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PAKISTAN STANDARD SPECIFICATION

FOR

MULTI NUTRIENT FERTILIZER

PAKISTAN STANDARDS AND QUALITY CONTROL AUTHORITY,
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Karachi.

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FOR

MULTINUTRIENT FERTILIZER

0. FOREWORD

0.1 This Pakistan Standard was adopted by the Pakistan Standards Institution on **23rd April,1973** on approval by the Chemical Division Council of the draft finalized on 26th March,1973 by the Fertilizer and Allied Products Sectional Committee.

0.2 The Sectional Committee responsible for the preparation of this draft felt that it is necessary to lay down specifications on multinutrient fertilizers to safeguard the interests of farming community and to protect them from using wrong types or grades of multinutrient fertilizers as well as to safeguard the interest of the manufacturers.

0.3 While preparing this standard the views of the producers, consumers and testing authorities were taken into consideration by the Sectional Committee. Due weightage to the need or international co-ordination among standard prevailing in different countries of the world was also given.

0.4 For the purpose of deciding whether the particular requirements of this standards complied with, the final value observed or calculated, expressing the result of a test or analysis shall be rounded off in accordance with or calculated expressing the result of a test or analysis, shall be rounded off in accordance with PS: 103 : 1960 "Rules for Rounding Off Numerical Values". The number of places retained in the rounded off value should be the same as those of the specified value in this standard.

0.5 This standard is intended mainly to cover the technical provisions relating to the supply of the material, and it does not cover all the necessary provision of a contract.

1. SCOPE

1.1 This standard provides requirement and methods of test for high analysis multinutrient fertilizers.

2. TERMINOLOGY

2.1 For the purpose of this standard, the following definitions, in addition to the definitions given in PS: 582:1966 "Glossary of Terms used in Fertilizer Industry", shall apply.

2.1.1 ***Straight Fertilizers***. Are fertilizers which are applied to provide one of the three nutrients (i.e. N P and K)

2.1.2 ***Multinutrient Fertilizers***. Are fertilizers which are applied to provide more than one nutrient to plant, and include the following types:

1. Compound Fertilizer
2. Complex Fertilizer
3. Mixed Fertilizer
4. Composite Fertilizer

2.1.3 **Compound Fertilizer**—It is a fertilizer which is applied to provide more than one nutrient to plants and every crystal granule or pellet of the product contains the nutrients in the same proportion as the fertilizer claim to possess. Such fertilizer are definite chemical compounds and should have definite melting points

2.1.4 **Composite Fertilizer**—Composite fertilizer are those multinutrient fertilizer in which more than one fertilizer are mixed together and they may react partially to form a new compound.

2.1.5 **Complex Fertilizer.** are fertilizers in which more than one fertilizer (straight or compound) are mixed together and the nutrient materials present are chemically linked giving grains with a constant proportion of these substances and making separation during transport or storage impossible.

2.1.6 **Mixed Fertilizer**. Are simple mixtures of more than one fertilizer in which interaction does not take place and they may be mixed in different proportions to be defined.

2.1.7 **Fertilizer Grade/Analysis**. refers to the minimum guaranteed percentage of the plant nutrient content in the fertilizer in terms of total nitrogen (N), available phosphorus pentoxide (P_2O_5) and water soluble potassium oxide (K_2O) expressed in that order.

2.1.8 **Fertilizer Ratio**. refers to the ratio or percentage of nitrogen (N) phosphorus pentoxide (P_2O_5) and potassium oxide (K_2O) content in a multinutrient fertilizer (a 20—20—0 grade has a 1—1—0 nutrient ratio).

2.1.9 **Available Phosphate**—It refers to the plant available phosphate soluble in a neutral ammonium citrate solution. (i.e Total (P_2O_5—citrate insoluble P_2O_5).

3. **REQUIREMNETS:**

3.1 **Description**—The material shall be free flowing and the granules, crystals or prills shall be uniform size and at least 80% of the crystals, prills and granules shall pass through 7 mesh and be retained on 18 mesh of P.S. 394: 1964. It shall not contain the following harmful ingredients more than the specified limits as prescribed below:-

Chloride—1.0% NaC1

Fluoride—0.5% F

Sodium Carbonate—0.3% as $NaHCO_3$

Biuret—1.5%

3.2 **Moisture**—The material shall not contain moisture more than 1—0 percent determined by the method described in P.S 217: 1962 “Specification for Urea”.

3.3 ***Total Nutrients***—The material shall contain total nutrients not less than 25 percent of the of the major nutrient i.e N.P. & K as determined by relevant methods given in this specification.

3.4 ***Free Phosphoric acid* (as P_2O_5)**—The material shall not contain free phosphoric acid more than 3.0 percent (as P_2O_5).

3.5 ***Phosphate soluble in water***.—The material shall contain phosphate soluble in water (as P_2O_5) not less than 80% of the total content claimed in compound fertilizers and not less than 50% in the case of multinutrient fertilizers other than compound fertilizers.

3.6 pH Value—The material shall have pH value 7±0.5 as determined by the method prescribed in PS 217: 1962 "Specification for Urea" 'Fertilizer'.

4. PACKING AND MARKING:

4.1 The material shall be packed in suitable bag lined with inner polythene or moisture-proof lining paper.

4.2 Each bag shall be securely closed, and marked with the name of manufacturer, recognized trade mark if any, weight in Kg & name of material and the guaranteed analysis in the form of minimum percentage of nitrogen available $P_2 O_5$ and water soluble K_2O content.

5. SAMPLING:

5.1 The representative samples of the material shall be drawn as described in Appendix "A".

APPENDIX 'A'

SAMPLING OF SOLID FERTILIZERS FROM PACKGES AND PREPARATION OF THE SAMPLE FOR ANALYSIS

A-1 SCOPE:

The method is applicable to the sample of granulated, crystalline or pulverized solid fertilizer materials from packages

A-2 SUMMARY OF METHOD

Representative portions of the fertilizer are selected by means of appropriate sampling devices and in accordance with prescribed sampling rates.

A-3 SCALE OF SAMPLING:

A-3.1 Lot—All the containers in a single consignment of the material drawn from a single batch of manufacture shall constitute the lot. If a consignment is declared to consist of different batches of manufacture, the batches shall be marked separately and the group of containers in each batch shall constitute separate lots.

A-3.2 *Gross Sample*—A number of bags, not less than the sample size indicated in Table I, shall be selected at random from a lot for the purpose of drawing samples for test. These bags shall constitute the gross sample.

TABLE I

MINIMUM NUMBER OF BAGS TO BE SELECTED FOR SAMPLING FROM VARIOUS SIZES OF LOTS

Lot Size	Sample Size
2 to 8	2
9 to 27	3
28 to 64	4
65 to 125	5
126 to 216	6
217 to 343	7
344 to 512	8
513 to 729	9
730 to 1,000	10

A-33 *Sampling Probe*—63-inch length, double tube, slotted. The slot width must be at least three times the diameter of the largest particle to be sampled. The probe or trier, must be constructed with partitions so as to divide it into compartments, each compartment having a length not greater than six inches. A suitable probe, shown in Figure 1, may be obtained under catalog No. 553 from the seedbure Equipment Company, 616 W. Jackson Boulevard, Chicage, Illinonis 60606.

A-4 **PROCEDURE**

A-4.1 *Test Samples from Bags*—Place the number of bags selected for sampling to the Table I in a horizontal position. Insert the closed probe shown in Figure 1 so that it extends into the bag from end to end at a maximum diagonal. Open probe, jab bag slightly to fill, close the probe and withdraw. Take one core of material per bag. The composite sample prepared by mixing the portions from each bag selected for sampling shall be no less than 250 gm (or 0.5 1bs). Reduced samples made out of the composite sample shall constitute the test sample.

A-4.2 *Test Sample*—Three sets of test samples, not less than 50 gm (or 2 oz) each representative of each heap, or wagon or package selected for sampling shall be transferred immediately to thoroughly dried bottles which are sealed air tight with glass stoppers. These shall labeled with all the particulars of sampling. One set of the test samples shall be sent to the purchaser and one to the vendor.

A-4.3 *Referee Sample*—The third set of the samples bearing the seals of the purchaser and the vendor, shall constitute the referee sample, to be used in case of dispute between the purchaser and the vendor, and it shall be kept at a place agreed between the purchaser and the vendor.

A-5 **TEST FOR ACCEPTANCE:**

A-5.1 *Examination and Tests*: The purchaser may examine and test each of the reduced samples constituting a test sample separately for compliance with the requirements of this standard or he may prepare, for the purpose of such examination and at any stage of the whole lot by mixing all the reduced samples constituting the test sample.

A-5.2 *Criterion for Judgment*—When the individual reduced samples in a test sample are separately examined and the results vary from one reduced sample to another, the criterion for judging the quality of the lot for the purpose of acceptance on the basis of the results obtained shall be at the discretion of the purchaser, unless otherwise previously agreed between the purchaser and the vendor.

APPENDIX ‘ B ’

TOTAL NITROGEN

B-0 Total nitrogen in a sample of mixed or complex fertilizer may include amide, ammoniacal and nitrate forms of nitrogen as well as some nitrogen in the organic matter present in mixed fertilizer.

This section includes the following four procedures for nitrogen estimation:-

B-1 Total nitrogen in nitrate free fertilizers.

B-2 Total nitrogen in fertilizers having nitrates.

B-3 Total ammoniacal nitrogen in fertilizers.

B-4 Total nitrogen in fertilizers having only nitrates a nitrate and ammoniacal nitrogen.

B-5 Biuret content of mixed fertilizers.]

Procedures B-3 and B-4 may be used t o determine the percentage of nitrate and ammoniacal nitrogen. A qualitative procedure for detection of nitrates is also included in this section.

B-0.1 Detection of Nitrates:

Mix 5g sample with 25 ml hot H_2O, and filter. To 1 volume of this solution add 2 volumes, H_2O_4 free form HNO_3 and oxides of N, and let it cool. Add few drops concentrated $FeSO_4$ solution in such a manner that fluids do not mix. If nitrates are present junction shows at first purple, afterwards brown, or if only minute quantity is present, reddish color. To another portion of solution add 1 ml 1% $NaNO_3$ solution and test as before to determine whether enough H_2O_4 was added in first test.

B-1 IMPROVED KJELDAHIL METHOD FOR NITROGEN CONTENT OF NITRATE-FREE FERTILIZERS

B-1.1 SCOPE:

This procedure is applicable to the analysis of nitrate-free fertilizers.

B-1.2 Summary:

Nitrogen in the sample is converted to ammonium sulfate by means of the kjeldahi method. Caustic soda is added and the liberated ammonia is distilled into a boric acid solution. The ammonia is titrated with a standard hydrochloric acid solution and the nitrogen content calculated from the data. Nitrogen content is reported in weight percent to the nearest 0.1%.

B-1.3 Apparatus:

(1) Kjeldahl Flask—500-800 m1. Capacity flask of hard moderately thick, well annealed glass.

(2) Digestion Unit—Consisting of heater (gas or electric) a refractory support for the flask and a bracket to hold the neck of the flask titled at an angle from the vertical. The heater should be capable of adjustment such that it can bring 250 m1. Of water in a kjeldahl flask from 25ºC to a rolling boil in five minutes.

(3) Distillation Unit—Use 500-800 m1. Kjeldahl or other suitable flask, with rubber stopper through which passes lower and of efficient scrubber bulb or trap to prevent mechanical carry-over of NaOH during distillation. Connect upper end of bulb tube to condenser tube by rubber tubing. Trap outlet of condenser in such way as to ensure complete absorption NH_3 distilled over into acid in receiver.

B-1.3 Reagents:

Unless otherwise indicated, the purity of all regents in intended to be of reagent grade.

(1) Mercury (or mercuric oxide, HgO)

(2) Potassium Sulfate, Powdered—(or anhydrous sodium sulfate)

(3) Sulfuric Acid—93 to 98% H2SO4, nitrogen free.

(4) Sulfide Solution (or thiosulfate solution).—Dissolve 40 grams of potassium sulfide or sodium sulfide in 1 litre of water (or dissolve 80 g. of sodium thiosulfate $Na_2S_2O_3.5H_2O$ in 1litre of water).

(5) Zinc.—Granular, 20-mesh.

(6) Sodium Hydroxide Solution—Dissolve 450 g of solid, nitrate-free sodium hydroxide in water, cool and finally dilute to 1 litre. The specific gravity of the solution should be 1.36 or higher in order to ensure that it will remain in a lower layer when add without agitation to the diluted sulfuric acid digestion mixture.

(7) Boric Acid Solution—Dissolve 50 g. of boric acid, H_3BO_3, in one litre of boiling water.

(8) Methyl Purple Indicator Solution—Available from most chemical supply companies in solution form.

(9) Standard Hydrochloric Acid Solution, N/10.—Dilute 8.4 ml of reagent grade hydrochloric acid (36.5—38%) to one litre with water and mix well. Standardize the solution against dried, primary standard grade sodium carbonate using methyl purple as the indicator.

B-1.5 Sampling: If the weight of sample as received at the laboratory is greater than one pound, reduce the gross sample to between one-half and one pound, by means of a riffle or quartering. Grind the sample to pass a No. 40 standard sieve (Tyler No. 35 sieve). Grind as rapidly as possible to avoid or gain of moisture during the operation. Mix the ground sample thoroughly and store in tightly stoppered bottles.

B-1.6 Procedure:

Reference to water in the following paragraphs mean distilled or deionized water:-

1. Weigh out 0.5 to 2.2 g. of the sample. Record the weight to the nearest 0.0001 g. The optimum sample weight is one which will require a 40 to 50-ml. titration in step (14).

2. Transfer the weighed sample to a kjeldahl flask. Avoid contacting the sides of the flask neck with the sample.

3. Add 0.65 g. of mercury (or 0.7 g. of mercuric oxide), 15 g. of powdered potassium sulfate (or 15 g. of ahhydrous sodium sulfate) and ml. of sulfuric acid (93-98%) to the flask. If a sample weight greater than 2.2 g. was used, the volume of sulfuric acid introduced should equal 10 ml. fo each gram of sample.

4. Run a blank determination alongwith each batch of samples. Add to another digestion flask the same quantities of mercury (or mercuric oxide), potassium sulfate (or sodium sulfate) and sulfuric acid that were added to the sample flask. Carry the blank through the following steps in exactly the same manner as the sample(s).

5. Place the flask on the heater and support the neck in a inclined position. Heat the flask gently until frothing ceases. A small amount of Paraffin may be added to reduce frothing.

6. Increase the heat and boil the solution briskly until it clears. Continue the boiling for 30 minutes after the solution has cleared (2 hours for samples containing organic matter).
7. Cool the solution and carefully add, with continuous swirling, 200 ml. of water. Cool the solution to 25ºC., or lower.

8. Add 25 ml of the sulfide solution (or thiosulfate solution) and swirl the flask to mix the contents and precipitate the mercury.

9. Measure 25 ml. of boric acid solution into a 300-ml Erlenmeyer flask means of a graduated cylinder and add 5 drops of methyl purple indicator solution.

10. Place the Erlenmeyer flask beneath the condenser of the distillation assembly so that the delivery tip is located below the surface of the acid solution. Tilt the flask to provide a grater depth of boric acid solution and make sure that the delivery tip extends as far as possible into the solution without actually touching the bottom of the flask. Attach the connecting tube and spray trap to the upper end of the condenser.

11. Add a few granules of zinc to the kjeldahl flask to prevent bumping, title the flask and carefully add 55 ml. of sodium hydroxide solution (450 g./1). Do not agitate the flask during the addition. The amount of sodium hydroxide added should be enough to make the solution strongly alkaline, when the solution is mixed in the following step.

12. Immediately connect the digestion flask to the spray trap. Swirl the flask to mix the contents thoroughly. Apply heat to the flask so as to bring the contents t a boil rapidly. Continue the heating until at least 150 ml. of distillate has been collected in the receiver.

13. Lower the receiver flask so that the deliver tip is above the surface of the solution and turn off the heat. Several minutes after turning of the heat, wash of the delivery tip of the condenser into the receiver with distilled water.

14. Titrate the solution in the receiving flask with the standard acid solution to the purple end point. The green color of the indicator fades into gray near the end point, and the end point is reached when the gray just disappears and only purple color remains. Record the volume of standard acid required to titrate the absorber solution.

B-1.7 Calculations:

Calculate the nitrogen content by means of the following equation:

$$C = \frac{(A-B)\times N\times 0.01401\times 100}{W}$$

Where

A is the volume of standard acid required to titrate the sample, in ml.
B is the volume of standard acid required to titrate the blank, in ml.
N is the normality of the Standard acid.
W is the weight of the sample, in g.
C is the concentration of nitrogen in the sample, in % (wt.)

B-1.8 Reporting:

Report the results as

Nitrogen_____% (wt.)

B-2 IMPROVED KJELDAHL METHOD FOR NITROGEN CONTENT OF FERTILIZERS CONTAINING NITRATES

B-2.1 **Scope:**
This method is intended for the determination of nitrogen in fertilizers containing nitrates.

B-2.2 **Summary:**

Nitrogen in the sample is converted to ammonium sulfate by means of the kjeldahl method. Conversion to ammonia of nitrogen present as nitrate is made possible by the inclusion of salicylic acid and sodium thiosulfate in the digestion mixture. Caustic soda is added and the liberated ammonia is distilled into a boric solution. The ammonia is titrated with a standard hydrochloric acid solution and the nitrogen content calculated from the data. Nitrogen concentration is reported in weight per cent to the nearest 0.1%

B-2.3 **Apparatus:**

(1) **Kjeldahl Flask**—500—800 ml capacity flask of hard moderately thick, well annealed glass.

(2) **Digestion Unit**—Consisting of a heater (gas or electric), a refractory support for the flask and a bracket to hold the neck of the flask titled at an angle from the vertical. The heater should be capable of adjustment such that is can bring 250 ml. of water in a kjeldahl flask from 25ºC to a rolling boil in five minutes.

(3) **Distillation Unit**—Use 500-800 ml kjeldahl or other suitable flask, fitted with runner stopper through which passes lower end of efficient scrubber bulb or trap to prevent mechanical carry-over of NaOH during distillation. Connect upper end of bulb tube to condenser tube by rubber tubing. Trap outlet of condenser in such way as to ensure complete absorption of NH_3 distilled over into acid in receiver.

B-2.4 **Reagents:**

Unless otherwise indicated, the purity of all reagents is intended to be of reagent-grade.

(1) Sulfuric Acid—93-98% H_2SO_4 nitrogen-free.

(2) Salicylic Acid—nitrogen-free

(3) Sodium Thiosulfate—crystals, $Na_2S_2O_3.5H_2O$. Zinc powder (dust) may be used in place of sodium thiosulfate, if desired.

(4) Mercury. (or mercuric oxide, Hg O.)

(5) Potassium Sulfate—Powdered (or anhydrous sodium sulfate).

(6) Sulfide Solution.(or thiosulfate solution).—Dissolve 40 g. of potassium sulfide or sodium sulfide in 1 litre of water (or dissolve 80 g. of sodium thiosulfate, $Na_2S_2O_3.5H_2O$in 1 litre of water).

(7) **Zinc**—Granular, 20-mesh.

(8) **Sodium Hydroxide Solution**—Dissolve 450 g. of solid, nitrate-free sodium hydroxide in water, cool and finally dilute to 1 litre. The specific gravity of the solution should be 1.36, or higher in order to ensure that it will remain in a lower layer when added to the diluted sulfuric acid digestion mixture.

(9) **Borci Acid Solution**—Dissolve 50 g. of boric acid, H_3BO_3, in one litre of boiling water.

(10) **Methyl Purple Indicator Solution**—Available from most chemical supply companies in solution form.

(11) **Standard Hydrochloric Acid Solution, N/10**—Dilute 8.4 ml of reagent hydrochloric acid (36.5—58%) to one litre with water and mix well. Standardize the solution against dried, primary standard grade sodium carbonate using methyl purple as the indicator.

B-2.5 **Sampling:**

Reduce the gross sample to a quantity sufficient of analysis, or grind out less than ½ pound of reduced sample without previous sieving. Grind the sample to pass a No 4 standard sieve (Tyler No. 35 sieve). Grind as rapidly as possible to avoid loss or gain of moisture during the operation. Mix the ground sample thoroughly and store in tightly stoppered bottles.

B-2.6 **Procedure:**

References to water in the following paragraphs mean distilled or deionized water:-

(1) Weigh out 0.5 to 2.2 g. of the sample. Record the weight to the nearest 0.0001 g. The optimum sample weight is one which will require a 40- to 50- ml. titration in step (16).

(2) Transfer the weighed sample to a kjeldahl flask, Avoid contacting the sides of the flask neck with the sample.

(3) Add 40 ml of sulfuric acid (93-98% $Na_2S_2O_3.5H_2O$). If desired, 2 g. of zinc dust (net granulated zinc or fillings) may be added in place of the sodium thiosulfate. Shake and let stand for five minutes.

(4) Add 5 g. sodium thiosulfate crystals ($Na_2S_2O_3.5H_2O$). If desired, 2 g. of zinc dust (net granulated zinc or fillings) may be added in place of the sodium thiosulfate. Shake and let stand for five minutes.

(5) Warm the flask over low heat until frothing ceases. Remove from the heat.

(6) Add 0.65 g. of mercury (0r 0.7 g. of mercuric oxide) and 15 g. of powdered potassium sulfate (or 15 g. or anhydrous sodium sulfate).

(7) Run a blank determination along with each batch of samples. Add to another digestion flask the same quantities of reagents that were added to the samples flask. Carry the blank through the following steps in exactly the same manner as the samples(s).

(8) Boil the solution until it clears. Continue the boiling for 30 minutes after the solution has cleared (2 hours for samples containing organic matter).

(9) Cool the solution and carefully add, with continues swirling 200 ml. of water. Cool the solution to 25ºC or lower.

(10) Add 25 ml of the sulfide solution (or thiosulfate solution) and swirl the flask to mix the contents and precipitate the mercury.

(11) Measure 25 ml of boric acid solution into a 300-ml. Erlenmeyer flask by means of a graduated cylinder and add drops of methyl purple indicator solution.

(12) Place the Erlenmeyer flask beneath the condenser of the distillation assembly so that the delivery tip is located below the surface of the acid solution. Tilt the flask to provide a greater depth of boric acid solution and make sure that the delivery tip extends as far as possible into the solution without actually touching the bottom of the flask. Attach the connecting tube and spray trap to the upper end of the condenser.

(13) Add a few granules of zinc to the kjeldahl flask to prevent bumping tilt the flask and carefully add 55 ml. of sodium hydroxide solution (450 g./1). Do not agitate the flask during the addition. The amount of sodium hydroxide added should be enough to make the solution strongly alkaline, when the solution is mixed in the following step.

(14) Immediately connect the digestion flask to the sprat trap. Swirl the flask to mix the contents thoroughly. Apply heat to the flask so as to bring the contents to boil rapidly. Continue the heating until at least 150 ml. of distillate has been collected in the receiver.

(15) Lower the receiving flask so that the delivery tip is above the surface of the solution and turn off the heat. Several minutes after turning off the heat, wash off the delivery tip of the condenser into the receiver with distilled water.

(16) Titrate the solution in the receiving flask with the standard acid solution to the purple end point. The green color of the indicator fades into gray near the end point, and the end point is reached when the gray just disappears and only purple color remains. Record the volume of standard acid required to titrate the absorber solution.

B-2.7 **Calculations:**

$$\% \text{ Nitrogen} = \frac{(A.B)\times N\times 0.01401\times 100}{S.}$$

Where

A is the volume of standard acid required to titrate the sample, in ml.

B is the volume of standard acid required to titrate the sample, in ml.

N is the normality of the standard acid

S is the weight of the sample, in g.

B-2.8 **Reporting:**

Report the result as

Nitrogen----------% (wt.)

B-3 **AMMONICAL NITROGEN IN COMPLEX FERTILIZERS:**

B-3.1 **Scope:**

The procedure is applicable to the determination of nitrogen present or available in solid fertilizers as ammonia or ammonium ion. It is not applicable to samples containing urea. Magnesium ammonium phosphate ($Mg\ NH_4\ PO_4$), or ferrous ammonium phosphate ($Fe\ NH_4\ PO_4$).

B-3.1 **Summary of Method**:

A weighed amount of the sample is steam distilled in the presence of magnesium oxide. Ammonia present as free ammonia or ammonium is driven over into a boric acid solution and the absorbed ammonia is titrated with standard acid. Results are reported as percent ammoniacal nitrogen to the nearest 0.1%.

B-3.3 **Apparatus**

(1) **Kjeldahl Flask**—800-ml. capacity flask of hard moderately thick, well annealed glass.

(2) **Distillation Until**—Consisting of a heater, a connecting tube fitted with a spray trap, and a condenser.

B-3.4 **Reagents:**

(1) Magnesium Oxide (carbonate free)

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(2) Standard Hydrochloric Acid Solution. N/10.—Dilute 8.4 ml. of regent grade hydrochloric acid (36.5—38%) to one litre with water and mix well. Standardize the solution against dried, primary standard grade sodium carbonate using methyl purple as the indicator.

(3) Boric Acid Solution—Dissolve 50 g. of boric acid $H_3 BO_3$, in one litre of boiling water.

(4) Methyl Purple Indicator Solution—available from most chemical supply companies in solution form.

B-3.5 **Procedure:**

(1) Weigh out 0.7 to 3.5 g. of the sample. The optimum sample weight is one which will require a 40 to 50-ml titration. Record the weight to the nearest 0.0001 g. Transfer the sample to the kjeldahl flask and add about 300 ml of distilled water.

(2) Measure 25 ml of boric acid solution into a 300 ml. Erlenmeyer flask by means of a graduated cylinder and add 5 drops of methyl purple indicator solution.

(3) Add 2 g. or more of the carbonate-free magnesium oxide to the kjeldahl flask. Connect immediately to the other end of the condenser tube. Mix the contents by shaking.

(4) Apply heat to the flask so as to bring the contents to a rapid boil. Continue the heating until at least 150 ml. of distillate has been collected in the receiver.

(5) Lower the receiving flask so that the delivery tip is above the surface of the solution and turn off the heat. When cool wash off the delivery tip of the condenser into the receiver with distilled water.

(6) Run a blank with each batch of samples. Add 300 ml of distilled water and 2 g. of magnesium oxide to a kjeldahl flask and follow the same steps that are used with the sample.

(7) Titrate the solution in the receiving flask with the standard acid solution to the purple end point. The green color of the indicator fades to a gray near the end point and the end point is reached when the gray disappears and only the purple color remains. Record the volume of the standard acid required to titrate the absorber solution.

B-3.6 Calculations:

Calculate the ammoniacal nitrogen content by the equation

$$\% \text{ Ammoniacal Nitrogen} = \frac{(A.B)\times N\times 0.0141\times 100}{S}$$

Where

A is the volume of standard acid required to titrate the sample, in ml.

B is the volume of acid required to titrate the blank, in ml.

N is the normality of the standard acid

S is the weight of the sample, in g.

B-3.7 **Reporting:**
Report the results to the nearest 0.1 % as

Ammoniacal Nitrogen----------%

B-4 AMMONIUM AND NITRATE NITROGEN BY DEVARD'S METHOD

B-4.1 **Scope:**
This procedure is applicable to the analysis of fertilizers containing only the two inorganic forms of ammoniacal and nitrate nitrogen. It is not applicable in the presence of organic matter, calcium cynamide and urea.

B-4.2 **Summary :**

Nitrate is reduced to ammonium by nascent hydrogen produced by the action of NaOH upon Zn and A1 (components of Devarda's alloy) and the total ammonium is volatilized as NH_3 into boric acid as in the total nitrogen procedure. The ammonia is titrated with a standard hydrochloric acid solution and the nitrogen content calculated in weight percent to the nearest 0.1%.

B-4.3 **Apparatus:**

(1) Kjeldahal flask, 800 ml. capacity flask of hard moderately thick well annealed glass.
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(2) Distillation Unit

Use 800 ml kjeldahl or other suitable flask, fitted with rubber stopper through which passes lower end of an efficient scrubber bulb or trap to prevent mechanical carry over of NaOH during distillation. Connect upper end of bulb tube by rubber tubing. Trap outlet of condenser in such a way as to ensure complete absorption of NH3 distilled over into acid in a receiver.

B-4.4 Reagents;

(1) **Devarda's Alloy**—Prepare this reagent by ball milling a good quality alloy until the product will pass a 100 mesh screen and at least 75 percent it will pass a 300 mesh screen. Store the finely divided alloy in a tightly stoppered bottle.

(2) **Sodium Hydroxide Solution**—Dissolve 450 g of solid nitrate free sodium hydroxide in water, cool and finally dilute to 1 litre. The specific gravity of the solution should be 1.36, or higher, in order to ensure that it will remain in a lower layer when added to the distillation flask.

(3) **Boric Acid Solution**—Dissolve 50 g. of Boric acid, H_3BO_3 in one litre of boiling water.

(4) **Methyl Purple Indicator Solution**—Available from most chemical companies in solution form.

(5) **Standard Hydrochloric Acid Solution. N/10**—Dilute 8.5 ml. of reagent grade hydrochloric acid (36.5—38 %) to one litre with water and mix well. Standardise the solution against dried, primary standard grade sodium carbonate using methyl purple as the indicator.

B-4.5 Procedure

Reference to water in the following paragraphs mean distilled or deionised water.

(1) Weigh out 0.35 to 0.5 g of the sample. Record the weight to the nearest 0.0001 g. The optimum sample weight is one which will require a 40 to 50 ml. titration in step 8.

(2) Transfer the weighed sample to 800 ml. Kjeldahl flask. Avoid contacting the sides of the flask neck with sample. Add 300 ml. of water.

(3) Measure 25 ml. of boric acid solution into a 300 ml. Urlenmeyer flask by means of a graduated cylinder and add 5 drops of methyl purple indicator solution.

(4) Place the Urlenmeyer flask beneath the condenser of the distillation assembly so that the delivery tip is located below the surface of the acid solution. Tilt the flask to provide greater depth of the boric acid solution and make sure that the delivery tip extends as far as possible into the solution without actually touching the bottom of the flask. Attach the connecting tube and spray trap to the upper end of the condenser.

(5) Add 3 g. fo Devard's alloy and add 55. Ml of sodium hydroxide solution (450 g/1) to the kjeldahl flask containing the fertilizer material and water. Do not agitate the flask during the addition. The amount of sodium hydroxide added should be enough to make the solution strongly alkaline, when the solution is mixed in the following step.

(6) Immediately connect the digestion flask to the spray trap. Swirl the flask to mix the contents thoroughly. Apply heat to the flask so as to bring the contents to boil rapidly. Continue the heating until at least 300 ml. or more of distillate has been collected in the receiver. It is necessary to carry the distillation nearly to dryness to obtain complete reduction of all nitrate.

(7) Run a blank determination along with each batch of samples. Add to another digestion flask the same quantities of reagents that were added to the sample flask. Carry the blank through all the steps in exactly the same manner as the sample(s).

(8) Titrate the solution in the receiving flask with the standard acid solution to the purple end point. The green colour of the indicator fades to a grey near the end point and the end point is reached when the grey disappears and only the purple colour remains. Record the volume of the standard acid required to titrate the absorber solution.

B-4.6 Calculations:

Calculate the nitrogen content (Ammoniacal+Nitrate) of the sample by the equation.

$$\% N = \frac{(A-B)\times N\times 0.0141\times 100}{S}$$

Where

A is the volume of standard acid required to titrate the sample, in ml.
B is the volume of acid required to titrate the blank, in ml.

N is the normality of the standard acid

S is the weight of the sample, in g.

B-4.7 Reporting:

Report the results to the nearest 0.1 % as total N (Ammoniacal+Nitrate nitrogen).

B-5 BIURET CONTENT OF MIXED FERTILIZERS COLORIMETRIC METHOD

B-5.1 Scope:
The method is intended for the determination of the biuret content of mixed fertilizers.

B-5.2 Summary of Method:
A known weight of sample is stirred in a $C0_2$—free distilled water to dissolve the biuret and the solution is filtered. The filtrate is passed through an ion exchange column to remove interference such as ammonium ions. The eluate is then treated with copper sulfate in the presence of alkaline tartrate solution; the biuret in the sample reacts to form a copper complex, the intensity of which is proportional to the biuret content. The color intensity is measured at 550 mu and with the absorbance known, the percent biuret is determined from the calibration curve. Results are reported to the nearest 0.01 weight percent.

B-5.3 Apparatus:

(1) Spectrophotometer—Capable of measuring absorbance at 555 mu, such as the Beckman instrument. Photoelectric colorimeters fitted with a 500—570 millimicron (or 520—580 millimicron) filter are acceptable.

(2) Absorption Cells—Hatched pair 50 mm. light path length.

(3) Water Baths—Capable of maintaining temperatures of 30±5ºC and 50±5ºC.

(4) Filter Paper—Whatman 1 or its equivalent.

B-5.4 Reagents:
Unless otherwise indicated, the purity of the following materials should be of reagent grade:-

(1) CO_2 Free Distilled Water—Prepare by boiling distilled water. Cool prepare fresh daily.

(2) Alkaline Tartrate Solution—Dissolve 40 g. of sodium hydroxide in 500 ml of water, stopper the container and allow to cool, add 50 g. of sodium potassium tartrate ($NaKC_4H406.4H20$), and agitate the solution to dissolve the crystals. Dilute to 1 litre and mix well. Allow the solution to stand one day before use.

(3) Copper Sulfate Solution—Dissolve 15 g of copper sulfate ($CuSO_45H20$), in CO_2—free distilled water and dilute to 1 litre.

(4) Biuret Standard Solution—Dissolve 1 mg./ml. Dissolve 250±1 mg. of biuret in CO_2—free distilled water and dilute to the mark in a 250 ml. volumetric flask.

(5) Methyl Red Indicator—Dissolve 1 g. of methyl red in 200 ml. of ethyl alcohol.

(6) Sulfuric Acid, 0.1N—Add 2.8 ml. of concentrated sulfuric acid to approximately 500 ml. of water in a 1-litre volumetric flask and fill to the mark with additional water. Mix well. Standardization of the solution is not required.

(7) Ion Exchange Resin—Fill a 50 ml. uret with 30 cm. column of Amberlite IR 120 (H) resin on a glass wool plug. (Regenerate the column after each use by passing 100 ml. of H_2SO_4 (1: 9) or HCI (1 : 4) through the column at 5 ml./min. then wash with water until the PH of the effluent is greater than 6. The Amberlin IR 120 (H) resin is available from Rohm and Haas, philadephia, Pennsylvania, or a comparable ion exchange resin may be used.

B-5.5 Calibration:

(1) Pipet separately 2, 10,20,30,40, and 50ml. of the biuret standard solution regant (4) in 100 ml. volumetric flasks. These will contain 2, 10, 20, 30, 40 and 50 mg. biuret, respectively.

(2) Adjust the volume in each flask to about 50 ml. with CO_2—free distilled water.

(3) Add one drop of methyl red into each flask and neutralize with 1 or 2 drops of 0.1N sulfuric acid to a pink color and swirl.

(4) While swirling, pipet into each flask 20 ml. of alkaline tartrate solution, Reagent (2), followed by 20 ml. of copper sulfate solution, Reagent (3).

(5) Fill each flask to the mark with CO_2—free distilled water and shake for 10 second.

(6) Allow the flasks to stand for 15 minutes at 30±5ºC. If the room temperature is not 30±5ºC, place the flasks in a water bath maintained at 30±5ºC.

(7) Prepare a reagent blank, using the same quantities of reagents and conditions but excluding the biuret standard solution.

(8) Fill one of the absorption cells with the regent blank and plight path in the spectrophotometer. Set the wavelength at 555 millimicrons. Adjust the absorbence to zero in accordance with instructions for the particular instrument.

(9) Fill the same cell with one of the calibration standards and determine the absorbance at 555 millimicrons. Record the absorbence reading.

(10) Repeat the absorbence measurement for each of the remaining calibration standards. All measurement should be conducted so that no standard is allowed to stand for more than 30 minutes measured from the time it was placed in the 30ºC bath.

(11) Prepare a calibration curve on rectilinear paper by plotting the absorbence values against the corresponding weights of biuret in the standards in mg.

B-5.6 **Procedure:**

(1) Weigh 10±0.1 g. of the sample under test into a 150 ml. beaker. Dissolve in 50 ml. of the CO_2–free distilled preheated at 50±5ºC.

(2) Stir the solution for 30 minutes and maintain the temperature at 50±5ºC by using a water bath capable of maintaining a temperature of 50±5ºC.

(3) Filter the solution into a 100 ml. volumetric flask using a medium sized filter paper. Rinse the beaker and the stirrer with small portions of CO_2–free distilled water and add the rinsings to the filter. Fill the flask to the mark with CO_2–free distilled water.

(4) Transfer 25 ml. aliquot of the filtrate into the ion exchange column ; adjust the flow to 4—5 ml./minute, collect the eluate in a 100 ml. volumetric flask.

(5) When the liquid level reaches the top of the resin bed, wash with two ml. portions of CO_2–free distilled water, and add the washings to the eluate in the flasks.

(6) Add 1 or 2 drops of methyl red indicator and IN NaOH to a yellow color. Add a few drops of 0.IN N_2SI4 until the solution just turns pin. Fill the flask to the mark CO_2—free distilled water, shake and mix thoroughly.

(7) Pipet 50 ml. of the solution into a 100 ml. volumetric flask and proceed as in CALIBRATION, steps (3) through (8).

(8) Fill the sample cell with the sample under test and determine the absorbence at 555 m/micron.

(9) From the calibration curve, determine the mg. of biuret that corresponds with the absorbence reading.

B-5.7 Calculation:

(1) Calculate the percent of biuret in the sample by the following equation:-

$$B = \frac{W1 \times 100}{W1 \times 1000 \times \frac{25}{100} \times \frac{50}{100}}$$

Simplifying:

$$B = \frac{W1}{W \times 1.25}$$

Where:

W is the weight of the sample in g.

W1 is the biuret content of the sample as read from the calibration curve in mg.

B is the wt percent biuret in the sample. The constant $\frac{25}{100}$ and $\frac{50}{100}$ are Aliquot portions.

B-5.8 Reporting:

Report the result to the nearest 0.01 % as :

Biuert Content _____%

APPENDIX 'C'

C.0 PHOSPHORUS CONTENT OF FERTILIZERS:

Available Phosphorus in fertilizers (mixed or compound) refers to the plant available phosphorus which includes both water soluble and citrate soluble forms.

This section includes the following test procedures:-

C1—Total Phosphorus content of fertilizers

C2—Water soluble Phosphorus content of fertilizers

C3—Citrate insoluble Phosphorus content of the fertilizers.

Test procedures C1 and C3 may be used to determine citrate soluble (Total Phosphorus 3/M citrate insoluble phosphorus) phosphorus content of the fertilizers.

C-1 PHOSPHORUS (TOTAL CONTENT OF FERTILIZERS)

C-1.1 Scope:

The procedure are applicable to phosphorus-containing fertilizers such as the superphosphates, mixed fertilizers, nitrophos and ammophos complexes and fertilizer raw materials. The spectrophotometric alternative is not applicable to materials yielding colored solutions or solutions containing ions other than orthophosphate which from colored complexes with molybdovanadate and is not recommended for basic slag. The volumetric method may be used in all cases.

C-1.2 Summary of Method:-

The sample is dissolved in acid and the phosphorus content of the solution determined by either a volumetric or spectrophotometric method. The volumetric option involves precipitation of the phosphate with molybdate solution, removal of the precipitate by filtration, dissolution of the precipitate in an excess of standard alkali solution and titration of the excess alkali with standard acid. In the spectrophotometric alternative the sample solution is reacted with molybdovanadate reagent and the absorbance of the resulting product measured in a spectrophotometric and the phosphorus content is reported as percent $P_2 0_5$ to the nearest 0.01%.

C-1.3 Apparatus:

(1) Agitator—A machine capable of shaking Erlenmeyer flasks such as a wrist-type shaker or any device capable of stirring the contents of a beaker, such as magnetic stirrer, may be used.

(2) Sintered Crucibles—Porcelain, 30 ml. capacity, fine porosity. Alternatively, 2.5ml Gooch crucibles prepared to retain fine precipitates may be used.

C-1.4 Reagents:

Reference to water in this and the following sections shall be understood to mean distilled water, or water of equivalent purity:

(1) Molybdate Solutions—Dissolve 100 g. of molydbic anhydrides (Mo03) in a mixture of 144 ml. of concentrated ammonium hydroxide and 271 ml. of water. Cool and pour the solution slowly, with constant stirring into a cool mixture of 489 ml. of concentrated nitric acid and 1148 ml. of water. Keep the final mixture in a warm place for several days until a portion heated to 40ºC deposit no yellow precipitate. Decant the solution from any sediment and store in glass stoppered containers. To each 100 ml of molybdate solution required for a batch of determinations add 5 ml of concentrated nitric and filter immediately before using.

(2) Standard Alkali Solution—Dilute 324.0 ml of carbonate-free IN sodium (or potassium) hydroxide solution to 1 liter. 50 ml. of this solution should neutralize 16.20 ml of 1.000 N acid solution. Adjust the solution if necessary, to this exact concentration. One ml. of the standard alkali solution equals 1 mg of or $P_2 0_5$ or 1% $P_2 0_5$ on the basis of 0.1 g. sample.

(3) Standard Acid Solution—Prepare a solution of hydrochloric or nitric acid corresponding in concentration to the standard alkali solution. Standardize the acid solution against the standard alkali solution using phenolphthalein as the indicator.

(4) Nitric Acid, Concentrated (67-71%).

(5) Hydrochloric Acid, Concentrated (36-38%).

(6) Perchloric Acid, (70-72%).

(7) Ammonium Hydroxide, Concentrated (28-30%).

(8) Ammonium Nitrate Solution—Dissolve 100 g. of phosphorus-free ammonium nitrate in water and dilute to 1 liter.

(9) Nitric Acid Dilute—Add 1 volume of concentrated nitric acid to 3 volumes of water and mix well.

(10) Methyl Red Indicator Solution—Dissolve 0.1 g. of methyl red in 60 ml of alcohol 95% ethyl alcohol, or ethyl alcohol that has been denatured with methyl alcohol.

(11) Phenolphthalein Indicator Solution—Dissolve 1 g. of phenolphthalein in 100 ml of alcohol (95% ethyl alcohol, or ethyl alcohol that has been denatured with methyl alcohol.

C-1.5 Preparation of Sample Solution:

Reference to water in this and the following sections shall be understood to mean distilled water, or water of equivalent purity:-

(1) Weigh ±0.1 g. of a uniform, representative portion of the sample into a 250 ml beaker. Record the weigh to the nearest 0.0001 g. as S.

(2) Dissolve the sample in accordance with the appropriate method below, depending upon the nature of the sample.

(a) ***Suitable for sample containing small quantities of organic matter***—Add 30 ml of concentrated nitric acid and 3-5 ml of concentrated hydrochloric acid to the beaker. Place a cover glass on the beaker and boil until any organic matter present is destroyed.

(b) ***Suitable for fertilizer containing much iron or aluminum phosphate and for basic slag***—Add 15-30 ml. of concentrated hydrochloric acid and 3-10 ml. of concentrated nitric acid to the sample beaker. Cover the beaker with a cover glass and boil until solution is complete.

(c) ***Suitable for all fertilizers***—Before using this technique read, and become thoroughly familiar with, the PRECAUTIONS section at the end of the method.

Transfer the weighed sample quantitatively to an Erlenmeyer flask (or kjeldahl flask preferably for samples containing large quantities of organic matter). Add 20-30 ml. of concentrated nitric acid and boil gently for 30-45 minutes to oxidize all easily oxidizable matter. Cool the flask and add 10-20 ml of 70-72% per chloric acid. Boil very gently until the solution is colorless, or nearly so, and dense white fumes appear in the flask. DANGER : Do not boil to dryness at any time. With samples containing large quantities of organic matter, the temperature should be raised to the fuming point (about 170 ºF) over a period of at least one hour. Cool slightly, add 50 ml. of water and boil for a few minutes.

(3) Cool the sample solution and transfer it quantitatively to a 200 ml. volumetric flask. Record this volume (200 ml.) as C. Dilute the solution to the mark, mix well and filter through a dry, quantitative filter paper. Collect the filtrate in a clean flask and stopper until ready for use.

C-1.6 Procedure:

(1) Pipet into a beaker or flask an aliquot of the sample solution corresponding to 0.4 g of sample if the P_2O_5 content of the sample is less than 5 %, 0.2 g. of sample if the P_2O_5 content is 5-20% or 0.1 g. of sample if the P_2O_5 or content is greater than 20%. Record the volume of the aliquot used and identify it as E.

(2) Add 7 m, of concentrated nitric acid (or 65 ml of ammonium nitrate solution). Add concentrated ammonium hydroxide until the precipitate that forms dissolves only slowly on vigorous stirring. If the sample solution does not give a precipitate with the ammonium hydroxide, make the solution slightly alkaline to limits paper with the ammonium hydroxide and then slightly acid with dilute nitric acid.

(3) Dilute the solution to 75-100 ml. and adjust the temperature to 25-30 ºC.

(4) Add to the neutralized solution 20-25 ml. of the molybdate solution if the $P_2 0_5$ content of the sample is less than 5 %, 30.35 ml. If the $P_2 0_5$ content is between 5 and 20% and enough molybdate solution to ensure complete precipitation for $P_2 0_5$ content greater than 20%.

(5) Place the solution in the shaking or stirring apparatus and agitate for 30 minutes at room temperature.

(6) Decent the supernatant liquid at once through a filter crucible. Wash the precipitate remaining in the vessel twice by adding 25-30 ml. portions of water, agitating thoroughly, allowing the precipitate to settle and decanting the wash into the filter crucible. Finally, transfer the precipitate to the filter and wash with cold water until the filtrate from two fillings of the crucible shows no acid reaction on the adding of two drops of methyl red solution.

(7) Transfer the crucible to a beaker and add sufficient standard alkali solution from a buret to dissolve the precipitate, avoiding an excess of more than 3 ml. Record the volume of alkali solution to the nearest 0.01 ml. agitate the beaker to dissolve all remaining particles of the precipitate.

(8) Dilute to 150 ml with water, add two drops of phenolphthalein indicator solution and titrate with the standard acid solution to the disappearance of the pink color. Record the volume of standard acid solution required to the nearest 0.01 ml.

C-1.7 Calculation:

(1) Calculate the phosphours content (as $P_2 0_5$) by the equation.

$$\% P_2 0_5 = \frac{A—B \times C \times 100}{S \times D \times 1000}$$

Where

A is the volume of standard alkali solution used dissolve the precipitate, in ml.

B is the volume of standard acid solution required to titrate the excess alkali solution, in ml.

C is the amount of sample weighed out under PREPARATION OF SAMPLE SOLUTION, in g.

D is the volume of the aliquot of sample solution taken in PROCEDURE, step (1) in ml.

B. SPECTROPHOTOMETRIC METHOD

C-1.8 Apparatus:

(1) **Spectrophotometer**—with matched pair of absorption cells. The light path length of the cells should be 1 cm. preferably, although cells up to 1.3 cm. in light path length may be used.

C-1.9 Reagents:

(1) ***Standard Phosphate Solution***—Dry several grams of potassium hydrogen phosphate (KH_2PO_4), primary standard grade, in an air oven at 105ºC. for two hours. Remove from

the oven and allow to cool in a desiccators, accurately weigh 1.5340 g. of the dried potassium hydrogen phosphate and dissolve in water. Transfer the solution to a 200 ml. volumetric flask and dilute to the reference mark with additional water. Stopper and mix well.

(2) ***Molybdornadate Solution***—Dissolve 40 g. of ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}$. $4H_2O$), in 400 ml. of hot water and allow to cool. Dissolve 2 g. of ammonium vanadate, NH_4VO_3, in 250 ml. of hot water, cool and add 450 ml. of 70% perchloric acid. Gradually add the molybdate solution to the vanadate solution with constant stiring. Dilute the final solution to 2 litres with water and mix well.

C-1.10 Calibration:

(1) Prepare a series of calibration solution by measuring into 100-ml volumetric flasks the volumes of standard phosphate solution, REAGENTS, (1), indicated in the table below. Measure the volumes carefully with a burette.

CALIBRATION

Calibration Solution	Concentration, mg. P_2O_5/ml.	Volume of Standard phosphate Solution, ml.
A	0.4	10.00
B	0.5	12.50
C	0.6	15.00
D	0.7	17.50
E	0.8	20.00
F	0.9	22.50
G	1.0	25.00

Dilute each solution to the reference mark with water and mix well.

(2) Pipet into 100-ml volumetric flasks 5-ml. aliquots of the seven calibration solutions. These flasks will contain 2,2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 mg P_2O_5. To each flask add 45 ml. of water, and within five minutes for the entire series, add 20 ml. of molybdovanadate solution by pipes, dilute to the mark with water and mix. Allow the solution to stand for 10 minutes.

(3) Fill the two absorption cells with the solution containing 2 mg P_2O_5. Set the spectrophotometer to 400 mμ and adjust to zero absorbance with one of the cells in the reference position. Move the other cell into the light path. If a negative absorbance is obtained, reverse the position of the cells and readjust to zero absorbance with the new cell in the light Path. Identify this cell permanently as the reference cell. If the absorbance of the sample cell is greater than 0.001, record it as the correction factor and correct all subsequent absorbance readings by subtracting this factor.

(4) Determine the absorbance of the other solution (2.5 through 5.0 mg. P_2O_5 retaining the 2-mg solution in the reference cell at zero absorbance. After each determination empty and refill the reference cell with fresh portions of the 2-mg solution to avoid any error that might arise from temperature changes.

(5) Prepare a calibration curve by plotting the observed absorbance values (corrected if necessary) against the respective quantities of P_2O_5 in the solutions prepared in step (2) i.e 2.0 through 5.0 mg. P_2O_5. When the calibration work has been completed, discard the seven calibration solutions (A-G). Do not attempt to use these solutions at a later date. The standard phosphate solutions, REAGENTS (1), may be retained.

C-1.11 ***Preparation of Sample Solution:***

(1) Weight 1±0.1 g. of uniform representative portion of the sample into a 250-ml. beaker. Record the weight to the nearest 0.0001 g.

(2) Dissolve the sample in accordance with step (2) of PREPARATION OF SAMPLE SOLUTION section under the VOLUMETRIC METHOD alternative.

(3) Cool the sample solution and transfer it quantitatively to a volumetric flask. If the P_2O_5 content is less than 5% use a 250-ml volumetric flask. If the P_2O_5 content is greater than 5% dilute to such volumetric that a 5- or 10-ml. aliquot will contain 2—5 mg. P_2O_5. Record the volume of the volumetric flask as V_1. Dilute the solution to the mark of the volumetric flask, mix well and filter through a dry quantitative filter paper. Collect the filtrate in a clean flask and stopper until ready for use.

C-1.12 ***Procedure***

(1) Prepare fresh calibration solutions A and D by measuring accurately from a buret 10.00 ml. and 17.50 ml. of the standard phosphate solution into 100-ml. volumetric flask. Dilute each aliquot to the reference mark with water and mix well

(2) Pipet into 100-ml volumetric flasks 5 ml. of the freshly prepared calibration solution A. Label the flask "2 mg. P_2O_5". Pipet into another 100-ml. volumetric flask 5 ml. of the freshly prepared calibration solution D and label the flask "3.5 mg. P_2O_5". Develop the color as under CALIBRATION step (2), starting with the addition of 45 ml. of water. Fill the reference cell with the "2 mg. P_2O_5" standard and adjust the instrument to zero absorbance at 400 m/µ. Determine the absorbance of "3.5 mg. P_2O_5" standard. The absorbance this standard should be practically identical with the corresponding value on the calibration curve.

(3) Pipet a 5- or 10-ml. aliquot of the sample solution from step (3) under PREPARATION OF SAMPLE SOLUTION into a 100-ml. volumetric flask. Record the volume of the aliquot used as V_2. Develop the color and determine the absorbance in the same manner as in step (2).

(4) Read, and record as W, the P_2O_5 content of the sample aliquot from the calibration curve.

C-1.13 Calibration:

(1) Determine the weight of sample represented by the aliquot used for the absorbance measurement by the equation.

$$S_A = S \times \frac{V_2}{V_1} =$$

Where

S is the weight of sample taken for analysis in g.

V_1 is the volume, in ml. to which the sample solution was diluted in step (3) of the PREPARTION OF SAMPLE SOLTUION section.

V_2 is the volume of the aliquot taken for the color development step (3) of PROCEDURE.

S_A is the weight of sample in the aliquot used for the absorbance measurement in mg.

(2) Calculate the total phosphorus content (as P_2O_5) by the equation.

$$\% P_2O_5 = \frac{W}{S_A} \times 100$$

Where

W is the weight of P_2O_5 in the sample aliquot, POROCEDURE step (4) in mg.

C-1.14 Reporting :

Report the result from the volumetric or the spectrophotometric determination as:

Phosphorus, Total (as P_2O_5)----------% P_2O_5 (1)

Indicate in the report which alternative was used to determine the total phosphours.

C-1.15 Precautions:

Contact of perhloric acid solution with oxidizable combustible materials or with dehydrating or Reducing agents may result in fire or explosion. Persons using this acid should be thoroughly familiar with its hazards, and safety practice should include the following:

(a) Remove spilled perchloric acid by immediate and thorough washing large quantities of water.

(b) Hoods and ducts for perchloric acid vapor should be made of chemically inert materials and so design that they can be thoroughly washed with water. The exhaust system should discharge in a safe location, and the fan should be accessible for cleaning.

(c) Avoid use of organic chemicals in hoods employed for perchloric acid digestions.

(d) Use goggles barrier shields, and other devices as may be necessary for personnel protection.

(e) In wet combustions with perchloric acid, treat the sample first with citric acid to destroy easily oxidizable organic matter.

(f) Contact of perchloric acid solution with strong dehydrating agents such as phosphorus pentoxide or concentrated sulfuric acid may result in formation of explosive anhydrous perchloric acid. Exercise special care in performing analysis requiring the use of perchloric acid with such agents.

C-2 PHOSPHORUS (WATER-SOLUBLE) CONTENT OF FERTILIZERS.

C-2.1 Scope

The procedure is applicable to phosphorus—containing fertilizers such the superphosphates, mixed fertilizers, nitrophos and ammophos complexes and fertilizer raw materials. The spectrophotometric alternative is not applicable to materials yielding colored water extracts or water extracts containing ions other than orthophosphate which from colored complexes with molybdovanadate, and is not recommended for basic slag. The volumetric alternative may be used in all cases.

C-2.2 Summary of Method:

A water extract of the sample is analyzed for phosphate content by either a volumetric or spectrohoametric method. The volumetric option involves precipitation of the phosphate with molydbate solution, removal of the precipitate by filtration, dissolution of the precipitate in an excess of standard alkali solution and titration of the excess alkali with standard acid. In the spectrophotometic alternative the sample solution is reacted with molybdovanadate reagent and the absorbance of the resulting product measured in a spectrophotometer. The phosphours content is reported percent P_2O_5 to the nearest 0.01%.

C-2.3 Preparation of Sample Solution:

Reference to water in this and the following sections shall be understood to mean distilled water, or water of equivalent purity:-

(1) Weigh 1± 0.1 g of a uniform, representative portions of the sample on a tared watch glass. Record the weight to the nearest 0.0001 g. as S.

(2) Transfer the sample quantitatively to a folded. 9-cm, quantitative, filter paper placed in a conical funnel. Wash the sample in the paper with small portions of room-temperature water, collecting the filtrate in a 250-ml volumetric flask. Allow each portions to pass through the filter completely before adding another portion. Continue the washing until the filtrate volume is approximately 240 ml. Use section if it be comes apparent that washing will not be complete within one hour. If the filtrate is turbid, add 1-2 ml of concentrated nitric acid. Dilute the solution to the mark with water and mix thoroughly. Record the volume of the solution as V_1.

(3) Determine the phosphate content of the water extract by one of the following procedures. If the water extract is colored, or contains ions other than orthophosphate that will form colored complexes with molybdovanadate, the volumetric method must be used

C-2.4 A. VOLUMETRIC METHOD:

C-2.5 Apparatus:

(1) ***Agitator***—A machine capable of shaking Erlenmeyer flask such as the wrist-type shaker or any device capable of stirring the contents of a beaker, such as a magnetic stirrer, may be used.

(2) ***Stinered Crucible***—Porcelain, 30-ml capacity, fine porosity. (Maximum pore radius, 3). Alternatively, 25-ml. Gooch crucible prepared to retain fine precipitates may be used.

C-2.6 Reagents:

(1) ***Molybdate Solution***—Dissolve 100 g of molybdic anhydride (MoO_3) in a mixture of 144 ml. of concentrated ammonium hydroxide and 271 ml of water. Cool and pour the solution slowly with constant stirring into a cool mixture of 489 ml. of concentrated nitric acid and 1148 ml. of water. Keep the final mixture in a warm place for several days or until a portion heated to 40 ºC deposits no yellow precipitate. Decant the solution from any sediment and store in glass stoppered containers. To each 100 ml of molybdate solution required for a a batch of determinations add 5 ml of concentrated nitric acid and filter immediately before using.

(2) ***Standard Alkali Solution***—Dilute 324.0 ml of carbonate-free IN sodium (or potassium) hydroxide solution to 1 litre. Fifty ml. of this solution should neutralize 16.20 ml. of IN acid solution. Adjust the solution, if necessary to this exact concentration. One ml. of the standard alkali solution equals 1 mg of $P_2 0_5$ or 1% $P_2 0_5$ on the basis of 0.1 g. of sample.

(3) ***Standard Acid Solution***—Prepare a solution of hydrochloric or nitric acid corresponding in concentration to the standard alkali solution. Standardize the acid solution against the standard alkali solution using phenolphthalein as the indicator. Adjust the solution, if necessary, so that 20.00 ml. of the acid is equivalent to 20.00±0.02 ml of the standard.

(4) ***Nitric Acid, reagent grade***—69-71%.

(5) ***Ammonium Nitrate Solution***—Dissolve 100 g. of phosphorus free ammonium nitrate in water and dilute to 1 litre.

(6) ***Ammonium Hydroxide, reagent grade***—28-30%.

(7) ***Methyl Red Indicator Solution***—Dissolve 0.1g. methyl red in 50 ml of alcohol (95% methyl alcohol, or ethyl alcohol that has been denatured with methyl alcohol). Dilute to 100 ml with water and mix well.

(8) ***Phenolphthalein Indicator Solution***—Dissolve 1 g. or phenolphthalein in 100 ml. of alcohol (95% ethyl alcohol, or ethyl alcohol that has been denatured with methyl alcohol).

C-2.7 Procedure:

(1) From the sample solution obtained in PREPARATION OF SAMPLE SOLUTION step, (2) pipet an aliquot that will contain 20-40 mg. of P_2O_5 into a beaker or flask, record the volume of the aliquot as V_2.

(2) Add 10 ml. of concentrated nitric acid (or 65 ml. of ammonium nitrate solution to the sample aliquot. Carefully add concentrated ammonium hydroxide until the precipitate that forms dissolves only slowly on vigorous stirring.

(3) Dilute the solution to 75-100 ml. and adjust the temperature to 25-30 C. If the sample solution does not give precipitate with the ammonium hydroxide in step (2) make the solution slightly alkaline to litmus paper with the ammonium hydroxide and then slightly acid with dilute nitric acid.

(4) Add the neutralized solution 20-30ml of the molybdate solution. Allow the precipitate to settle momentarily and test for completeness of precipitation by adding 1 ml of molybdate solution to the clear, supernatant liquid. If a precipitate forms, continue to add molybdate solution until precipitation is complete. Place the solution in the shaking or stirring apparatus agitate for 30 minutes at room temperature.

(5) Decant the supernatant liquid at once through a filter crucible. Wash the precipitate remaining in the vessel twice by adding 25 to 30 ml portions of water, agitating thoroughly, allowing the precipitate to settle, and decanting the wash water into filter crucible. Finally, transfer the precipitate to the filter and wash with boiled water, until the filtrate from two fillings of the crucible shows no acid reaction on the addition of two drops of methyl red indicator.

(6) Transfer the crucible to a beaker and add sufficient standard alkali solution form a buret to dissolve the precipitate, avoiding an excess of more than 3 ml. Record the volume of alkali solution to the nearest 0.01 ml. Agitate the beaker to dissolve all remaining particles of the precipitate.

(7) Dilute to 150 ml with water, add two drops of phenolphthalein solution and titrate with the standard acid solution to the disappearance of the pink color. Record the volume of standard acid solution required to the nearest 0.01 ml.

C-2.8 Calculation:

Calculate the concentration of water-soluble phosphorus in the sample as:

$$\% P_2O_5 = \frac{(A-B) \times V_1 \times 100}{S \times V_2 \times 1000}$$

A is the volume of standard alkali solution used to dissolve the precipitate, in ml.

B is the volume of standard acid solution required to titrate the excess alkali solution in ml.

V_1 is the volume of the sample solution from PREPARATION OF SAMPLE SOLUTION, step (2) in ml.

S is the weight of sample, PREPARATION OF SAMPLE SOLTUION, step (1) in g.

V_2 is the volume of the aliquot of sample solution taken in PROCEDURE, step (1) in ml.

B. SPECTROPHOTOMETRIC METHOD

C-2.9 Apparatus:

(1) ***Spectrophotometer***—with matched pair of absorption cells. The light path of the cells should be 1 cm. preferably, although cells up to 1.3 cm. in light path length may be used.

C-2.10 Reagents:

(1) ***Standard Phosphate Solution***—Dry several grams of potassium hydrogen phosphate, KH_2PO_4), primary standard grade, in an air oven at 105ºC. for two hours. Remove from the oven and allow to cool in a desiccators. Accurately weigh 1.5340 g. of the dried potassium hydrogen phosphate and dissolve in water. Transfer the solution to a 200-ml volumetric flask and dilute to the reference mark with addition water Stopper and mix well.

(2) ***Molybdovanadate Solution***—Dissolve 40 g. of ammonium molybdate tetrahydrate, $(NH_4)_6 MO_7O_{24}\ 4H_2O$, in 400 ml. of hot water and allow to cool. Dissolve 2 g of ammonium vanadate $NH_4\ VO_3$ in 250 ml. of hot water, cool and add 250 ml. of 70% perchloric acid. Gradually add the molybdate solution to the vanadate solution with constant stirring dilute the final silution to 2 liters with water and mix well.

C-2.11 Calibration

(1) Prepare a series of calibration solutions by measuring into 100 ml. volumetric flasks the volumes of standard phosphate solution REAGENTS, (1) indicated in the table below: Measure the volumes carefully with a buret.

Calibration Solution	Concentration mg. P_20_5 /ml.	Volumes of Standard Phosphate Solution ml.
A	0.4	10.00
B	0.5	12.50
C	0.6	15.00
D	0.7	17.50
E	0.8	20.00
F	0.9	22.50
G	1.0	25.00

Dilute each solution to the reference mark with water and mix well.

(2) Pipet into 100 ml. volumetric flaks 5 ml aliquots of the seven calibration solutions. These flasks will contain 2, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 mg. P_20_5. To each flask add 45 ml. of water and within five minutes for the entire series, add 20 ml. of molybdovanadate solution by pipet, dilute to the marks with water and mix. Allow the solutions to stand for ten minutes.

(3) Fill the absorption cells with the solution containing 2 mg P_20_5. Set the spectrophotometer to 400 mμ and adjust to zero absorbance with one of the cells in the reference position. Move the other cell into the light path. If a negative absorbance is obtained, reverse the position of the cells and readjust to zero absorbance with the new cell in the light Path. Identify this cell permanently as the reference cell. If the absorbance of the sample cell is greater than 0.001, record it as the correction factor and correct all subsequent absorbance readings by subtracting this factor.

(4) Determine the absorbance of the other solution (2.5 through 5.0 mg. P_20_5 retaining the 2-mg solution in the reference cell at zero absorbance. After each determination empty and refill the reference cell with fresh portions of the 2-mg solution to avoid any error that might arise from temperature changes.

(5) Prepare a calibration curve by plotting the observed absorbance values (corrected if necessary) against the respective quantities of P_20_5 in the solutions prepared in step (2) i.e 2.0 through 5.0 mg. P_20_5. When the calibration work has been completed, discard the seven calibration solutions (A-G). Do not attempt to use these solutions at a later date. The standard phosphate solutions, REAGENTS (1), may be retained.

C-2.12 Procedure:

(1) Prepare fresh calibration solutions A and D by measuring accurately from a buret 10.00 ml. and 17.50 ml. of the standard phosphate solution into 100-ml. volumetric flask. Dilute each aliquot to the reference mark with water and mix well.

(2) Pipet into 100-ml volumetric flasks 5 ml. of the freshly prepared calibration solution A. Label the flask "2 mg. P_2O_5". Pipet into another 100-ml. volumetric flask 5 ml. of the freshly prepared calibration solution D amd label the flask "3.5 mg. P_2O_5". Develop the color as under CALIBRATION step (2), starting with the addition of 45 ml. of water. Fill the reference cell with the "2 mg. P_2O_5" standard and adjust the instrument to zero absorbance at 400 m/μ. Determine the absorbance of "3.5 mg. P_2O_5" standard. The absorbance this standard should be practically identical with the corresponding value on the calibration curve.

(3) If the sample solution from step (2) of PREPARATION OF SAMPLE SOLUTION contain more than 5 mg of P_2O_5 in 5 ml. of solution it will be necessary to dilute the solution. Pipet a 10-or 25 ml. aliquot of the sample solution into a volumetric flask of such volume that 5 or 10 ml of the diluted solution will contain 2—5 mg. of P_2O_5. Record the volume of the aliquot used for the dilution as V_3 and the volume of the diluted solution as V_4.

(4) If a 10-ml. aliquot of the sample solution from PREPARATION OF SAMPLE SOLUTION step (2) contain less than 2 mg of P_2O_5 discard the solution and repeat the preparation of the sample solution with a larger weight of sample.

(5) Pipet a 5- or 10-ml. aliquot of the sample solution from step (3) under PREPARATION OF SAMPLE SOLUTION step (2) or PROCEDURE, step (3) or step (4) into 100 ml volumetric flask. Record the volume of the aliquot as V_2. Add 45 ml of water and, within five minutes, add 20 ml of molybdovanadate solution from a pipet. Dilute to the mark with water and mix. Allow the solution to stand for ten minutes.

(6) Fill the reference absorption cells with a fresh portion of the " 2 mg. P_2O_5". Solution and adjust the spectrophotometer, if necessary to zero absorbance. Fill the sample cell with the reacted sample solution from step (5) and determine its absorbance at 400 m/ micron.

(7) Read, and record as W, the P_2O_5 content of the sample aliquot from the calibration curve.

C-2.13 Calculation:

(1) Determine the weight of sample represented by the aliquot used for the absorbance measurement by the equation.

$$S_A = S \times 1000 \frac{V_2 \times V_3}{V_1 \times V_4}$$

Where

S is the weight of sample taken for analysis in g.

V_1 is the volume, in ml. to which the sample solution was diluted in step (3) of the PREPARTION OF SAMPLE SOLTUION, step (2) in ml.

V_2 is the volume of the aliquot taken for the color development step (3) of PROCEDURE.

S_A is the weight of sample in the aliquot used for the absorbance measurement in mg.

Omit terms V_3 and V_4 from the calculation if no dilution of the sample solution was required.

(2) Calculate the concentration of water—soluble P_2O_5 in the sample as:

$$\% \text{ Water—Soluble Phosphorus (as } P_2O_5) = \frac{W \times 100}{S_A}$$

Where

W is the weight of P_2O_5 in the aliquot taken for the absorbance measurement in POROCEDURE step (7) in mg.

C-2.14 Reporting :

Report the concentration of water—soluble phosphorus (as P_2O_5) as:

Water—Soluble Phosphorus (AM—S 600.46)--------(as P_2O_5)

Indicate in the report which alternative procedure was used to obtain the result.

C-3 CITRATE—INSOLUBLE P_2O_5 AND AVAILABLE P_2O_5 IN FERTILIZER

C-3.1 Scope

The procedure is applicable to phosphorus—containing fertilizers such as the superphosphates, mixed fertilizers, nitrophos complexes and fertilizer raw materials. The spectrophotometric alternative is not applicable to materials yielding colored solutions or solutions containing ions other than orthophosphate which from colored complexes with molybdovanadate, nor is it recommended for basic slag. The volumetric alternative may be used in all cases.

C-3.2 Summary of Method

A sample of the fertilizer is successively extracted with water and ammonium citrate solution. The latter extraction is carried out under prolonged agitation at an elevated temperature. After filtration and ignition, the residue is dissolved and the solution is analyzed for P_2O_5 content by either a spectrophotometric or volumetric method. In the spectrophotometric alternative the sample solution is reacted with molybdovanadate regent and the absorbance of the resulting product measured in a spectrophotometer. The volumetric option involves precipitation of the phosphate with molybdate solution, removal of the precipitate by filtration, dissolution of the precipitate in an excess of standard alkali and titration of the excess alkali with standard acid. The percent citrate insoluble P_2O_5 is calculated and reported as percent of the original sample.

Available P_2O_5 is calculated as the difference between the % citrate-insoluble P_2O_5 and the % total P_2O_5 (C-1) and reported as percent of the original sample.

C-3.3 Apparatus

(1) ***Shaking Machine***—capable of shaking 250-ml. volumetric flasks while maintaining them at a temperature of 65±2ºC. for two hours. A wrist-type shaker positioned so that one arm enters an opening in the side of an air oven that is held 35ºC. is a suggested arrangement.

C-3.4 Reagents

Reference to water in this and the following sections shall be understood to mean distilled water, or water of equivalent purity:-

(1) ***Ammonium Citrate Solution***—Dissolve 37 g. of crystallized citric acid in 1½ litres of water and nearly neutralize by adding 345 ml of concentrated ammonium hydroxide (28-29 % NH_3). If the concentration of ammonia is less than 28 add a correspondingly larger volume and dissolve the citric acid in a correspondingly smaller volume of water. Cool and adjust the pH of the solution to 7.0 by adding, carefully, small portions of ammonium hydroxide. Mix thoroughly and measure the neutrality of the solution if necessary to specific gravity 1.09 at 20ºC. The volume should be about 2 litres. Store the solution in tightly stoppered bottles and check pH from time to time.

C-3.5 Preparation of Sample Solution

(1) Weigh 1±0.1 g. of a uniform, representative portion of the sample on a tared watch glass. Record the weight to the nearest 0.0001 g. as S.

(2) Transfer the sample quantitatively to a 9 cm. folded filter paper in a funnel and wash with successive small portions of water until the volume of filtrate is about 225 ml. Allow each portion of wash water to pass through the filter before adding more water. Use suction if after 30 minutes. It is obvious, that the filtration cannot be completed in one hour.

(3) With one hour transfer the filter paper containing the water-insoluble residue to a 250-ml. volumetric flask and add 100-ml of ammonium citrate solution previously heated to 65ºC. Close the flask with a smooth rubber stopper, shake vigorously to disintegrate the paper. Relieve the pressure by removing the stopper momentarily. Replace the stopper tightly and clamp the flask in the shaking machine. Shake the flask for one hour while maintaining its temperature at 65ºC. in the oven. Shaking should be vigorous enough so that the sample is dispersed throughout the solution and so that all of the interior of the flask and the underside of the stopper are continually in contact with the solution.

(4) At the end of the 1 hour agitation, remove the flasks from the shaker and filter the contents immediately by suction as rapidly as possible on a dry, quantitative filter paper (Whatman—5 or equivalent). The paper may be placed in a Buchner funnel or in a conventional funnel using a platinum or other cone to support the paper. Wash the residue with water at 65ºC. until the volume of the filtrate is about 350 ml. Allow time for thorough draining before adding more water. If the material is of the type that will yield a cloudy filtrate, wash the residue with 5% ammonium nitrate solution in place of the hot water.

(5) Dry the filter paper and contents carefully, being careful not to lose any of the residue. Transfer the paper to a clean crucible and ignite until all organic matter is destroyed. Digest the ignited until all organic matter is destroyed. Digest the ignited residue with 10 to 15 ml. of concentrated hydrochloric acid until all phosphate has dissolved.

(6) If the spectrophotometric finish step is to b employed, dilute the solution to 100-150 ml. with water, mix well and filter through a dry quantitative filter paper into a 200 ml volumetric flask. Dilute the solution to the mark with water and mix well. Record the volume of the volumetric flask as V_1.

(7) If the volumetric procedure is to be followed, evaporate the hydrochloric acid solution to a small volume. Avoid spattering and do not allow to go to dryness. Dilute the solution to about 10 ml. with water, proceed with the volumetric determination.

C.3.6 A. SPECTROPHOTOMETRIC METHOD

C-3.7 Apparatus:

(1) ***Spectrophotometer***—with matched pair of absorption cells. The light path of the cells should be 1 cm. preferably, although cells up to 1.3 cm. in light path length may be used.

C-3.8 Reagents:

(1) ***Standard Phosphate Solution***—Dry several grams of potassium hydrogen phosphate, KH_2PO_4), primary standard grade, in an air oven at 105ºC. for two hours. Remove from the oven and allow to cool in a desiccators. Accurately weigh 1.5340 g. of the dried potassium hydrogen phosphate and dissolve in water. Transfer the solution to a 200-ml volumetric flask and dilute to the reference mark with addition water Stopper and mix well.

(2) ***Molybdovanadate Solution***—Dissolve 40 g. of ammonium molybdate tetrahydrate, $(NH_4)_6$ MO_7O_{24} $4H_2O$, in 400 ml. of hot water and allow to cool. Dissolve 2 g of ammonium vanadate NH_4 VO_3 in 250 ml. of hot water, cool and add 250 ml. of 70% perchloric acid.

Gradually add the molybdate solution to the vanadate solution with constant stirring dilute the final silution to 2 liters with water and mix well.

C-3.9 Calibration

(1) Prepare a series of calibration solutions by measuring into 100 ml. volumetric flasks the volumes of standard phosphate solution REAGENTS, (1) indicated in the table below: Measure the volumes carefully with a buret.

Calibration Solution	Concentration mg. P_2O_5 /ml.	Volumes of Standard Phosphate Solution ml.
A	0.4	10.00
B	0.5	12.50
C	0.6	15.00
D	0.7	17.50
E	0.8	20.00
F	0.9	22.50
G	1.0	25.00

Dilute each solution to the reference mark with water and mix well.

(2) Pipet into 100 ml. volumetric flaks 5 ml aliquots of the seven calibration solutions. These flasks will contain 2, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 mg. P_2O_5. To each flask add 45 ml. of water and within five minutes for the entire series, add 20 ml. of molybdovanadate solution by pipet, dilute to the marks with water and mix. Allow the solutions to stand for ten minutes.

(3) Fill the absorption cells with the solution containing 2 mg P_2O_5. Set the spectrophotometer to 400 mμ and adjust to zero absorbance with one of the cells in the reference position. Move the other cell into the light path. If a negative absorbance is obtained, reverse the position of the cells and readjust to zero absorbance with the new cell in the light Path. Identify this cell permanently as the reference cell. If the absorbance of the sample cell is greater than 0.001, record it as the correction factor and correct all subsequent absorbance readings by subtracting this factor.

(4) Determine the absorbance of the other solution (2.5 through 5.0 mg. P_2O_5 retaining the 2-mg solution in the reference cell at zero absorbance. After each determination empty and refill the reference cell with fresh portions of the 2-mg solution to avoid any error that might arise from temperature changes.

(5) Prepare a calibration curve by plotting the observed absorbance values (corrected if necessary) against the respective quantities of P_2O_5 in the solutions prepared in step (2) i.e 2.0 through 5.0 mg. P_2O_5. When the calibration work has been completed, discard the seven calibration solutions (A-G). Do not attempt to use these solutions at a later date. The standard phosphate solutions, REAGENTS (1), may be retained.

C-3.10 Procedure:

(1) Prepare fresh calibration solutions A and D by measuring accurately from a buret 10.00 ml. and 17.50 ml. of the standard phosphate solution into 100-ml. volumetric flask. Dilute each aliquot to the reference mark with water and mix well.

(2) Pipet into 100-ml volumetric flasks 5 ml. of the freshly prepared calibration solution A. Label the flask "2 mg. P_2O_5". Pipet into another 100-ml. volumetric flask 5 ml. of the freshly prepared calibration solution D amd label the flask "3.5 mg. P_2O_5". Develop the color as under CALIBRATION step (2), starting with the addition of 45 ml. of water. Fill the reference cell with the "2 mg. P_2O_5" standard and adjust the instrument to zero absorbance at 400 m/μ. Determine the absorbance of "3.5 mg. P_2O_5" standard. The absorbance this standard should be practically identical with the corresponding value on the calibration curve.

(3) Pipet a 5- or 10-ml. aliquot of the sample solution from step (3) under PREPARATION OF SAMPLE SOLUTION step (2) or PROCEDURE, step (3) or step (4) into 100 ml volumetric flask. Record the volume of the aliquot as V_2. Add 45 ml of water and, within five minutes, add 20 ml of molybdovanadate solution from a pipet. Dilute to the mark with water and mix. Allow the solution to stand for ten minutes.

(4) Fill the reference absorption cells with a fresh portion of the " 2 mg. P_2O_5". Solution and adjust the spectrophotometer, if necessary to zero absorbance. Fill the sample cell with the reacted sample solution from step (3) and determine its absorbance at 400 m/ micron.

(7) Read, and record as W, the P_2O_5 content of the sample aliquot from the calibration curve.

C-3.11 Calibration:

(1) Determine the weight of sample represented by the aliquot used for the absorbance measurement by the equation.

$$S_A = S \times 1000 \frac{V_2 \times V_3}{V_1 \times V_4}$$

Where

S is the weight of sample taken for analysis in g.

V_1 is the volume, in ml. to which the sample solution was diluted in step (3) of the PREPARTION OF SAMPLE SOLTUION, step (2) in ml.

V_2 is the volume of the aliquot taken for the color development step (3) of PROCEDURE.

S_A is the weight of sample in the aliquot used for the absorbance measurement in mg.

Omit terms V_3 and V_4 from the calculation if no dilution of the sample solution was required.

(2) Calculate the concentration of water—soluble P_2O_5 in the sample as:

$$\% \text{ Water—Soluble Phosphorus (as } P_2O_5) = \frac{W \times 100}{S_A}$$

Where

W is the weight of P_2O_5 in the aliquot taken for the absorbance measurement in POROCEDURE step (7) in mg.

C-3.12 B. VOLUMETRIC METHOD:

C-3.13 Apparatus:

(1) ***Agitator***—A machine capable of shaking Erlenmeyer flask such as the wrist-type shaker or any device capable of stirring the contents of a beaker, such as a magnetic stirrer, may be used.

(2) ***Filter Crucible***—Porcelain, 30-ml capacity, fine porosity. (Maximum pore radius,3).Alternatively, 25-ml. Gooch crucible prepared to retain fine precipitates may be used.

C-2.6 Reagents:

(1) ***Molybdate Solution***—Dissolve 100 g of molybdic anhydride (MoO_3) in a mixture of 144 ml. of concentrated ammonium hydroxide and 271 ml of water. Cool and pour the solution slowly with constant stirring into a cool mixture of 489 ml. of concentrated nitric acid and 1148 ml. of water. Keep the final mixture in a warm place for several days or until a portion heated to 40 ºC deposits no yellow precipitate. Decant the solution from any sediment and store in glass stoppered containers. To each 100 ml of molybdate solution required for a a batch of determinations add 5 ml of concentrated nitric acid and filter immediately before using.

(2) ***Standard Alkali Solution***—Dilute 324.0 ml of carbonate-free IN sodium (or potassium) hydroxide solution to 1 litre. Fifty ml. of this solution should neutralize 16.20 ml. of IN acid solution. Adjust the solution, if necessary to this exact concentration. One ml. of the standard alkali solution equals 1 mg of P_2O_5 or 1% P_2O_5 on the basis of 0.1 g. of sample.

(3) ***Standard Acid Solution***—Prepare a solution of hydrochloric or nitric acid corresponding in concentration to the standard alkali solution. Standardize the acid solution against the standard alkali solution using phenolphthalein as the indicator. Adjust the solution, if necessary, so that 20.00 ml. of the acid is equivalent to 20.00±0.02 ml of the standard.

(4) ***Nitric Acid, reagent grade***—69-71%.

Reporting :

Report the concentration of water—soluble phosphorus (as P_2O_5) as:

Water—Soluble Phosphorus (AM—S 600.46)--------(as P_2O_5)

Indicate in the report which alternative procedure was used to obtain the result.

C-3 CITRATE—INSOLUBLE P_2O_5 AND AVAILABLE P_2O_5 IN FERTILIZER

C-3.1 Scope:

The procedure is applicable to phosphorus-containing fertilizers such as the superphosphates, mixed fertilizers, nittrophos complexes and fertilizer raw materials. The spectrophotometric alternative is not applicable to materials yielding colored solutions containing ions other than orthophosphate which form colored complexes with molybdovanadate, nor is it recommended for basic slag. The volumetric method may be used in all cases.

C-3.2 Summary of Method:

A sample of the fertilizer is successively extracted with water and ammonium citrate solution. The l;ater extraction is carried out under prolonged agitation at an elevated temperature. After filtration and ignition, the residue is dissolved and the solution is analyzed for P_2O_5 content by either a spectrophotmetric or volumetric method. In the spectrophotometric alternative the sample solution is reacted with molybdovanadate reagent and the absorbance of the resulting product measured in a spectrophotometer. The volumetric option involves precipitation of the phosphate with molybdate solution, removal of the precipitate by filtration, dissolution of the precipitate in an excess of standard alkali and titration of the excess alkali with standard acid. The percent citrate insoluble P_2O_5 is calculated and reported as percent of the original sample.

Available P_2O_5 is calculated as the difference between the % citrate-insoluble P_2O_5 and the % total P_2O_5 (C-1) and reported as percent of the original sample.

C-3.3 Apparatus:

(1) Shaking Machine—capable of shaking 250-ml volumetric flaks while maintaining them at a temperature 65±2°C for two hours. A wrist-type shaker positioned so that one arm enters an opening in the side of an air oven that is held at 35°C is a suggested arrangement.

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C-3.4 Reagents:

Reference to water in this and the following sections shall be understood to mean distilled water, or water of equivalent purity:-

(1) Ammonium Citrate Solution—Dissolve 37 g. of crystallized citric acid in 1½ litres of water and nearly neutralize by adding 345 ml of concentrated ammonium hydroxide (28-29% NH_3). If the concentration of ammonia is less than 28% add a correspondingly larger volume and dissolve the citric acid in a correspondingly smaller volume of water. Cool and adjust the pH of the solution to 7.0 by adding, carefully, small portion of

ammonium hydroxide. Mix thoroughly and measure the neutrality of the solution after each addition with a pH meter. Dilute solution if necessary to specific gravity 1.09 at 20°C. The volume should be about 2 litres. Store the solution in tightly stoppered bottles and check pH from time to time.

C-3.5 Preparation of Sample Solution:

(1) Weigh 1±0.1 g. of a uniform, representative portion of the sample on a tared watch glass. Record the weight to the nearest 0.0001 g. as S.

(2) Transfer the sample quantitatively to a 9 cm., folded filter paper in a funnel and wash with successive small portions of water until the volume of filtrate is about 225ml. Allow each portion of wash water to pass through the filter before adding more water. Use suction if after 30 minutes, it is obvious that the filtration cannot be completed in one hour.

(3) Within one hour transfer the filter paper containing the water-insoluble residue to 250-ml. volumetric flask and add 100-ml of the ammonium citrate solution previously heated to 65°C. Close the flask with a smooth rubber stopper, shake vigorously to disintegrate the paper. Relieve the pressure by removing the stopper momentarily. Replace the stopper tightly and clamp the flask in the shaking machine. Shake the flask for one hour while maintaining its temperature at 65°C in the oven. Shake should be vigorous enough so that the sample is dispersed throughout the solution and so that all of the interior of the flask and the underside of the stopper are continually in contact with the solution.

(4) At the end of the 1 hour agitation, remove the flasks from the shaker and filter the contents immediately by suction as rapidly as possible on a dry, quantitative filter paper (Whatman–5 or equivalent). The paper may be placed in a Buchner funnel or in a conventional funnel using a platinum or other cone to support the paper. Wash the residue with water at 65°C until the volume of the filtrate is about 350 ml. Allow time for thorough draining before adding more water. If the material is of the type that will yield a cloudy filtrate, wash the residue with 5% ammonium nitrate solution in place of the hot water.

(5) Dry the filter paper and contents carefully, being carefully not to lose any of the residue. Transfer the paper to a clean crucible and ignite until all organic matter is destroyed. Digest the ignited residue with 10 to 15 ml. of concentrated hydrochloric acid until all phosphate has dissolved.

(6) If the spectrophotometric finish step is to be employed, dilute the solution to 100-150 ml. with water, mix well and filter through a dry quantitative filter paper into a 200 ml volumetric flask. Dilute the solution to the mark with water and mix well. Record the volume of the volumetric flask as V_1.

(7) If the volumetric procedure is to be followed, evaporate the hydrochloric acid solution to a small volume. Avoid spattering and do not allow to go to dryness. Dilute solution to about 10 ml with water proceed with the volumetric determination.

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C-3.6 A. SPECTROPHOTOMETRIC METHOD

C-3.7 Apparatus:

(1) Spectrophotometer—with matched pair of absorption cells.—The light path length of the cells should be 1 cm. preferably although cells up to 1.3 cm, in light path length may be used.

C-3.8 Reagents:

(1) Standard Phosphate Solution—Dry several grams of potassium hydrogen phosphate (KH_2PO_4), primary standard grade, in an air oven at 105°C for two hours. Remove from

the oven and allow to cool in a desiccators. Accurately weigh 1.5340 g. of the dried potassium hydrogen and dissolve in water. Transfer the solution to a 200-ml volumetric flask and dilute to the reference mark with additional water. Stopper and mix well.

(2) Molybdovandate Solution—Dissolve 40 g. of ammonium molybdate, $(NH_4)_6MO_7O_{24}$ $4H_{20}$ in 400ml of hot water, and allow to cool. Dissolve 2 g of ammonium vanadate, NH_4 VO_3, in 250 ml of hot water, cool and add 450 ml of 70% perchloric acid. Gradually add the molybdate solution to the vanadate solution with constant stirring. Dilute the final solution to 2 litres with water and mix well.

C-3.9 Calibration:

(1) Prepare a series of cal bration solution by measuring into 100 ml. volumetric flasks the volumes of standard phosphate solution [REAGENTS, (1)] indicated in the table below. Measure the volumes carefully with a buret.

Calibration Solution	Concentration mg. P_2O_5/ml	Volume of Standard Phosphate Solution, ml.
A	0.4	10.00
B	0.5	12.50
C	0.6	15.00
D	0.7	17.50
F	0.8	20.00
F	0.9	22.50
G	1.0	25.00

Dilute each solution to the reference mark with water and mix well.

(2) Pipet into 100 ml volumetric flask 5 ml. aliquots of the 7 calibration solutions. These flasks will contain 2.2.5, 3.0, 3.5, 4.0, 4.5 mg. P_2O_5. To each flask add 45 ml of water, and within five minutes for the entire series, add 20 ml of molybdovanadate solution by pipet, dilute to the mark with water and mix. Allow the solutions to stand for ten minutes.

(3) Fill the two absorption cells with the solution containing 2 mg P_20_5. Set the spectrophotometer to 400 m/micron and adjust to zero absorbance with one of the cells in the reference position. Move the other cell into the light path. If a negative absorbance is obtained, reverse the position of the cells and readjust to zero absorbance with the new cell in the light Path. Identify this cell permanently as the reference cell. If the absorbance of the sample cell is greater than 0.001, record it as the correction factor and correct all subsequent absorbance readings by subtracting this factor.

(4) Determine the absorbance of the other solution (2.5 through 5.0 mg). (P_20_5) retaining the 2-mg solution in the reference cell at zero absorbance. After each determination empty and refill the reference cell with fresh portions of the 2-mg solution to avoid any error that might arise from temperature changes.

(5) Prepare a calibration curve by plotting the observed absorbance values (corrected if necessary) against the respective quantities of P_20_5 in the solutions prepared in step (2) i.e 2.0 through 5.0 mg. P_20_5. When the calibration work has been completed, discard the seven calibration solutions (A to G). Do not attempt to use these solutions at a later date. The standard phosphate solutions, REAGENTS (1), may be retained.

C-2.10 Procedure:

(1) Prepare fresh calibration solutions A and D by measuring accurately from a buret 10.00 ml. and 17.50 ml. of the standard phosphate solution into 100-ml. volumetric flask. Dilute each aliquot to the reference mark with water and mix well.

(2) Pipet into 100-ml volumetric flasks 5 ml. of the freshly prepared calibration solution A. Label the flask "2 mg. P_20_5". Pipet into another 100-ml. volumetric flask 5 ml. of the

freshly prepared calibration solution D amd label the flask "3.5 mg. P_2O_5". Develop the color as under CALIBRATION step (2), starting with the addition of 45 ml. of water. Fill the reference cell with the "2 mg. P_2O_5" standard and adjust the instrument to zero absorbance at 400 m/micron. Determine the absorbance of "3.5 mg. P_2O_5" standard. The absorbance this standard should be practically identical with the corresponding value on the calibration curve.

(3) Pipet a 5- or 10-ml. aliquot of the sample solution from step (3) under PREPARATION OF SAMPLE SOLUTION step (2) or PROCEDURE, step (3) or step (4) into 100 ml volumetric flask. Record the volume of the aliquot as V_2. Add 45 ml of water and, within five minutes, add 20 ml of molybdovanadate solution from a pipet. Dilute to the mark with water and mix. Allow the solution to stand for ten minutes.

(4) Fill the reference absorption cells with a fresh portion of the "2 mg. P_2O_5" solution and adjust the spectrophotometer, if necessary to zero absorbance. Fill the sample cell with the reacted sample solution from step (3) and determine its absorbance at 400 m/ micron.

(5) Read, and record as W, the P_2O_5 content of the sample aliquot from the calibration curve.

C-3.11 Calculation:

(1) Determine the weight of sample represented by the aliquot used for the absorbance measurement by the equation.

$$S_A = S \times 1000 \times \frac{V_2}{V_1}$$

Where

S is the weight of sample taken for analysis in g.

V_1 is the volume, in ml. to which the sample solution was diluted in step (3) of the PREPARTION OF SAMPLE SOLTUION, step (6) in ml.

V_2 is the volume of the aliquot taken for the color development step (3) in ml.

S_A is the weight of sample in the aliquot used for the absorbance measurement in mg.

(2) Calculate the concentration of water—soluble P_2O_5 in the sample as:

$$\% P_2O_5 = \frac{W}{S_A}$$

Where

W is the weight of P_2O_5 in the aliquot taken for the absorbance measurement in POROCEDURE step (5) in mg.

C-3.12 B. *VOLUMETRIC METHOD*

C-3.13 *Apparatus:*

(1) *Agitator.-A* machine capable of shaking Erlenmeyer flasks such as the wrist-type shaker or any device capable of stirring the contents of a beaker such as a magnetic Stirrer may be used.

(2) *Filter* Crucible.-Porcelain, 30 ml. Capacity, fine porosity. A suitable item is Seals crucible No. 3001. Alternatively, 25-ml. Gooch crucibles prepared to retain fine precipitates may be used.

C-3.14 *Reagents*

(1) *Molybdate* Solution.-Dissolve 100g-of molybdade anhydride (Mo03) in a mixture of 144 ml. of concentrated ammonium hydroxide and 271 ml. of water. Cool and pour the

solution slowly, with constant stirring into a cool mixture of 489 ml. of concentrated nitric acid and 1148 ml. of water. Keep the final mixture in a warm place for several days or until a portion heated to 40 °C, deposits no yellow precipitate.

Decant the solution from any sediment and store in glass stoppered containers. To each 100 ml. of n10lyhda1c solution required for a batch of determinations add 5 ml. of concentrated nitric acid and filter immediately before using.

(2) **Standard Alkali Solution** -Dilute 324.0 ml. of carbonate-free, l N sodium (or Potassium) hydroxide solution to 1 liter. 50 ml. of this solution should neutralize 16.20 ml. of 1 N acid solution. Adjust the solution if necessary, to this exact concentration 1ml of the standard alkali solution equals 1mg. of $P_2 0_5$, or 1% $P_2 05$ on the basis of a 0. lg. sample.

(3) **Standard Acid solution**.-Prepare a solution of hydrochloric or nitric acid corresponding in concentration to the stand• are alkali solution. Standardize the acid solution against the standard alkali solution using phenolphthalein as the indicator. Adjust the solution, if necessary, so that 20.00 ml. of the acid is equivalent to 20.00 ± 0.02 ml. of the standard alkali.

(4) **Nitric Acid, Concentrated** (69—71%) :

(5) **Ammonium Nitrate Solution** – Dissolve *100* g. of phosphorus-free ammonium nitrate in water and dilute to 1 liter.

(6**) Ammonium Hydroxide. Concentrated** (28-30%)

(7) **Methyl Red Indicator Solution** - Dissolve 0.1 g. of methyl red in 60 ml of alcohol 95% ethyl alcohol, or ethyl alcohol that has been denatured with methyl alcohol).

(8**) Phenolphthalein Indicator Solution.**-*Dissolve* 1g of phenolphthalein 1OO ml. of alcohol (95%

ethyl alcohol, or ethyl alcohol that has been denatured with methyl alcohol).

C-3.15 Procedure *:*

(I) To the sample solution from PREPARATION OF SAMPLE SOLUTION step (7) add 5 ml. of concentrated nitric acid (or 65 ml. of ammonium nitrate solution). Carefully add concentrated ammonium hydroxide until the precipitate that forms dissolves only slowly on vigorous stirring.

(2) Dilute the solution to 75-100 ml. and adjust the tem• perature to 25-30°C. If the sample solution does not give a precipitate withthe ammonium hydroxide in step (1) make the solution slightly alkaline to litmus paper with the ammonium hydroxide and then slightly acid with dilute nitric acid.

(3) Add to the neutralized solution 20-25 ml. of the molybdate solution. Place the solution in the shaking or stirring apparatus and agitate for 30 minutes at room temperature.

(4) Decant the supernatant liquid at once through a filter crucible. Wash the precipitate remaining in the vessel twice by adding 25 to 30 ml. portions of water, agitating thoroughly, allowing the precipitate to settle and decanting the wash water into the filter crucible. Finally transfer the precipitate to the filter and wash with cold water until the filtrate from two fillings of the crucible shows no acid reaction on the addition of two drops of methyl red indicator.

(5) Transfer the crucible to a beaker and add sufficient standard alkali solution from a buret to dissolve the precipitate avoiding an excess of more than 3 ml. Record the volume of alkali solution to the nearest 0.01 ml. Agitate the beaker to dissolve all remaining particles of the precipitate.

(6) Dilute to 150 m Lwith water, add two drops of phenolphthalein indicator solution and titrate with the standard acid solution to the disappearance of the pink color. Record the volume of standard acid solution to the nearest 0.01 ml.

C-3.16 **Calculation:**

Calculate the concentration of citrate-insoluble phosphorus in the sample as under

$$\%P_2O_5 = \frac{(A-B) \times 100}{S \times 1000}$$

Where,

A is the volume of standard alkali solution used to dissolve the precipitate, in ml

B is the volume of standard acid solution required to titrate the excess alkali solution in ml.

S is the weight of sample used (PREPARATION OF SAMPLE SOLUTION) Step (1), in g.

C-3.17 **Reporting:**

Report the concentration of citrate-insoluble Phosphorus (as P_2O_5) as

Citrate-insoluble phosphorus----------%(P_2O_5)

Indicate the report which alternative was used to determine the citrate-insoluble phosphorus by inserting as A in the parentheses after % P_2O_5 for the spectrometric method or a B for the volumetric procedure.

If "percent available phosphorus " is required by the specification or the sample submitter, subtract the % citrate-insoluble P_2O_5 (as determined by C-1 and report the difference as

Available phosphorus----------%(P_2O_5)

APPENDIX D

D-1 POTASSIUM CONTENT OF FERTILIZERS

D-1.1 **Scope**:

The procedure is intended for the determination of soluble potassium in solid fertilizers

D-1.2 Summary of Method:

In the volumetric procedure the potassium salt are extracted from a portion of the sample and the potassium precipitated with a measured volume of sodium tetraphenylboron. The excess reagents titrated with a standard quaternary ammonium chloride solution. The flame photometric method involves a similar extraction of the sample which is followed by passing the extract through an ion exchange column to remove interfering anions. The treated solution is aspirated into a flame photometer and the emission intensity at 767m/micron is measured. Results are calculated as percent K_2O and reported to the nearest 0.1%

D-1.3 Precision:

Duplicate results obtained by the same operator should not be considered suspected unless they differ by more than the following amounts at the indicated concentration level.

$\%K_2O$ Level	Sodium Tetraphenylboron Method	Flame Photometric Method
8 & 12 %	0.48	0.79
30 %	0.62	1.6
60 %	1.3	2.2

A- SODIUM TETRAPHENYLBORON METHOD

D-1.4 **Reagents**

Reference to water in this and the following sections shall be understood to mean distilled water, or water of equivalent purity:

(1) Ammonium Oxalate Solution. 4 % - Dissolve 4±0.1g of ammonium oxalate, $(NH_4)_2\ C_2\ O_4.\ H_2O$ in 100ml of water.

(2) Sodium Hydroxide Solution, 20% – Dissolve 20± 0.1 g of sodium hydroxide in 100ml of water.

(3) Formaldehyde Solution, 37% (wt.) – Available in this concentration from most chemical supply companies.

(4) Standard Quaternary Ammonium Chloride Solution---
Dilute 50ml of 12.8% Zephiran Chloride (Alkaldimethyl Benzyl Ammonium Chloride) to 1 litre with water and Mix. The concentration of the resulting solution will be approximately 0.625% Cetyltrimethyl ammonium bromide from most chemical supply companies may be substituted for the Zephiran chloride. If the bromide compound is used, dissolve 6.2±0.1g. in water and dilute to 1 litre with additional water.

Standardize the solution as follows. Pipet 2.00ml of the unstandardized sodium tetraphenylboron solution (STPB) REAGENTS (5) into a 125ml. Wrlenmeyer flask and add 20-25ml of water. Pipet 1ml of 20% sodium hydroxide, 2.5ml of 37% formaldehyde solution and 1.5ml of 4% ammonium oxalate into the flask and add 6-8 drops of clyton yellow indicator solution. Titrate the solution with the quaternary ammonium chloride reagents to the pink end point, using a 10ml buret graduated in 0.05ml subdivisions. Adjust the concentration of the quaternary ammonium chloride, solution so that 2.00±0.02ml. of the STPB solution. The solution is relatively stable. Normally this ratio should be checked every two weeks and adjustments made as required.

(5) Standard Sodium Tetraphenylboron Solution—Dissolve 12g of sodium tetraphenylboron, NAB $(C_6\ H_5)_4$ in approximately 800ml of water. Add 20-25g of aluminum hydroxide, Al $(OH)_3$, Stir for 5minutes and filter through filter paper (Whatman#42, or equivalent) into a 1litre volumetric flask. Rinse the beaker sparingly with water and add the washings to the filter, collecting the filtrate in the volumetric flask. Add 2ml of 20% sodium hydroxide solution to the filtrate, dilute to the mark with water and mix well. Allow the solution to stand for 48hours and standardize in the following manner.

Dissolve 2.500g of primary-standard grade potassium hydrogen phosphate KH_2PO_4, in water and transfer to a 250ml volumetric flask. Add 50ml of 4% ammonium oxalate solution dilute to the mark with water and mix. Transfer a 15ml aliquot (equivalent) to 52.87 mg. K_2O, or 43.88 mg. K) to a 100ml volumetric flask. Pipet 2ml of 20% sodium hydroxide solution and 5m of 37%formaldehyde solution into the flask. Carefully

transfer 43.00ml of of the sodium tetraphenylboron (STPB) solution from a buret into the flask. Dilute the solution to the reference mark with water and mix thoroughly. Allow the solution to stand for 5-10 minutes and filter through a dry filter paper.. Pipet a 50ml aliquot of the filtrate into a 125ml. Erlenmeyer flask, add 6-8 drops of clayton yellow indicator solution and titrate the excess STPB with the standardized quaternary ammonium chloride solution to the pink end point.

Calculate the titer of the solution by the equation

$$F = \frac{34.58}{A-B}$$

Where,

A is the volumetric STPB solution added (=43.00ml)

B is the volume of quaternary ammonium chloride solution required to titrate the excess STPB, in ml

F is the titer, expressed as % K_2O /ml of STPB

The facto F applies on ly when 2.5g of sample has been diluted to 250ml and a 15ml aliquot taken for the titration.

(6) Clayton yellow Indicator Solution. 0.04%- dissolve 40mg of clayton yellow in 100ml of water This compound is listed as Titen yellow in some chemical catalogs.

D-1.5 Procedure:

(1) Weight 2.500±0.001 g of a uniform, representative portion of the sample on a tared watch glass. Transfer the sample quantitatively to a 250ml . Volumetric flask. Content If the K_2O content of the sample is known to be greater than 50% weight out 1.250±0.001g of sample instead of the 2.500g

(2) Add 50ml of 4% ammonium oxalate and 125ml of water to the flask and boil the contents for 30 minutes/ Agitate the flask occasionally during the early stage of the heating to make sure that the sample has not caked on the bottom of the flask.

(3) Allow the solution to cool, dilute to the mark on the flask with water and mix thoroughly. Filter the solution through dry filter paper (What man #5, or equivalent) or allow the solution to stand until clear.

(4) Pipet at 15ml aliquot of the clear solution into a 100ml volumetric flask. Pipet 2ml of 20% sodium hydroxide and 5ml of 37% formaldehyde solution into the flask. Using a uret, carefully measure into the solution 1ml of the STPB solution for each 1% K_2O expected in the sample. Measure an additional 8ml of the STPB solution into the flask and record to the nearest 0.01ml., the total volume of STPB used. Do not swirl or attempt to mix the solution in the volumetric flask while the STPB is being used, Intense foaming may accrue making it virtually impossible to bring the volume accurately to the reference mark. After the addition of STPB, dilute to the mark with water and then mix thoroughly.

(5) Allow the solution to stand for 5-10 minutes and filter through a dry filter paper (Whatman 2#,or equivalent)

(6) Pipet 50ml of the filtrate into a 125ml Erlenmeyer flask, add 6-8 drops of the clayton yellow indicator solution and titrate with the quaternary ammonium chloride solution to the pink end point. Record the volume of titrant required to the nearest 0.01ml.

D-1.6 **Calculation:**

(1) Calculate the concentration of potassium (as K_2O) in the samples as follow:

"Potassium (%K_2O)=(V-D) F"

Where,

C is the volume of STPB added in step (4), in ml.

D is the volume of quaternary ammonium chloride required to titrate the excess STPB in step (6) in ml

F is the titer of the STPB solution, in $\%K_2O$/ml Multiply the result by 2 if a 1.25g sample was used.

D-1.7 **B. FLAME PHOTOMETRIC METHOD**

D-1.8 Apparatus:

References to water in this, and the following section shall be understood to mean distilled water, or water of equivalent purity:

(1) Flame Photometer:

(2) Ion Exchange Column- made from a 12 inch length of 2.5m O.D, No.4 rubber stopper through which is inserted a 2-way stopcock or glass tubing connected to rubber tubing over which is placed a compressor clamp. See Fig.1 for detail of construction. Do not allow to stopcock tubing to protrude above the stopper. The stopper should be large enough so that there is no space between the stopper vertex and the column wall. Insert a glass wool plug in the bottom of the column.

Prepare the resin according to the following instructions. Place about 1.5lb of anion exchange resin in a 4liter beaker and add enough 5% sodium hydroxide solution(2-3) liters) to completely float the resin when it is being stirred. Stir the mixture with an electric stirrer for 30minutes. Let the resin settle and decant the sodium hydroxide solution from the beaker. Repeat the treatment with 5% sodium hydroxide solution two more times, decanting the solution from the resin after each treatment.

Add 3 liters of water to the resin, stir for a few minutes, allow the resin to settle and decant the wash water. Repeat the water washing three or four times. The resin is now in the free base form. Regenerate the resin to the nitrate from by treating it three times with 5% nitric acid, using the same technique as with the sodium hydroxide solution. Wash the resin against the corresponding concentrations, in ppm. Prepare a standard curve of emission by plotting the observed values against the corresponding concentrations, as ppm on linear paper.

D-1.11 (1) Weight 1.506±0.001g of a uniform representative portion of the sample on a tared watch glass

(2) Transfer the sample quantitatively to a 250ml volumetric flask (500ml) flask if the

sample contain more than 30% K_2O), and add 100ml of water followed by 20ml of ammonium carbonate solution. Oil the solution for five minutes and cool the room temperature. Dilute the solution to the reference mark with water, mix well and filter through a dry filter paper (Whatman#1), or equivalent). Collect the filtrate in a clean dry container. Stopper the container until ready for use.

(3) Pipet 10ml of the filtered sample solution into 250ml beaker. Add 1 drop of methyl red indicator and neutralize the solution to the oink end point with dilute nitric acid.

(4) Adjust the water level in the ion exchange column so that it is level with the top of the resin. Transfer the neutralized sample aliquot quantitatively to the column. Open the stopcock carefully to give a flow rate of 2drops/second, collecting the effluent in a 250ml. volumetric flask. Wash the sample solution into the column with 2-3 small portions of water

(5) Collect 50-75ml of effluent in the flask. Open the stopcock and collect an additional 100ml of effluent while pouring water into the top of the column making certain that the

water level dose not fall below the top of the resin bed. Close the stopcock and dilute the effluent in the volumetric flask to the reference mark with water. If an internal standard instrument is being used, add an amount of lithium nitrate equal to that used in the calibration before diluting the effluent to volume.

(6) Check the instrument conditions and adjustment by aspirating several of the calibration solutions into the burner and comparing the emission readings with those of the calibration curve. Make any necessary adjustments so that the observed values agree with those on the calibration curve. This step should be performed each day that the instrument is used.

(7) Aspirate the treated sample solution in to the flame and measure the emission in the same manner as under CALIBRATION. Record the percent transmission (or dial reading).

(8)Obtain the corresponding potassium concentration in ppm, from the calibration curve.

D1.12 **Calculations**:

(1) If the sample solution was made up to 250ml in PROCEDURE, step (2) calculate the concentration of potassium in the sample by the equation.

$$\%K_2O = \frac{A}{2}$$

Where,

A is the concentration of potassium, in ppm obtained from the calibration curve, in PROCEDURE, step (8)

(2) If the sample solution was made up to 500ml in PROCEDURE step (2) calculate the concentration by the equation

$$\%K_2O = A$$

D-1.13 **Reporting:**

Report the result as:

Potassium --------$\%K_2O$

Indicate in the report which alternative was used to determine the potassium content by inserting an A in the ~arentheses after % K20 for the sodium tetra phenyl boron· method or a B for the flame photometric procedure.

_____XXX_____XXX_____XXX_____