STATUTORY INSTRUMENTS

1980 No. 1130

AGRICULTURE

The Fertilisers (Sampling and Analysis) (Amendment) Regulations 1980

Made - - - -	30*th July* 1980
Laid before Parliament	12*th August* 1980
Coming into Operation	1*st November* 1980

The Minister of Agriculture, Fisheries and Food, the Secretary of State for Scotland and the Secretary of State for Wales, acting jointly, in exercise of the powers conferred by sections 66(1), 74A, 75(1), 76(1), 77(4), 78(6), 79(1), (2) and (9) and 84 of the Agriculture Act 1970**(a)** and now vested in them**(b)**, and of all other powers enabling them in that behalf, hereby make the following regulations after consultation with such persons or organisations as appear to them to represent the interests concerned:—

Citation, commencement and interpretation

1.—(1) These regulations may be cited as the Fertilisers (Sampling and Analysis) (Amendment) Regulations 1980 and shall come into operation on 1st November 1980.

(2) In these regulations "the principal regulations" means the Fertilisers (Sampling and Analysis) Regulations 1978**(c)**.

Amendment of regulation 1 of the principal regulations

2. Regulation 1(2) of the principal regulations shall be amended by adding immediately after the definition of "the Act" the following definitions—

"EEC fertiliser" has the meaning assigned to it by regulation 1(2) of the Fertilisers Regulations 1977**(d)**;

"the 1977 regulations" means the Fertilisers Regulations 1977.

New regulation 6

3. For regulation 6 of the principal regulations there shall be substituted the following new regulation—

"**6.**—(1) The methods by which analysis of fertilisers shall be made for the purposes of the Act shall be those set out in Schedules 2 and 2A.

(2) Analytical constituents of materials listed in Groups 1(a), 1(b), 2(a) and 3(a) of Section A and Groups 1 to 4 of Section B of the table in Schedule 1 to the 1977 regulations shall be determined by the appropriate method of analysis prescribed in Schedule 2.

(3) In the case of "Phosphated slag" and "Rock phosphate" in Group 2(b) of Section A and "Phosphatic fertiliser" in Group 2(d) of Section A of

(a) 1970 c. 40; Section 74A was inserted by the European Communities Act 1972 (c. 69), section 4(1) and Schedule 4, paragraph 6.
(b) In the case of the Secretary of State for Wales by virtue of S.I. 1978/272.
(c) S.I. 1978/1108.
(d) S.I. 1977/1489, as amended by S.I. 1978/1108.

the said table, the amount of phosphorus pentoxide soluble in 2% formic acid shall be determined by the method prescribed in Schedule 2.

(4) In the case of "Basic slag medium concentration" and "Granular basic slag" in Group 2(b) of Section A of the said table, fineness shall be determined by the method prescribed in Schedule 2.

(5) In respect of analytical constituents of materials not provided for in paragraphs (2), (3) and (4) of this regulation, the methods of analysis prescribed in Schedule 2A shall apply.".

Amendment of Regulation 10 of the principal regulations

4. For regulation 10 of the principal regulations, there shall be substituted the following regulation—

"**10.** As respects their application to fertilisers, regulations 3, 4, 5, 15, 16 and 17 and Parts I, II and IV of Schedule 1, Schedule 6 and Part I of Schedule 8 of the Fertilisers and Feeding Stuffs Regulations 1973**(a)** shall cease to have effect on 1st November 1980.".

New Schedule 2A

5. The provisions of the Schedule to these regulations shall be inserted as Schedule 2A to the principal regulations.

Amendment of Schedule 3 to the principal regulations

6. The Form of Certificate of Analysis specified in Schedule 3 to the principal regulations shall be amended by substituting for note (11) thereto the following new note—

"(11) In the case of analysis of substances for which no analytical method is prescribed by regulation 6 and Schedules 2 and 2A here indicate the method used. If analysis cannot be carried out because no suitable method exists then the certificate should state this.".

Amendment of the 1977 regulations

7. Regulation 2(2) of the 1977 regulations shall be amended by substituting for the words "organic substance" the words "organic nutrients of animal or vegetable origin".

In Witness whereof the Official Seal of the Minister of Agriculture, Fisheries and Food is hereunto affixed on 24th July 1980.

(L.S.)

Peter Walker,
Minister of Agriculture, Fisheries and Food.

28th July 1980.

George Younger,
Secretary of State for Scotland.

30th July 1980.

Nicholas Edwards,
Secretary of State for Wales.

(a) S.I. 1973/1521, as amended by S.I. 1976/840, 1977/115.

SCHEDULE Regulation 5

PROVISIONS TO BE INSERTED AS SCHEDULE 2A TO THE PRINCIPAL REGULATIONS

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SCHEDULE 2A

METHODS OF ANALYSIS

1. **General**

(*a*) When two or more methods are prescribed in this Schedule to determine a component of a fertiliser the choice of the method shall, except where otherwise indicated, be left to the agricultural analyst concerned; the method used must, however, be indicated in the certificate of analysis.

(*b*) Any reference to water in this Schedule means purified water as defined in the European Pharmacopoeia.

2. **Reagents and Apparatus**

(*a*) All reagents used shall be of analytical quality.

(*b*) For the determination of any form of nitrogen, water must be free of all nitrogenous compounds and carbon dioxide.

(*c*) Solutions for which no solvents are prescribed must be aqueous.

(*d*) Only special instruments or apparatus requiring special standards are mentioned in the descriptions of the methods of analysis.

3. **Methods of Analysis**

1. Preparation of the sample for analysis
2. Determination of moisture
3. Determination of total nitrogen—chromium powder reduction method
4. Determination of urea

5a. Extraction of phosphorus—by mineral acids (total phosphorus)
5b. Extraction of phosphorus—by 2% citric acid
5c. Extraction of phosphorus—by water

6a. Determination of extracted phosphorus—gravimetric method
6b. Determination of extracted phosphorus—spectrophotometric method

7a. Determination of potassium—gravimetric method
7b. Determination of potassium—flame photometric method

8. Determination of total magnesium

9a. Determination of boron—titrimetric method
9b. Determination of boron—spectrophotometric method

10. Determination of cobalt
11. Determination of molybdenum
12. Determination of copper
13. Determination of iron
14. Determination of manganese
15. Determination of the neutralising value in liming materials
16. Determination of fineness of products other than potassic basic slag
17. Determination of fineness of potassic basic slag

1. PREPARATION OF THE SAMPLE FOR ANALYSIS

1. Introduction

The preparation of a sample for analysis from the final sample received at the laboratory is a series of operations, usually sieving, grinding and mixing, carried out in such a way that the smallest amount weighed, as prescribed by the method of analysis chosen, is representative of the final sample. The sample should be ground to the fineness required by the method of analysis. (Over-grinding must be avoided in cases where this will affect the solubility in various reagents.) With some materials, fine grinding may lead to loss or gain of moisture and allowance for this must be made.

2. Scope and Field of Application

This method is applicable to fertilisers in Groups 1(c), 1(d), 2(b), 2(c), 2(d), 3(b), 3(c), 4(a), 4(b), 4(c) of Section A and Group 5 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977. It is also applicable to products in Group 5(a) of Section A in the said table when the determination of total magnesium is required.

This method is also applicable to liquid fertilisers.

The determination of the fineness of fertilisers is carried out on the sample as received.

3. Principle

3.1 *Solid fertilisers:* the whole final sample is ground to the required fineness. All the ground sample is thoroughly mixed before each test portion is taken.

3.2 *Liquid fertilisers:* the final sample is thoroughly mixed before each test portion is taken.

4. Apparatus

4.1 Sample grinder capable of grinding the fertiliser to pass the specified sieve.

4.2 Mortar and pestle of suitable material and size.

4.3 Sieves having square apertures of 0·18mm, 0·5mm and 1·0mm. Test sieves conforming to British Standard 410:1976 are suitable.

4.4 Sample containers of non-corrodible materials, with air-tight closures.

5. Procedure

WARNING

All operations connected with this procedure should be carried out as quickly as possible to minimise absorption or loss of water. Care should be taken during grinding that the temperature of the fertiliser does not rise above 45°C to avoid loss of volatile constituents. Grinding beyond the fineness required must in all cases be avoided.

5.1 *Grinding and sieving*

The procedure in 5.1.1 should be followed except when a grinding machine is not available, in which case 5.1.2 is applicable.

5.1.1 Grind the final sample until all the sample has passed through, or for the specified time, depending on the type of grinder (4.1). To check that the grinding has been adequate, sieve a small portion of the ground sample through a 0·5mm sieve (4.3) and discard it. If the whole of this portion does not pass the sieve, return the remainder of the sample to the grinder and repeat the grinding until satisfactory grinding is achieved.

5.1.2 Sieve the whole final sample through a 0·5mm sieve (4.3). Grind the residue on the sieve, using the pestle and mortar (4.2), until all the material passes through the sieve. Carefully mix the sample.

5.2 Place the prepared sample in a clean container (4.4) and seal it until required for analysis.

5.3 Before taking each test portion for analysis, the whole sample must be well mixed. Form the material into a flattened cone and using a spatula take the required test portion at random in small increments.

5.4 If the sample contains foreign matter which cannot be ground this shall be removed, weighed and allowed for in the results of the analysis. This material shall be retained and if possible its nature recorded.

6. **Special Cases**

6.1 *Samples not to be ground*

For those samples where the amount of phosphorus pentoxide soluble in 2% citric acid and the fineness of grinding are to be determined, the sample should be well mixed (soft lumps may be disintegrated by lightly crushing) and divided into two parts, which are as identical as possible. The above-mentioned determinations shall be carried out on the unground sample. All other determinations shall be carried out on the sample prepared in accordance with the directions in paragraph 5.1.

6.2 *Products which may be difficult to grind mechanically, including products with abnormal moisture or products which become doughy through grinding*

Some products such as superphosphate may become doughy if ground mechanically. In these cases crush the sample in a mortar (4.2) so that all the material passes through a 1·0mm sieve (4.3). Place the material so crushed in a clean container (4.4) and seal it until required for analysis.

6.3 *Organic materials*

Some organic materials may be of such a nature that the procedures given above cannot be used (for example fresh guano, leather, wool and animal residues). In these cases the analyst should use the best practicable means to obtain a representative sample.

6.4 *Fertilisers comprising several different materials*

These fertilisers include materials with marked differences in texture or mechanical properties (hardness, density, etc.). They may be difficult to grind entirely (for example mixtures of organic and inorganic materials) or they may segregate during handling (for example "Kalimagnesia"). Special procedures are necessary in these cases:—

6.4.1 for mixtures other than those in 6.4.2, follow the procedure in 5.1.1, replacing the 0·5mm sieve by one with apertures of 0·18mm. A grinding machine, capable of grinding the whole of the sample to the required fineness in one pass, is strongly recommended;

6.4.2 in the case of mixtures containing one or more very hard components, or mixtures containing organic materials, it may be difficult to grind and homogenise all the components. To avoid overgrinding some of the softer components proceed as follows:—

grind the sample as in 5.1.1 or 5.1.2 to pass a 0·5mm sieve. Re-sieve the sample through a 0·18mm sieve and reduce the residue to a convenient size by further grinding or other practicable means. Thoroughly remix the sample and place in a clean container (4.4).

7. **Liquid Fertilisers**

Mix thoroughly by shaking, ensuring that any insoluble matter is thoroughly dispersed, immediately before drawing a portion of the sample for analysis.

2. DETERMINATION OF MOISTURE

1. **Scope and Field of Application**

This method is applicable to all fertilisers where a correction for moisture is necessary.

2. **Principle**

The sample is dried to constant weight in an oven at 100°C. The loss in weight corresponds to the moisture content of the sample.

3. **Apparatus**

3.1 Suitable containers with lids ensuring air-tight closure; the dimensions should allow the sample to be spread at about 0·3g per cm^2.

3.2 Electrically heated oven, suitably ventilated and capable of being maintained at 100±2°C.

4. **Preparation of Sample**

See Method 1.

5. **Procedure**

Weigh to the nearest 0·001g, 5g of the prepared sample and transfer to a previously weighed container (3.1). Place the uncovered container and the lid in the oven (3.2) for 2 to 3 hours. Replace the lid on the container, remove from the oven and allow to cool in a dessicator and weigh. Reheat for another hour, cool and reweigh. If the difference in weight exceeds 0·01g continue the heating and cooling procedure until a weight constant within 0·01g is attained.

6. **Expression of the Result**

Calculate the total loss of weight and express it as a percentage of the original weight.

3. DETERMINATION OF TOTAL NITROGEN—CHROMIUM POWDER REDUCTION METHOD

1. **Scope and Field of Application**

This method is applicable to fertilisers in Groups 1(c), 1(d), 3(b), 4(a) and 4(c) of Section A and Group 5 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977 in respect of which the indication of total nitrogen is required.

2. **Principle**

The nitrate is reduced to ammonia by chromium powder in an acid medium. Organic and ureic nitrogen is converted into ammonium sulphate by digestion with concentrated sulphuric acid using a catalyst. The ammonia is distilled from an alkaline solution and absorbed in standard acid. The excess acid is titrated with standard alkali.

3. **Reagents**

3.1 Sodium hydroxide solution: 40g per 100ml, ammonia free.

3.2 Sulphuric acid, 0·1N solution.

3.3 Sulphuric acid, 0·2N solution.

3.4 Sulphuric acid, 0·5N solution.

3.5 Sodium hydroxide, 0·2N solution, carbonate free.

3.6 Chromium metal powder, 100 mesh, low nitrogen content.

3.7 Anti-bump granules of pumice stone, washed in hydrochloric acid and ignited.

3.8 Anti-foaming agent, paraffin wax.

3.9 Sulphuric acid (d = 1·84g/ml).

3.10 Hydrochloric acid (d = 1·18g/ml).

3.11 Catalyst mixture: 1000g potassium sulphate and 50g copper sulphate pentahydrate. The ingredients must be ground and thoroughly mixed.

3.12 Indicator solutions:

3.12.1 Mixed indicator:
mix 50ml of 2g/litre ethanolic solution of methyl red with 50ml of 1g/litre ethanolic solution of methylene blue.

3.12.2 Methyl red indicator:
dissolve 0·1g methyl red in 50ml ethanol. This indicator may be used instead of the preceding one.

3.13 pH indicator paper, wide range.

4. **Apparatus**

Apparatus for mineral acid digestion and distillation according to Kjeldahl's method.

5. Preparation of Sample

See Method 1.

6. Procedure

6.1 *Reduction*

Weigh, to the nearest 0·001g, between 0·5 and 2·0g of the prepared sample, containing not more than 0·06g nitric nitrogen and 0·235g total nitrogen, and transfer to a Kjeldahl flask. Add sufficient water to make the total volume 35ml. Allow the flask to stand for 10 minutes with occasional gentle swirling to ensure solution of all nitrate salts.

Add 1·2g chromium powder (3.6) and 7ml hydrochloric acid (3.10), mix well and allow the flask to stand for at least 5 minutes but not more than 10 minutes at ambient temperature. Heat the flask gently so that the contents just begin to boil in about 7 minutes. Continue boiling gently for 10 minutes. Remove the flask from the heat and allow to cool.

6.2 *Hydrolysis, when the fertiliser is known not to contain organic matter*

Place the flask (6.1) in a fume cupboard, add a small quantity of anti-bump granules (3.7) and then carefully add 25ml sulphuric acid (3.9). Mix the contents of the flask and heat gently until boiling. Continue heating until dense white fumes of sulphuric acid are evolved for at least 15 minutes. Allow the mixture to cool and then carefully add 250ml water. Allow to cool to room temperature and continue as described in 6.4.

6.3 *Digestion, when the fertiliser is known to contain organic matter*

Add a small quantity of anti-bump granules (3.7), 10g of the catalyst mixture (3.11) and then carefully add 25ml sulphuric acid (3.9) (see *NOTE*). Add 0·5g paraffin wax (3.8) to reduce foaming and mix. Heat the flask moderately at first, shaking from time to time until frothing ceases and the liquid is practically colourless. Continue the digestion for at least a further 60 minutes. Allow the mixture to cool and then carefully add 250ml water. Allow to cool to room temperature, and continue as described in 6.4.

NOTE: If organic matter other than urea exceeds 1·0g add an additional 1·0ml sulphuric acid for each 0·1g organic matter in excess of 1·0g.

6.4 *Distillation*

Transfer an appropriate volume of 0·1N, 0·2N or 0·5N sulphuric acid (3.2, 3.3, 3.4) to the collecting flask of the distillation apparatus, according to the presumed level of nitrogen; add a few drops of indicator solution (3.12.1 or 3.12.2). Taking precautions against the loss of ammonia, carefully add to the contents of the Kjeldahl flask (6.2 or 6.3) 100ml sodium hydroxide solution (3.1). Mix well and connect immediately to the distillation apparatus. Heat the flask so that approximately 150ml of the liquid are distilled in 30 minutes. At the end of this time, lower the collecting flask so that the tip of the condenser is above the surface of the liquid. Test the subsequent distillate by means of the indicator paper (3.13) to ensure that all the ammonia is completely distilled. Remove the source of heat. Titrate the excess acid with 0·2N sodium hydroxide solution (3.5) to the end point of the indicator.

6.5 *Blank test*

Carry out a blank test (omitting only the sample) under the same conditions and allow for this in the calculation of the final results.

7. Expression of the Results

Determine the quantity of sulphuric acid consumed.

1ml 0·1N sulphuric acid ≡ 0·0014g nitrogen.
1ml 0·2N sulphuric acid ≡ 0·0028g nitrogen.
1ml 0·5N sulphuric acid ≡ 0·0070g nitrogen.

Express the result as the percentage of nitrogen (N) contained in the fertiliser as received for analysis.

4. DETERMINATION OF UREA

1. **Scope and Field of Application**

This method is applicable to fertilisers in Group 1(d) of Section A and Group 5 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977.

2. **Principle**

The sample is suspended in acid solution with a clarifying agent and filtered. The urea content of the filtrate is determined after the addition of 4-dimethylaminobenzaldehyde (4-DMAB) by measuring the absorbance at 435nm.

3. **Reagents**

3.1 Activated charcoal.

3.2 Carrez solution I:

Dissolve 21·9g zinc acetate dihydrate in water, add 3ml glacial acetic acid and dilute to 100ml with water.

3.3 Carrez solution II: 10·6g potassium ferrocyanide per 100ml.

3.4 Hydrochloric acid solution, 0·02N.

3.5 Sodium acetate solution: 136g sodium acetate trihydrate per litre.

3.6 4-dimethylaminobenzaldehyde solution:

Dissolve 1·6g of 4-dimethylaminobenzaldehyde (4-DMAB) in 100ml 96% ethanol and add 10ml of hydrochloric acid (d = 1·18g/ml).

3.7 Urea standard solution: 1·0g per 100ml (1ml of this solution = 10mg urea).

4. **Apparatus**

Spectrophotometer with 10mm cells.

5. **Preparation of Sample**

See Method 1.

6. **Procedure**

6.1 *Preparation of the solution for analysis*

Weigh to the nearest 0·001g, 2g of the prepared sample, or a suitable amount expected to contain between 50 and 500mg of urea, and transfer it to a 500ml graduated flask. Add 150ml 0·02N hydrochloric acid solution (3.4), shake for 30 minutes then add 10ml sodium acetate solution (3.5) and mix well. Add 2g activated charcoal (3.1) to the flask, shake well, and allow to stand for a further 15 minutes. Add 5ml Carrez solution I (3.2), followed by 5ml Carrez solution II (3.3), mixing well between additions. Dilute to volume with water and mix well. Filter a portion of the solution through a dry filter paper into a clean dry 250ml beaker.

6.2 *Determination*

Transfer 10ml of the filtrate (6.1) to a 50ml graduated flask, add 10ml 4-DMAB solution (3.6), dilute to 50ml with water, mix well and allow to stand for 10 minutes. Measure the absorbance of the solution at 435nm, in a 10mm cell against a reference solution prepared by diluting 10ml 4-DMAB solution (3.6) to 50ml with water.

6.3 *Calibration curve*

Transfer amounts of standard urea solution (3.7) corresponding to 50, 100, 150 and 250mg of urea into a series of 250ml graduated flasks; add 75ml 0·02N hydrochloric acid solution (3.4) and proceed as described above (6.1) commencing at ". . . shake for 30 minutes . . .". Measure the absorbance of the solutions, and construct a calibration graph relating the absorbances to the amounts of urea present.

7. **Expression of the Results**

Determine the amount of urea in the sample by reference to the calibration graph. Express the result in terms of percentage ureic nitrogen of the sample:

(mg urea × 0·4665 = mg ureic nitrogen).

5a. EXTRACTION OF PHOSPHORUS BY MINERAL ACIDS (TOTAL PHOSPHORUS)

1. Scope and Field of Application

This method is applicable to fertilisers in Groups 2(b), 2(c), 2(d), 3(b) and 4(c) of Section A and Group 5 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977 in respect of which the indication of total phosphorus is required.

2. Principle

The phosphorus is extracted from the fertiliser with a mixture of nitric acid and sulphuric acid.

3. Reagents

3.1 Sulphuric acid (d = 1·84g/ml).

3.2 Nitric acid (d = 1·42g/ml).

4. Apparatus

Kjeldahl flask, with a capacity of at least 500ml, or a 250ml round-bottomed flask with a glass tube forming a reflux condenser.

5. Preparation of the Sample

See Method 1.

6. Procedure

6.1 *Extraction*

Weigh to the nearest 0·001g, 2·5g of the prepared sample and place it in a dry Kjeldahl flask (4). Add 15ml water and stir so as to suspend the substance. Add 20ml nitric acid (3.2) and carefully add 30ml sulphuric acid (3.1) (see *NOTE*). When the initial violent reaction has ceased, slowly bring the contents of the flask to boiling and boil for 30 minutes. Allow to cool and then carefully add with mixing about 150ml water. Boil for 15 minutes. Cool completely and transfer the liquid quantitatively to a 500ml graduated flask. Make up to volume, mix and filter through a dry fluted filter, discarding the first portion of the filtrate.

6.2 *Determination*

Determine the phosphorus according to Method 6a or Method 6b on an aliquot part of the clear filtrate.

NOTE: If the sample contains cellulosic matter, the following procedure is suggested to avoid excessive frothing during digestion:

Weigh to the nearest 0·001g, 2·5g of the prepared sample and place it in a dry Kjeldahl flask. Add 30ml sulphuric acid (3.1) and carefully boil until most of the organic matter has been destroyed. Allow to cool, add 15ml water and 20ml nitric acid (3.2); bring to the boil and continue boiling for 30 minutes. Continue as described in 6.1 from "Allow to cool and then . . .".

5b. EXTRACTION OF PHOSPHORUS BY 2% CITRIC ACID

1. Scope and Field of Application

This method is applicable to fertilisers in Groups 2(b), 3(b) and 4(b) of Section A of the table in Schedule 1 of the Fertilisers Regulations 1977 in respect of which an indication of the phosphorus soluble in 2% citric acid is required.

2. Principle

The phosphorus is extracted from the fertiliser with a 2% citric acid solution (20g per litre) in given conditions.

3. Reagent

2% citric acid solution (20g per litre), prepared from citric acid monohydrate.

4. Apparatus

Rotary shaker: 35–40 turns per minute.

5. Preparation of the Sample

The analysis is carried out on the product as received after carefully mixing the original sample to ensure it is homogeneous.

See Method 1.

6. Procedure

6.1 *Extraction*

Weigh to the nearest 0·001g, 5g of the prepared sample, and place it in a dry flask with a sufficiently wide neck, with a capacity of 600ml, allowing the liquid to be shaken thoroughly. Add 500ml of the citric acid solution (3) at 20±1°C. When adding the first few ml of the reagent, shake vigorously by hand to stop the formation of lumps and to prevent the substance sticking to the sides of the flask. Close the flask with a rubber stopper and shake it in the rotary shaker (4) for exactly 30 minutes at a temperature of 20±2°C. Filter immediately through a dry fluted filter, into a dry glass receiver and discard the first 20ml of the filtrate. Continue the filtering until a sufficient quantity of filtrate is obtained to carry out the phosphorus determination.

6.2 *Determination*

Determine the phosphorus according to Method 6a or Method 6b on an aliquot part of the clear filtrate.

5c. EXTRACTION OF PHOSPHORUS BY WATER

1. Scope and Field of Application

This method is applicable to fertilisers in Group 5 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977 in respect of which an indication of the phosphorus soluble in water is required.

2. Principle

The phosphorus is extracted with water by shaking under specific conditions.

3. Apparatus

3.1 Rotary shaker, 35–40 turns per minute.

3.2 500ml graduated flask (for example Stohmann flask).

4. Preparation of Sample

See Method 1.

5. Procedure

5.1 *Extraction*

Weigh to the nearest 0·001g, 5g of the prepared sample and place it in a 500ml graduated flask. Add to the flask 450ml water, the temperature of which must be between 20 and 25°C. Shake on the rotary shaker (3.1) for 30 minutes. Then make up to the mark with water, mix thoroughly by shaking and filter through a dry fluted filter, into a dry container.

5.2 *Determination*

Determine the phosphorus according to Method 6a or Method 6b on an aliquot part of the clear filtrate.

6a. DETERMINATION OF EXTRACTED PHOSPHORUS—GRAVIMETRIC METHOD

1. Scope and Field of Application

This method is for the determination of the phosphorus extracted in Methods 5a, 5b and 5c.

2. Principle

2.1 After hydrolysis, phosphorus is precipitated in an acid solution in the form of quinoline phosphomolybdate. The precipitate is collected, washed, dried at 250°C and weighed.

2.2 In the above conditions, compounds likely to be found in the solution (mineral and organic acids, ammonium ions, soluble silicates, etc) will not interfere, provided that a reagent based on sodium molybdate or ammonium molybdate is used in the precipitation.

3. Reagents

3.1 Nitric acid (d = 1·42g/ml).

3.2 Molybdate reagent:

3.2.1 *Preparation of the reagent based on sodium molybdate*

Solution A: dissolve 70g sodium molybdate dihydrate in 100ml water.
Solution B: dissolve 60g citric acid monohydrate in 100ml water and add 85ml concentrated nitric acid (3.1).
Solution C: stir solution A into solution B to obtain solution C.
Solution D: to 50ml water add 35ml concentrated nitric acid (3.1), then 5ml freshly distilled quinoline. Add this solution to solution C, mix thoroughly and leave standing overnight in the dark. Make up to 500ml with water, mix again and filter through a sintered glass funnel (4.3).

3.2.2 *Preparation of the reagent based on ammonium molybdate*

Solution A: dissolve 100g ammonium molybdate in 300ml water, heating gently and stirring from time to time.
Solution B: dissolve 120g citric acid monohydrate in 200ml water and add 170ml of concentrated nitric acid (3.1).
Solution C: add 10ml freshly distilled quinoline to 70ml of concentrated nitric acid (3.1).
Solution D: stirring well, slowly pour solution A into solution B. After thoroughly mixing, add solution C to this mixture and make up to 1 litre with water. Leave standing for two days in a dark place and filter through a sintered glass funnel (4.3).

The reagents 3.2.1 and 3.2.2 can be used in the same way; both must be kept in the dark in stoppered polyethylene bottles.

4. Apparatus

4.1 Filter crucible with porosity of 5 to 20 microns.

4.2 Drying oven regulated at 250°C±10°C.

4.3 Sintered glass funnel with porosity of 5 to 20 microns.

5. Procedure

5.1 *Treatment of the solution*

With a pipette take an aliquot part of fertiliser extract containing about 0·01g of P_2O_5 and put it in a 500ml Erlenmeyer flask. Add 15ml concentrated nitric acid (3.1) and dilute with water to about 100ml.

5.2 *Hydrolysis*

Bring the contents of the Erlenmeyer flask to the boil slowly and keep at this temperature for 1 hour to complete hydrolysis.

Care must be taken to avoid losses by splashing and excessive evaporation which would reduce the initial volume by more than half, by fitting a reflux condenser. After hydrolysis make up to the initial volume with distilled water.

5.3 *Weighing the crucible*

Dry the filter crucible (4.1) for at least 15 minutes in the drying oven (4.2). Cool the crucible in a desiccator and weigh.

5.4 *Precipitation*

Heat the acid solution in the Erlenmeyer flask until it begins to boil and then precipitate the quinoline phosphomolybdate by adding 40ml of the precipitating reagent (3.2.1 or 3.2.2) drop by drop, stirring continuously. Place the Erlenmeyer flask in a steam bath, leave it there for 15 minutes, shaking it from time to time. The solution can be filtered immediately or after it has cooled down.

5.5 *Filtering and washing*

Filter the solution under vacuum by decantation. Wash the precipitate in the Erlenmeyer flask with 30ml water. Decant and filter the solution. Repeat this process five times. Quantitatively transfer the rest of the precipitate into the crucible washing in with water. Wash four times with 20ml water, allowing the liquid to drain from the crucible before each addition.

5.6 *Drying and weighing*

Wipe the outside of the crucible with a filter paper. Place the crucible in the drying oven (4.2) and keep it there until its weight remains constant at a temperature of 250°C (usually 15 minutes); leave it to cool in a desiccator to ambient temperature and weigh immediately.

5.7 *Blank test*

For each series of determinations make a blank test under the same conditions (omitting only the sample) and allow for this in the calculation of the final result.

5.8 *Control test*

Carry out the determination using an aliquot part of a potassium dihydrogen phosphate solution containing 0·01g of P_2O_5.

6. **Expression of the Results**

Calculate the percentage phosphorus content of the sample as P_2O_5 or P, taking into account the weight of the test sample and the volume of the aliquot part taken for the determination.

Conversion factors:

quinoline phosphomolybdate to P_2O_5 = 0·032074;

quinoline phosphomolybdate to P = 0·013984.

6b. DETERMINATION OF EXTRACTED PHOSPHORUS—SPECTROPHOTOMETRIC METHOD

1. **Scope and Field of Application**

This method is for the determination of the phosphorus extracted in Methods 5a, 5b and 5c.

2. **Principle**

An acidic solution of the extracted phosphorus is treated with molybdovanadate reagent and the absorbance of the yellow solution is measured at 430nm.

3. **Reagents**

3.1 Nitric acid (d = 1·42g/ml).

3.2 Molybdovanadate reagent: dissolve separately 20g ammonium molybdate and 0·47g ammonium vanadate in water, mix, acidify with 140ml nitric acid (3.1) and dilute to 1 litre with water.

3.3 Phosphorus standard solution: dissolve 4.387g potassium dihydrogen phosphate, previously dried at 105°C for 1 hour, in water and dilute to 1 litre.
1ml of this solution contains 1mg phosphorus (P) or 2·29 mg phosphorus pentoxide (P_2O_5).

3.4 Sodium hydroxide, approximately 5N solution.

4. Apparatus

Spectrophotometer with 10mm cells.

5. Procedure

5.1 *Determination*

5.1.1 *For Total Phosphorus*

Dilute, if necessary, the prepared extract to obtain a phosphorus concentration of about 20μg/ml. Transfer 10ml of this solution to a glass-stoppered test tube, add 10ml freshly prepared molybdovanadate reagent (3.2) and mix. Allow to stand for 10 minutes at 20°C and then measure the absorbance of the solution at 430nm against a freshly prepared reference solution made by adding 10ml molybdovanadate reagent (3.2) to 10ml water.

5.1.2 *For Water Soluble Phosphorus and Citric Acid Soluble Phosphorus*

Dilute, if necessary, the prepared extract to obtain a phosphorus concentration of about 80μg/ml. Transfer 25ml of this solution to a 100ml conical flask, add 5ml nitric acid (3.1) and boil gently for 30 minutes. Cool the solution and neutralise with sodium hydroxide solution (3.4). Cool the solution to 20°C, transfer quantitatively to a 100ml graduated flask and make up to the mark with water. Transfer 10ml of this solution to a glass-stoppered test tube, add 10ml freshly prepared molybdovanadate reagent (3.2) and mix. Proceed as described in 5.1.1 from "Allow to stand . . .".

5.2 *Calibration*

From the standard solution (3.3) prepare a series of solutions containing respectively 5, 10, 20, 30 and 40μg/ml of phosphorus (P). Transfer 10ml of each solution into glass-stoppered test tubes, add 10ml molybdovanadate reagent (3.2), mix and proceed as described in 5.1.1 from "Allow to stand . . .".

Construct a graph relating the absorbance to the amount of phosphorus present. The calibration curve should be prepared at the same time as the determination is carried out.

6. Expression of the Results

Determine the amount of phosphorus in the sample by reference to the calibration curve. Express the result in terms of percentage phosphorus (P) or percentage phosphorus pentoxide (P_2O_5) of the sample:

mg phosphorus (P) × 2·29 = mg phosphorus pentoxide (P_2O_5).

7a. DETERMINATION OF POTASSIUM—GRAVIMETRIC METHOD

1. Scope and Field of Application

This method is applicable to fertilisers in Groups 3(b), 3(c), 3(d) and 4(c) of Section A and Group 5 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977 in respect of which an indication of total potassium is required.

2. Principle

The sample is ashed and dissolved in dilute hydrochloric acid or, if it contains no organic substances, it is dissolved directly in dilute hydrochloric acid. After the removal of interfering substances the potassium is precipitated in a slightly alkaline medium in the form of potassium tetraphenylborate (KTPB).

3. Reagents

3.1 Formaldehyde, 25–35% solution, filtered if necessary before use.

3.2 Potassium chloride.

3.3 Sodium hydroxide, 10N solution. Care should be taken to ensure that the sodium hydroxide is free from potassium.

3.4 Indicator solution: dissolve 0·5g phenolphthalein in 100ml 90% ethanol.

3.5 EDTA solution: 4g of the dihydrated disodium salt of ethylenediaminetetra-acetic acid (EDTA) per 100ml. Store this reagent in a plastic container.

3.6 STPB solution: dissolve 32·5g sodium tetraphenylborate in 480ml of water, add 2ml of sodium hydroxide solution (3.3) and 20ml of a magnesium chloride solution (100g of $MgCl_2.6H_2O$ per litre). Stir for fifteen minutes and filter through a fine, ashless filter. Store this reagent in a plastic container.

3.7 Liquid for washing: dilute 20ml of the STPB solution (3.6) to 1 litre with water.

3.8 Hydrochloric acid (d= 1·18g/ml).

4. Apparatus

4.1 Filter crucibles with a porosity of 5 to 20 microns.

4.2 Oven regulated at 120°C±10°C.

5. Preparation of Sample

See Method 1.

6. Procedure

6.1 *Preparation of the solution for analysis*

6.1.1 *Fertilisers containing little or no organic matter*

Weigh to the nearest 0·001g, 2·5g of the prepared sample and transfer to a 400ml beaker. Add 50ml water and 5ml hydrochloric acid (3.8) and evaporate to dryness on a steam bath. Add 5ml hydrochloric acid (3.8) and 50ml water. Bring the contents to the boiling point, breaking down any crystals or lumps with a glass rod. Dilute the solution with water to about 100ml and boil gently for a few minutes. Allow to cool, transfer to a 250ml graduated flask, dilute to the mark with water and mix; filter through a dry paper.

6.1.2 *Fertilisers containing organic matter*

Weigh to the nearest 0·01g, 10g of the prepared sample into a suitable crucible and place in a cold muffle furnace. Gradually raise the temperature to about 475°C (not to exceed 500°C). Maintain at this temperature for at least 16 hours and then open the furnace and allow the crucible to cool. Grind the residue to eliminate any lumps, add 50ml water and 10ml hydrochloric acid (3.8) and evaporate to dryness on a steam bath. Proceed as in 6.1.1, commencing "Add 5ml hydrochloric acid (3.8) and 50ml water.".

6.2 *Determination*

6.2.1 Transfer by pipette an aliquot part of the filtrate (6.1.1 or 6.1.2), containing 25–50mg of potassium (30–60mg K_2O) into a 250ml beaker; make up to 50ml with water.

6.2.2 To remove interferences, add 10ml of the EDTA solution (3.5), several drops of the phenolphthalein solution (3.4) and stir in, drop by drop, sodium hydroxide solution (3.3) until it turns red, then finally add a few more drops of sodium hydroxide to ensure an excess (usually 1ml of sodium hydroxide is sufficient to neutralise the sample and ensure an excess).

6.2.3 To eliminate most of the ammonia boil gently for 15 minutes. Add water to make the volume up to 60ml. Bring the solution to the boil, remove the beaker from the heat and add 10ml formaldehyde (3.1). Add several drops of phenolphthalein solution (3.4) and if necessary, more sodium hydroxide solution until a distinct red colour appears. Cover the beaker with a watch glass and place it on a steam bath for fifteen minutes.

6.3 *Weighing the crucible*

Dry the filter crucible (4.1) to constant weight in the oven at 120°C (4.2) (about 15 minutes).

Allow the crucible to cool in a desiccator and then weigh it.

6.4 *Precipitation*

Remove the beaker from the steam bath and stir in *drop by drop* 10ml of the STPB solution (3.6). This addition should take about 2 minutes; allow to stand for at least 10 minutes before filtering.

6.5 *Filtering and washing*

Filter under vacuum into the weighed crucible, rinse the beaker with the liquid for washing (3.7), wash the precipitate three times with the liquid for washing (60ml in all of the liquid for washing) and twice with 5 to 10ml of water.

6.6 *Drying and weighing*

Wipe the outside of the crucible with a filter paper and place in the oven (4.2) for one and a half hours at a temperature of 120°C. Allow the crucible to cool in a desiccator to ambient temperature and weigh rapidly.

6.7 *Blank test*

Make a blank test under the same conditions (omitting only the sample) and allow for this in the calculation of the final result.

6.8 *Control test*

Carry out the determination on an aliquot part of an aqueous solution of potassium chloride, containing at the most 40mg of K_2O.

7. Expression of the Results

Calculate the percentage potassium content of the sample as K_2O, taking into account the weight of the test sample, the volume of the aliquot part taken for the determination and the value of the blank determination. (Conversion factor, KTPB to K_2O = 0·1314.)

7b. DETERMINATION OF POTASSIUM— FLAME PHOTOMETRIC METHOD

1. Scope and Field of Application

This method is applicable to fertilisers in Groups 3(b), 3(c), 3(d) and 4(c) of Section A and Group 5 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977 in respect of which an indication of total potassium is required.

2. Principle

The sample is ashed and dissolved in dilute hydrochloric acid or, if it contains no organic substances, it is dissolved directly in dilute hydrochloric acid. The solution is diluted and the potassium content of the extract is determined by flame photometry.

3. Reagents

3.1 Ammonia solution (30% V/V): dilute 30ml concentrated ammonia solution (d = 0·88g/ml) to 100ml.

3.2 Ammonium oxalate solution: saturated aqueous solution.

3.3 Hydrochloric acid (d = 1·18g/ml).

3.4 Potassium dihydrogen phosphate: dried for one hour at 105°C.

3.5 Potassium solution (stock): dissolve 3·4807g potassium dihydrogen phosphate (3.4) in water and dilute to 1 litre.

3.6 Potassium solution (dilute): dilute 50ml stock solution (3.5) to 1 litre with water. 1ml contains 50μg potassium (K).

4. Apparatus

Flame photometer.

5. Preparation of Sample

See Method 1.

6. Procedure

6.1 *Preparation of the solution for analysis*

6.1.1 *Fertilisers containing little or no organic matter*

Weigh to the nearest 0·001g, 2·5g of the prepared sample and transfer to a 400ml beaker. Add 50ml water and 5ml hydrochloric acid (3.3) and evaporate to dryness

on a steam bath. Add to the residue 125ml water and 50ml ammonium oxalate solution (3.2) and boil for 30 minutes. If necessary, a small quantity of potassium-free antifoaming agent may be added. Cool the mixture, add a slight excess of ammonia solution (3.1) and allow to cool. Transfer to a 250ml graduated flask, dilute to the mark with water, mix and filter through a dry paper.

6.1.2 *Fertilisers containing organic matter*

Weigh to the nearest 0·01g, 10g of the prepared sample into a suitable crucible and place in a cold muffle furnace. Gradually raise the temperature to about 475°C (not to exceed 500°C). Maintain at this temperature for at least 16 hours and then open the furnace and allow the crucible to cool. Grind the residue to eliminate any lumps, add 50ml water and 10ml hydrochloric acid (3.3) and evaporate to dryness on a steam bath. Add to the residue 125ml water and 50ml ammonium oxalate solution (3.2) and boil for 30 minutes. Cool the mixture, add a slight excess of ammonia solution (3.1) and allow to cool. Transfer to a 500ml graduated flask, dilute to the mark with water, mix and filter through a dry paper.

6.2 *Blank solution*

Prepare a blank solution from which only the sample has been omitted and allow for this in the calculation of the final results.

6.3 *Determination*

6.3.1 *Preparation of sample and blank test solutions*

Dilute sample solutions (6.1.1 or 6.1.2) and the blank solution (6.2) to a concentration within the optimal measuring range of the flame photometer.

6.3.2 *Preparation of the calibration solutions*

By diluting the standard solution (3.6), prepare at least five standard solutions of increasing concentration corresponding to the optimal measuring range of the flame photometer.

6.4 *Measurement*

Set the flame photometer to measure the potassium emission according to the manufacturer's instructions. Spray successively, in triplicate, the standard solutions (6.3.2), the sample solution and the blank solution (6.3.1), washing the instrument through with distilled water between each spraying. Plot the calibration curve using the median emissions as the ordinates and the corresponding concentrations of potassium in μg/ml as the abscissae. Determine the concentration of potassium in the final sample solution by reference to the calibration curve.

The concentration of potassium in the final solution may be confirmed as follows:

prepare two further dilutions of the standard potassium solution to contain respectively 1mg/litre more and 1mg/litre less than the estimated potassium 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. Take the median result of each of the three readings and calculate the potassium content of the sample solution.

7. **Expression of the Results**

Calculate the percentage potassium content of the sample as K taking into account the weight of the test sample and the dilutions carried out in the course of the analysis. (Conversion factor K to K_2O = 1·204.)

8. DETERMINATION OF TOTAL MAGNESIUM

1. **Scope and Field of Application**

This method is applicable to all fertilisers, except magnesium ammonium nitrate, in Group 1(a) of Section A of the table in Schedule 1 of the Fertilisers Regulations 1977.

2. **Principle**

The sample is ashed and dissolved in dilute hydrochloric acid or, if it contains no organic substances, it is dissolved directly in dilute hydrochloric acid. The solution is diluted and the magnesium content of the extract is determined by atomic absorption spectrophotometry.

3. **Reagents**

3.1 Hydrochloric acid (d = 1·18g/ml).

3.2 Hydrochloric acid, 6N solution (approximately).

3.3 Hydrochloric acid, 0·5N solution.

3.4 Magnesium solution: dissolve 1·013g magnesium sulphate ($MgSO_4.7H_2O$) in 0·5N hydrochloric acid solution (3.3) and dilute to 100ml with this acid. 1ml of this solution contains 1mg of magnesium (Mg).

OR Weigh out 1·658g of magnesium oxide, previously calcined at 600°C for 2 hours, place in a beaker with 100ml of water and 120ml of approximately N hydrochloric acid. After dissolution, transfer quantitatively into a 1 litre graduated flask, make up the volume with water and mix. 1ml of this solution contains 1mg of magnesium (Mg).

3.5 Releasing agent

3.5.1 Strontium chloride solution: dissolve 76·08g strontium chloride ($SrCl_2.6H_2O$) in 0·5N hydrochloric acid solution (3.3) and dilute to 500ml with this acid. 1ml contains 0·05g Sr.

3.5.2 Lanthanum oxide solution: moisten 117·3g lanthanum oxide (La_2O_3), low in magnesium content, with water. Slowly add 350ml hydrochloric acid (d = 1·18g/ml) (3.1) and stir until the lanthanum oxide is dissolved. Allow to cool and dilute to 1 litre with water. 1ml contains 0·1g La.

4. **Apparatus**

Atomic absorption spectrophotometer with a magnesium lamp (285·2nm).

5. **Preparation of Sample**

See Method 1.

6. **Procedure**

6.1 *Preparation of the solution for analysis*

6.1.1 *In the absence of organic matter*

Weigh, to the nearest 0·001g, 5g of the prepared sample (in the case of liming materials about 1g of the sample). Place it in a 400ml beaker and carefully add 50ml water and 5ml hydrochloric acid (3.1) (there may be a vigorous reaction due to carbon dioxide formation). Add more hydrochloric acid if necessary. When effervescence has stopped, evaporate to dryness on a steam bath, stirring occasionally with a glass rod. Add 15ml 6N hydrochloric acid solution (3.2) and 120ml water. Stir with the glass rod, which should be left in the beaker, and cover the beaker with a watch glass. Boil the solution gently until dissolution appears complete and then filter through a filter paper(a) into a 250ml graduated flask. Wash the beaker and filter with 5ml of hot 6N hydrochloric acid solution (3.2) and twice with boiling water. Cool and make up to the mark with water (the hydrochloric acid concentration of this solution should be about 0·5N).

6.1.2 *In the presence of organic matter*

Weigh to the nearest 0·001g, 5g of the prepared sample into a silica or platinum crucible and place the crucible in a cold muffle furnace. Close the furnace and gradually raise the temperature to 450–475°C over about 90 minutes. Maintain this temperature for at least 16 hours and then open the furnace and allow the crucible to cool. Moisten the ash with water and transfer it into a 250ml beaker. Wash the crucible with about 5ml hydrochloric acid (3.1) and add the latter slowly and carefully to the beaker (there may be a vigorous reaction due to carbon dioxide formation). If necessary, add more hydrochloric acid (3.1) with stirring, until all effervescence has stopped.

Evaporate the solution to dryness, occasionally stirring with a glass rod. Add 15ml 6N hydrochloric acid solution (3.2) and 120ml water. Stir with the glass rod, which should be left in the beaker, and cover with a watch glass. Boil the solution gently until dissolution appears complete and filter through a filter paper(a) into

(a) Whatman 541 or equivalent.

a 250ml graduated flask. Wash the beaker and filter with 5ml of hot 6N hydrochloric acid solution (3.2) and twice with boiling water. Cool, and make up to the mark with water. (The hydrochloric acid concentration of this solution should be about 0·5N.)

6.2 *Blank solution*

Prepare a blank solution from which only the sample has been omitted.

6.3 *Determination*

6.3.1 *Preparation of sample and blank test solutions*

Dilute the sample solutions (6.1.1 or 6.1.2) and the blank test solution (6.2), with 0.5N hydrochloric acid (3.3) to a concentration within the working range of the spectrophotometer. Add sufficient releasing agent (3.5.1 or 3.5.2) to the final solution to give a concentration of 0.5g Sr or 1.0g La per 100ml.

6.3.2 *Preparation of the calibration solutions*

By diluting the standard solution (3.4) with 0.5N hydrochloric acid solution (3.3), prepare at least 5 standard solutions of increasing concentration corresponding to the optimal measuring range of the spectrophotometer. Add sufficient releasing agent (3.5.1 or 3.5.2) to the final solution to give a concentration of 0.5g Sr or 1.0g La per 100ml.

6.4 *Measurement*

Set up the spectrophotometer (4), at a wavelength of 285·2nm using an oxidising air-acetylene flame. Spray successively, in triplicate, the standard solutions (6.3.2), the sample solution and the blank solution (6.3.1), washing the instrument through with distilled water between each spraying. Plot the calibration curve using the mean absorbances as the ordinates and the corresponding concentrations of magnesium in µg/ml as the abscissae. Determine the concentration of magnesium in the sample and blank solutions by reference to the calibration curve.

7. **Expression of the Results**

Calculate the quantity of magnesium (Mg) or magnesium oxide (MgO) (conversion factor Mg to MgO=1·66) in the sample taking into consideration the blank.

Express the result as a percentage of the sample.

9a. DETERMINATION OF BORON—TITRIMETRIC METHOD

1. **Scope and Field of Application**

This method is applicable to all fertilisers where the levels of boron are greater than 1000mg/kg.

2. **Principle**

The sample is dissolved in acid, the solution treated with lead nitrate in order to remove phosphate, and the borate in the filtrate is titrated potentiometrically in the presence of mannitol.

3. **Reagents**

3.1 Calcium oxide.

3.2 Mannitol.

3.3 Sodium carbonate.

3.4 Hydrochloric acid solution 50% (V/V): dilute 50ml concentrated hydrochloric acid (d=1·18g/ml) with water to 100ml.

3.5 Hydrochloric acid, 0·5N solution.

3.6 Lead nitrate solution, 10g per 100ml.

3.7 Sodium hydroxide, 0·5N solution.

3.8 Sodium hydroxide, 0·05N solution, carbonate free.

3.9 Methyl red indicator solution: dissolve 0·1g of methyl red in 50ml 95% ethanol, make up to 100ml with water and filter if necessary.

3.10 Phenolphthalein indicator solution: dissolve 0·25g phenolphthalein in 150 ml 95% alcohol and dilute with water to 250ml.

4. Apparatus

pH meter.

5. Preparation of Sample

See Method 1.

6. Procedure

6.1 *Preparation of the solution for analysis*

6.1.1 *In the absence of organic matter*

Weigh to the nearest 0·001g, 2g of the prepared sample if the boron content is 0·5% or less, or 1g if the boron content is from 0·5–1·0%, and place in a 400ml beaker. Add 100ml water, a few drops of phenolphthalein indicator solution (3.10) and sufficient sodium carbonate (3.3) to make the solution slightly alkaline. Boil gently and keep the boiling solution alkaline, adding more sodium carbonate (3.3) as necessary until all the ammonia which may be present has been evolved. Cool the solution and add 12ml hydrochloric acid solution (3.4).

6.1.2 *In the presence of organic matter*

Weigh to the nearest 0·001g, 2g of the prepared sample if the boron content is 0·5% or less, or 1g if the boron content is from 0·5–1·0%, and place it in a silica dish. Add 0·2g calcium oxide (3.1) for each 1g of sample, moisten with water, mix thoroughly, evaporate the mixture to dryness and transfer the crucible to a cold muffle furnace. Raise the temperature slowly to 450±10°C and then ignite for about 3 hours. Remove the crucible from the furnace, cool and moisten the ash with 10ml of hydrochloric acid solution (3.4). Warm the solution on a steam bath for 15 minutes, covering the dish with a watch glass. Transfer the contents of the dish quantitatively into a 400ml beaker, add a few drops of phenolphthalein indicator solution (3.10) and dilute to about 120ml with water.

6.2 *Determination*

To the prepared solution (6.1.1 or 6.1.2), add 20ml lead nitrate solution (3.6) for each 12% P_2O_5 in the sample if 2g of the sample has been used; add 10ml lead nitrate solution for each 12% P_2O_5 in the sample if 1g of the sample has been used. Heat to boiling, remove from the source of heat, and make slightly alkaline by addition of sodium carbonate (3.3). Warm the solution on a steam bath for five minutes, cool and transfer the solution quantitatively into a 200ml graduated flask. Make up to the mark with water, mix and filter through a 24cm filter paper(a), rejecting the first 10–20ml of the filtrate.

Transfer 100ml of the filtrate into a 250ml beaker, add a few drops of methyl red indicator (3·9) and acidify the solution with 0·5N hydrochloric acid solution (3.5). Heat almost to boiling, stir vigorously to remove carbon dioxide, keeping the solution acidic, by adding if necessary more 0·5N hydrochloric acid solution (3.5). Neutralise the solution with 0·5N sodium hydroxide solution (3.7), and then make just acid by addition of 0·5N hydrochloric acid solution (3.5). Cover the beaker with a watch glass and boil the solution gently for 5 minutes in order to expel any remaining carbon dioxide.

Cool the solution rapidly and using the pH meter (4), adjust the pH of the solution to 6·3 by the addition of 0·05N sodium hydroxide solution (3.8). Add 10g mannitol (3.2) and titrate the solution with 0·05N sodium hydroxide solution to a pH of 6·3. Continue to add further 10g portions of mannitol (3.2) and to re-adjust the pH to 6·3 until after the final addition of mannitol the pH remains constant at 6·3. The total amount of 0·05N sodium hydroxide solution used after the first addition of mannitol corresponds to the amount of boron present in the sample solution. Allow a standard value of 0·1ml 0·05N sodium hydroxide solution as 'blank' value.

(a) Whatman 42 or equivalent.

7. Expression of the Results

The percentage boron content of the sample is given by the formula

$$\frac{0{\cdot}1082 \times (T - 0{\cdot}1)}{M}$$

where:

T = ml of 0·05N sodium hydroxide solution used after the addition of the mannitol.

M = weight of the sample in grams.

9b. DETERMINATION OF BORON— SPECTROPHOTOMETRIC METHOD

1. Scope and Field of Application

This method is applicable to all fertilisers for levels of boron up to 1000mg/kg.

2. Principle

The sample is ashed in the presence of calcium oxide and the residue is dissolved in hydrochloric acid. The resulting solution is treated with carmine to form a coloured complex with boron, the absorption of which is measured at 625nm.

3. Reagents

3.1 Calcium oxide.

3.2 Sulphuric acid (d = 1·84g/ml).

3.3 Carminic acid solution: dissolve 0·025g carminic acid in sulphuric acid (3.2) and dilute to 100ml with sulphuric acid (3.2).

3.4 Hydrochloric acid solution 20% (V/V): dilute 20ml hydrochloric acid (d = 1·18g/ml) with water to 100ml.

3.5.1 Boron solution (stock): weigh to the nearest 0·001g, 1·905g boric acid, dissolve in water and dilute to 1 litre with water. 1 ml of this solution = 0·333mg boron.

3.5.2 Boron solution (working standard): dilute 10ml of boric acid stock solution (3.5.1) with water to 100ml. Transfer 5, 10, 15, 20 and 25ml respectively into separate 100ml graduated flasks and dilute to the marks with water. These solutions contain 5, 10, 15, 20 and 25μg of boron per 3ml of solution.

3.6 Hydrazine hydrate (approximately 60% W/W solution).

WARNING: Hydrazine hydrate is toxic and corrosive, causing burns; avoid contact with eyes and skin.

4. Apparatus

Spectrophotometer with 10mm cells.

5. Preparation of the Sample

See Method 1.

6. Procedure

6.1 *Preparation of the solution for analysis*

Weigh to the nearest 0·001g, 5g of the prepared sample and place it in a silica dish. Add 1g calcium oxide (3.1), moisten with water, mix thoroughly, evaporate the mixture to dryness and then transfer the crucible to a cold muffle furnace. Raise the temperature slowly to 450 ± 10°C and ignite for about 3 hours. Remove the crucible from the furnace, cool and add hydrochloric acid solution (3.4) until the resulting mixture is acid, then add 5ml hydrochloric acid solution (3.4) in excess. Heat the mixture at 70°C for 15 minutes, cool and filter through a filter paper(a) into a suitable graduated flask

(a) Whatman 42 or equivalent.

washing both the dish and the filter with water. Make up to the mark with water and mix. Dilute an aliquot of this solution so that 3ml contains between 5 and 25μg of boron.

6.2 *Blank test*

Carry out a blank test omitting only the sample.

6.3 *Determination*

Transfer 3ml of the prepared solution (6.1) to a small conical flask, add cautiously 15ml sulphuric acid (3.2), swirl the flask and add 10ml carminic acid solution (3.3). Cool the flask rapidly to room temperature, mix well and allow to stand for 2 hours. Measure the absorbance in the spectrophotometer (4) at 625nm with water as reference. Determine the quantity of boron in the solution by reference to the calibration curve (6.4).

6.4 *Calibration curve*

Transfer 3ml of each working standard solution (3.5.2) into a series of small conical flasks and proceed as described in 6.3 commencing at ". . . add cautiously 15ml sulphuric acid (3.2) . . .". Plot a calibration curve of the absorbance of the solutions against the corresponding quantities of boron, in μg.

7. **Expression of the Results**

The boron content in mg/kg is given by the formula:

$$\frac{A \times V \times F}{3 \times M}$$

where:

A = weight of boron in the 3ml aliquot taken for colour development after allowing for the blank reading (μg);

V = volume of prepared solution before dilution;

F = factor allowing for dilution under 6.1;

M = weight of the sample in grams.

NOTE

The colour of the boron-carmine complex is affected by nitrate nitrogen. When this form of nitrogen is known to be present in the sample, the "Determination" procedure (6.3) should be modified by the addition of 0·5ml hydrazine hydrate (3.6) before the addition of the sulphuric acid (3.2) which should be carried out under conditions of extreme caution because of the violent nature of the reaction. (The use of a burette for the addition of the sulphuric acid is recommended.)

The hydrazine hydrate (3.6) has no influence on the absorption of the boron-carmine complex and therefore is not added to the standard solutions in the preparation of the calibration curve. However, in order to equalise the volumes of the solutions of both samples and standards, add 0·5ml water to the latter.

10. DETERMINATION OF COBALT

1. **Scope and Field of Application**

This method is applicable to all fertilisers.

2. **Principle**

The sample is dissolved in hydrochloric acid (after ashing if necessary) and the solution is treated with citric acid in order to prevent precipitation of iron and phosphate. Cobalt is extracted as its 2-nitroso-1-naphthol complex into toluene. The cobalt content is measured at 367nm, by reference to a calibration curve.

3. **Reagents**

3.1 Sodium sulphate, anhydrous.

3.2 Toluene.

3.3 Hydrochloric acid, 2N solution.

3.4 Hydrochloric acid solution, 50% (V/V): dilute 50ml concentrated hydrochloric acid solution (d = 1·18g/ml) to 100ml with water.

3.5 Hydrogen peroxide solution, 3% (10 volume).

3.6 Nitric acid solution, 30% (V/V): dilute 30ml nitric acid (d = 1·42g/ml) with water to 100ml.

3.7 2-nitroso-1-naphthol solution: dissolve 1g of 2-nitroso-1-naphthol in 100ml glacial acetic acid and add 1g activated carbon. Shake the solution before use and filter off the required amount.

3.8 Sodium citrate solution: 40g per 100ml.

3.9 Sodium hydroxide, 2N solution.

3.10 Cobalt solution (stock): weigh to the nearest 0·001g, 0·670g ammonium cobaltous sulphate, $[(NH_4)_2\,Co(SO_4)_2.6H_2O]$ dissolve in water and make up to 100ml with water. 1ml of this solution contains 1000μg cobalt.

3.11 Cobalt solution (working standard): dilute the stock cobalt solution (3.10) as required so that 1ml contains 1μg cobalt. Prepare the solution freshly before use.

4. Apparatus

Spectrophotometer with 10mm cells.

5. Preparation of the Sample

See Method 1.

6. Procedure

6.1 *Preparation of the solution for analysis*

6.1.1 *In the absence of organic matter*

Weigh to the nearest 0.001g, 5g of the prepared sample, place in a 100ml beaker, add 10ml hydrochloric acid solution (3.4) and evaporate to dryness on a steam bath. Extract the soluble salts with three successive 10ml portions of boiling 2N hydrochloric acid solution (3.3), decanting the solution each time through the the same filter paper(a) into a 50ml graduated flask. Wash the filter paper with a little water, cool the solution to room temperature and make up to the mark with water.

6.1.2 *In the presence of organic matter*

Weigh to the nearest 0·001g, 5g of the prepared sample into a silica dish and place a silica cover on top. Transfer the dish to a cold muffle furnace, raise the temperature to about 475°C (do not exceed 500°C). Maintain at this temperature for at least 16 hours and then open the furnace and allow the crucible to cool. Add 10ml hydrochloric acid solution (3.4) and evaporate to dryness on a steam bath. Extract the soluble salts with two successive 10ml portions of boiling 2N hydrochloric acid solution (3.3), decanting the solution each time through the same filter paper(a) into a 50ml graduated flask. Add 5ml hydrochloric acid solution (3.4) and 5ml nitric acid solution (3.6) to the residue in the dish and evaporate the mixture to dryness on a hot plate at low heat. Add 10ml boiling hydrochloric acid solution (3.3) to the residue and filter the solution through the same filter paper into the 50ml graduated flask. Wash the filter paper with water, cool the solution to room temperature and make up to the mark with water.

6.2 *Determination*

6.2.1 Transfer a suitable aliquot of the solution prepared in 6.1 (containing not more than 15μg cobalt) to a 100ml beaker, add 15ml sodium citrate solution (3.8), dilute to about 50ml with water and adjust the pH to between 3 and 4 by adding 2N hydrochloric acid solution (3.3). (A precipitate of ferric hydroxide may form but this can be dissolved by heating the solution.) Cool to room temperature, add 10ml hydrogen peroxide solution (3.5) and, after 5 minutes,

(a) Whatman 541 or equivalent.

1ml 2-nitroso-1-naphthol solution (3.7). Heat the solution to about 90°C and then allow to stand for 30 minutes at room temperature. Transfer the solution to a 125ml separating funnel, add 10ml toluene (3.2), shake vigorously for 2 minutes, allow the phases to separate and discard the lower aqueous phase.

6.2.2 To the toluene extract add 20ml 2N hydrochloric acid solution (3.3), shake for 1 minute and discard the lower aqueous phase. Add 20ml 2N sodium hydroxide solution (3.9), shake for 1 minute and again discard the lower aqueous phase. Repeat the washing with a further 20ml of 2N sodium hydroxide solution (3.9). Finally run off the toluene solution through a little anhydrous sodium sulphate (3.1) into a clean dry stoppered tube. Carry out a blank determination repeating the procedure, but omitting the sample. Measure the absorbance of the magenta coloured solutions at a wave length of 367nm in the spectrophotometer (4) with toluene (3.2) as reference. Determine the quantity of cobalt in the solution by reference to the calibration curve (6.3).

6.3 *Calibration curve*

Measure amounts of cobalt working standard solution (3.11) corresponding to 3, 6, 9, 12 and 15μg cobalt into five separate 100ml beakers and proceed as described in 6.2 commencing at ". . . add 15ml sodium citrate solution (3.8) . . .". Plot a calibration graph of the absorbance of the solutions against the corresponding amounts of cobalt (μg).

7. **Expression of the Results**

The cobalt content in mg/kg is given by the formula:

$$\frac{A \times 50}{V \times M}$$

where:

A = weight of cobalt taken for colour development as read from the calibration graph after allowing for the blank reading (μg);

V = volume in millilitres of sample taken for colour development;

M = weight of sample in grams.

11. DETERMINATION OF MOLYBDENUM

1. **Scope and Field of Application**

This method is applicable to all fertilisers.

2. **Principle**

The sample is dissolved in hydrochloric acid (after ashing if necessary) and the molybdenum complexed with thiocyanate in the presence of stannous chloride. The red coloured complex is extracted into an organic solvent mixture and its absorbance measured at 470nm.

3. **Reagents**

3.1 Hydrochloric acid, 50% (V/V): dilute 50ml concentrated hydrochloric acid solution (d = 1·18g/ml) to 100ml with water.

3.2 Hydrochloric acid, 2N solution.

3.3 Hydrochloric acid, N solution.

3.4 Nitric acid solution, 30% (V/V): dilute 30ml nitric acid (d = 1·42g/ml) with water to 100ml.

3.5.1 Molybdenum solution (stock): dissolve 1·84g ammonium molybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in water and dilute with water to 1 litre.

3.5.2 Molybdenum solution (working standard): dilute 1·0ml stock solution (3.5.1) to 1 litre with water (1ml = 1μg molybdenum).

Prepare this solution immediately prior to use.

3.6 Ammonium ferrous sulphate solution, 4g per 100ml.

3.7 Potassium thiocyanate solution, 40g per 100ml.

3.8 Sodium sulphate, anhydrous.

3.9 Stannous chloride solution: suspend 40g stannous chloride dihydrate in 20ml 6·5N hydrochloric acid, add water to dissolve and dilute to 100ml. Filter if turbid.

3.10 Solvent mixture: mix equal volumes of carbon tetrachloride and 3-methylbutan-1-ol.

4. **Apparatus**

Spectrophotometer with 10mm cells.

5. **Preparation of the Sample**

See Method 1.

6. **Procedure**

6.1 *Preparation of the solution for analysis*

6.1.1 *In the absence of organic matter*

Weigh to the nearest 0·001g, 5g of the prepared sample, place in a 100ml beaker, add 10ml hydrochloric acid solution (3.1) and evaporate to dryness on a steam bath. Extract the soluble salts with three successive 10ml portions of boiling 2N hydrochloric acid solution (3.2), decanting the solution each time through the same filter paper**(a)** into a 50ml graduated flask. Wash the filter paper with a little water, cool the solution to room temperature and make up to the mark with water.

6.1.2 *In the presence of organic matter*

Weigh to the nearest 0·001g, 5g of the prepared sample into a silica dish and place a silica cover on top. Transfer the dish to a cold muffle furnace and gradually raise the temperature to about 475°C (not to exceed 500°C). Maintain at this temperature for at least 16 hours and then open the furnace and allow the crucible to cool. Add 10ml hydrochloric acid solution (3.1) and evaporate to dryness on a steam bath. Extract the soluble salts with two successive 10ml portions of boiling 2N hydrochloric acid solution (3.2), decanting the solution each time through the same filter paper**(a)** into a 50ml graduated flask. Add 5ml hydrochloric acid solution (3.1) and 5ml nitric acid solution (3.4) to the residue in the dish and evaporate the mixture to dryness on a hot plate at low heat. Add 10ml boiling hydrochloric acid solution (3.1) to the residue and filter the solution through the same filter paper into the 50ml graduated flask. Wash the filter paper with water, cool the solution to room temperature and make up to the mark with water.

6.2 *Determination*

6.2.1 Transfer a suitable aliquot of the solution, prepared as in 6.1, to a 125ml separating funnel, add 1ml ammonium ferrous sulphate solution (3.6) and sufficient N hydrochloric acid (3.3) to bring the volume to 50ml (see *NOTE*), then add 1ml potassium thiocyanate solution (3.7) and mix. Add 1ml stannous chloride solution (3.9) and mix again. Add exactly 7ml solvent mixture (3.10), shake vigorously for two minutes and allow to separate for fifteen minutes. Filter the lower layer through a 7cm paper into a small stoppered tube. (If the lower layer is not clear or if filtration is difficult, filter through a suitable column packed with anhydrous sodium sulphate (3.8), solid stannous chloride and plugged with cotton wool.)

6.2.2 Carry out a blank determination repeating the procedure but omitting the sample. Measure the absorbance of the solutions at a wave length of 470nm, in the spectrophotometer (4) with water as reference. Determine the quantity of molybdenum in the solution by reference to the calibration curve (6.3).

NOTE: The acidity of the final solution must not exceed 1·5N with respect to hydrochloric acid; with more strongly acid conditions, fading of the colour will occur.

(a) Whatman 541 or equivalent.

6.3 *Calibration curve*

Transfer by pipette, 0, 5, 10, 15, 20 and 25ml standard molybdenum solution (3.5.2) into a series of 125ml separating funnels. To each funnel add 1ml ammonium ferrous sulphate solution (3.6) and 25ml of 2N hydrochloric acid (3.2); dilute to 50ml with water where necessary and proceed as described at 6.2.1, commencing at ". . . then add 1ml potassium thiocyanate solution (3.7) and mix . . .". Plot a calibration curve of the absorbance of the solutions against the corresponding amounts of molybdenum (μg).

7. **Expression of the Results**

The molybdenum content in mg/kg is given by the formula:

$$\frac{A \times 50}{V \times M}$$

where:

A = weight of molybdenum in the aliquot taken for colour development as read from the calibration curve after allowing for the blank reading (μg);

V = volume in millilitres of aliquot taken for colour development;

M = weight of sample in grams.

12. DETERMINATION OF COPPER

1. **Scope and Field of Application**

This method is applicable to all fertilisers.

2. **Principle**

The sample is ashed and dissolved in dilute hydrochloric acid or, if it contains no organic substances, it is dissolved directly in dilute hydrochloric acid. The solution is diluted and the copper content is determined by atomic absorption spectrophotometry.

3. **Reagents**

3.1 Hydrochloric acid (d = 1·18g/ml).

3.2 Hydrochloric acid, 6N solution.

3.3 Hydrochloric acid, 0·5N solution.

3.4 Hydrogen peroxide, approximately 100 volume, 30% by weight.

3.5.1 Copper solution**(a)** (stock): weigh to the nearest 0·001g, 1g pure copper, dissolve in 25ml 6N hydrochloric acid solution (3.2), add 5ml hydrogen peroxide (3.4) and dilute to 1 litre with water.

1ml of this solution = 1000μg of copper (Cu).

3.5.2 Copper solution (dilute): dilute 10ml of stock solution (3.5.1) to 100ml with water and then dilute the resulting solution, 10ml to 100ml with water, 1ml. of the final dilution = 10μg of copper (Cu).

4. **Apparatus**

Atomic absorption spectrophotometer with a copper lamp (324·8nm).

5. **Preparation of Sample**

See Method 1.

6. **Procedure**

6.1 *Preparation of the solution for analysis*

6.1.1 *In the absence of organic matter*

Weigh to the nearest 0·001g, 5g of the prepared sample, place it in a 400ml beaker, add carefully 5ml hydrochloric acid (3.1) (there may be a vigorous reaction due to carbon dioxide formation). Add more hydrochloric acid, if necessary. When

(a) Commercially available standard copper solution may be used.

effervescence has stopped, evaporate to dryness on a steam bath, stirring occasionally with a glass rod. Add 15ml 6N hydrochloric acid solution (3.2) and 120ml water. Stir with the glass rod, which should be left in the beaker, and cover the beaker with a watch glass. Boil the solution gently until dissolution appears complete and then filter through a filter paper(a) into a 250ml graduated flask. Wash the beaker and filter with 5ml hot 6N hydrochloric acid solution (3.2) and twice with boiling water. Cool and make up to the mark with water (the hydrochloric acid concentration of this solution should be about 0·5N).

6.1.2 *In the presence of organic matter*

Weigh to the nearest 0·001g, 5g of the prepared sample into a silica or platinum crucible and place the crucible into a cold muffle furnace. Close the furnace and gradually raise the temperature to 450–475°C over about 90 minutes. Maintain this temperature for at least 16 hours and then open the furnace and allow the crucible to cool. Moisten the ash with water and transfer it into a 250ml beaker. Wash the crucible with about 5ml hydrochloric acid (3.1) and add the latter slowly and carefully to the beaker (there may be a vigorous reaction due to carbon dioxide formation). If necessary, add more hydrochloric acid (3.1) with stirring, until all effervescence has stopped. Evaporate the solution to dryness, occasionally stirring with a glass rod. Add 15ml 6N hydrochloric acid solution (3.2) and 120ml water. Stir with the glass rod, which should be left in the beaker, and cover with a watch glass. Boil the solution gently until dissolution appears complete and filter through a filter paper(a) into a 250ml graduated flask. Wash the beaker and filter with 5ml of hot 6N hydrochloric acid solution (3.2) and twice with boiling water. Cool and make up to the mark with water. (The hydrochloric acid concentration of this solution should be about 0·5N.)

6.2 *Blank solution*

Prepare a blank solution from which only the sample has been omitted and allow for this in the calculation of the final results.

6.3 *Determination*

6.3.1 *Preparation of sample and blank test solutions*

Dilute the sample solutions (6.1.1 or 6.1.2) and the blank test solution (6.2) with 0·5N hydrochloric acid solution (3.3) to a concentration within the optimal measuring range of the spectrophotometer.

6.3.2 *Preparation of the calibration solution*

By diluting the standard solution (3.5.2) with 0·5N hydrochloric acid solution (3.3) prepare at least 5 standard solutions corresponding to the optimal measuring range of the spectrophotometer.

6.4 *Measurement*

Set up the spectrophotometer (4) at a wavelength of 324·8nm using an oxidising air-acetylene flame. Spray successively, in triplicate, the standard solution (6.3.2), the sample solution and the blank test solution (6.3.1), washing the instrument through with distilled water between each spraying. Plot the calibration curve using the mean absorbances as the ordinates and the corresponding concentrations of copper in μg/ml as the abscissae.

Determine the concentration of copper in the final sample and blank solutions by reference to the calibration curve.

7. Expression of the Results

Calculate the copper content of the sample taking into account the weight of the test sample and the dilutions carried out in the course of the analysis. Express the result either as a percentage or as mg/kg.

(a) Whatman 541 or equivalent.

13. DETERMINATION OF IRON

1. Scope and Field of Application

This method is applicable to all fertilisers.

2. Principle

The sample is ashed and dissolved in dilute hydrochloric acid or, if it contains no organic substances, it is dissolved directly in dilute hydrochloric acid. The solution is diluted and the iron content of the extract is determined by atomic absorption spectrophotometry.

3. Reagents

3.1 Hydrochloric acid (d = 1·18g/ml).

3.2 Hydrochloric acid, 6N solution.

3.3 Hydrochloric acid, 0·5N solution.

3.4 Hydrogen peroxide, approximately 100 volume, 30% by weight.

3.5.1 Iron solution(a) (stock): weigh to the nearest 0·001g, 1g pure iron, dissolve in 200ml 6N hydrochloric acid solution (3.2), add 16ml hydrogen peroxide solution (3.4) and dilute to 1 litre with water.

1ml of this solution = 1000μg of iron (Fe).

3.5.2 Iron solution (dilute): dilute 10ml of stock solution (3.5.1) to 100ml with water.

1ml of this solution = 100μg of iron (Fe).

3.6 Lanthanum chloride solution: dissolve 12g lanthanum oxide in 150ml water, add 100ml 6N hydrochloric acid solution (3.2) and dilute to 1 litre with water.

4. Apparatus

Atomic absorption spectrophotometer with an iron lamp (248·3nm).

5. Preparation of Sample

See Method 1.

6. Procedure

6.1 *Preparation of the solution for analysis*

6.1.1 *In the absence of organic matter*

Weigh to the nearest 0·001g, 5g of the prepared sample, place it in a 400ml beaker, add carefully 5ml hydrochloric acid (3.1) (there may be a vigorous reaction due to carbon dioxide formation). Add more hydrochloric acid, if necessary. When effervescence has stopped, evaporate to dryness on a steam bath, stirring occasionally with a glass rod. Add 15ml 6N hydrochloric acid solution (3.2) and 120ml water. Stir with the glass rod, which should be left in the beaker, and cover the beaker with a watch glass. Boil the solution gently until dissolution appears complete and then filter through a filter paper(b) into a 250ml graduated flask. Wash the beaker and filter with 5ml of hot 6N hydrochloric acid solution (3.2) and twice with boiling water. Cool and make up to the mark with water. (The hydrochloric acid concentration of this solution should be about 0·5N.)

6.1.2 *In the presence of organic matter*

Weigh to the nearest 0·001g, 5g of the prepared sample into a silica or platinum crucible and place the crucible in a cold muffle furnace. Close the furnace and gradually raise the temperature to 450–475°C over about 90 minutes. Maintain this temperature for at least 16 hours and then open the furnace and allow the crucible to cool. Moisten the ash with water and transfer it into a 250ml beaker. Wash the crucible with about 5ml hydrochloric acid (3.1) and add the latter slowly and carefully to the beaker (there may be a vigorous reaction due to carbon

(a) Commercially available standard iron solution may be used.
(b) Whatman 541 or equivalent.

dioxide formation). If necessary, add more hydrochloric acid (3.1) with stirring, until all effervescence has stopped. Evaporate the solution to dryness, occasionally stirring with a glass rod. Add 15ml 6N hydrochloric acid solution (3.2) and 120ml water. Stir with the glass rod, which should be left in the beaker, and cover with a watch glass. Boil the solution gently until dissolution appears complete and filter through a filter paper(a) into a 250ml graduated flask. Wash the beaker and filter with 5ml of hot 6N hydrochloric acid solution (3.2) and twice with boiling water. Cool and make up to the mark with water. (The hydrochloric acid concentration of this solution should be about 0·5N.)

6.2 *Blank solution*

Prepare a blank solution from which only the sample has been omitted and allow for this in the calculation of the final results.

6.3 *Determination*

6.3.1 *Preparation of sample and blank test solutions*

Dilute the sample solutions (6.1.1 or 6.1.2) and the blank test solution (6.2) with 0·5N hydrochloric acid solution (3.3) to a concentration within the optimal measuring range of the spectrophotometer. The final solution must contain 10% (V/V) of the lanthanum chloride solution (3.6).

6.3.2 *Preparation of the calibration solutions*

By diluting the standard solution (3.5.2) with 0·5N hydrochloric acid solution (3.3) prepare at least 5 standard solutions of increasing concentration corresponding to the optimal measuring range of the spectrophotometer. The final solutions must contain 10% (V/V) of the lanthanum chloride solution (3.6).

6.4 *Measurement*

Set up the spectrophotometer (4), at a wave length of 248·3nm using an oxidising air-acetylene flame. Spray successively, in triplicate, the standard solutions (6.3.2) the sample solution, and the blank test solution (6.3.1), washing the instrument through with distilled water between each spraying. Plot the calibration curve using the mean absorbances as the ordinates and the corresponding concentrations of iron in μg/ml as the abscissae. Determine the concentration of iron in the final sample and blank solutions by reference to the calibration curve.

7. **Expression of the Results**

Calculate the iron content of the sample taking into account the weight of the test sample and the dilutions carried out in the course of the analysis. Express the result either as a percentage or as mg/kg.

14. DETERMINATION OF MANGANESE

1. **Scope and Field of Application**

This method is applicable to all fertilisers.

2. **Principle**

The sample is ashed and dissolved in dilute hydrochloric acid or, if it contains no organic substances, it is dissolved directly in dilute hydrochloric acid. The solution is diluted and the manganese content of the extract is determined by atomic absorption spectrophotometry.

3. **Reagents**

3.1 Hydrochloric acid (d = 1·18g/ml).

3.2 Hydrochloric acid, 6N solution.

3.3 Hydrochloric acid, 0·5N solution.

3.4.1 Manganese solution(b) (stock): weigh to the nearest 0·001g, 1g pure manganese, dissolve in 25ml 6N hydrochloric acid solution (3.2) and dilute to 1 litre with water. 1ml. of this solution = 1000μg of manganese (Mn).

(a) Whatman 541 or equivalent.
(b) Commercially available standard manganese solution may be used.

3.4.2 Manganese solution (dilute): dilute 10ml of stock solution (3.4.1) to 1 litre with water. 1 ml. of this solution = 10μg of manganese.

3.5 Lanthanum chloride solution: dissolve 12g lanthanum oxide in 150ml water, add 100ml 6N hydrochloric acid solution (3.2) and dilute to 1 litre with water.

4. Apparatus

Atomic absorption spectrophotometer with a manganese lamp (279·5nm).

5. Preparation of Sample

See Method 1.

6. Procedure

6.1 *Preparation of the solution for analysis*

6.1.1 *In the absence of organic matter*

Weigh to the nearest 0·001g, 5g of the prepared sample, place it in a 400ml beaker, add carefully 5ml hydrochloric acid (3.1) (there may be a vigorous reaction due to carbon dioxide formation). Add more hydrochloric acid, if necessary. When effervescence has stopped, evaporate to dryness on a steam bath, stirring occasionally with a glass rod. Add 15ml 6N hydrochloric acid solution (3.2) and 120ml water. Stir with the glass rod, which should be left in the beaker, and cover the beaker with a watch glass. Boil the solution gently until dissolution appears complete and then filter through a filter paper(a) into a 250ml graduated flask. Wash the beaker and filter with 5ml of hot 6N hydrochloric acid solution (3.2) and twice with boiling water. Cool and make up to the mark with water. (The hydrochloric acid concentration of this solution should be about 0·5N.)

6.1.2 *In the presence of organic matter*

Weigh to the nearest 0·001g, 5g of the prepared sample into a silica or platinum crucible and place the crucible into a cold muffle furnace. Close the furnace and gradually raise the temperature to 450–475°C over about 90 minutes. Maintain this temperature for at least 16 hours and then open the furnace and allow the crucible to cool. Moisten the ash with water and transfer it into a 250ml beaker. Wash the crucible with about 5ml hydrochloric acid (3.1) and add the latter slowly and carefully to the beaker (there may be a vigorous reaction due to carbon dioxide formation). If necessary add more hydrochloric acid (3.1) with stirring, until all effervescence has stopped. Evaporate the solution to dryness, occasionally stirring with a glass rod. Add 15ml 6N hydrochloric acid solution (3.2) and 120ml water. Stir with the glass rod, which should be left in the beaker, and cover with a watch glass. Boil the solution gently until dissolution appears complete and filter through a filter paper(a) into a 250ml graduated flask. Wash the beaker and filter with 5ml of hot 6N hydrochloric acid solution (3.2) and twice with boiling water. Cool and make up to the mark with water. (The hydrochloric acid concentration of this solution should be about 0·5N.)

6.2 *Blank solution*

Prepare a blank solution from which only the sample has been omitted and allow for this in the calculation of the final results.

6.3 *Determination*

6.3.1 *Preparation of sample and blank test solutions*

Dilute the sample solutions (6.1.1 or 6.1.2) and the blank test solution (6.2), with 0·5N hydrochloric acid solution (3.3) to a concentration within the optimal measuring range of the spectrophotometer. The final solution must contain 10% (V/V) of the lanthanum chloride solution (3.5).

6.3.2 *Preparation of the calibration solutions*

By diluting the standard solution (3.4.2) with 0·5N hydrochloric acid solution (3.3) prepare at least 5 standard solutions of increasing concentration corresponding to the optimal measuring range of the spectrophotometer. The final solutions must contain 10% (V/V) of the lanthanum chloride solution (3.5).

(a) Whatman 541 or equivalent.

6.4 *Measurement*

Set up the spectrophotometer (4), at a wave length of 279·5nm using an oxidising air-acetylene flame. Spray successively, in triplicate, the standard solutions (6.3.2), the sample solution and the blank test solution (6.3.1), washing the instrument through with distilled water between each spraying. Plot the calibration curve using the mean absorbances as the ordinates and the corresponding concentrations of manganese in μg/ml as the abscissae. Determine the concentration of manganese in the final sample and blank solutions by reference to the calibration curve.

7. Expression of the Results

Calculate the manganese content of the sample taking into account the weight of the test sample and the dilutions carried out in the course of the analysis. Express the result either as a percentage or as mg/kg.

15. DETERMINATION OF THE NEUTRALISING VALUE IN LIMING MATERIALS

1. Scope and Field of Application

This method is applicable to products in Groups 5(a) and 5(b) of Section A of the table in Schedule 1 of the Fertilisers Regulations 1977.

2. Principle

The sample is dissolved in a measured quantity of standard hydrochloric acid, the excess of which is titrated with a standard solution of sodium hydroxide.

3. Reagents

3.1 Hydrochloric acid, 0·5N solution.

3.2 Sodium hydroxide, 0·5N solution (carbonate free).

3.3 Phenolphthalein indicator solution: dissolve 0·25g phenolphthalein in 150ml 95% ethanol and dilute with water to 250ml.

4. Preparation of Sample

Rapidly grind 50g of the representative lime sample to pass through a 1mm sieve.

5. Procedure

Weigh to the nearest 0·001g, 0·5g of the prepared sample and transfer to a 300ml conical flask. Add 50ml of 0·5N hydrochloric acid (3.1), cover the flask with a watch glass and boil the contents gently for five minutes. Cool the mixture to room temperature, add two or three drops of the phenolphthalein indicator (3.3) and titrate with 0·5N sodium hydroxide solution (3.2) to the end point of the indicator.

6. Expression of the Results

Determine the amount of hydrochloric acid consumed by the sample.
1ml 0·5N hydrochloric acid ≡ 0·01402g calcium oxide (CaO).
The neutralising value is expressed as a percentage by weight of calcium oxide (CaO).

16. DETERMINATION OF FINENESS OF PRODUCTS OTHER THAN POTASSIC BASIC SLAG

1. Scope and Field of Application

This method is applicable to "Rock phosphate" in Group 2(b) and to products in Groups 4(c), 5(a) and 5(b) of Section A of the table in Schedule 1 of the Fertilisers Regulations 1977.

2. Principle

By hand sieve shaking, the proportion of material passing through the prescribed sieve is determined.

3. Apparatus

Sieves having square apertures of 45mm, 6·7mm, 6·3mm, 5mm, 3·35mm, 1·0mm and 150 microns; lower receiver to fit sieve. Test sieves conforming to British Standard 410:1976 are suitable.

4. Procedure

4.1 *For sieving through 3·35mm, 1·0mm and 150 micron sieves*

Thoroughly mix the sample and quarter down until a portion of about 100g is obtained. Heat this portion at 100°C until dry and thoroughly mix. Weigh to the nearest 0·01g, 20g and transfer to the sieve with the lower receiver attached. Proceed as described in 4.4.

4.2 *For sieving through 6·7mm, 6·3mm and 5mm sieves*

Oven dry the sample at 100°C for 24 hours and thoroughly mix. Weigh to the nearest 0·1g, 200g and transfer to the sieve with the lower receiver attached. Proceed as described in 4.4.

4.3 *For sieving through a 45mm sieve*

If the sample appears moist or damp, oven dry at 100°C for 24 hours, but if the sample appears dry, heating is not necessary. Thoroughly mix the sample and weigh to the nearest 0·1g, 500g and transfer to the sieve with the lower receiver attached. Proceed as in 4.4.

4.4 *Sieving*

Shake the sieve for 5 minutes, frequently tapping the side. Disintegrate soft lumps such as can be caused to crumble by the application of the fibres of a soft brush, taking care that the hard part of the brush does not make contact with the sieve, and that the brush is not used to brush particles through the sieve. Brush out the powder in the lower receiver and weigh. Replace the receiver and repeat the shaking and tapping procedure for 2 minutes. Add the powder in the receiver to the first portion and weigh. Repeat the process until not more than 0·04g passes through the sieve during 2 minutes.

5. Expression of the Results

Calculate the fineness by expressing the weight of the material passing through the sieve as a percentage of the weight of the portion of the dried (or as the case may be, undried) sample taken for sieving.

17. DETERMINATION OF FINENESS OF POTASSIC BASIC SLAG

1. Scope and Field of Application

Exclusively to "Potassic basic slag" in Group 3(b) of Section A of the table in Schedule 1 of the Fertilisers Regulations 1977.

2. Principle

By hand sieve shaking and dissolution of the soluble salts, the proportion of slag passing through the prescribed sieve is determined.

3. Apparatus

Sieve having square apertures of 0·5mm (500 microns); lower receiver to fit sieve. Test sieves conforming to British Standard 410:1976 are suitable.

4. Procedure

4.1 *Preparation of the sample*

Thoroughly mix the sample and quarter down until a portion of about 100g is obtained. Heat this portion at 100°C until dry, and thoroughly mix.

4.2 *Sieving*

Weigh to the nearest 0·1g, 20g of the dry sample and transfer to the sieve with the lower receiver attached. Shake the sieve for five minutes, frequently tapping the sides. Disintegrate soft lumps that can be caused to crumble by the application of a soft brush, taking care that the hard part of the brush does not make contact with the sieve and that the brush is not used to brush particles through the sieve.

Transfer the finer portion from the container into a 500ml beaker and add 200ml of previously boiled water. Stir and then filter through a weighed sintered glass crucible. Thoroughly wash the residue with water, dry and re-weigh the crucible. Calculate the weight of slag in the mixture with a particle size of less than 0·5mm (A).

Weigh to the nearest 0·01g, about 20g of the dry sample and transfer to a 500ml conical flask. Add 200ml previously boiled water and shake for 30 minutes. Filter through a weighed, sintered glass crucible, wash the residue thoroughly with water, dry and re-weigh the crucible. Calculate the total weight of slag in the mixture (B).

5. Expression of the Results

Express the fineness of the slag as $\frac{A}{B} \times 100$. ".

EXPLANATORY NOTE

(*This Note is not part of the Regulations.*)

These regulations, made under Part IV of the Agriculture Act 1970 (as amended by Schedule 4E to the European Communities Act 1972), apply throughout Great Britain and are made after consultation with persons and organisations representing the interests concerned.

The regulations amend the Fertilisers (Sampling and Analysis) Regulations 1978 (the principal regulations) in order to:—

(*a*) prescribe additional methods of analysis (regulation 5 and the Schedule);

(*b*) extend the application of the principal regulations to fertilisers marked in accordance with the Fertilisers and Feeding Stuffs Regulations 1973 (regulations 3 and 5); and

(*c*) revoke the Fertilisers and Feeding Stuffs Regulations 1973, as amended, in so far as they apply to the sampling and analysis of fertilisers (regulation 4).