

FERTILIZERS REGULATIONS

ARRANGEMENT OF REGULATIONS

REGULATIONS

1. Citation
2. Interpretation

PART I

QUALITY OF FERTILIZER

3. Composition and fineness of fertilizers
4. Approval of brand [Revoked by G.N. 64/1996]
5. Appeals against decisions of registering Officer [Revoked by G.N. 64/1996]

PART II

LABELLING OF CONTAINERS

6. Labelling of containers
7. Information on invoices [Revoked by G.N. 64/1996]

PART III

SAMPLING AND ANALYSIS

8. Taking of samples
9. Analysis and sampling at the request of purchaser
10. Certificate of sampling
11. Results of analysis
12. Limits of variation
13. Method of analysis
14. Imported fertilizer not complying with requirements

PART IV

GENERAL

15. Labelling of containers
16. Offences and penalties

Schedules

G.N. 142/1970

123/1985

64/1996

FERTILIZERS REGULATIONS

under s. 16

1. Citation

These Regulations may be cited as the Fertilizers Regulations.

2. Interpretation

In these Regulations, unless the context otherwise requires—

“fee” means the appropriate fee prescribed in the First Schedule;

“form” means the appropriate form prescribed in the Second Schedule;

“specified composition” in relation to a fertilizer or type of fertilizer means the required composition thereof as specified by the Minister from time to time by notice published in the Gazette.

PART I

QUALITY OF FERTILIZER G.N. 64/1996

3. Composition and fineness of fertilizers

(1) Fertilizers listed in the Third Schedule shall have the specified composition set out in relation to such fertilizer in the Third Schedule. G.N. 64/1996

(2) Fertilizers listed in the Fourth Schedule shall comply with the minimum fineness requirements listed in relation to such fertilizer in the Fourth Schedule.

(3) No product shall be imported, sold or distributed as fertilizer if such product is contaminated with heavy metal or other substance that would be harmful to the soil, or the environment, or to public health.

4.

[Revoked by G.N. 64/1996.]

5.

[Revoked by G.N. 64/1996.]

PART II

LABELLING OF CONTAINERS

6. Labelling of containers

(1) The container in which a fertilizer is sold shall be duly and legibly marked or labelled in English with the relevant information set out in the Third Schedule. G.N. 64/1996

(2) Any figures or numerals used for representing the chemical composition of a fertilizer shall be preceded or followed by the appropriate symbol.

7.

[Revoked by G.N. 64/1996.]

PART III

SAMPLING AND ANALYSIS

8. Taking of samples

(1) The manner of taking samples of fertilizers shall be as follows—

(a) where the fertilizer is packed in containers, samples shall be taken at random from different parts of the whole quantity, as follows: G.N. 123/1985

(i) if the quantity of fertilizer does not exceed three tonnes, from not less than two unopened containers per 1.01 tonne or part thereof; and G.N. 123/1985

(ii) if the quantity exceeds 3.03 tonnes, from one additional unopened container for every additional 1.01 tonne or part thereof:

Provided that in no case need samples be taken from more than twenty containers;

(b) where the fertilizer is not packed in containers, not less than six samples shall be taken from different parts of the whole quantity, where possible in the ratio of two samples per 1.01 tonne or part thereof:

Provided that in all not more than fifty samples need be taken.

(2) Where the fertilizer is packed in containers the samples shall be taken by means of a sampling probe not less than 0.03 metre in diameter. G.N. 123/1985

(3) Where the fertilizer is not packed in containers the samples shall be taken by means of a sampling probe not less than 0.3 meter in diameter or by such other means as will ensure as far as is practicable, the taking of a representative sample.

(4) The samples taken in accordance with subregulation (1) in respect of a whole consignment shall form a bulk sample which shall not be less than 4.50 kg in weight and need not exceed 6.75 kg in weight. G.N. 123/1985

(5) The bulk sample thus obtained shall be thoroughly mixed, formed into a flattened heap and quartered. One quarter randomly selected shall then be rejected and the remainder remixed and requartered. This procedure of mixing, quartering and rejection shall be repeated until the original bulk sample has been reduced to approximately 1.35 kg in weight. The resultant sample shall then be dealt with as specified in section 12 (3) of the Act. G.N. 123/1985

(6) In the case of liquid fertilizers, the samples shall be taken by such means as will ensure as far as is practicable the taking of a representative sample.

9. Analysis and sampling at the request of purchaser

(1) The purchaser of a fertilizer may request an inspector to sample and analyse such fertilizer in the manner prescribed in section 12 (3) of the Act and regulation 8.

(2) The purchaser shall pay the appropriate fee for such sampling and analysis.

10. Certificate of sampling

The certificate referred to in section 12 (3) of the Act shall be in form No. 3.

11. Results of analysis

The analyst to whom a sample of a fertilizer has been submitted in accordance with section 12 (3) of the Act shall state the results of the analysis on form No. 4.

12. Limits of variation

A fertilizer shall be deemed to comply with these Regulations if, upon analysis, the composition is found not to differ from the specified composition by more than the variations set out in the Fifth Schedule. G.N. 64/1996

13. Method of analysis

The methods of analysing fertilizers for the purposes of the Act shall be those set out in the Sixth Schedule.

14. Imported fertilizer not complying with requirements

(1) If an examination, analysis or test of samples of fertilizer being imported into Malawi shows that any such fertilizer does not comply with the requirements of the Act or these Regulations, the Minister may—

(a) order such fertilizer:

(i) to be destroyed without compensation; or

(ii) at the option of the importer to be removed from Malawi within a specified period; or

(b) permit the removal thereof from the port of entry subject to such conditions as he may impose.

PART IV

GENERAL

15. Labelling of containers

No person shall— G.N. 64/1996

(a) add to or abstract from any fertilizer any substance or portion so as to alter its composition with the intention that the fertilizer so treated may be sold under its name in an altered state;

(b) knowingly sells fertilizer under the brand or name of such fertilizer but altered in its composition.

16. Offences and penalties

Any person not complying with any of the requirements of these Regulations shall be guilty of an offence and shall be liable to a fine of K 1,000 and to imprisonment for six months. G.N. 64 of 1996

FIRST SCHEDULE (reg. 2)

FEES

The fee for the analysis of a sample at the request of the purchaser shall be K2 for each determination, with a maximum charge of K8 for any one sample.

G.N. 64/1996

SECOND SCHEDULE (reg. 2)

PRESCRIBED FORMS

[FORMS No. 1 and No. 2 deleted by G.N. 64/1996]

FORM No. 3

FERTILIZERS, FARM FEEDS AND REMEDIES ACT

CERTIFICATE OF SAMPLING

To be completed in triplicate

I hereby certify that the accompanying are samples of
..... taken by me on at (full address)
..... from stock in charge of
..... in the presence of (state name and address of
witness)

.....

The following further particulars are given in connexion with the samples—

Samples	No.BrandNameQuantity	represented	by
sample.....
.....

Other particulars:

.....

.....

.....

..... Signature of WitnessInspector

Place:

Date:

NOTE— A copy of this certificate shall be handed or forwarded to the owner or seller or to his agent. The second copy shall be forwarded to the analyst and the third copy shall be retained by the Inspector.

FORM No. 4

FERTILIZERS, FARM FEEDS AND REMEDIES ACT

CERTIFICATE OF ANALYSIS OF FERTILIZER

To be completed in triplicate

Brand

Name of Fertilizer

Sample Size

Sample Number

Name of Laboratory

ANALYTICAL REPORT

Actual analysis per centum	Registered analysis per centum	Total nitrogen (expressed as N)
.....Ammoniacal	nitrogen	(expressed as N)
.....Nitric	nitrogen	(expressed as N)
.....Water-soluble	phosphorus	(expressed as P2O5)
.....Citric acid-soluble	phosphorus	(expressed as P2O5)
.....Total	phosphorus	(expressed as P2O5)
.....Potassium		(expressed as K2O)
.....Chloride (expressed as Cl)	Boron (expressed as B)

Observations:

.....

.....

.....

Date:Analyst

THIRD SCHEDULE (regs. 3, 6 and 7), G.N. 64/1996

PART A

FERTILIZER MIXTURES

Compound Fertilizers NP2O5K2OSBZnB: 4:18:15Max5201740.1Min316134C: 6:18:15Max8201740.1Min5161340.1D: 8:18:15Max10201740.1Min71613S: 6:18:6Max8207Min5165X:

20:10:5Max22126Min1884J: 15:5:20Max17622Min134183:2:1 (25)Max13216Min1017440.123:21:0 +
 4SMax25225Min20283 0:22:30Max2432Min2028Diammonium Phosphate
 (DAP)Max19480.15Min1744Monoammonium Phosphate (MAP)Max12520.15Super B
 (5.33:24:20)Max626220.15Min422186Super C: (8:24:20)Max1026220.15 Min622186Super D:
 (10:24:20)Max1226220.15Min92218610:20:20Max122222Min8181820:20:5+ 4S+
 0.1ZnMax2222660.1ZnMin18184

Calcium Nitrate (15.5%N+ 19.0% Calcium) (Water soluble)

Urea—S:(8:l) (40%N + 5% SO₄)

Mixture B, and C should contain 0.1 per cent Boron and Mixture S should contain at least 0.04 per cent Boron.

PART B

STRAIGHT FERTILIZERS

FERTILIZERS SPECIFICATION

(i) PhosphatesP₂O₅Total% Citric Soluble% Water SolubleP₂O₅FERTILIZERStraightsSingle
 Superphosphate19.018.519.0Double Superphosphate44.844.044.8(ii) Nitrogen% Nitrate %
 AmmoniaTotalUrea—4646Calcium Ammonium Nitrate131325—30Ammonium Sulphate—2121Nitrate of
 Soda16—16Ammonium Nitrate171734(iii) Potash% K% K₂O Muriate of Potash5060Sulphate of
 Potash4048

FOURTH SCHEDULE (reg. 3)

MINIMUM REQUIRED FINENESS

FertilizerFineness RequirementsBasic slag, rock phosphate, fused magnesium phosphateGround so that
 not less than 80 per cent will pass through a sieve, mesh No. 100.Bone mealGround so that not less than
 85 per cent will pass through a sieve, mesh No. 8.Bone flourGround so that 100 per cent will pass
 through a sieve, mesh No. 8, and not less than 50 per cent will pass through a sieve, mesh No. 16.

FIFTH SCHEDULE (reg. 13)

FertilizerLimits of VariationAll fertilizers not mentioned elsewhere in this ScheduleAll forms of nitrogen
 (expressed as N): not more than 1/10th of the specified composition above and below the specified
 composition with a minimum of 0.3 per cent of N and a maximum of 1.0 of N.All forms of phosphorus
 (expressed as P₂O₅): not more than 1/15th of the specified composition above and below the specified
 composition with a minimum of 0.5 per cent of P₂O₅ and a maximum of 2.0 per cent of P₂O₅.Potassium
 (expressed as K₂O): not more than 1/15th of the specified composition above and below the specified
 composition with a minimum of 0.7 per cent of K₂O.Chloride (expressed as Cl): not more than 0.5 per
 cent of chloride (Cl) above and below the specified composition.Boron (expressed as B): where the
 boron content is 0.05 per cent of B or less, not more than 1/3rd of the specified composition above and

below the specified composition. Where the boron content is greater than 0.05 per cent of B, not more than 1/5th of the specified composition above and below the specified composition. Straight Fertilizers The tolerance for Straight Fertilizers shall not be more than 1/20th of the specified composition above and below the specified composition with a minimum and a maximum of either N or P₂O₅ or K₂O provided under this Schedule. Ammoniated superphosphates and bone products Total nitrogen (expressed as N): not more than 0.5 per cent of nitrogen above and below the specified composition. All forms of phosphorus (expressed as P₂O₅): not more than 1/20th of the specified composition above and below the specified composition with a minimum of 0.5 per cent. of P₂O₅ and a maximum of 2.0 per cent. of P₂O₅. Guanos Total nitrogen (expressed as N): not more than 1/5th of the specified composition with a minimum of 0.3 per cent. of N. and a maximum of 1.5 per cent. of N. Total phosphorus (expressed as P₂O₅): not more than 1/10th of the specified composition above and below the specified composition with a minimum of 0.5 per cent. of P₂O₅ and a maximum of 2.0 per cent. of P₂O₅. Potassium (expressed as K₂O): not more than 1/5th of the specified composition above and below the specified composition. Boron and fertilizer borate Boron (expressed as B): not more than 1/10th of the specified composition above and below the specified composition with a maximum of 1.0 per cent. of B.

SIXTH SCHEDULE

METHODS OF ANALYSIS

1. Preparation of the sample for analysis

1.1 If the sample contains any extraneous matter which cannot be conveniently ground and homogenized with the rest of the material, such matter should be removed, weighed and allowed for in calculating the results of the analysis.

1.2 Where a fertilizer is too moist to be ground in its original condition, the sample should be thoroughly mixed and a portion thereof taken for moisture determination as described at 2.1 below.

The remaining portion shall be dried at 100°C., except where the fertilizer may lose ammonia on heating or contains soluble phosphorus compounds. In these latter cases, the sample should be dried either by placing it in a desiccator over anhydrous calcium chloride or silica gel, or alternatively by passing dry air at room temperature over it until it is in a suitable condition for grinding. The dried sample should then be treated appropriately as described under 1.4 and 2.2 below.

1.3 The results of analysis of the dried sample should be adjusted to and expressed on the "as received" basis.

1.4 Crystalline, dry powder or granular fertilizers.—Grind the sample to pass through a mesh No. 16 sieve, mix thoroughly and finely grind a portion of about 250 g. in a mortar.

1.5 Basic slag.—Grind the sample to pass through a mesh No. 100 sieve.

1.6 Liquid fertilizers.—The sample should be thoroughly mixed before analysis. The prepared portion of the sample shall be stored in a non-corrodible container fitted with an air-tight screw-cap or stopper.

2. Determination of moisture

2.1 In absence of volatile constituents.—In duplicate, weigh to the nearest mg. about 5 g. of the sample, heat in the oven at 100°C. for 5 hours, cool in a desiccator, and weigh again.

In the case of sodium nitrate, ammonium sulphate and potassium salts, heat to constant weight at 130°C.

2.2 In presence of volatile constituents.—In duplicate, weigh to the nearest mg. about 5 g. of the sample and dry by placing in a vacuum desiccator overnight under not less than 20 in. vacuum, or by subjection to passage of dry air at room temperature overnight, as mentioned at 1.2 above. Weigh again.

2.3 Calculate the loss in weight as a percentage of the original weight.

3. Preparation of extracts

3.1 If the fertilizer is mixture or a substance in an impure state, extract it for the required elements as described under the respective headings below.

3.2 If the material is a pure compound, however, and is soluble in water (e.g. sulphate of ammonia, muriate of potash or sulphate of potash), extract it by dissolving an accurately weighed (correct to the nearest mg.) portion of the sample in a measured volume of water and determine the required constituents on aliquots drawn from such solutions.

4. Determination of nitrogen

4.1 Reagents to be used:

- (a) Concentrated sulphuric acid (preferably nitrogen-free).
- (b) Salicylic acid (analytical reagent grade).
- (c) Zinc dust or sodium thiosulphate.
- (d) Mixed catalyst.—Grind and mix together: 160 g. anhydrous potassium sulphate (K_2SO_4) or sodium sulphate (Na_2SO_4) 10 g. cupric sulphate ($CuSO_4 \cdot 5H_2O$) 3 g. selenium powder.
- (e) Capryl alcohol or paraffin wax.
- (f) Sodium hydroxide: 46 per cent. aqueous solution.
- (g) Boric acid: 2 per cent. aqueous solution, dissolved in boiling water.

(h) Mixed indicator.—To 3 parts of 0.1 per cent., bromcresol green in 90 per cent. ethyl alcohol, add 2 parts of 0.1 per cent. methyl red in 90 per cent. ethyl alcohol.

(i) N/70 Hydrochloric acid.—Add 1.23 ml. concentrated hydrochloric acid (analytical reagent grade) to water and dilute to 1 litre.

(j) Ammonium alum.

(k) Sucrose (analytical reagent grade).

(l) Indigo solution.—Cautiously add 40 ml. of concentrated sulphuric acid to 1 g. of indigo carmine and stir until dissolved. Pour the solution into 800 ml. of water and dilute to 1 litre. Adjust the strength of the solution to comply with the following test:

Add 20 ml. to a solution of 4 mg. of potassium nitrate in 20 ml. of water. Add rapidly 40 ml. of concentrated sulphuric acid and heat to boiling: the blue colour is just discharged in 1 minute.

(m) Ferrous sulphate.

(n) Sodium nitrate.

(o) Magnesium oxide (carbonate-free): Analytical reagent grade magnesium oxide heated at 600-700°C. in a muffle furnace for 2 hours and stored in a desiccator over potassium hydroxide pellets.

4.2 Test for absence of nitrates.

(a) Shake 5 g. of the sample with 80 ml. of water in 100ml. volumetric flask. Add 1 g. of ammonium alum, dilute to 100 ml. shake well and filter into a dry beaker. Dilute 1 ml. of the filtrate with 8 ml. of water. Add 1 ml. of standard indigo solution and 10 ml. of concentrated sulphuric acid. Heat to boiling point. If the blue colour is not discharged, regard the sample as free from nitrates, or

(b) Shake 5 g. of the sample with 25 ml. of hot water and filter. To 1 volume of this solution add 2 volumes of concentrated sulphuric acid (nitrogen-free), and allow to cool. Add a few drops of concentrated ferrous sulphate solution in such a way that the fluids do not mix. If nitrates are present, a purple colour appears at the junction which afterwards turns brown or, if only minute quantities of nitrates exist, a reddish colour. (To another portion of the solution add 1 ml. of 1 per cent. sodium nitrate solution and test as above to determine whether sufficient sulphuric acid was added in the first test.)

4.3 Total nitrogen (organic and ammoniacal) in absence of nitrates:

(i) In duplicate, weigh to the nearest mg. about 1 g. of the sample (or an amount containing not more than 250 mg. of nitrogen) and transfer to a Kjeldahl digestion flask. Add 15 ml. of concentrated sulphuric acid followed by 1.7 g. of mixed catalyst. * Add a few glass beads or porcelain chips to avoid local overheating and control bumping. Heat gently until frothing ceases, adding 2-3

drops of capryl alcohol, or about 0.5 g. of paraffin wax, if frothing is excessive. Increase the heat and continue the digestion until the liquid is clear (pale green or practically colourless). Continue heating for a further hour. Cool, transfer to a 100 ml. volumetric flask and make up to the mark with water. Carry out a blank determination on the reagents using 1 g. of sucrose in place of the sample.

(ii) Transfer a 2 ml. (or suitable) aliquot of the extract obtained at 4.3 (i) above to a Markham still. Add 5 ml. of 46 per cent. sodium hydroxide solution (or enough to ensure an excess of alkali) through the funnel of the still with the stoprod in position. Then lift the stoprod and allow most of the alkali to pass into the still; wash the funnel with 5–10 ml. of water, letting most of the washings run into the still too. Steamdistil, collecting the distillate in a 100 ml conical flask containing 10 ml. of 2 per cent. boric acid to which 5 drops of the mixed indicator have been added and in which the delivery tube of the still dips. Distil until the wine-red colour turns green, taking care not to lose any of the liberated ammonia. Proceed for 1 minute after the green colour has appeared, and then continue distilling for a further minute with the tube above the solution in the receptacle. The rate of distillation should be at least 5 ml. per minute.

(iii) Titrate the recovered ammonia against N/70 hydrochloric acid from a microburette until the original wine-red colour reappears. Express the result in terms of percentage total nitrogen in the sample as received.

1 ml. N/70 HCl=0.2 mg. nitrogen

4.4 Total nitrogen (organic, ammoniacal and nitric) in presence of nitrates

(i) In duplicate, weigh to the nearest mg. about 1 g. of the sample (or an amount containing not more than 250 mg. of nitrogen) and transfer to a Kjeldahl digestion flask. Add 15 ml. of concentrated sulphuric acid and 0.5 g. of salicylic acid, swirl and allow to stand for 30 minutes. Add 1 g. of zinc dust or 5 g. of sodium thiosulphate followed by 1 g. of mixed catalyst and a further 10 ml. of concentrated sulphuric acid. Carry on the extraction as described from the point marked * in paragraph 4.3 (i) above and continue to complete the determination as in paragraphs 4.3 (ii) and (iii), expressing the result as percentage total nitrogen in the sample as received.

1 ml. N/70 HCl=0.2 mg. nitrogen

4.5 Ammoniacal nitrogen

(i) In duplicate, weigh to the nearest mg. about 2 g. of the sample, transfer to a 100 ml. volumetric flask, dissolve or take up by shaking in about 80 ml. of water, make up to the mark and filter if necessary.

(ii) Transfer 5 ml. of the solution (or a quantity containing not more than 25 mg. of nitrogen) to a Markham still, and add a little water. Add 2 ml. of 46 per cent. sodium hydroxide solution through the funnel of the still as described in paragraph 4.3 (ii). (If the sample contains urea, 0.5 g. of carbonatefree light magnesium oxide suspended in water should be used instead of 46 per cent. sodium hydroxide.) Steam-distil and proceed to complete the determination as described in paragraphs 4.3 (ii)

and (iii). Carry out a blank test on the re-agents. Express the result as percentage ammoniacal nitrogen in the sample as received.

1 ml. N/70 HCl=0.2 mg. nitrogen

4.6 Ammoniacal and nitrate nitrogen

(i) In duplicate, weigh to the nearest mg. about 1 g. of the sample, transfer to a 100 ml. volumetric flask, add 80 ml. of water, shake well to dissolve, dilute to volume and filter if necessary.

(ii) Transfer 5 ml. of the solution or filtrate (or a volume containing not more than 25 mg. of nitrogen) to a Markham still. Add 0.5 g. of zinc dust by washing with water through the funnel of the still. Add 2 ml. of 46 per cent. sodium hydroxide solution (or 0.5 g. of carbonate-free light magnesium oxide if urea is known to be present in the sample). Add as much water as the inner jacket of the still can hold without hindering the steam distillation process. Allow to stand in the cold for 15 minutes with the delivery tube of the still dipping in 10 ml. of 2 per cent. boric acid to which 5 drops of mixed indicator have been added, in a 250 ml. conical flask. Then warm gently by passing steam at a slow rate for up to 30 minutes. Slowly increase the temperature and distil at the rate of 5 ml. per minute for 30 minutes, i.e. until about 150 ml. distillate has been collected.

(iii) Titrate the recovered ammonia as described in paragraph 4.3 (iii). Carry out a reagent blank determination in which only the sample is omitted. Express the result as percentage ammoniacal plus nitrate nitrogen in the sample as received.

1 ml. N/70 HCl=0.2 mg. nitrogen

(Note—The difference between the result obtained in this determination and that in the determination in section 4.5 gives the amount of nitrate nitrogen in the sample.)

5. Determination of phosphorus

5.1 Colorimetric ammonium phosphomolybdate methods

(i) Reagents to be used

(a) 50 per cent. (volume/volume) hydrochloric acid.

(b) Ammonium molybdate reagent (1.5 per cent. ammonium molybdate solution in 3.5 N hydrochloric acid).—Dissolve 15 g. ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ in about 300 ml. of water warmed to 50°C., filtering if necessary. Cool; then slowly add 350 ml. of concentrated hydrochloric acid, stirring rapidly. Cool and make up to 1 litre with water. Store in a brown glass-stoppered bottle.

(Note—This reagent must be renewed every 2 months.)

(c) Stannous chloride.—Dissolve 1.25 g. stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 5.6 ml. concentrated hydrochloric acid, warming slightly if necessary to dissolve. Cool and make up to 50 ml. with freshly boiled and cooled water.

(d) Calcium acetate solution.—Dissolve 120 g. calcium acetate in litre of water and slowly add 1 litre of alcohol.

(ii) Extraction

In duplicate, weigh to the nearest mg. about 0.5 g. of the sample into an evaporation basin. (If the sample contains organic matter, saturate with calcium acetate solution and ignite in the muffle furnace at a temperature not exceeding 550°C . until all organic matter is destroyed, i.e. until a uniformly grey ash is obtained. Allow to cool.) Add 10 ml. of 50 per cent. hydrochloric acid, swirling carefully to mix. Evaporate to dryness in a sand bath on a hotplate. Remove, allow to cool somewhat and take up in 2.5 ml. of 50 per cent. hydrochloric acid. Add some hot water and filter into a 100 ml. volumetric flask, using a policeman to loosen and remove the residue from the basin. Wash through the filter paper several times with small portions of hot water, collecting the washings in the flask. Cool, make up to the mark with water and mix well.

(iii) Determination

Pipette a 2 ml. aliquot of the extract into a 50 ml. volumetric flask and * add from a burette 10 ml. of the ammonium molybdate reagent. Make up to the mark with water and then add 0.25 ml. of the stannous chloride reagent from a microburette. Shake to mix thoroughly. Stand to allow maximum colour development and measure the intensity of the blue colour on the Hilger absorptiometer after 5 minutes but within 20 minutes (N.B. The colour fades after 20 minutes) using Filter 70 and a 2 cm. cell.

Determine the amount of phosphorus (as percentage P_2O_5) in the sample from known dilution factors and the weight of the sample, making use of a calibration curve prepared by plotting absorptiometer scale readings against known concentrations of phosphorus in a series of standard solutions prepared as described under paragraph 5.1.1 (iv) below.

(iv) Calibration curve

Phosphorus (P) stock solution.—Dissolve in water 0.2195 g. of analytical grade potassium dihydrogen phosphate (KH_2PO_4), previously dried at 105°C . for 1 hour, and add 25 ml. of 7N sulphuric acid. Make up to 1 litre in a volumetric flask. This solution contains 50 mg. of phosphorus per litre (i.e. 50 mg. P/litre).

Phosphorus P standard solutions.—From a burette measure into a series of 50 ml. volumetric flasks 0.5, 1.0, 1.5, 2.0, 3.5, 5.0, 7.5 and 10 ml. of the 50 mg. P/litre stock solution (i.e. 0.025, 0.050, 0.075, 0.100, 0.175, 0.250, 0.375 and 0.500 mg. P) and dilute to 50 ml. with water. Withdraw 2 ml. aliquots ** from each flask, transfer to a corresponding second series of 50 ml. volumetric flasks and proceed with the determination as described from the point marked * in paragraph 5.1.1 (iii) above.

Plot a calibration curve relating absorptiometer scale readings to the phosphorus concentrations represented by the 2 ml. aliquots withdrawn and referred to at ** in the paragraph immediately above.

5.1.2 Colorimetric phosphomolybdate method for total phosphorus in basic slag

(i) Extraction

In duplicate, weigh to the nearest mg. about 0.5 g. of the sample into a 400 ml. beaker, wet thoroughly with 20 ml. of water and then add a further 80 ml. of water with continuous stirring. Warm the mixture and add dropwise with stirring 10 ml. of concentrated hydrochloric acid, followed by 5 ml. of concentrated nitric acid. Gently boil the solution for 10 minutes, cool and dilute to about 200 ml. with water. Stir to mix and then filter the solution into a 250 ml. volumetric flask through a filter paper which has previously been washed with 20-30 ml. of a solution of 2 per cent. strength (v/v) in respect of nitric acid and 4 per cent. in respect of hydrochloric acid. Wash through the filter paper with several small portions of water into the flask and make up to the mark. Shake to mix thoroughly.

(ii) Determination

Proceed as in paragraph 5.1.1 (iii).

5.1.3 Colorimetric phosphomolybdate method for citric acid-soluble phosphorus in all fertilizers

(i) Extraction

In duplicate weigh to the nearest mg. about 0.5 g. of the sample and transfer to a stoppered bottle of about 500 ml. capacity. Add 250 ml. of a 2 per cent. solution of pure crystallized citric acid (monohydrate) to the sample in the bottle, shaking to avoid possible caking. Shake the bottle continuously for 30 minutes. Pour the whole of the liquid at once onto a large filter paper and collect the filtrate. If the filtrate is not clear, pass it again through the same filter.

(ii) Determination

Proceed as in paragraph 5.1.1 (iii).

5.1.4 Colorimetric phosphomolybdate method for water-soluble phosphorus in all fertilizers

(i) Extraction

In duplicate, weigh to the nearest mg. about 1 g. of the sample and transfer to a stoppered bottle of about 500 ml. capacity. Add 200 ml. of water and shake the bottle continuously for 30 minutes. Filter into a 250 ml. volumetric flask. Wash through the filter with 2-3 large portions of water, make up to the mark and mix well.

(ii) Determination

Proceed as in paragraph 5.1.1 (iii).

5.2 Spectrophotometric vanadophosphomolybdate methods

5.2.1 Reagents to be used

- (a) Concentrated hydrochloric acid.
- (b) Concentrated nitric acid.
- (c) Calcium acetate solution.—Dissolve 120 g. calcium acetate in 1 litre of water and slowly add 1 litre of alcohol.
- (d) Crystallized citric acid (monohydrate).
- (e) Potassium dihydrogen phosphate (KH_2PO_4).—Containing at least 99.8 per cent. of monopotassium dihydrogen phosphate.
- (f) Vanadium molybdate reagent.—Dissolve separately 20 g. of ammonium molybdate and 1 g. of ammonium vanadate in hot water. Cool and then mix by slowly adding the molybdate solution to the vanadate solution. Acidify with 140 ml. of concentrated nitric acid and dilute to 1 litre.
- (g) 1-N Sodium hydroxide.—Dissolve 40.00 g. of sodium hydroxide in water, cool and make up to 1 litre in a volumetric flask. Store in a waxed brown glass bottle.
- (h) Standard phosphate solution.—Dissolve in water 1.9173 g. of potassium dihydrogen phosphate previously dried at 105°C . for 1 hour, and dilute to 1 litre. Make a 5-fold dilution. [1 ml.=0.2 mg. phosphoric acid (P_2O_6)].

5.2.2 Spectrophotometric vanadophosphomolybdate method for total phosphorus in all fertilizers except basic slag

(i) Extraction

(a) In the absence of organic matter

In duplicate, weigh to the nearest mg. about 5 g. of the sample into a 400 ml. beaker, add 100 ml. of water and stir thoroughly. Heat to boiling and, to the boiling mixture, add 10 ml. of concentrated hydrochloric acid in a thin stream, followed by 10 ml. of concentrated nitric acid. Boil gently for 10 minutes, cool, transfer to a 500 ml. volumetric flask and dilute to the mark. Mix well and filter the solution through a dry filter paper into a dry flask, discarding the first 10–20 ml. and retaining the rest of the filtrate.

(b) In the presence of organic matter

In duplicate, weigh to the nearest mg. about 5 g. of the sample into an evaporation basin of about 5 cm. diameter and saturate with calcium acetate solution. Dry the contents slowly and ignite in a muffle furnace at a temperature not exceeding 550°C . until all organic matter is destroyed. Allow to cool and carefully transfer the contents to a 400 ml. beaker.

Add 100 ml. of water, stir thoroughly and heat to boiling. To the boiling mixture add slowly 10 ml. of concentrated hydrochloric acid and 10 ml. of concentrated nitric acid and continue boiling for a further 10 minutes. Cool, transfer to a 500 ml. volumetric flask and dilute to the mark. Mix well and filter through a dry filter paper into a dry flask, discarding the first 10–20 ml. of the filtrate and retaining the rest.

(ii) Standardization of the spectrophotometer (calibration graph)

From a burette measure into a series of 100 ml. volumetric flasks 25.0, 26.0, 27.0, 28.0, 29.0, 30.0 and 31.0 ml. of the standard phosphate solution (i.e. 5.0, 5.2, 5.4, 5.6, 5.8, 6.0 and 6.2 mg. P₂O₅). Add 25 ml. of the vanadomolybdate reagent to each flask and dilute to 100 ml. with water, making sure the reagent and the dilution water are at room temperature. Shake and allow to stand for 10 minutes.

Set the spectrophotometer to a correct wave-length (say 4,000 or 4,200 Å), fill two 1 cm. cells with the 5 mg. P₂O₅ solution and check the optical density of the cells. If there is a small difference, select the cell with the smaller reading as the standard reference cell.

Determine the apparent optical density at room temperature (corrected for cell differences) of the 5.2, 5.4, 5.6, 5.8, 6.0 and 6.2 mg. P₂O₅ solutions referred to the 5.0 mg. P₂O₅ solution as standard.

Plot a calibration graph of scale readings against known P₂O₅ contents.

(iii) Determination (procedure for all determinations except water-soluble phosphorus)

Successively dilute a portion of the extract prepared so that the final volume of about 25 ml. contains between 5.5 and 6.2 mg. P₂O₅, taking care that the dilution water is at room temperature.

Transfer this final volume to a 100 ml. volumetric flask, add 25 ml. of the vanadomolybdate reagent at room temperature, dilute to the mark, mix and allow to stand for 10 minutes. Measure the difference in optical density at room temperature between the two solutions and determine the P₂O₅ content of the volume of the unknown solution from the calibration curve.

From the known dilution factors and weight of the sample, calculate the P₂O₅ content of the sample.

Note:—Prepare a fresh reference standard for each series of readings on the instrument.

5.2.3 Spectrophotometric vanadophosphomolybdate method for total phosphorus in basic slag

(i) Extraction

In duplicate, weigh to the nearest mg. about 2.5 g. of the sample into a 400 ml. beaker, wet thoroughly with 20–30 ml. of water with continuous stirring, and then add a further 70 ml. of water. Warm the mixture and add dropwise with stirring 10 ml. of concentrated hydrochloric acid, followed by

10 ml. of concentrated nitric acid. Gently boil the solution for 10 minutes, cool and dilute to 250 ml. in a volumetric flask. Mix well and filter the solution through a dry filter paper into a dry flask, rejecting the first 20–30 ml. of the filtrate and retaining the rest.

(ii) Determination

Proceed as described in paragraph 5.2.2 (iii) above.

5.2.4 Spectrophotometric vanadophosphomolybdate method for citric acid-soluble phosphorus in all fertilizers

(i) Extraction

In duplicate, weigh to the nearest mg. about 2.5 g. of the sample and transfer to a glass-stoppered bottle of about 500 ml. capacity. Add 250 ml. of a 2 per cent. solution of pure crystallized citric acid (monohydrate), shaking the bottle to avoid possible caking. Shake continuously for 30 minutes. Pour the whole of the liquid at once onto a large filter paper and collect the filtrate. If the filtrate is not clear, pass it again through the same filter.

(ii) Determination

Proceed as described in paragraph 5.2.2 (iii) above.

5.2.5 Spectrophotometric vanadophosphomolybdate method for water-soluble phosphorus in all fertilizers

(i) Extraction

In duplicate, weigh to the nearest mg. about 10 g. of the sample and transfer to a glass-stoppered bottle of about 500 ml. capacity. Add 400 ml. of water and shake continuously for 30 minutes. Transfer the contents to a 500 ml. volumetric flask make up to the mark, mix well and filter, collecting the filtrate in a dry flask.

(ii) Determination

To 25 ml. of the extract add 1 ml. of concentrated nitric acid. Heat to almost boiling on a hotplate and maintain at this temperature for 10 minutes. Cool, neutralize with 1-N sodium hydroxide solution and complete the determination as in paragraph 5.2.2 (iii) above.

6. Determination of potassium

6.1 Flame photometric methods

6.1.1 Reagents to be used

(a) Concentrated hydrochloric acid.

(b) Ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4$.—A saturated aqueous solution.

(c) Concentrated ammonia, NH_4OH .—A solution of specific gravity 0.96.

(d) Potassium dihydrogen phosphate, KH_2PO_4 : Containing at least 99.8 per cent. of monopotassium dihydrogen phosphate.

(e) Standard potash solution.—Dissolve 5.779 g. of potassium dihydrogen phosphate (KH_2PO_4) previously dried for 1 hour at 105°C . and dilute to 1 litre in a volumetric flask. Shake well. Transfer 50 ml. of this solution to a 1 litre volumetric flask and dilute to the mark. Shake well. This final solution now contains 100 mg. K_2O per litre (i.e. 100 mg. $\text{K}_2\text{O}/\text{l}$.).

6.1.2 Method for potassium salts other than those containing ammonium, calcium, iron, aluminium or other interfering substances

(i) Extraction

In duplicate, weigh to the nearest mg. about 0.5 g. of the sample and transfer to a 400 ml. beaker. Add 10 ml. of concentrated hydrochloric acid and 50 ml. of water and bring to boiling, using a stirring with a flattened end to break down any crystals or lumps. Dilute with water to about 100 ml. and boil gently for a few minutes. Cool, transfer to a 250 ml. volumetric flask and make up to the mark. Mix well and filter through a dry filter paper.

Successively dilute a measured portion of the extract so that the final solutions contains approximately 16 mg. $\text{K}_2\text{O}/\text{l}$. and determine the potash content of the extract as described under paragraph 6.1.2 (iii) below.

(ii) Standardization of the flame photometer (calibration graph)

From the standard (100 mg. $\text{K}_2\text{O}/\text{l}$.) potash solution obtained under paragraph 6.1.1 (e) above, prepare a set of accurate dilutions containing 10, 12, 14, 16, 18 and 20 mg. $\text{K}_2\text{O}/\text{l}$. (e.g. by correspondingly diluting 10, 12, 14, 16, 18 and 20 ml. of the standard solution to 100 ml. in a series of 100 ml. volumetric flasks). Set the sensitivity of the flame photometer so that 100 scale divisions (i.e. full-scale deflection) are equivalent to the 20 mg. $\text{K}_2\text{O}/\text{l}$. solution. Spray the 10, 12, 14, 16 and 18 mg. $\text{K}_2\text{O}/\text{l}$. solutions three times. Take the median reading (not the mean) and construct a calibration graph. (N.B.—After spraying each different strength solution, spray the 20 mg. $\text{K}_2\text{O}/\text{l}$. solution again to ensure that the sensitivity of the flame photometer has not changed.)

(iii) Determination

Reset the photometer at 100 scale divisions with the 20 mg. $\text{K}_2\text{O}/\text{l}$. solution. Spray the diluted fertilizer extract obtained as described under paragraph 6.1.2 (i) above, and read the approximate K_2O content of the solution from the graph prepared as described in paragraph 6.1.2 (ii) above.

Prepare two further dilutions of the standard K_2O solution to contain respectively 1 mg. $\text{K}_2\text{O}/\text{l}$. more and 1 mg. $\text{K}_2\text{O}/\text{l}$. less than the estimated K_2O content of the diluted solution of the

sample. Successively spray the low standard solution, the diluted solution of the sample, and the high standard solution. Repeat this twice more. Take the median result of each set of three readings and calculate the K₂O content of the sample solution and hence of the fertilizer, from the proportionality of the radiation given by the sample solution and that given by the two standard solutions containing respectively 1 mg. K₂O/1. more and 1 mg. K₂O/1. less than the predicated K₂O content.

(Note.—Diluted standard solutions should be freshly prepared, and the photometer must be set up in a vibration-free position and a dust-free atmosphere.)

6.1.3 Method for potassium in mixed fertilizers containing little or no organic matter, or in salts containing ammonium, calcium, iron, aluminium or other interfering substances

(i) Extraction

In duplicate, weigh to the nearest mg. about 2.5 g. of the sample and place in a 400 ml. beaker. Add 125 ml. of water and 50 ml. of saturated ammonium oxalate solution. Boil for 30 minutes, adding, if necessary, a small quantity of a potassium-free anti-foaming agent (e.g. capryl alcohol). Cool, add a slight excess of concentrated ammonia solution and cool to room temperature. Dilute to 250 ml. in a volumetric flask, mix and filter through a dry filter paper.

Successively dilute a measured portion of the extract so that the final solution contains approximately 16 mg. K₂O/1. and determine the potash content as described in paragraph 6.1.2 (iii) above.

6.1.4 Method for potassium in mixed fertilizers containing organic matter

(i) Extraction

In duplicate, weigh to the nearest mg. about 10 g. of the sample into an evaporation basin and gently incinerate in a muffle furnace at a temperature not exceeding 500°C. to destroy organic matter. Grind the residue to eliminate any lumps. Add 125 ml. of water and 50 ml. of saturated ammonium oxalate solution and boil for 30 minutes. Cool, add a slight excess of concentrated ammonia solution, cool to room temperature, and dilute to 500 ml. in a volumetric flask. Mix well and filter through a dry filter paper.

Successively dilute a measured portion of the extract so that the final solution contains approximately 16 mg. K₂O/1. and determine the potash content as described in paragraph 6.1.2 (iii) above.

7. Determination of calcium

7.1 Volumetric method

7.1.1 Reagents to be used

(a) 0.02N versenate solution.—Dissolve 3.723 g. of disodium ethylenediamine tetracetate (EDTA) and make up to 1 litre with water. Standardize this solution at least once per month against 0.02N calcium chloride solution (1.001 g. of analytical reagent grade calcium carbonate previously dried at 105°C., dissolved in about 250 ml. of water containing 5 ml. of concentrated analytical reagent grade hydrochloric acid, boiled, cooled and made up to 1 litre with water=0.02N calcium chloride), using 2 ml. of 10 per cent. potassium hydroxide solution in a volume of about 50 ml. for buffering but omitting reagent (b) below.

(b) Sodium diethyldithiocarbamate (0.3 per cent. aqueous solution). Shake vigorously to dissolved; filtering is not necessary.

(c) Potassium hydroxide (10 per cent. aqueous solution).

(d) Concentrated hydrochloric acid.

(e) Murexide/sodium chloride mixture as an indicator.—To 100 g. sodium chloride add 0.5 g. ammonium purpurate; grind to mix well.

OR

(f) Alizarin indicator.—Dissolve 0.5 g. of the indicator solid in 75 ml. of triethanolamine and make up to 100 ml. with absolute ethanol.

7.1.2 Procedure

(i) Extraction

In duplicate, weigh to the nearest mg. about 0.4 g. of the sample into a 250 ml. beaker and add 10 ml. of concentrated hydrochloric acid. Heat, if necessary, to dissolve. Add 20 ml. of water and boil down to about 5 ml. Then dilute and filter while hot into a 100 ml. volumetric flask. Cool and make up to the mark with water.

(ii) Determination

Pipette a suitable aliquot (2 ml. is adequate if the sample has a high calcium content) into a 250 ml. conical flask. Add 1 ml. of 0.3 per cent. sodium diethyldithiocarbamate, 20 ml. of 10 per cent. potassium hydroxide solution, and about 0.3 g. of murexide/sodium chloride (or 6 drops of alizarin) indicator. Titrate against 0.02N versenate (EDTA) solution, using a microburette. (The colour change at the end point is from wine-red to violet.) Calculate the calcium content from the titre obtained and from the weight of the sample equivalent to the aliquot of the extract taken.

1 ml. 0.02N EDTA=0.4008 mg. Ca.

Express the result in terms of percentage calcium oxide in the sample.

$\% \text{CaO} = \% \text{Ca} * 1.40$

7.2 Gravimetric method

7.2.1 Reagents to be used

- (a) Concentrated hydrochloric acid.
- (b) Ammonium oxalate solutions.—6 per cent. and 0.1 per cent. aqueous solutions.
- (c) Ammonium hydroxide (1:1).—50 per cent. aqueous solution (v/v).
- (d) Methyl red indicator.—Dissolve 0.1 g. of methyl red in 250 ml. of ethanol.

7.2.2 Procedure

(i) Extraction

In duplicate, weigh to the nearest mg. about 0.5 g. of the sample and place in a 400 ml. beaker. Add 10 ml. of water and 10 ml. of concentrated hydrochloric acid, and heat, if necessary, to dissolve. Dilute to about 200 ml. with water. Filter if necessary (i.e. if suspended impurities are present). Add 3–4 drops of methyl red indicator and heat to boiling. While boiling, add 500 ml. of warm 6 per cent. ammonium oxalate solution. To the hot solution add dropwise, with stirring, 1:1 ammonium hydroxide, maintaining the temperature at about 80°C. or above, until the solution is neutral or faintly alkaline. Stand warm for at least 1 hour. After the precipitate has settled, test for complete precipitation by adding a few drops of 6 per cent. ammonium oxalate solution (run the solution down a glass rod).

If precipitation is complete, filter through paper suitable for fine precipitates (e.g. Whatman No. 40 paper), washing the precipitate of calcium oxalate chloride-free with cold 0.1 per cent. ammonium oxalate. (Test for chloride by taking 5 ml. of the washings and adding dilute nitric acid followed by a few drops of dilute silver nitrate solution: if no precipitate forms, then the calcium oxalate precipitate is chloride-free; if a precipitate forms with silver nitrate, continue washing with cold 0.1 per cent. ammonium oxalate till chloride-free.)

(ii) Determination

Then transfer the precipitate and the filter paper to a tared crucible previously ignited at 500°C. and cooled. Dry in the oven at 110–120°C. When dry, ignite in the muffle furnace for 2 hours with the temperature maintained at 500°C. or just below. (Note.—Cover the crucible with a lid during ignition but slightly tilt the lid over to one side to permit oxidation.) Cool the crucible in a desiccator and weigh the resultant calcium carbonate. Return to the furnace and ignite at 500°C. for a further 1 hour. Cool and reweigh.

(If a change in weight occurs, some of the carbonate has been converted to oxide: moisten with a few drops of a saturated ammonium carbonate solution, dry in the oven at 110°C. cool and weigh. Gain in weight proves oxide was present.) Calculate the percentage calcium content from the weight of the calcium carbonate obtained and that of the sample taken:

$\% \text{ Ca} = \text{wt. of CaCO}_3 \times 0.4004 \times 100 \dots \text{wt. of sample taken}$

(Note.—In this gravimetric method, calcium may also be finally determined as the oxide by igniting the calcium carbonate precipitate obtained and subjecting it to dissociation at 900°C. until constant weight is attained. The percentage calcium content is then calculated from the weight of the calcium oxide obtained and that of the sample taken:

$\% \text{ Ca} = \text{wt. of CaO} \times 0.7147 \times 100 \dots \text{wt. of sample taken}$

8. Determination of magnesium (e.g. in dolomite)

8.1 Reagents to be used

- (a) 0.02N versenate (EDTA) solution.—As described under paragraph 7.1.1 (a).
- (b) Sodium diethyldithiocarbamate (0.3 per cent. aqueous solution).—As under paragraph 7.1.1 (b).
- (c) Ammonium chloride/ammonium hydroxide buffer solution (pH 10).—Dissolve 67.5 g. of ammonium chloride in 570 ml. of concentrated ammonium hydroxide solution and make up to 1 litre with water.
- (d) Eriochrome Black-T indicator.—Dissolve 0.5 g. of Eriochrome Black-T powder and 4.5 g. of hydroxylamine hydrochloride in 100 ml. of 95 per cent. ethanol.
- (e) Concentrated hydrochloric acid.

8.2 Procedure

- (i) Extraction (for magnesium in presence of calcium e.g. dolomite)

Follow the procedure described in paragraph 7.1.2 (i).

- (ii) Determination

Pipette a suitable aliquot (2 ml. is adequate if calcium content is high) into a 250 ml. conical flask. Add 1 ml. of 0.3 per cent. sodium diethyldithiocarbamate, 5 ml. of ammonium chloride/ammonium hydroxide buffer solution and 10 drops of Eriochrome Black-T indicator solution. Titrate with 0.02N versenate (EDTA) solution, using a microburette. (The end-point colour change is from wine-red to blue.) In presence of calcium, the total amount of EDTA solution added to reach this end-point gives a measure of the sum of calcium and magnesium. The difference between the quantity of EDTA solution used to determine the content of calcium alone and that used to determine the sum of calcium and magnesium in an equivalent aliquot of the extract represents the magnesium content of the aliquot.

In the absence of calcium, the titre obtained represents the amount of magnesium present in the aliquot.

Calculate the magnesium content of the sample from the direct or differential titre obtained (whichever is applicable) and from the weight of the sample equivalent to the aliquot of the extract taken.

1 ml. 0.02N EDTA=0.2432 mg. Mg.

Express the result in terms of percentage magnesium oxide in the sample.

% MgO= % Mg \times 1.66

9. Determination of boron

9.1 Reagents to be used

- (a) 5 per cent. nitric acid solution.
- (b) Bismuth nitrate solution.—Dissolve 22 g. of bismuth nitrate in 8 ml. of concentrated nitric acid and dilute to 100 ml. with water.
- (c) 10 per cent. sodium hydroxide solution.
- (d) 0.02N sodium hydroxide solution.—Carbon dioxide free.
- (e) Mannitol.
- (f) Bromothymol blue indicator solution.

9.2 Procedure

(i) Extraction

In duplicate, weigh to the nearest mg. about 2.5 g. of the sample and transfer to a 400 ml. beaker. Add 2 ml. of concentrated nitric acid and 50 ml. of water, stir, warm, and dilute to 100 ml. with water. Warm to 75°–85°C. (do not boil as boric acid is volatile) and slowly add from a burette with continuous stirring 5 ml. of bismuth nitrate solution for each 25 mg. of phosphorus (P₂O₅) present. Keep the solution hot during precipitation. Allow the precipitate to settle, cool, wash into a 250 ml. volumetric flask and dilute to the mark. Filter through a dry paper, discarding the first 10–20 ml.

(ii) Determination

To a 100 ml. aliquot add a few drops of bromothymol blue indicator solution and then 10 per cent. sodium hydroxide solution until the indicator turns blue. Filter and wash the precipitate several times with cold water to give a total volume of filtrate of 150–200 ml. Using a pH meter, adjust to pH 5, adding 5 per cent. nitric acid solution. Heat to about 85°C. (do not boil) and stir vigorously to expel carbon dioxide.

Cool and titrate with 0.02N sodium hydroxide solution to pH 6.3. Add 10 g. of mannitol and readjust to pH 6.3 with 0.02N sodium hydroxide solution. Continue to add 10 g. portions of mannitol

and to adjust to pH 6.3 until, after the final addition of mannitol, the pH remains constant at 6.3. The total amount of 0.02N sodium hydroxide solution used after the first addition of mannitol corresponds to the amount of boron present in the solution.

Carry out a reagent blank determination.

Calculate the amount of boron in the portion taken for analysis from the factor:

1.0 ml. 0.02N NaOH=0.216 mg. B

10. Determination of chloride

10.1 Reagents to be used

- (a) Dilute nitric acid.—Dilute 1 volume of concentrated nitric acid with 1 volume of water.
- (b) Nitrobenzene.—Analytical reagent grade.
- (c) 0.1N silver nitrate solution.
- (d) 0.1N potassium thiocyanate solution.
- (e) Ferric alum indicator solution.—Prepare a saturated solution of ferric ammonium sulphate and add a small quantity of dilute nitric acid.

10.2 Procedure

(i) Extraction

In duplicate, weigh to the nearest mg. about 5 g. of the sample and transfer to a stoppered bottle of about 500 ml. capacity marked at 250 ml. Add 200 ml. of water and shake continuously for 30 minutes. Transfer through a filter paper into a 250 ml. volumetric flask, washing several times with small portions of water. Make up to the mark and shake to mix well.

(ii) Determination

Dilute an aliquot of the extract (containing about 70 mg. Cl) to 100 ml. with water, add 10 ml. of dilute nitric acid, an excess of 0.1N silver nitrate solution, 2–3 ml. of nitrobenzene and 1 ml. of ferric alum indicator. Shake vigorously to coagulate the precipitate. Titrate the residual silver nitrate with 0.1N potassium thiocyanate solution until a faint reddish-brown colour persists. Carry out a reagent blank determination.

Calculate the amount of chloride in the portion taken for analysis from the relationship:

1 ml. 0.1N AgNO₃=3.55 mg. Cl

11. Determination of sulphate

11.1 Reagents to be used

- (a) Concentrated hydrochloric acid.
- (b) Concentrated nitric acid.
- (c) 5 per cent. barium chloride (BaCl_2) solution.

11.2 Procedure

(i) Extraction

In duplicate, weigh to the nearest mg. about 1 g. of the sample and transfer to a 250 ml. beaker. Add 20 ml. of concentrated hydrochloric acid followed by 4 ml. of concentrated nitric acid. Evaporate just to dryness on a hotplate in the fume chamber, covering the beaker with a watchglass to avoid loss through spattering. Cool, add 2 ml. of concentrated hydrochloric acid and dilute to about 200 ml. with hot water. Filter into a 500 ml. volumetric flask, washing 4–5 times with hot water. Cool, make up to the mark and shake well.

(ii) Determination

To a 100 ml. aliquot in a 400 ml. beaker, add water until the volume is about 200 ml. Heat to boiling and slowly add 20 ml. of 5 per cent. barium chloride solution with stirring. Maintain at gentle boiling for about 15 minutes, allow the precipitate to settle and add a few drops of the 5 per cent. barium chloride solution to confirm that precipitation is complete. Stand for at least 2 hours (preferably overnight) to obtain a coarse, easily-filtered precipitate.

Filter by decantation through filter paper of suitable texture (e.g. Whatman No. 40), washing the precipitate with hot water. Transfer the precipitate quantitatively to the filter paper and continue washing with hot water until the filtrate is chloride-free (i.e. until a clear solution, or no more than a very faint opalescence, results after adding dilute silver nitrate solution to a portion of the washings acidified with about 1 ml. of dilute (2N) nitric acid).

Place the filter paper plus the precipitate in a previously ignited, cooled and weighed silica or porcelain crucible, and dry in the oven at 100°C . Transfer to the muffle furnace and gradually raise the temperature until the paper begins to char. (N.B.—The paper must not catch fire.) Then heat at $500\text{--}600^\circ\text{C}$. until incineration is complete.

Cool in a desiccator and weigh as barium sulphate, BaSO_4 .

(iii) Calculation

As barium sulphate contains 41.153 per cent. sulphate, the amount of sulphate in the sample can be calculated from the relationship:

$\% \text{SO}_4 \text{ in sample} = \text{wt. of } \text{BaSO}_4 \text{ precipitate obtained} \times 41.153 \dots \text{wt. of sample}$
equivalent to the aliquot of extract taken