations includes 8:16:24:6:0.5:0.15 (denoting individual levels of N, P, K, S, Zn and B) manufactured by Tata Chemical Limited, is targeted at potato grown in Agra, Aligarh, Farrukhabad districts of Uttar Pradesh (U.P). Another formulation, 10:13:12:6:2:0 has been specially designed for sweet sorghum cultivated in Nanded, Maharashtra. Likewise, Coromandel Industries Limited has received the nod for two customized formulations, 15:15:15:9:0.5:0.2 and 20:0:15:0:0.2, meant for groundnut in Anantapur and maize in Warangal districts of Andhra Pradesh (A.P). Few more formulations as prepared by the different industries have been presented in Table 7.

Table 7: Different Customized Fertilizer Formulations available in India

SI. No	Company	Crops Formulations (N:P:K:S:Zn:B)/ N:P:K: Zn		Geography		
			N:P:K:S:Mg:Zn:B:Fe/ N:P:K:S:Zn:B)			
1		Potato	8:16:24:6:0.5:0.15	Agra, Aligarh, Budaun, Bulandshahar and Baghpath		
2		Wheat	10:18:25:3:0.5:0	Muzaffarnagar, Barielly, Bijnore, Hathras, Pilibhit, Mathura, Meerut and Etah		
3		Sugarcane	7:20:18:6:0.5:0	Moradabad, KR Nagar, Farukhabad and Ferozabad		
4	ра	Rice	8:15:15:0.5:0.15:0	GB Nagar, Ghaziabad, Rampur, Shahjahanpur, Mainpuri and US Bagar		
5	ata Chemicals Limited	Mentha	8:20:20:4:0.3:0.2	JP Nagar and Lakhimpur Kheri		
6	nical	Paddy	15:32:8:0.5,18:33:7: 0.5,18:27:14:0.5	Andhra Pradesh		
7	E Rice(Basal)		11:24:06:3:0.5	Adilabad, Nizamabad and Medak		
8	ata	Maize (Basal)	14:27:10:4:0.5	Karimnagar, Warangal and Ranga Reddy		
9		Grape,	10:20:10:5:2:0.5:0.3:0.2	Aurangabad, Nasik, Pune and		
		Sugarcane		Ahmednagar		
10	_	Grape,	20:10:10:5:2:0.5:0.3:0.2	Nasik, Dhule, Jalgaon, Pune, Ahmednagar and		
	atier	Pomegranate,		Aurangabad		
	nod.	Paddy,				
	<u> </u>	Sugarcane, Tomato.				
	cals	Courds and				
	ш	Leafy				
	rock	vegetables				
11	Deepak Fertilizers & Petrochemicals Corporation	Grape, Cotton,	15:15:15:5:2:0.5:0:0.2	-da-		
	3 213	Onion, Banana,				
	tilize	Tomato,				
	Fer	Gourds &				
	spak	Leafy and				
	Dee	Vegetable				

12		igarcane,	10:20:20:3:2:0.5:0.3:0.2	-do-
	Cit	trus		
13	Gr	roundnut	15:15:15:9:0.5:0.2	Andhra Pradesh
14	Ma	aize	20:0:15:0:0:0.2	Andhra Pradesh
15	Pa	addy	16:22:14:4:1:0	East Godawari, West Godawari,
	(Ba	asal)		Krishna, Guntur
16	Ma	aize	14:20:15:4:0.6:0	Karimnagar, Warangal and
	(Ba	asal)		Nizamabad
17	Gr	oundnut	17:17:17:4:0.5:0.2	Anantapur, Chittoor, Kadapa, Kurnool and
	(Ba	asal)		Mahaboobnagar

Customized fertilizers to be used for basal application shall be granular in size with minimum 90% of the material remains between 1-4 mm IS sieve and the material passing through sieve having size less than 1 mm IS sieve should not exceed 5%. The moisture content should not exceed 1.5%. For foliar application, however, the grades should be 100% water soluble. The minimum nutrient contents should be 30 units of all nutrients combined.

Customized Fertilizers and Opportunity

In order to meet the simultaneous challenges of ensuring food and nutritional security customized fertilizers can undertake a huge initiative. Customized fertilizer presents agronomic as well as marketing opportunity both.

Agronomic Opportunity

Widespread deficiency of micronutrients is recognized as one of the major reason for crop yield stagnation. However, low use efficiency of micronutrients due to improper dose and method of application discourages farmer from their use. As more and more micronutrients are becoming deficient, farmers will find it extremely difficult to acquire knowledge and skill to address such emerging issues. As customized fertilizers are the most efficient carriers of micronutrients, they provide an excellent opportunity for ease and regularity of micronutrients use besides their improved use efficiency.

Marketing Opportunity

Fertilizer industry operates under regulation and it is unlikely that many of these regulations will be eased soon. However, in case of customized fertilizers, there has been an exception. Liberal provisions of customized fertilizers quidelines issued by Government of India present an opportunity to the segment of fertilizer industry and competent entrepreneurs. For this segment of industries having fiscal and technological capabilities, it is possible to set high standard of production and marketing for the benefits of farmers. These standards are to be strictly adhered to, leaving no scope for Government' scrutiny. Notwithstanding there can be challenging time for the Government and the customized fertilizers industry for the development of policy guidelines to ensure its adherence. They have to stop non-serious players to evade the guidelines and exploit it when fertilizer supplies are scare. The risk for the customized fertilizers industry, however, lies in making heavy capital investment in state of the art manufacturing facility for the customized fertilizer. This is because there is no long-term assurance from the government to keep the policy intact throughout the years. Most likely in the situation of shortage situation government may disallow use of subsidized fertilizers for manufacturing customized fertilizers. This could make the investment in the manufacturing plant unviable and thus redundant. Global experience shows two vital things; one there is vital policy support for the customized fertilizers industry and two there is high level technology support for the manufacture of quality products. In agriculturally advanced countries, more than 50 per cent of fertilizer is used in the form of customized fertilizers. Even in China, more than 40 per cent fertilizers used are re-customized. In India different grades of NPK are used which account for 15 per cent or less of consumption. This justifies that customized fertilizers are the future fertilizers for country like India as it improves fertilizers use efficiency.

Fertilizer Mixing

Fertilizer Mixing

Before mixing two or more different fertilizers varying in physical and chemical composition it has to be ensured that it does not yield any adverse effects. However, fertilizers which are to be mixed must be compatible both chemically and physically:

- Chemically, so that no gaseous loss will occur nor any decrease in nutrient availability or caking due to chemical reactions
- Physically, i.e. of similar granule size (2-4 mm, or 1-3.5 mm), to prevent segregation during transport and spreading.

Fertilizer Compatibility and Storage

When mixing fertilizers that contain a common element (for example Potassium Nitrate together with Potassium Sulphate) the solubility of the fertilizers is decreased. In such case, one cannot refer to the fertilizer solubility data alone. The same happens when the water used for dissolution is highly rich with minerals, e.g. calcium,

magnesium or sulphate. In such cases, additional chemical reactions come into play, and calculations become more complex. Usually, these are not calculated in the field and instead, trial-and-error practices are common. Again some fertilizers should not be mixed together in one stock tank because an insoluble salt may form very quickly. An example for such incompatibility is mixing fertilizers that contain calcium with those that contain phosphate or sulphate. Improper mixing and storage of fertilizers can result in large nutrient losses. Some important aspects (Fig 11) to consider in fertilizer mixing and storage include the following:

- Urea should not be mixed with ammonium calcium nitrate (CAN), KCI, SSP or TSP.
- Urea can be mixed with most other fertilizers but fertilizer mixtures containing urea should be applied immediately after mixing.
- Do not store fertilizer mixtures containing urea.
- Ammonium phosphates and super phosphates should not be mixed with lime, slag, rock phosphate or CAN.
- Potassium chloride and sulfate of potash can be mixed with most fertilizers, but mixtures of these fertilizers with urea and calcium ammonium nitrate should not be stored.
- CAN should not be mixed with basic slag but can be mixed with urea, single super phosphate, and ammonium phosphates immediately prior to application.

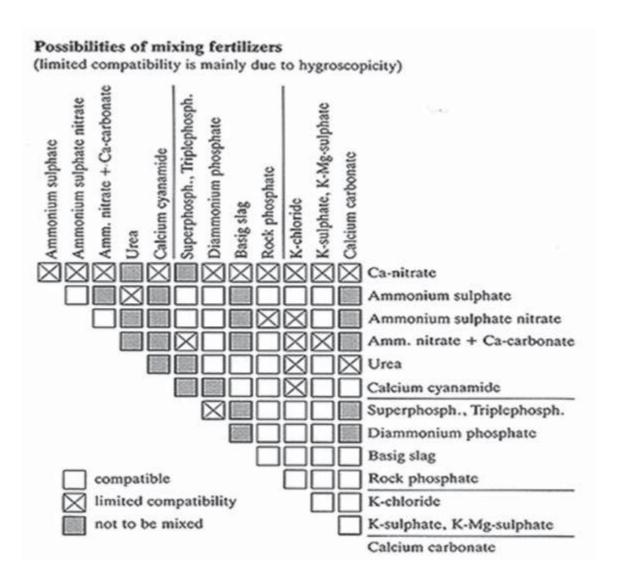


Fig 11. Fertilizer compatibility chart (Possibilities of mixing fertilizers)

Fertilizers shouldn't be stored in damp or dirty places. One needs to make sure that bags of fertilizer in the store do not absorb moisture from leaky roofs or water seepage through walls and floors. Fertilizers tend to absorb water from the atmosphere (they are hygroscopic) and can become caked and almost cement-like and impossible to apply properly. Fertilizers will start to absorb water when the CRH is exceeded (Table 8). Fertilizers that have a low CRH will absorb atmospheric moisture first (e.g., urea with a CRH of 70 will begin to clump together before SA which has a CRH of 79). When applying fertilizers through the irrigation water, it is essential that one shouldknow some important facts about the fertilizers solubility.

Table 8: Critical relative humidity (CRH) values for selected fertilizers

Fertilizer	CRH(%)
Ammonium nitrate	58
Urea	70
Potassium chloride	76
Ammonium sulphate	79
Triple upper phosphate	95
Sulphate of potash	96

Solubility of a Fertilizer

The solubility of a fertilizer is defiend as the maximal amount of the fertilizer, that can be completely dissolved in a given amount of distilled water at a given temperature. Manufacturers may provide the solubility data of their fertilizers upon request. Solubility data of various fertilizers (expressed in g/litre) have been presented in Table 9..

Different manufacturers may provide slightly different solubility data for the same fertilizer. This is because they use different additives in their products. There are also some fertilizers that may contain insoluble residues.

Table 9: Solubility for selected fertilizers at different temperature

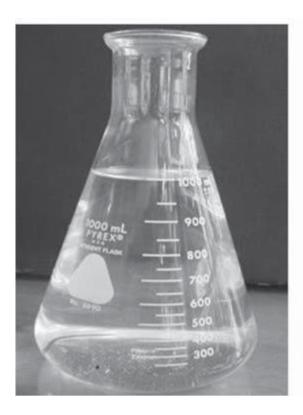
Fertilizer/ Temperature (C°)	Solubility g/l					
	5	10	20	25	30	40
Potassium nitrate	133	170	209	316	370	458
Ammonium nitrate	1183	1510	1920	NA	NA	NA
Ammonium sulfate	710	730	750	NA	NA	NA
Calcium nitrate	1020	1130	1290	NA	NA	NA
Magnesium Nitrate	680	690	710	720	NA	NA
MAP (Mono	NA	290	370	NA	NA	NA
Ammonium Phosphate)						
MKP (Mono Potassium	110	180	230	250	NA	NA
Phosphate)						
Potassium chloride	229	238	255	264	275	NA
Potassium sulfate	80	90	111	120	NA	NA
Urea	780	850	1060	1200	NA	NA

During dissolving a fertilizer, one should not exceed its solubility. Otherwise, a precipitate may form and might clog the irrigation system. Moreover, the nutrients you intend to provide through the solution may not be fully available. For example, according to the data in the table above, the solubility of Potassium Nitrate in 20°C is 209 g/l and the fertilizer contains 38% Potassium. If you attempt

to dissolve 300 g/l in the fertilizer stock tank, you will not get 114 g/l of Potassium (38% of 300g), but only 80g. The remaining 34g will precipitate and will not be available.

What is the Practical Way out?

The Jar Test: It is pertinent that when mixing fertilizers, one must be familiar with the solubility data of the fertilizers used, as well as with the chemical reactions that may take place. In order to avoid unwanted precipitates, a common recommendation is to perform a "jar test". In this test, the fertilizers are initially mixed in a jar containing the same water used for irrigation. The fertilizers should be mixed exactly in the same concentration as intended to be used in the stock tanks. If a precipitate forms or if the solution has a "milky" appearance, the test should be repeated with lower concentrations of the fertilizers.



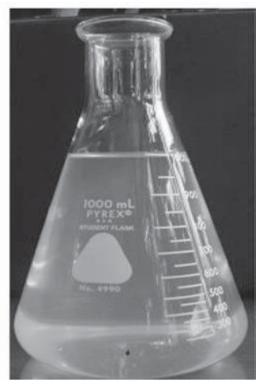


Fig 12. Complete dissolution Formation of a precipitate

Quality Control of Fertilizer

The contribution and impact of Extension in generation and transfer of appropriate technologies for rainfed farming need to be constantly improved because it is from these areas that further increases in production have to come to meet the growing demands of the population. Extension systems have to come up with technological options to provide improved livelihoods for this burgeoning population over the foreseeable future. The problem of quality control is major limitations to the efficient use of fertilizer in modern commercial agriculture. The major problems in quality control are adulteration/misbranding (70% problem), deliberate manufacturing of low quality fertilizers: (20 % problem), short weight of bags (5% problem) and black marketing or over charging price. This warrants the intervention of a vibrant extension system and facilities as well as the enhancement of its technical and human resources, which will strengthen its control on the regional scale. Among different remedial measures popularizing the quick testing kits for quick detection of adulteration in the field by extension workers are going to be a key in years to come. In this perspective quick testing kits will definitely help in reshaping the fortunes of Indian farmers.

Introduction

Agricultural growth relies on the use of fertilizers very heavily. Fertilizers have been considered as an essential input to Indian agriculture for meeting the food grain requirements of the growing population of the country. Chemical fertilizers bear a direct relationship with food grain production along with a number of supporting factors like High Yielding Varieties (HYVs), irrigation, access to credit, enhanced total factors of productivity, the tenurial conditions, size of the product market and prices they face both for inputs and the outputs etc. In the Post Green Revolution period, more than 50% of additional foodgrains production has been contributed by the fertiliser alone. To ensure adequate availability of right quality of fertilizers at reasonable price to the farmers in the country, the 'Fertiliser' was declared as an Essential Commodity in March, 1957 and the Fertiliser Control Order (FCO) was promulgated by the Central Government under section 3 of the Essential Commodities Act (ECA), 1955 to regulate the trade, price, quality and distribution of Fertilisers in the Country.

India is the third largest producer and consumer of fertilisers in the world after China and USA. It contributes to 12.1% of world production and 12.6% of world consumption but sustains 1/6 of world population. India is the second largest producer of Urea & DAP after China/ USA respectively. About 20 grades of various fertilisers are produced in 58 Major N & P manufacturing units and 73 SSP Manufacturing units. About 36.56 million tonnes of fertiliser material (17.36 mt nutrients) are distributed through a network of 2.83 Lakh dealers of both private and institutional channel. The occasional shortage of some fertilisers in sporadic pockets and high cost of fertilisers specially after decontrol of phosphatic and potassic fertilisers, are often exploited by the unscrupulous elements for adulteration/misbranding.

Status quality control of fertilizers in India

The Fertiliser Control Order, issued under section 3 of the Essential Commodities Act, provides for compulsory registration of fertiliser manufacturers, importers and dealers, specification of all fertilisers manufactured/imported and sold in the country, regulation on manufacture of fertiliser mixtures, packing and labelling on the fertiliser bags, appointment of enforcement agencies, setting up of quality control laboratories and prohibition on manufacture/import and sale of non-standard/spurious/adulterated fertilisers. The order also provides for cancellation of authorization letter/registration certificates of dealers and mixture

manufacturers and also imprisonment from 3 months to 7 years with fine to offenders under ECA. The FCO offence has also been declared as cognizable and non bailable.

The FCO has been amended periodically to keep it abreast with the changing scenario. A number of amendments have been made during last 4 decades and a few recently in 2003, which includes replacement of Dealers Registration Certificate with Authorisation letter, providing grievances redressal mechanism through Referee Analysis and tolerances in Moisture and particle size, for the first time prescribing specification of provisional fertilizers for commercial trials, specification of new grades of 100% water soluble NPK fertilizers, maintaining of minimum laboratory facilities for all Fertilizer Control Laboratories for ensuring accuracy of results, reduced time limit from sampling to communication of results, provision for secrecy of samples, reprocessing of damaged stock during transit in special situation and methods of analysis of different fertilizers etc.

Major problems of quality control

The problem of quality control is major limitations to the efficient use of fertilizer in modern commercial agriculture. The major problems in quality control are:-

Adulteration/misbranding - (70% problem)

- NPK(Mixtures)/SSP (Granular) ------DAP/NPK Complexes
- Magnesium Sulphate -----Zinc Sulphate
- Common Salt/sand ------MDP
- Gypsum/Fly ash/Clay -----SSP/DAP/Complexes.

Deliberate manufacturing of low quality fertilisers : (20 % problem)

- NPK Mixtures
- **922**
- Micronutrient Fertilisers

Short weight of bags (5% problem)

Black marketing or over charging price

The problem of quality control in fertilizer, can be exploited by the unscrupulous elements. However, certain fertilizers are more prone where adulteration/mixing of cheap foreign material having physical similarities is quite easily possible without detection by the ordinary means or where the inputs/ingredients can be easily manipulated for affecting the finished product to a lower quality. These are called as Prone Fertilizers. At Macro level based on the samples found Non-standard in different states, the following prone fertilizers have been identified in order of severity Fertilizer Mixtures, SSP, Micronutrient fertilizers and DAP & Complexes.A list of commonly used adulterant materials with the common fertilizers is listed in Table 10.

Table 10: Commonly used adulterant materials with the common fertilizers

Table to. Commonly used additer and makerials with the common tertilizers					
Fertilizer	Adulterant				
	Macro nutrient fertilizer				
Urea	Normal Salt				
DAP	Granular SSP, Rock phosphate				
SSP Ash, Gypsum					
MOP Sand, Normal salt, <i>Morram</i>					
NPK	Superphospahe, Rock phosphate				
Micro nutrient fertiliser					
Ca	Black soil, Ammonium nitrate, Gypsum				
Zinc sulphate	Magnesium sulfate				
Ferrus sulphate	Sand, Normal salt				
Cupper sulphate	Sand, Normal salt				

Weaknesses in quality control

The main reasons for non standard material in fertilizer mixtures and micronutrient fertilizers are due to use of lesser quantity of ingredients/raw material or their lower quality, the non standard sample in SSP is either due to this account or inadequate curing or use of the excess quantity of fillers and non homogenous mixing. The following seven weaknesses due to which the magnitude of the problem rises by leaps and bound.

- i)No full time Inspectors :-In states except Haryana, J & K, Gujarat, Maharashtra and Orissa only the part time inspectors have been assigned the responsibility of fertilizers, which is not very effective.
- ii)Multiplicity of Grades :-A large number of grades of NP & NPK having the common nutrient ratio are being produced and consumed which often creates problem in the field because of variable price and demand.
- iii)Inadequate Laboratory Facility:- Against minimum 5.66 lakh samples to be drawn analysed from 2.83 lakh dealers, the existing capacity of 67 laboratory is only around 1.25 lakh sample which is only 20% of minimum requirement.
- iv) Drawing samples from Non prone Fertilizers: In many of the states inspite of repeated advice by the Government of India, around 30-40% of samples drawn by the field inspectors are of Urea, MOP etc. which is not prone for adulteration and so less attention given on the problem fertiliser.
- v) **Very Low prosecution**:-Though about 4000-5000 samples are declared non standard by the laboratories every year, the legal prosecutions are only in 5-6% cases(Rajasthan, UP, Gujarat, TN and MP) and unfortunately the convictions by the courts is hardly to the extent of 2-3%. This dilutes the quality control system.
- vi) No Testing facility for Dealers and Farmers: The Government Laboratories normally do not accept the private samples of dealers and farmers. There is also no private laboratory in the Country to cater the need of dealers or farmers.
- vii)Non Participation in Training Programmes:- Though Clause FCO provides for mandatory training for Fertilizer Inspectors & Analysts in training programmes organized at Central Fertilizer Quality Control & Training Institute, Faridabad and RFCL, Kalyani . The participation from different states is also not satisfactory.
- viii) Non submission of reports by State Governments:- Half Yearly reports are required to be sent by State Governments regarding the number of samples received and analysed, follow up action on Nonstandard samples and also the details of non standard Urea etc. to the Institute.

Remedial measures

Following remedial measures may be advocated for a sustainable solution.

- i)Full Time Regular Inspectors:-To be appointed by redeployment from the existing agricultural officers. This will require only one inspector at each of 5000 blocks and 3 Inspectors at the district headquarter making the total of about 6000 Inspectors in the Country instead of existing about 20,000 inspectors.
- ii)Relationalisation of Product Pattern: As per the recommendation of GVK Rao Committee and as approved by the Government the new product pattern should be nitrogen as Urea, Phosphate as DAP, SSP and Nitrophosphate and Potash as MOP. The other grades of NP/NPK complexes having common nutrient ratio, need to be restricted to the barest minimum with high nutrient value.
- iii)Restriction on Granulated NPK mixtures:-Since the major problem of quality control is the granulated NPK mixtures and granular SSP, which are used as a adulterant in DAP and popular grades of complexes, there is urgent need to discourage any further expansion in the NPK mixtures in most of the States.
- iv) Sampling Priority and adequate training:- Based on the identification of problem fertilizers at micro level in the States, the stress should be made on the problem fertilizers for sampling and analysis. Adequate training to Fertiliser Inspectors are required in both technical and legal aspects of quality control for proper presentation of cases in courts of law for successful convictions.
- v)Setting up of Input diagnostic Centres by the Entrepreneurs:-Like the medical facilities, private entrepreneurs need to be encouraged for setting up of the testing laboratories to provide the testing facility to the dealers and farmers for advisory purposes in respect of major inputs like fertilizers, seeds and pesticides.
- vi)Popularizing the Quick Testing Kits for Quick Detection of Adulteration in the field: To instill the confidence of farmers in the fertilizers purchased by them and also to help the enforcement agencies in segregating the suspected stocks in the field for quick follow up action, the Quick Testing Kit (Table 2) need to be popularized at the gross root level.
- viii) Creating awareness amongst farmers for use of consumer forums: For seeking compensation for the purchase of non standard fertilizers from the dealers, the farmers need to be well educated for approaching the consumer Forums, in addition to the legal action by Government Agencies.

Quick Testing Kits for quality control

There are different on spot quick testing methods available which could be used for effective and qualitative judge of the input material. In Table. If the test procedures have been mentioned.

Table 11: Methodology for quick testing of fertilizer

Fertilizer Method				
Macro nutrient fertilizer				
Urea	Take I g urea fertilizer in a test tube. Heat the sample, complete melting ensures good quality/ Take			
	I g urea fertilizer in test tube. Add 5 ml normal water. Mix it. Add 5-6 drops of 1% AgNO₃			
	.Appearance of white coloured solution ensures presence of adulterant.			
DAP	Pure DAP granules are not completely round shaped. If the DAP granules on heating doubles its			
	size, it ensures good quality. To test the presence of nitrogen in DAP add lime with one gram of DAP.			
	If there is bad odour /pungency of NH3 that ensures presence of nitrogen.			
SSP Take 1 g SSP fertilizer in a test tube. Add 5 ml normal water. Filter it. Add one drop				
	drop of AgNO3 in the filtrate. If there is yellow precipitate which ensures presence of phosphate in			
	the fertilizer.			
MOP In presence of fire/heat if it converts to yellow coloured substance it ensures				
	adulterant. Crystals of MOP are completely soluble in water with the red part floating in water.			
Micro nutrient fertiliser				
Zinc sulphate	White crystalline powder of ZnSO4 is not completely soluble in water and on dissolving in water does			
	not impart cooling effect. Take 1 g ZnSO4 fertilizer in a test tube. Add 5 ml normal water. Filter it.			
	Add eight to ten drops of NaOH in the filtrate. If there is white jelly like formation and subsequently			

further addition of 8-10 drops of NaOH the gelly dissolves that ensures right grade of ZnSO4.

Fertilizer is an input that allows considerable farmer experimentation, and there is much evidence to support the view that farmers are able to arrive at economically efficient fertilizer practices and evaluation of quality control through their own experience. In this perspective quick testing kits will definitely help in reshaping the fortunes of Indian farmers. Quality testing of fertilizers has to be ensured and supplies of spurious inputs have to be checked. Threats to availability of quality input are real and cannot be ignored anymore.

Fertilizer Control Order

Fertilizer Control Order, 1985

Fertilizer is the key input for sustainable agriculture. In the Post Green Revolution period, more than 50% of additional foodgrains production has been contributed by the fertilizer alone. To ensure adequate availability of right quality of fertilizers at reasonable price to the farmers in the country, the 'Fertilizer' was declared as an Essential Commodity in March, 1957 and the Fertilizer Control Order (FCO) was promulgated by the Central Government under section 3 of the Essential Commodities Act (ECA), 1955 to regulate the trade, price, quality and distribution of Fertilizers in the Country.

The Fertilizer Control Order provides for compulsory registration of fertilizer manufactures, importers and dealers, specification of all fertilizers manufactured/imported and sold in the country, regulation on manufacture of fertilizer mixtures, packing and labeling on the fertilizer bags, appointment of enforcement agencies, setting up of quality control laboratories and prohibition on manufacture/import and sale of nonstandard/ spurious/adulterated fertilizers. The order also provides for cancellation of authorization letter/registration certificates of dealers and mixture manufacturers and also imprisonment from 3 months to 7 years with fine to offenders under ECA. The FCO offence has also been declared as cognizable.

The FCO has been amended periodically to keep it abreast with the changing scenario. A number of amendments have been made during last 4 decades and a few in 2003, which includes replacement of Dealers Registration Certificate with Authorization letter, providing grievances redressal mechanism through Referee Analysis and tolerances in Moisture and particle size, for the first time prescribing specification of provisional fertilizers for commercial trials, specification of new grades of 100% water soluble NPK fertilizers, maintaining of minimum laboratory facilities for all Fertilizer Control Laboratories for ensuring accuracy of results, reduced time limit from sampling to communication of results, provision for secrecy of samples, reprocessing of damaged stock during transit in special situation and methods of analysis of different fertilizers etc. A new concept of customized fertilizers has been introduced in FCO and lately non edible deciled cake fertilizers have been included in FCO.

Penal provisions

The FCO provides for administrative action against offenders while ECA provides for penal provisions. The offenders of FCO are prosecuted under Section 7 of ECA, 1955. The following penalities have been prescribed under ECA:-

- i) 3 months to 7 years imprisonment with fine under Section 7(i)(a)(ii).
- ii) Making any false information is punishable up to 5 years imprisonment.
- iii) The fertilizer stock and also its receptacle can be forfeited under section 7(i) (ii).
- iv) The FCO offences are cognizable under section 10 A.
- v) All offences are to be tried by the Courts of 1st Class Magistrate only, who can impose imprisonment upto 1 year and fine.
- vi) The Authorization letter of dealers can be suspended/cancelled/debarred under clause 31 of FCO.

Various grades of various fertilizers are produced in 19 Major N & P manufacturing units and over 82 SSP Manufacturing units. About 56 million tonnes of fertilizer material (28.12 mt nutrients) are distributed through a network of 2.75 Lakh dealers of both private and institutional channel. The occasional shortage of some fertilizers in sporadic pockets and high cost of fertilizers especially after decontrol of phosphatic and potassic fertilizers, are often exploited by the unscrupulous elements for adulteration/misbranding.

Enforcement agencies

The State Govts. are primarily responsible for implementing the FCO provisions through appointment of Enforcement agencies like Fertilizer Inspectors, Registering Authority/Notified Authority and Appellate Authority, who have been given adequate powers under the Order. They also set up quality control laboratories for testing of samples. The Central Govt. only oversees the activities and assist the State Govts. through periodical executive guidelines, making necessary amendment in FCO provisions as and when required and

training of their Enforcement Officers at the Central Fertilizer Quality Control & Training Institute & its 3 Regional Laboratories located at Navi Mumbai. Chennai and Kalvani (WB). The Fertilizer Inspectors, who are the back bone for implementing the FCO provisions, are notified by the State Govts. under clause 27 of FCO. They are empowered to draw samples from importers, manufacturing units, distribution network and dealers, seek any information about manufacture, import and sale of any fertilizer, enter upon and search any premises where fertilizer is manufactured or sold, seize any fertilizer and also books of 27 accounts in case any contravention of FCO provisions is anticipated and also to stop the sale of fertilisers. They are also empowered to check the illegal inter-state movement of fertilizers under Fertiliser Movement Control Order (FMCO). The Registering Authority/Notified Authority is notified by the State Govts. under clause 26 and 26A respectively. Registering Authority is empowered for issuance and renewal of Certificate of Manufacture for fertilizer mixtures, special mixtures, Bio fertilizers and organic fertilizers. Notified Authority is empowered to issue and renew the Letter of Authority to dealers for sale of fertilizers. They are also empowered to suspend/cancel/debar these certificates/Letter of Authority in case of violation of FCO provisions. The Appellate Authority is notified under Clause 32/32 A by the Central/State Governments to hear appeal against the orders of Registering Authority/Notified Authority regarding refusal to grant or renew Registration Certificates/Authorization Letter and its suspension/ cancellation/debarment. The Appellate Authority is also empowered to order for reanalysis of Non standard fertilizer samples. The State Fertilizer Inspectors regularly draw samples of all imported and indigenous fertilisers and send to State Quality Control Laboratory, who analyze as per prescribed procedure and communicate the result within 30 days. If sample is found Non-standard the administrative/legal action is taken against offender by designated officer. The Central Govt. has also notified a limited number of Fertilizer Inspectors posted at Central Fertilizer Quality Control & Training Institute and its 3 Regional Laboratories and defined their area of jurisdiction as throughout the country. They mainly inspect the imported fertilizers at the discharge ports and randomly the indigenous manufacturing units and their distribution network to supplement the activities of State Governments. Samples are analyzed in the Central Institute and Regional Laboratories and the reports are sent to the State Govts. for further follow up action on non standard samples as per provisions of FCO, 1985.

Quality control laboratories

With the sustained efforts of Government, the number of laboratories have increased from 27 during 5th Plan to 44 by the end of 6th Plan (1984-85) and 47 during 7th Plan. Now, there are 74 Fertilizer Quality Control Laboratories in the country, which includes 4 laboratories of Govt. of India with total annual analyzing capacity of two lacs samples. Most of the States have one or more labs. However, 7 States namely: Arunachal Pradesh, Sikkim, Manipur, Tripura, Meghalaya, Delhi, Goa and all U.Ts. (except Pondicherry) do not have any laboratory and they are presently being catered from Govt. of India Laboratories.

Salient features of FCO, 1985 :

1/ Definitions

Clause 2 of FCO (1985) includes the definition of various terms including 'Fertilizer', 'Inspector', 'Dealer', 'Grade' & 'Prescribed', 'standard', etc.

Fertilizer

Means any substance used or intended to be used as a fertilizer of the soil and/or crop & specified in part A, of schedule I or a mixture of fertilizers and special mixture of fertilizers. No material can be sold as fertilizer which is not listed in Schedule I of the Fertilizer (Control) Order and the material sold as fertilizer should, apart from being listed in Schedule I should also adhere to specifications given therein.

Mixtures of Fertilizers

Means a mixture of fertilizers made by physical mixing of two or more fertilizers with or without inert material in physical or granular form & includes a mixture of NPK fertilizers, a mixture of micro-nutrient fertilizers and a mixture of NPK with micronutrient fertilizers.

Dealer

Means a person carrying on the business of selling fertilizers whether wholesale or retail or industrial use and includes a manufacturer, importer and a pool handling agency carrying on such business and the agents of such person, manufacturer, importer or pool handling agency.

Retail Dealer

Means a dealer who sells fertilizers to farmers or plantations for agricultural use such as for fertilization of soil and increasing productivity of crops.

Wholesale Dealer

Means a dealer who sells fertilizers otherwise than in retail for agricultural use such as for fertilization of soil and increasing productivity of crops.

Industrial Dealer

Means a dealer who sells fertilizer for industrial purposes.

2) Regulation on trade of fertilizers

Under clause 7 of FCO, every person is required to obtain the "Certification of Registration" (DRC) and follow its terms and conditions before carrying on the business of selling fertilizers. Thus trading of fertilizer is not allowed without DRC.

2a) Procedure for obtaining Certificate of Registration

- a) Apply in duplicate in Form 'A' along with prescribed fee and certificate of source in Form 'O';
- b) Apply separately for wholesale and retail dealer to the designated Registering Authority.

2b) Conditions for grant of Certificate of Registration (CR)

The Registering Authority shall grant DRC in form 'B' within 30 days of receipt of application EXCEPT when :

- a) The person has been convicted for any offence under ECA or any Order under
- the Act within 3 years preceding the date of application;
- b) Form "O" is not enclosed;
- c) Application is uncomplete;
- d) Previous CR is under suspension;
- e) Previous CR was cancelled within one year preceding the date of application.

For each sale depot, separate DRC is required. CR should be displayed prominently in the place of business. State Governments are authorized to grant exemption under clause 7 to deal with the special situations like exempting small dealers from obtaining DRC from payment of fee, sale of fertilizers through Mobile Vans in the mandis, providing one time DRC to the manufacturers/importers from State Head quarter for their buffer go-downs instead of by individual Registering Authorities, where it is located. It is mandatory that Certificate of source must be attached for each and every product of each manufacturer that the dealer wishes to sell. This he can do at the time of obtaining DRC, or can get it included at a later date (but before trading of that specific product) on payment of prescribed fees.

2c) Validity period

Every CR granted or renewed is valid for a maximum period of 3 years from the date of issue.

2d) Renewal of DRC

Every dealer should get renewed before expiry date. (or within one month from expiry date with additional late fee).

2e) Procedure for renewal of CR

- a) Apply to designated registering authority in Form 'C' in duplicate :
- b) Enclose Certificate of Source in Form 'O' & submit prescribed fee.

2f) Condition for renewal of CR

On receipt of application, the registering authority shall renew the CR, EXCEPT when :

- a) Application is incomplete;
- b) Certificate of source is not attached:
- c) The application did not sell fertilizer during preceding one year of expiry date.

Applicant is deemed to possess valid DRC until the registering authority passes order to the contrary on renewal application.

3) Price control

The Government of India has power to fix Maximum Retail Price (MRP) for sale of any fertilizer. However, presently only Urea is under such statutory price control. It is mandatory for dealers to sell fertilizers only at the specified price. They cannot charge higher than the MRP fixed by the Government printed on the bags of decontrolled fertilizers. However for sale of small packets, the retail dealer can charge additional cost per pack from farmers the rates of which are also notified by the Government. The issue of cash/credit memo is mandatory in the specified form by the dealer to each purchaser.

4) Display of stock position & price list

- i) Every retail dealer is required to display prominently in his place of business
- a) Opening stock of fertilizers
- b) Price/rate of fertilizers
- ii) Maximum retail price except local taxes, whenever specified.

5) Restriction on manufacture/import/sale of fertilizers

The manufacture/import/sale/stock distribution etc. s prohibited under clause 19 of fertilizer:

- a) Which is not of prescribed standard,
- b) Which is not packed and marked as specified,
- c) Which is an imitation or a substitute for another fertilizer,
- d) Which is adulterated.
- e) Whose label or container gives fictitious address of manufacturer or any false or misleading information,
- f) Whose label or container does not exhibit the grade, and
- q) Which is in fact not a fertilizer.

6) Printing & marking on fertilizer bags

- a) Every container or bag of fertilizer should be printed in the manner, specified by controller under clause 21.
- b) No information, other than required under notified order, be printed.
- c) Every container should be so packed (lead sealed in case of hand stitching) that contents thereof cannot be tapered with without a visible break in stitching or seal.

7) Bulk sale of fertilizers

- a) Retail dealer may keep one bag of each variety in open condition for sale.
- b) One manufacturer/importer can sell in bulk to the other manufacturer of mixture/special mixture/complex fertilizer.
- c) Central Government may also authorize any manufacturer to sell his product in bulk to farmers along with certificate of quaranteed nutrients. However, no such authorization has been issued by Government to any manufacturer at present.

8) Disposal of non-standard fertilizers

As non-standard fertilizers cannot be sold to farmers, following provision has been made for disposal of such stock lying with dealers/manufacturer:

- a) Apply to registering authority in form-H with reason for stock becoming non standard.
- b) Drawal of representative sample from stock by Fertilizer Inspector and its analysis in State Government Laboratories.
- c) Enclose the copy of analysis report of sample drawn by Fertilizer Inspector.
- d) The registering authority to fix the per unit price of non-standard fertilizer on pro-rata basis.
- e) The registering authority to issue authorization for sale non-standard fertilizer in Form-I.
- f) Such stock to be sold only to manufacturers of fertilizer mixtures, special mixtures, or research farm of Government or Universities.
- g) put 'X' mark and print 'Non-standard' in red ink on each bag.

9) Restrictions on use of fertilizers

- a) Fertilizers should be used only for agricultural purposes i.e. fertilization of soil and increasing productivity of crops.
- b) Only 'Industrial dealer' can sell the fertilizer for industrial use
- c) The rates for industrial purposes are inclusive of Custom/Excise duty or any other tax chargeable. No subsidy is admissible on sale of fertilizers for industrial purposes.
- d) Central Government may also permit any person to sell or use fertilizer for industrial purposes.

10) Enforcement authorities

There are 4 types of enforcement authorities under FCO:

- i) Controller of fertilizers
- ii) Registering authority
- iii) Fertilizer Inspector
- iv) Appellate authority

i) Controller of Fertilizers

a) Controller of Fertilizers is appointed under section 5 of ECA, 1955 read with

clause 2(e) of FCO. Presently Joint Secretary (Fert) in Dept. of Agri. & Coop.

Government of India is the Controller of Fertilizers.

- b) He has the power to make orders and to issue notifications under section 3 of ECA and relevant provisions of FCO.
- c) He is also registering authority for industrial dealers.

ii) Registering Authority

- a) Registering authorities are appointed under clause 26 of FCO, by State Governments.
- b) Their area of jurisdiction is also defined.
- c) Main functions of the registering authority include :
- To grant the Certificate of Registration and its renewal to retail and

wholesale dealers;

- To grant the certificate of manufacture under clause and its renewal;
- To grant the certificate of authorization for sale of non-standard fertilizers;
- To grant the duplicate copies of certificate of registration or manufacture, and
- To amend the certificate of registration.
- d) He has the power to refuse to grant/renew the Certificate of Registration or Manufacture, giving reasons in writing.
- e) He may also suspend/cancel such Certificates giving reasons in writing.

iii) Fertilizer Inspectors

- a) Central or State Governments appoint fertilizer inspectors through notifications.
- b) Their area of jurisdiction is also defined.
- c) Qualifications for appointment :
- Graduate in agriculture or science (with Chemistry)
- Training or experience in quality control of fertilizers
- Working in Central/State Dept. of Agriculture
- d) Powers of Fertilizer Inspectors :
- To seek any information from any manufacturer, importer, dealer or pool handling agency regarding manufacture, storage or disposal of any fertilizer manufactured or handled by them.
- To draw the sample of any fertilizer as per procedure given in schedule II part A of FCO.
- To enter upon and search any premises where fertilizer is manufactured or stored or exhibited for sale if he has reason to believe that it is contrary to FCO provisions.
- To seize any books of accounts or documents regarding fertilizer.

- e) Main duties and responsibilities :
- *He should regularly visit the dealers and manufacturers randomly and check.
- Certificate or registration (CR) and Certificate of Manufacture (CM) to ensure its validity.
- Compliance of specific conditions of CR & CM regarding its display, qualification of manufacturer, laboratory requirements etc.
- Stock position, cash memo stock register
- Packing and marking requirement on bags.
- *He could detain/seize fertilizer in case of serious contravention of FCO provisions.
- *He should launch prosecution against offender after taking approval of competent authority.

iv) Appellate Authority

The State Governments notify the appellate authority under clause 32 of FCO. Any aggrieved person may appeal to him within 60 days of the receipt of an order of

- *Refusing to grant, amend or renew the CR
- *Refusing to grant or renew the CM
- *Suspension or Cancellation of CR or CM
- *Non issuance of CR within stipulated period

The decision of appellate authority is final.

11) Follow up action against offenders

Administration Action : Legal Action :

- i) Stop Sale/detention notice i) Launching prosecution (Cl.28 (1) (d) & 28 (2)
- ii) Seizure of stock Cl.28 (1) (d) a) directly in special
- iii)Interim suspension of CR/CM CI.31(2) Court OR
- iv)Cancellation of CR/CM (Cl.31(1) b) FIR in Police Station

12) Penalties for non-compliance of FCO

Severe penalties for violation of provision of ECA/FCO, including imprisonment or fine or both have been provided. All offences under ECA are cognizable and non-bailable which means that the Police can arrest without Arrest Warrant and bail can be given only by Special Court or High Court.

13) Sampling of fertilizers

Detailed procedure for drawal of fertilizer samples, its sealing and analysis has been laid down in Schedule II.

Appendix

Table1: List of fertiliser manufacturer/supplier from Private/Public and PSU sector

Some of the public sector companies in India fertilizer industry:

- National Fertilizers Limited
- Fertilizers & Chemicals Travancore Limited
- Rashtriya Chemicals & Fertilizers Limited
- Madras Fertilizers Limited
- Steel Authority Of India Limited
- Neyveli Lignite Corporation Limited
- Paradeep Phosphates Limited
- Pyrites, Phosphates & Chemicals Limited
- Hindustan Fertilizer Corporation Limited
- Fertilizer Corporation of India Limited (FCIL)
- Projects &Development India Limited (PDIL)
- FCI Aravali Gypsum & Minerals India Limited, Jodhpur

Some of the private sector companies in Indian fertilizer industry:

- Chambal Fertilizers & Chemicals Limited
- Ajay Farm-Chem Private Limited
- Balaji Fertilizers Private Limited
- Deepak Fertilizer and Petrochemicals Corporation Limited
- Bharat Fertilizer Industries Limited
- Coromandal Fertilizers Limited
- Gujarat Narmada Valley Fertilizer Co. Limited
- Meerut Agro Chemicals Private Limited
- Duncans Industries Limited
- Karnataka Agro Chemicals
- Godavari Fertilizers & Chemical Limited
- Shri Amba Fertilizers (I) Private Limited
- Tuticorin Alkali Chemi & Fertilizer Limited
- Gujarat State Fertilizers & Chemicals Limited
- Indo-Gulf Fertilizers & Chemicals Corporation Limited
- Southern PetroChemical Industries Corporation Limited
- Maharashtra Agro Industrial Development Corporation
- Zuari Industries Limited- Fertilizer Limited
- Mangalore Chemicals & Fertilizers Limited

Public sector undertakings

- IFFCO
- KRIBHCO



Fig 1. Map showing the Location of Major Fertilizer Plants in India

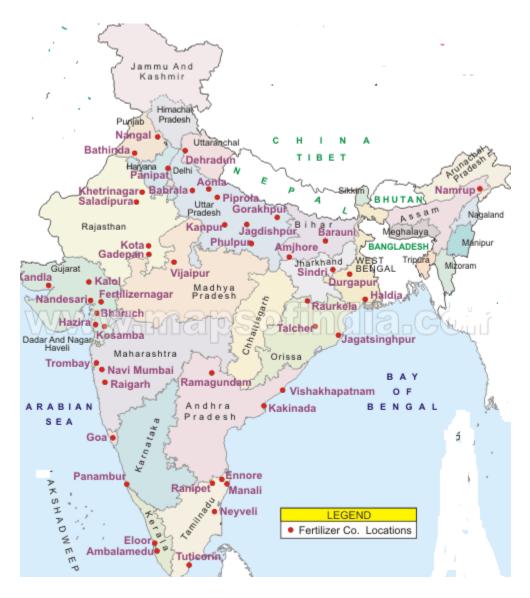


Fig 2. Map showing the Location of Major Fertilizer Companies in India

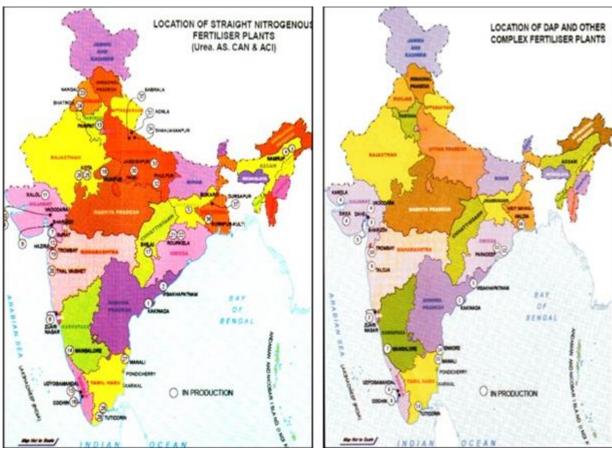


Fig 3. Map showing the Location of different fertilizer plants in India

Important aspects of fertilizer bag

Labels on fertilizer bags or other containers can vary markedly from place to place and from supplier to supplier. Probably the most noticeable difference from places is language. However, this is unavoidable and necessary to convey the required information to the local customers/farmers. Additionally, each supplier may have their own company logo and/or brand name for its products. This is a tool used by suppliers to identify and market their products as distinct from other supplier's products. However, there is certain information that should be contained on all labels regardless of the supplier or the language in which it is presented. A description of this information follows.

- Grade, as previously defined, is a short version of the guarantees for nitrogen (N), phosphorus (P or P2Os), and potassium (K or K2O) with each guarantee separated by a hyphen/dash or dot. Examples are 15-15-15 and 15-15-15. Some countries also allow for the secondary nutrients or micronutrients to be included in the grade. Examples are 15-15-15-5S and 15-15-15-1B. The grade is usually displayed in large numbers at the top of the bag.
- Guaranteed Analysis is the supplier's or manufacturer's guarantee for the claimed nutrients in aspecific order and format and is considered to be alegal guarantee.
- Net Weight as defined above refers to the actual weight of the bag or container with fertilizer minus the weight of the bag or container. This weight should be displayed prominently on each bag or container of fertilizer.
- Name and Address refers to the name and address of the person or company responsible for the guarantees made on the label.

- Directions for Use should be included on the label when a fertilizer is produced for use on a specific crop or if the use of a fertilizer might be detrimental to the development and yield of certain crops.
- ❖ Bag The most commonly used fertilizer bag is the pillow-shaped polypropylene (WPP) bag with either a loose inner bag liner or a liner laminated to the inner surface. Inner liners for fertilizer bags are constructed of either low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), or polypropylene of various densities. Most common bag capacity is 50- kilogram. Dimensions of bags (55-60 cm width and 90-100 cm length) are determined based on the bulk density of the fertilizer as well as the desired capacity.

Brief Fertilizer Profile

Total No. of Units	Urea:31;DAP:12;Complexes:19;SSP:80				
Private sector produced ne	Private sector produced nearly 45 % of nitrogenous fertilizers and 65 % of phosphatic fertilizers				
	India is the third (after China and USA) largest producer and second largest consumer of fertilizer in the world.Indian fertilizer				
	industry started in 1906 with SSP production facility at Ranipet near Chennai .Started operating in a big scale since 1940s, when the				
Fertilizer & Chemicals Travancore of India Ltd. and the Fertilizers Corporation of India were set up in Kerala and Bihar.					
Share of different	88% urea ,10% DAP & 2% ammonium fertilizers.				
nitrogenous fertilizers					
Market capitalisation	25% of GDP				

Conversion Factors of Plant nutrients

From oxide to elemental							
P ₂ O ₅	χ	0.44	=	Р			
K ₂ D	χ	0.83	=	K			
CaO	χ	0.71	=	Са			
MgO	Х	0.60	=	Mg			
SO ₃	χ	0.40	=	2			
B_2O_3	Х	0.31	=	В			
From elemental to oxide	From elemental to oxide						
Р	Х	2.29	=	$P_2 O_5$			
K	χ	1.20	=	K ₂0			
Ca	Х	1.40	=	CaO			
Mg	χ	1.66	=	MgD			
2	χ	2.50	=	SO ₃			
В	χ	3.22	=	B ₂ O ₃			

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