STATUTORY INSTRUMENTS

1978 No. 1108

AGRICULTURE

The Fertilisers (Sampling and Analysis) Regulations 1978

Made - - - - -	28th July 1978
Laid before Parliament - -	16th August 1978
Coming into Operation - -	6th September 1978

ARRANGEMENT OF REGULATIONS

The Minister of Agriculture, Fisheries and Food and the Secretaries of State for Scotland and Wales, acting jointly, in exercise of the powers conferred on them by sections 66(1), 67(5), 74A (inserted by section 4(1) of, and paragraph 6 of Schedule 4 to, the European Communities Act 1972 (**a**)), 75(1), 76(1), 77, 78(2), (4) and (6), 79(1), (2) and (9) and 84 of the Agriculture Act 1970 (**b**), as read with article 2(3) of, and Schedule 1 to, The Transfer of Functions (Wales) (No. 1) Order 1978 (**c**) 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—

(**a**) 1972 c.68. (**b**) 1970 c.40. (**c**) S.I. 1978/272.

Citation, commencement and interpretation

1.—(1) These regulations may be cited as the Fertilisers (Sampling and Analysis) Regulations 1978, and shall come into operation on 6th September 1978.

(2) In these regulations, unless the context otherwise requires—

"the Act" means the Agriculture Act 1970, as amended by section 4(1) of, and paragraph 6 of Schedule 4 to, the European Communities Act 1972;

AND other expressions have the same meaning as in the Act.

(3) The Interpretation Act 1889(**a**) shall apply to the interpretation of these regulations as it applies to the interpretation of an Act of Parliament and as if these regulations and the regulations hereby revoked were Acts of Parliament.

(4) Any reference in these regulations to a numbered regulation or schedule shall, unless the context otherwise requires, be construed as a reference to the regulation or schedule bearing that number in these regulations.

(5) Any reference in these regulations to a numbered section shall, unless the reference is to a section of a specified Act, be construed as a reference to the section bearing that number in the Act.

Prescribed amount for the purposes of the definition of sampled portion

2.—(1) The prescribed amount of material for the purposes of the definition of sampled portion in section 66(1) shall be determined in accordance with the provisions of this regulation.

(2) In relation to solid fertiliser in packages, the prescribed amount shall be the quantity of material present or 5 tonnes, whichever is the less.

(3) In relation to solid fertiliser in bulk containers, the prescribed amount shall be the contents of the lowest number of containers which together hold not less than 5 tonnes, save that if all the containers together hold less than 5 tonnes or if all the fertiliser is in one container, the prescribed amount shall be the quantity of material present, or if any such bulk containers hold not less than 5 tonnes, the prescribed amount shall be the contents of any such bulk container.

(4) In relation to solid fertiliser which is loose in heaps or bays, the prescribed amount shall be the contents of the lowest number of heaps or bays which together contain not less than 5 tonnes, save that if all the heaps or bays together contain less than 5 tonnes or if all the fertiliser is in one heap or bay, the prescribed amount shall be the quantity of material present, or if any such heaps or bays contain not less than 5 tonnes, the prescribed amount shall be the content of any such heap or bay.

(5) In relation to liquid or semi-liquid fertiliser in containers, the prescribed amount shall be the contents of the lowest number of containers which together hold not less than 5,000 litres, save that if all the containers together hold less than 5,000 litres or if all the fertiliser is in one container, the prescribed amount shall be the quantity of material present, or if any such containers hold not less than 5,000 litres, the prescribed amount shall be the content of any such container.

Manner of taking, dividing, marking, sealing and fastening of samples

3. The manner in which samples are to be taken, divided, marked, sealed and fastened in cases where under Part IV of the Act they are taken in the prescribed manner shall be as set out in Schedule 1.

(**a**) 1889 c.63.

Methods of sending part of a sample

4. Any part of a sample required to be sent to any person in pursuance of subsection (1)(b) or (2) of section 77 shall be sent by registered post or by the recorded delivery service or may be delivered or given by hand.

Qualifications of agricultural analysts and deputy agricultural analysts

5. The prescribed qualifications for an agricultural analyst or a deputy agricultural analyst for the purposes of section 67 (5) and for the purposes of these regulations are that he shall be a Chartered Chemist, being a Fellow or a Member of the Royal Institute of Chemistry, and that his practical experience of the analysis and examination of fertilisers shall be attested by another agricultural analyst or deputy agricultural analyst appointed under section 67(3) of the Act or in accordance with section 11 of the Fertilisers and Feeding Stuffs Act 1926(**a**).

Application of the methods of analysis

6.—(1) The methods of analysis prescribed in Schedule 2 shall apply, as respects materials specified in Schedule 1 to the Fertilisers Regulations 1977(**b**), as follows:—

(a) in the case of those materials set out in Groups 1(a), 1(b), 2(a) and 3(a) of Section A, and Groups 1 to 4 inclusive of Section B, determination of all analytical constituents;

(b) in the case of "Nitrogenous fertiliser" in Group 1(d) of Section A, and "Compound fertiliser" in Group 5 of Section B, determination of ureic nitrogen; and

(c) in the case of "Phosphated slag" and "Rock phosphate" in Group 2(b) of Section A, and "Phosphatic fertiliser" in Group 2(d) of the said Section A, determination of phosphorus pentoxide soluble in 2% formic acid.

(2) As respects materials or analytical constituents not specified or referred to in paragraph (1) of this regulation the requirements of Schedule 6 of the Fertilisers and Feeding Stuffs Regulations 1973(**c**) shall apply thereto.

(3) As respects analytical constituents for which methods of analysis are specified in Schedule 2 to these regulations, and in Schedule 6 to the Fertilisers and Feeding Stuffs Regulations 1973, the methods of analysis to be made for the purpose of the Act shall be those respectively set out in the said Schedules.

Form of certificate of analysis

7. The certificate of an agricultural analyst of the analysis shall be in the form set out in Schedule 3.

Amendment as respects metrication

8. In relation to any material to which these regulations apply the operation of the provisions of sections 66(1) and 76(5) shall be modified as follows:—

(a) the definition of "sampled portion" in the said section 66(1) shall have effect as if the words "five tonnes or 5,000 litres" were substituted for the words "five tons or 1,000 gallons or the prescribed metric substitution"; and

(**a**) 1926 c.45. (**b**) S.I. 1977/1489. (**c**) S.I. 1973/1521.

(b) section 76(5) shall have effect as if the words "six kilograms" were substituted for the words "fourteen pounds or the prescribed metric substitution".

Amendment of the Fertilisers Regulations 1977

9. The Fertilisers Regulations 1977 shall be amended as follows:—

(a) regulation 1(1)(b) shall be amended by substituting for the words "when they shall come into operation on 1st June 1978" the words "when they shall, in the case of fertilisers sold or offered for sale in bulk or in packages or containers exceeding 25 kilograms or 10 litres, as the case may be, come into operation on 1st June 1978, and in the case of fertilisers sold or offered for sale in packages or containers not exceeding 25 kilograms or 10 litres, as the case may be, come into operation on 1st June 1980";

(b) the following regulation shall be substituted for regulation 3:—

"**3.**—(1) Any material, which is sold or offered for sale in bulk or in packages or containers exceeding 25 kilograms or 10 litres, as the case may be, manufactured on or after 1st June 1978 and not designated as an EEC fertiliser, shall comply with the requirements of these regulations and any such material manufactured before 1st June 1978 shall, subject to the provisions of regulation 14, comply with the requirements of the Fertilisers and Feeding Stuffs Regulations 1973 as amended (**a**) until 31st December 1979.

(2) Any material, which is sold or offered for sale in packages or containers not exceeding 25 kilograms or 10 litres, as the case may be, manufactured on or after 1st June 1980 and not designated as an EEC fertiliser, shall comply with the requirements of these regulations and any such material manufactured before 1st June 1980 shall, subject to the provisions of regulation 14, comply with the requirements of the Fertilisers and Feeding Stuffs Regulations 1973 as amended until 31st May 1983.";

(c) regulation 13 shall be amended by substituting for the words "1st January 1980" the words "1st June 1983";

(d) regulation 14 shall be amended by substituting for the words "in the case of all other fertilisers" the words "in the case of fertilisers sold or offered for sale in bulk or in packages or containers exceeding 25 kilograms or 10 litres, as the case may be, or before 1st June 1980 in the case of all other fertilisers";

(e) Schedule 2 shall be amended by inserting after the words "other than a bulk container" in paragraph 3 of Part II thereof, the words "or a container of liquid fertilisers of a capacity not exceeding 10 litres".

Revocations

10. Regulations 3, 4, 5, 15, 16 and 17 and Parts I, II and IV of Schedule 1 and Part I of Schedule 8 of the Fertilisers and Feeding Stuffs Regulations 1973, and regulations 2(1), (2), (7), (8), (9), (16) and (18) and 3(2) and Schedule 8 of the Fertilisers and Feeding Stuffs (Amendment) Regulations 1976 (**b**) shall cease to have effect as respects their application to fertilisers on 1st June 1983.

(**a**) The relevant amending instrument is S.I. 1976/840. (**b**) S.I. 1976/840.

In Witness whereof the Official Seal of the Minister of Agriculture, Fisheries and Food is hereunto affixed on 27th July 1978.

(L,S.)

John Silkin,
Minister of Agriculture,
Fisheries and Food.

Bruce Millan,
Secretary of State for Scotland.

28th July 1978.

John Morris,
Secretary of State for Wales.

28th July 1978.

SCHEDULE 1

MANNER OF TAKING, DIVIDING, MARKING, SEALING AND FASTENING OF SAMPLES

(Sections 66(1), 74A, 75(1), 76(1), 77(1), (2) and (3), 78(2) and (4) and 79(1) and (2) and Regulation 3)

PART I

DEFINITIONS

In this Schedule:—

"sampled portion" means a quantity of a material constituting a unit and having characteristics presumed to be uniform;

"incremental sample" means a quantity taken from one point in the sampled portion;

"aggregate sample" means an aggregate of incremental samples taken from the same sampled portion;

"reduced sample" means a representative part of the aggregate sample obtained from the latter by a process of reduction;

"final sample" means a representative part of the reduced sample or, where no intermediate reduction is required, of the aggregate sample; and

"unit" means a material identifiable as such by reason of its manufacturer, packer, uniform manner of packaging or labelling.

PART II

GENERAL INSTRUCTIONS FOR THE TAKING OF SAMPLES

1. In the case of fertiliser in packages or containers, only unopened packages or containers which appear to the inspector proposing to take the sample to be the original packages or containers of the fertiliser shall be selected for the purpose of the sample.

2. The sample shall be taken and prepared as quickly as possible having regard to the precautions necessary to ensure that it remains representative of the sampled portion. Instruments, surfaces and containers used in sampling shall be clean and dry.

3. No sample shall be drawn from any part of the sampled portion which appears to be damaged.

4. When stones are naturally present in a fertiliser, they shall, if possible, be broken up and mixed with the quantity from which a sample is to be drawn. Failing this they shall be removed from the mixture from which a sample is to be drawn and the weight of the residue of that mixture and the weight of the stones ascertained and reported to the analyst. In addition, a representative sample of the stones shall be sent to the analyst with the final sample.

5. An inspector who intends to take a sample in accordance with the provisions of section 76(1) on premises (not being premises used only as a dwelling) on which he has reasonable cause to believe that there is any fertiliser which the occupier of the premises has purchased, shall:—

(a) satisfy himself that the conditions in which the fertiliser is stored are not such as might cause undue deterioration of the said fertiliser, and that the fertiliser appears not to have been contaminated by any other material;

(b) where he has reasonable cause to believe that fertiliser in packages or containers is only part of an original consignment, select the number of packages or containers to be sampled as if not less than the whole consignment were still present, except that sampling shall not take place if fewer than the minimum number of packages or containers prescribed in table 1 of Part VI for the purposes of paragraph 2(a) and (c) of Part III of this Schedule are present.

The provisions of this paragraph shall not apply as respects any fertiliser purchased for the purpose of resale in the course of trade.

7. The sampling apparatus shall be made of materials which cannot affect the characteristics of the materials to be sampled.

8. In the case of a sampling spear its dimensions shall be appropriate to the characteristics of the sampled portion in all respects including depth of container, dimensions of the bag and particle size of the fertilizer.

9. Notwithstanding the provisions of these regulations, a sampling spear shall not be used if, prior to the taking of a sample, objection is raised thereto by the manufacturer on the ground that the material is unsuitable.

10. Mechanical apparatus may be used for the sampling of moving fertilisers, provided that such equipment is capable of taking samples right across the flow of the product.

11. Apparatus designed to divide the sample into approximately equal parts may be used for taking incremental samples and for the preparation of reduced and final samples.

12. A sample taken in accordance with the methods described below shall be deemed to be representative of the sampled portion.

PART III

Quantitative Requirements

1. Sampled portion

The sampled portion in compliance with regulation 2 shall be such that each of its constituent parts can be sampled in accordance with the requirements of this Schedule.

2. Incremental sample

The incremental samples shall be selected in the following manner:—

(a) in the case of fertilisers in packages—

(i) where the content of each of the packages contained in the sampled portion is greater than 1 kg in weight, the number of packages shall be selected in accordance with table 1 in Part VI of this Schedule;

(ii) where the content of each of the packages contained in the sampled portion does not exceed 1 kg in weight, the number of packages shall be selected in accordance with table 1 in Part VI of this Schedule, except that the number selected shall be not less than four.

(b) in the case of loose fertilisers the number of incremental samples shall be selected in accordance with table 2 in Part VI of this Schedule;

(c) in the case of liquid or semi-liquid fertilisers—

(i) where each container in the sampled portion contains not more than 200 litres the number of containers shall be selected in accordance with table 3 in Part VI of this Schedule;

(ii) where each container in the sampled portion contains more than 200 litres an incremental sample shall be drawn from each container.

3. Aggregate sample

A single aggregate sample per sampled portion is required. The weight or volume, as appropriate, of the aggregate sample shall be not less than the following:—

(a) packaged fertilisers—	
(i) packages of more than 1 kg	4 kg
(ii) packages not exceeding 1 kg	2 kg
(b) loose fertilisers	4 kg
(c) liquid or semi-liquid fertilisers—	
(i) containers not exceeding 200 litres	1 litre
(ii) containers of more than 200 litres	See table 4 in Part VI of this Schedule

4. Final sample

The amount of material in each final sample shall be not less than 500g in the case of solid fertilisers and 250ml in the case of liquid or semi-liquid fertilisers.

PART IV

Taking and Preparation of Samples

1. Incremental samples

Incremental samples of approximately equal sizes shall be taken at random throughout the whole sampled portion in the following manner:—

(a) in the case of packaged fertilisers—

(i) having selected the required number of packages for sampling in accordance with paragraph 2(a) of Part III of this Schedule, part of the content of each selected package shall be taken as the incremental sample, except in the case of material to which sub-paragraph (iv) of this paragraph applies;

(ii) where necessary, each selected package shall be emptied and worked up with a shovel separately, and one shovelful taken as the incremental sample;

(iii) when the material is of a suitable nature the incremental sample may be taken from each selected package by means of a sampling spear or by divider;

(iv) when the material is so packed or of such a nature that a shovel or spear or divider cannot be used, or where the content of the package does not exceed 1kg, the whole package shall be taken as the incremental sample;

(v) where the fertiliser is in a coarse or lump condition incremental samples shall be taken in accordance with sub-paragraph (ii) or (iv) of this paragraph as appropriate. These shall be crushed immediately and the whole passed through a sieve with meshes 31·8mm square;

(vi) where the fertiliser consists of bulky material, uneven in character and likely to get matted together, each selected package shall be emptied separately and the matted portions torn up and the whole of the contents of each package shall be thoroughly mixed. The incremental samples shall then be taken in accordance with sub-paragraphs (ii) or (iv) of this paragraph as appropriate;

(b) in the case of loose fertilisers—

(i) an imaginary division shall be made of the sampled portion into a number of approximately equal parts, corresponding to the number of incremental samples required in accordance with paragraph 2(b) in Part III of this Schedule and at least one incremental sample shall be taken at random from each of these parts;

(ii) when sampling is being carried out while the material comprising the sampled portion is in motion, the incremental samples shall be taken from the randomly selected parts as required in sub-paragraph (b) (i) of this paragraph;

(iii) when a sampling spear is used the sample shall be taken at an angle to the base of the heap;

(iv) where the fertiliser is in a coarse or lump condition, or consists of bulky material, uneven in character and likely to get matted together, the incremental samples shall be taken in accordance with the relevant provisions of paragraph 1(a)(v) or 1(a)(vi), as appropriate;

(c) in the case of liquid or semi-liquid fertilisers in containers each containing not more than 200 litres, the number of containers to be selected shall be taken in accordance with paragraph 2(c)(i) of Part III of this Schedule, and

(i) where the containers each contain not more than 1 litre the entire contents of the selected containers shall be transferred into a clean dry vessel of suitable material;

(ii) where the containers each contain more than 1 litre and not more than 200 litres the selected containers shall be well shaken or the contents agitated or otherwise treated to ensure uniformity. An approximately equal proportion of fluid shall then be taken immediately from each of the selected containers and transferred into a clean dry vessel of suitable material;

(d) in the case of liquid or semi-liquid fertilisers in containers each containing more than 200 litres—

(i) when a consignment is being withdrawn from the container and there is a tap in the outlet pipe from which it is suitable to draw a sample, a quantity in accordance with paragraph 3(c)(ii) in Part III of this Schedule shall be drawn from the tap (after first withdrawing sufficient to remove any residues in the pipe) into a clean dry vessel of suitable material, made up of portions of not less than 0·5 litres and of approximately equal size taken at regular intervals; otherwise

(ii) if the liquid is homogeneous, about 1 litre shall be drawn from a convenient outlet in the container (after first withdrawing sufficient to remove any residues in the outlet) into a clean dry vessel of suitable material, or

(iii) if the liquid is not homogeneous, the contents shall be well stirred or otherwise agitated and sampling shall then proceed as in sub-paragraph (ii), but

(iv) if it is not possible to make the liquid homogeneous, in the manner described in sub-paragraph (iii), or if the inspector considers that the procedure in sub-paragraphs (i), (ii) and (iii) may not be appropriate, the contents shall be sampled by lowering an open tube (which must be long enough to reach the bottom of the container) perpendicularly into the container. One or both ends of the tube shall then be closed and the contents transferred into a clean dry vessel of suitable material. If sampling by tube is impracticable, portions shall be taken from various levels of the container with a sampling bottle so as to obtain a quantity fairly representative of the whole. The appropriate process shall be repeated until a quantity in accordance with paragraph 3(c)(ii) of Part III of this Schedule has been withdrawn;

(v) where a sampled portion consists of two or more containers, incremental samples of approximately equal size shall be taken from each, drawn in the manner described in sub-paragraph (i), (ii), (iii) or (iv), as appropriate, and shall be placed in a clean dry vessel of suitable material.

2. Aggregate sample

The incremental samples shall be thoroughly mixed to form a single aggregate sample. In the case of solid fertilisers the material in the aggregate sample shall be carefully mixed to obtain an homogenised sample. Any lumps inconsistent with the nature of the material shall be broken up (if need be by separating them out and returning them to the aggregate sample).

3. Reduced sample

(a) In the case of solid fertilisers the aggregate sample shall, if necessary, be reduced to not less than 2 kg in the following manner:—

(i) the material shall be heaped to form a "cone", which shall then be flattened and quartered. Two diagonally opposite quarters shall be rejected, and the remainder shall then be mixed and the quartering and rejection continued as necessary, or

(ii) the reduction method effected by the use of a mechanical device.

(b) In the case of liquid or semi-liquid fertilisers if the aggregate sample consists of approximately 1 litre this may be taken as the final sample. In all other cases the aggregate sample shall be thoroughly mixed and a quantity of at least 1 litre transferred immediately into a clean dry vessel of suitable material.

4. Final samples

The final samples shall be obtained in the following manner:—

(a) in the case of solid fertilisers, the reduced sample or where necesssary the aggregate sample shall be thoroughly mixed and divided into three or, in the circumstances set out in section 77(2), four similar and approximately equal parts, and each part placed in an appropriate airtight container;

(b) in the case of liquid or semi-liquid fertilisers the reduced sample or where necessary the aggregate sample shall be thoroughly mixed and at once divided into three or, in the circumstances set out in section 77(2), four similar and approximately equal parts by pouring successive portions into appropriate airtight containers.

The containers used shall be such that the characteristics of the fertiliser at the time of sampling are preserved.

PART V

MARKING, SEALING AND FASTENING OF THE FINAL SAMPLE

1. Each container of a final sample shall be so secured and sealed by the person taking the sample that the container cannot be opened without breaking the seal; alternatively the container may be placed in a stout envelope or in a linen, cotton or plastic bag, and this further receptacle then secured and sealed in such a manner that the contents cannot be removed without breaking the seal or the receptacle.

2. A label shall be attached to the container or receptacle containing the final sample and sealed in such a manner that it cannot be removed without the seal being broken. The label shall be marked with the following particulars, which shall be visible without the seal being broken:—

(a) name of the inspector as well as the department to which he belongs;

(b) identification mark given by the inspector to the sample;

(c) place of sampling;

(d) date of sampling;

(e) name of the material; and

(f) identification code, batch reference number or consignment identification of the material sampled, where readily available.

3. The container or receptacle may also be sealed, or the label also signed or initialled, by the holder of the material sampled or person acting on his behalf.

PART VI

SAMPLING TABLES

TABLE 1

PACKAGED FERTILISERS

Number of packages in the sampled portion	*Number of packages to be selected for sampling*
1 to 4	All packages
5 to 16	not less than 4
17 to 25	„ 5
26 to 36	„ 6
37 to 49	„ 7
50 to 64	„ 8
65 to 81	„ 9
82 to 100	„ 10
101 to 121	„ 11
122 to 144	„ 12
145 to 169	„ 13
170 to 196	„ 14
197 to 225	„ 15
226 to 256	„ 16
257 to 289	„ 17
290 to 324	„ 18
325 to 361	„ 19
362 and above	„ 20

TABLE 2

Loose Fertilisers

Size of sampled portion in tonnes	*Number of incremental samples required*
Up to and including 2·5	Not less than 7
Greater than 2·5 and up to and including 3	„ 8
„ 3 „ 4	„ 9
„ 4 „ 5	„ 10
„ 5 „ 6	„ 11
„ 6 „ 7	„ 12
„ 7 „ 8	„ 13
„ 8 „ 9	„ 14
„ 9 „ 11	„ 15
„ 11 „ 12	„ 16
„ 12 „ 14	„ 17
„ 14 „ 16	„ 18
„ 16 „ 18	„ 19
„ 18 „ 20	„ 20
„ 20 „ 22	„ 21
„ 22 „ 24	„ 22
„ 24 „ 26	„ 23
„ 26 „ 28	„ 24
„ 28 „ 31	„ 25
„ 31 „ 33	„ 26
„ 33 „ 36	„ 27
„ 36 „ 39	„ 28
„ 39 „ 42	„ 29
„ 42 „ 45	„ 30
„ 45 „ 48	„ 31
„ 48 „ 51	„ 32
„ 51 „ 54	„ 33
„ 54 „ 57	„ 34
„ 57 „ 61	„ 35
„ 61 „ 64	„ 36
„ 64 „ 68	„ 37
„ 68 „ 72	„ 38
„ 72 „ 76	„ 39
„ 76	„ 40

TABLE 3

Liquid and Semi-Liquid Fertilisers

Number of containers in sampled portion	*Number of containers to be selected for sampling*
1 to 3	All containers
4 to 20	4
21 to 60	6
61 to 100	8
101 to 400	10
More than 400	20

TABLE 4

Liquid and Semi-Liquid Fertilisers

Size of sampled portion in litres				*Size of aggregate sample in litres*	
Greater than 200	and up to and including	5,000		not less than	1·0
„ 5,000	„	25,000		„	1·5
„ 25,000	„	50,000		„	2·0
„ 50,000	„	75,000		„	2·5
„ 75,000	„	100,000		„	3·0
„ 100,000	„	250,000		„	3·5
„ 250,000	„	500,000		„	5·0
„ 500,000				„	10·0

SCHEDULE 2

METHODS OF ANALYSIS

(Sections 68(5), 69(5), 70(4), 71(3), 74A, 75(1), 77(4), 78(6) and 79(3) and Regulation 6)

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 ammoniacal nitrogen
- 3.a Determination of nitric and ammoniacal nitrogen—Ulsch method
- b Determination of nitric and ammoniacal nitrogen—Arnd method
- c Determination of nitric and ammoniacal nitrogen—Devarda method
- 4.a Determination of total nitrogen in calcium cyanamide—in the absence of nitrate
- b Determination of total nitrogen in calcium cyanamide—in the presence of nitrate
5. Determination of total nitrogen in urea
6. Determination of cyanamide nitrogen
7. Determination of biuret in urea
- 8.a Determination of different forms of nitrogen—in the presence of cyanamide nitrogen
- b Determination of different forms of nitrogen—in the absence of cyanamide nitrogen
- 9.a Extraction of phosphorus—by mineral acids
- b Extraction of phosphorus—by 2% formic acid
- c Extraction of phosphorus—by 2% citric acid
- d Extraction of phosphorus—by neutral ammonium citrate
- e Extraction of phosphorus—by alkaline ammonium citrate (Petermann's method) at 65°C
- f Extraction of phosphorus—by alkaline ammonium citrate (Petermann's method) at ambient temperature

g Extraction of phosphorus—by alkaline ammonium citrate (Joulie's method)

h Extraction of phosphorus—by water

10. Determination of extracted phosphorus

11. Determination of potassium

12.a Determination of water-soluble magnesium—atomic absorption spectrophotometric method

b Determination of water-soluble magnesium—EDTA method

13.a Determination of total magnesium—atomic absorption spectrophotometric method

b Determination of total magnesium—EDTA method

14. Determination of chlorides, in the absence of organic matter

15.a Determination of fineness of grinding—dry method

b Determination of fineness of grinding—for soft natural phosphates

1. Preparation of the Sample for Analysis

1. Scope

The following procedure is to be used for the preparation of the sample for analysis, taken from the final sample.

2. Principle

The preparation of a final sample received at the laboratory is a series of operations, usually sieving, grinding and mixing, carried out in such a way that:—

(a) the smallest amount weighed out laid down by the methods of analysis is representative of the laboratory sample; and

(b) the fineness of the fertiliser has not been changed by the preparation to the extent that its solubility in the various extraction reagents is appreciably affected.

3. Apparatus

3.1 Sample divider (optional).

3.2 Sieves with apertures of 0·2mm and 0·5mm.

3.3 250ml flasks, stoppered.

3.4 Porcelain pestle and mortar or grinder.

4. Choice of Treatment to be Used

Preliminary remark: if the product is suitable, only a representative part of the final sample need be kept.

4.1 *Final samples which must not be ground*
Calcium nitrate, calcium magnesium nitrate, sodium nitrate, Chile nitrate, calcium cyanamide, nitrogenous calcium cyanamide, ammonium sulphate, ammonium nitrates of over 30% N, urea, basic slag, natural phosphate rendered partially soluble, precipitated dihydrated di-calcium phosphate, calcined phosphate, aluminium calcium phosphate, soft ground rock phosphate.

4.2 *Final samples which must be divided and part of which must be ground*
These are products in respect of which certain determinations are carried out without previous grinding (fineness of grinding for example) and other determinations after grinding. They include all compound fertilisers containing the following phosphate ingredients: basic slag, aluminium calcium phosphate, calcined phosphate, soft ground rock phosphate and natural phosphate rendered partially soluble. To that end, divide the final sample into two parts, which are as identical as possible, using a sample divider or by quartering.

4.3 *Final samples in respect of which all determinations are carried out on a ground product*

These are all the other fertilisers in Groups 1(a), 2(a) and 3(a) of Section A, and Groups 1 to 4 of Section B of the table in Schedule 1 of the Fertiliser Regulations 1977 which are not to be found under 4.1 and 4.2. The whole final sample shall be ground.

5. Method

The part of the final sample referred to under 4.2 and 4.3 is sieved rapidly through a sieve with apertures of 0·5mm. The residue is ground *roughly* so as to obtain a product in which there is a minimum of fine particles, and it is then sieved. The grinding must be done in conditions such that the substance is not appreciably heated. The operation is repeated as many times as is necessary until there is no residue, and it must be effected as quickly as possible in order to prevent any gain or loss of constituents (water, ammonia). The whole ground and sieved product is placed in a non-corrodible container provided with an air-tight closure.

Before any weighing is carried out for the analysis, the whole sample must be thoroughly mixed.

6. Special Cases

(a) *Fertilisers comprising a blend of several categories of crystals*

In this case, separation frequently occurs. It is therefore *absolutely* essential to crush and pass the sample through a sieve with apertures of 0·2mm (for example, mixtures of ammonium phosphate and potassium nitrate). The grinding of the whole of the final sample is recommended in the case of these products.

(b) *Residue which is difficult to grind and does not contain fertilising substances*

Weigh the residue and take account of its mass when calculating the final result.

(c) *Products which decompose on heating*

Grinding must be carried out in such a way as to avoid any heating. It is preferable in this case to use a mortar for grinding (for example, compound fertilisers containing calcium cyanamide and urea).

(d) *Products which are abnormally moist or made into a paste by grinding*

To ensure homogeneity, a sieve is to be chosen which has the smallest apertures compatible with the destruction of lumps by hand or with the pestle. This may be the case of mixtures, certain ingredients of which contain water of crystallisation.

2. Determination of Ammoniacal Nitrogen

1. Scope

This method is for the determination of ammoniacal nitrogen.

2. Field of Application

All nitrogenous fertilisers, including compound fertilisers, in which nitrogen is found exclusively either in the form of ammonium salts, or ammonium salts together with nitrates.

It is not applicable to fertilisers containing urea, cyanamide or other organic nitrogenous compounds.

3. Principle

Displacement of ammonia by means of an excess of sodium hydroxide; distillation; determining the yield of ammonia in a given volume of a standard sulphuric acid and titration of the excess acid by means of a standard solution of sodium or potassium hydroxide.

4. Reagents

4.1 Hydrochloric acid solution, 50% (V/V): dilute an appropriate volume of hydrochloric acid (d = 1·18g/ml) with an equal volume of water.

4.2 Sulphuric acid, 0·1N solution.
4.3 Sodium or potassium hydroxide, 0·1N solution, carbonate free. } for variant (a)

4.4 Sulphuric acid, 0·2N solution.
4.5 Sodium or potassium hydroxide 0·2N solution, carbonate free. } for variant (b) (See *Note* on page 18)

4.6 Sulphuric acid, 0·5N solution.
4.7 Sodium or potassium hydroxide, 0·5N solution, carbonate free. } for variant (c) (See *Note* on page 18)

4.8 Sodium hydroxide solution, 30g per 100ml, ammonia free.

4.9 Indicator solutions:

4.9.1 Mixed indicator:

Solution A: dissolve 1g methyl red in 37ml sodium hydroxide solution 0·1N and make up to 1 litre with water.

Solution B: dissolve 1g methylene blue in water and make up to 1 litre.

Mix 1 volume of solution A and 2 volumes of solution B.

This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0·5ml (10 drops) of this indicator solution.

4.9.2 Methyl red indicator solution:

dissolve 0·1g methyl red in 50ml ethanol (95%) make up to 100ml with water and filter if necessary. This indicator may be used (4 to 5 drops) instead of the preceding one.

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

4.11 Ammonium sulphate.

5. Apparatus

5.1 Distillation apparatus consisting of a round-bottomed flask of suitable capacity connected to a condenser by means of a splash head.

Examples of the different types of equipment recommended for this determination are reproduced in Figures 1, 2, 3 and 4 in the Appendix.

5.2 Rotary shaker, 35 to 40 turns per minute.

6. Preparation of Sample

See Method 1.

7. Procedure

7.1.1 *Solubility test*

Carry out a solubility test on the sample in water at room temperature in the proportion of 2g per 100ml.

7.1.2 *Preparation of the solution*

Weigh to the nearest 0·001g, according to the indications in the Table on page 19, a quantity of 5, 7 or 10g of the prepared sample and place it in a 500ml graduated flask. From the result of the solubility test, proceed as follows:

(a) *Products completely soluble in water*

Add to the flask the quantity of water needed to dissolve the sample; shake, and when completely dissolved, make up the volume and mix thoroughly.

(b) *Products not completely soluble in water*

Add to the flask 50ml water and then 20ml hydrochloric acid solution (4.1). Shake and leave undisturbed until the evolution of carbon dioxide has ceased. Add 400ml water and shake for half an hour with the rotary shaker (5.2). Make up to volume with water, mix and filter through a dry filter into a dry receiver.

7.2 *Determination*

According to the variant chosen, place in the collecting flask a measured quantity of standard sulphuric acid as indicated in the Table on page 19. Add the appropriate quantity of the chosen indicator solution (4.9.1 or 4.9.2) and, if necessary, water in order to obtain a volume of at least 50ml. The condenser outlet must be below the surface of the standard acid in the collecting flask.

Transfer by pipette, according to the details given in the Table, an aliquot part of the clear solution into the distillation flask of the apparatus. Add water to obtain a volume of about 350ml and several grains of pumice in order to control the boiling.

Assemble the distillation apparatus, and taking care to avoid any loss of ammonia, add to the contents of the distillation flask 10ml of concentrated sodium hydroxide solution (4.8) or 20ml of the reagent in the cases where 20ml hydrochloric acid (4.1) have been used in order to dissolve the sample. Warm the flask gently and when boiling commences distil at such a rate that about 250ml are distilled in 30 minutes.

When no more ammonia is likely to be evolved, lower the receiving flask so that the tip of the condenser is above the surface of the liquid.

Test the subsequent distillate by means of an appropriate reagent to ensure that all the ammonia is completely distilled. Wash the condenser extension with a little water and titrate the excess acid with the standard solution of sodium or potassium hydroxide prescribed for the variant adopted (see *Note*).

Note: Standard solutions of different strengths may be used for the titration provided that the volumes used for the titration do not, as far as possible, exceed 40 to 45ml.

7.3 *Blank*

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

7.4 *Control test*
Before carrying out analyses, check that the apparatus is working properly and that the correct application of the method is used, using an aliquot part of a freshly prepared solution of ammonium sulphate (4.11) containing the maximum quantity of nitrogen prescribed for the chosen variant.

8. Expression of the Result

Express the result of the analysis as the percentage of ammoniacal nitrogen in the fertiliser as received for analysis.

TABLE FOR METHOD 2

Determination of the ammoniacal nitrogen and of the ammoniacal and nitric nitrogen in fertilisers.

Table of the weighing, dilution and calculation to be carried out for each of the variants (a) (b) and (c) of the method.

Variant (a) Approximate maximum quantity of nitrogen to be distilled = 50mg.
Sulphuric acid 0·1N to be placed in the receiving flask = 50ml.
Titration with sodium or potassium hydroxide, 0·1N solution.

Declaration N%	Amount to be weighed (g)	Dilution (ml)	Solution of sample to be distilled (ml)	Expression of the result[a] N% = (50-A)F
0 - 5	10	500	50	(50-A) × 0·14
5 - 10	10	500	25	(50-A) × 0·28
10 - 15	7	500	25	(50-A) × 0·40
15 - 20	5	500	25	(50-A) × 0·56
20 - 40	7	500	10	(50-A) × 1·00

Variant (b) Approximate maximum quantity of nitrogen to be distilled = 100mg.
Sulphuric acid 0·2N to be placed in receiving flask = 50ml.
Titration with sodium or potassium hydroxide, 0·2N solution.

Declaration N%	Amount to be weighed (g)	Dilution (ml)	Solution of sample to be distilled (ml)	Expression of the result[a] N% = (50-A)F
0 - 5	10	500	100	(50-A) × 0·14
5 - 10	10	500	50	(50-A) × 0·28
10 - 15	7	500	50	(50-A) × 0·40
15 - 20	5	500	50	(50-A) × 0·56
20 - 40	7	500	20	(50-A) × 1·00

Variant (c) Approximate maximum quantity of nitrogen to be distilled = 200mg.
Sulphuric acid 0·5N to be placed in the receiving flask = 35ml.
Titration with sodium or potassium hydroxide, 0·5N solution.

Declaration N%	Amount to be weighed (g)	Dilution (ml)	Solution of sample to be distilled (ml)	Expression of the result[a] N% = (35-A)F
0 - 5	10	500	200	(35-A) × 0·175
5 - 10	10	500	100	(35-A) × 0·350
10 - 15	7	500	100	(35-A) × 0·500
15 - 20	5	500	100	(35-A) × 0·700
20 - 40	5	500	50	(35-A) × 1·400

[a] For the purposes of the formula for expression of the result:

50 or 35 = millilitres of standard solution of sulphuric acid to be placed in the receiving flask.

A = millilitres of sodium or potassium hydroxide used for the titration.

F = factor taking into account the weight of sample, the dilution, the volume of the aliquot part distilled and the volumetric equivalent.

3a. Determination of Nitric and Ammoniacal Nitrogen— Ulsch Method

1. Scope

This method is for the determination of nitric and ammoniacal nitrogen with reduction according to Ulsch.

2. Field of Application

All nitrogenous fertilisers, including compound fertilisers, in which nitrogen is found exclusively in nitrate form, or in ammoniacal and nitrate form.

3. Principle

Reduction of nitrates and nitrites to ammonia by means of metallic iron in an acid medium, and displacement of the ammonia thus formed by the addition of an excess of sodium hydroxide; distillation of the ammonia, and determination of the yield of ammonia in a known volume of standard sulphuric acid solution. Titration of the excess sulphuric acid by means of a standard solution of sodium or potassium hydroxide.

4. Reagents

4.1 Hydrochloric acid solution, 50% (V/V): dilute an appropriate volume of hydrochloric acid (d = 1·18g/ml) with an equal volume of water.

4.2 Sulphuric acid, 0·1N solution.

4.3 Sodium or potassium hydroxide, 0·1N solution, carbonate free.

4.4 Sulphuric acid solution, approximately 30% H_2SO_4 (W/V), ammonia free.

4.5 Powdered iron reduced in hydrogen. (The prescribed quantity of iron must be able to reduce at least 0·05g nitric nitrogen).

4.6 Sodium hydroxide solution, 30g per 100ml, ammonia free.

4.7 Indicator solutions:

4.7.1 Mixed indicator:

Solution A: dissolve 1g methyl red in 37ml 0·1N sodium hydroxide solution and make up to 1 litre with water.

Solution B: dissolve 1g methylene blue in water and make up to 1 litre.

Mix 1 volume of solution A with 2 volumes of solution B.

This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution; use 0·5ml (10 drops).

4.7.2 Methyl red indicator solution:

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

This indicator may be used (4 to 5 drops) instead of the preceding one.

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

4.9 Sodium nitrate.

5. Apparatus

See Method 2.

6. Preparation of Sample

See Method 1.

7. Procedure

7.1 *Preparation of the solution*
See Method 2.

7.2 *Determination*
Place in the receiving flask an exactly measured quantity of standard sulphuric acid (4.2) as indicated in the table of Method 2 (variant (a)) and add the appropriate quantity of indicator solution (4.7.1 or 4.7.2). The end of the extension tube of the condenser must be below the surface of the standard acid in the receiving flask.

Using a pipette, transfer an aliquot part of the clear solution as indicated in the table of Method 2 (variant (a)) and place it in the distilling flask of the apparatus. Add 350ml water, 20ml 30% sulphuric acid solution (4.4), stir, and add 5g of reduced iron (4.5). Wash the neck of the flask with several ml water, and place in the neck of the flask a small, long stemmed funnel. Heat in a boiling water bath for an hour and then wash the stem of the funnel with a few ml water.

Taking care to avoid any loss of ammonia, add to the contents of the distilling flask 50ml concentrated sodium hydroxide solution (4.6), or in the cases where 20ml hydrochloric acid (4.1) has been used to dissolve the sample, add 60ml of concentrated sodium hydroxide solution (4.6). Assemble the distillation apparatus. Distil the ammonia according to the procedure given in Method 2. Titrate the excess acid with the standard solution of sodium or potassium hydroxide (4.3).

7.3 *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 result.

7.4 *Control test*
Before analysis, check that apparatus is working properly and that the correct application of the method is used by using an aliquot part of a freshly prepared solution of sodium nitrate (4.9) containing 0·045g to 0·050g of nitrogen.

8. Expression of the Results

Express the results of analysis as a percentage of nitric nitrogen or combined ammoniacal and nitric nitrogen contained in the fertiliser as received for analysis.

3b Determination of Nitric and Ammoniacal Nitrogen – Arnd Method

1. Scope

This method is for the determination of nitric and ammoniacal nitrogen with reduction according to Arnd (modified for each of the variants (a), (b) and (c)).

2. Field of Application

See Method 3a.

3. Principle

Reduction of nitrates and nitrites to ammonia in a neutral aqueous solution by means of a metallic alloy composed of 60% Cu and 40% Mg (Arnd's alloy) in the presence of magnesium chloride.

Distillation of the ammonia, and determination of the yield in a known volume of standard sulphuric acid solution. Titration of the excess acid by means of a standard solution of sodium or potassium hydroxide.

4. Reagents

4.1 Hydrochloric acid solution, 50% (V/V): dilute an appropriate volume of hydrochloric acid (d = 1·18g/ml) with an equal volume of water.

4.2 Sulphuric acid, 0·1N solution.

4.3 Sodium or potassium hydroxide, 0·1N solution, carbonate free.

} for variant (a) (page 19)

4.4 Sulphuric acid, 0·2N solution.

4.5 Sodium or potassium hydroxide, 0·2N solution, carbonate free.

} for variant (b) (page 19) (See *Note* on page 18)

4.6 Sulphuric acid, 0·5N solution.

4.7 Sodium or potassium hydroxide, 0·5N solution, carbonate free.

} for variant (c) (page 19) (See *Note* on page 18)

4.8 Sodium hydroxide solution, approximately 2N.

4.9 Arnd's alloy—powdered so as to pass through a sieve with apertures less than 1·0mm square.

4.10 20% Magnesium chloride solution:

dissolve 200g magnesium chloride ($MgCl_2.6H_2O$) in approximately 600 – 700ml water in a 1 litre flat-bottomed flask. To prevent frothing, add 15g magnesium sulphate ($MgSO_4.7H_2O$). After dissolution add 2g magnesium oxide and a few anti-bump granules of pumice stone, and concentrate the suspension to 200ml by boiling, thus expelling any trace of ammonia from the reagents. Cool, make up the volume to 1 litre and filter.

4.11 Indicator solutions:

4.11.1 Mixed indicator:

Solution A: dissolve 1g methyl red in 37ml 0·1N sodium hydroxide solution and make up to 1 litre with water.

Solution B: dissolve 1g methylene blue in water and make up to 1 litre.

Mix 1 volume of A with 2 volumes of B.

This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0·5ml (10 drops).

4.11.2 Methyl red indicator solution:

dissolve 0·1g methyl red in 50ml 95% ethanol, make up to 100ml with water and filter if necessary. This indicator may be used (4 to 5 drops) instead of the preceding one.

4.11.3 Congo red indicator solution:

dissolve 3g Congo red in 1 litre warm water and filter if necessary after cooling. This indicator may be used, instead of the two described above, in the neutralisation of acid extracts before distillation, using 0·5ml per 100ml of liquid to be neutralised.

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

4.13 Sodium nitrate.

5. Apparatus

See Method 2.

6. Preparation of Sample

See Method 1.

7. Procedure

7.1 *Preparation of the solution for analysis*
See Method 2.

7.2 *Determination*
According to the chosen variant, place in the receiving flask a measured quantity of standard sulphuric acid as indicated in the table of Method 2. Add the appropriate quantity of chosen indicator solution (4.11.1 or 4.11.2) and if necessary water to give a volume of at least 50ml. The end of the extension tube of the condenser must be below the surface of the solution.

Using a pipette, take, according to the table, an aliquot part of the clear solution and place in the distillation flask.

Add sufficient water to obtain a total volume of about 350ml (see *Note*), 10g Arnd's alloy (4.8), 50ml magnesium chloride solution (4.10) and a few fragments of pumice stone (4.12). Rapidly connect the flask to the distillation apparatus. Heat gently for about 30 minutes. Then increase the heating to distil the ammonia. Continue the distillation for about an hour. After this time, *the residue in the flask ought to have a syrupy consistency*. When the distillation has finished, titrate the quantity of excess acid in the receiving flask according to the procedure in Method 2.

Note: When the sample solution is acid (addition of 20ml hydrochloric acid (4.1) to dissolve the sample) the aliquot part taken for analysis is neutralised in the following way:

to the distillation flask containing the aliquot part add about 250ml water, the necessary quantity of one of the indicators (4.11.1, 4.11.2, 4.11.3) and shake carefully. Neutralise with 2N sodium hydroxide solution (4.8) and acidify again with a drop of hydrochloric acid (4.1). Then proceed as indicated in 7.2.

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

7.4 *Control test*
Before analysis, check that apparatus is working properly and that the correct technique is applied using a freshly prepared solution of sodium nitrate (4.13) containing 0·050g to 0·150g nitrogen depending on the variant chosen.

8. Expression of the Results

Express the results of analysis as a percentage of nitric nitrogen or combined ammoniacal and nitric nitrogen contained in the fertiliser as received for analysis.

3c. Determination of Nitric and Ammoniacal Nitrogen—Devarda Method

1. Scope

This method is for the determination of nitric and ammoniacal nitrogen with reduction according to Devarda (modified for each of the variants (a), (b) and (c)).

2. Field of Application

See Method 3a.

3. Principle

Reduction of nitrates and nitrites to ammonia in a strongly alkaline solution by means of a metallic alloy composed of 45% Al, 5% Zn, and 50% Cu (Devarda alloy). Distillation of the ammonia and determination of the yield in a known volume of standard sulphuric acid; titration of the excess sulphuric acid by means of a standard solution of sodium or potassium hydroxide.

4. Reagents

4.1 Hydrochloric acid solution, 50% (V/V): dilute an appropriate volume of hydrochloric acid (d = 1·18g/ml) with an equal volume of water.

4.2 Sulphuric acid, 0·1N solution.
4.3 Sodium or potassium hydroxide, 0·1N solution, carbonate free. } for variant (a) (page 19)

4.4 Sulphuric acid, 0·2N solution.
4.5 Sodium or potassium hydroxide, 0·2N solution, carbonate free. } for variant (b) (page 19) (see *Note* on page 18)

4.6 Sulphuric acid, 0·5N solution.
4.7 Sodium or potassium hydroxide, 0·5N solution, carbonate free. } for variant (c) (page 19) (see *Note* on page 18)

4.8 Devarda's alloy—powdered so that 90 to 100% will pass through a sieve with apertures less than 0·25mm square, 50 to 75% will pass through a sieve with apertures of less than 0·075mm square. (Pre-packed bottles containing a maximum of 100g are recommended).

4.9 Sodium hydroxide solution, 30g per 100ml, ammonia free.

4.10 Indicator solutions:

4.10.1 Mixed indicator:

Solution A: dissolve 1g methyl red in 37ml 0·1N sodium hydroxide solution and make up to 1 litre with water.

Solution B: dissolve 1g methylene blue in water and make up to 1 litre.

Mix 1 volume of A with 2 volumes of B.

This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0·5ml (10 drops).

4.10.2 Methyl red indicator:

dissolve 0·1g methyl red in 50ml 95% ethanol. Make up to 100ml with water and filter if necessary.

This indicator (4 to 5 drops) may be used instead of the preceding one.

4.11 Ethanol, 95%.

4.12 Sodium nitrate.

5. Apparatus

5.1 Distillation apparatus consisting of a round-bottomed flask of suitable capacity, connected to a condenser by means of a splash head, equipped, in addition, with a bubble trap on the receiving flask to prevent any loss of ammonia.

An example of the type of apparatus recommended for this determination is reproduced in Figure 5 in the Appendix.

6. Preparation of the Sample

See Method 1.

7. Procedure

7.1 *Preparation of the solution for analysis*
See Method 2.

7.2 *Determination*
According to the variant chosen, place in the receiving flask an exactly measured quantity of standard sulphuric acid as indicated in the Table on page 19. Add the appropriate quantity of the chosen indicator solution (4.10.1 or 4.10.2) and finally, sufficient water to give a volume of 50ml. The end of the extension tube of the condenser must be below the surface of the solution. Fill the bubble trap with distilled water.

Using a pipette, take an aliquot part of the clear solution as indicated in the table and place in the distillation flask. Add sufficient water to the distillation flask to obtain a volume of 250-300ml, 5ml ethanol (4.11) and 4g Devarda's alloy (4.8).

(*Note:* In the presence of calcium salts such as calcium nitrate and calcium ammonium nitrate, it is necessary to add, before distillation for each gram of sample present in the aliquot part, 0·700g disodium hydrogen phosphate ($Na_2HPO_42H_2O$) to prevent the formation of calcium hydroxide.)

Taking the necessary precautions to avoid loss of ammonia, add to the flask about 30ml 30% sodium hydroxide solution (4.9) and finally, in the case of acid soluble samples an additional quantity sufficient to neutralise the quantity of hydrochloric acid (4.1) present in the aliquot part taken for the analysis. Connect the distillation flask to the apparatus, ensuring the tightness of connections. Carefully shake the flask to mix the contents.

Warm gently, so that the release of hydrogen decreases appreciably over about half an hour and the liquid will boil. Continue the distillation, increasing the heat so that at least 200ml liquid distils in about 30 minutes. (Do not prolong the distillation beyond 45 minutes.) 2r

When the distillation is complete, disconnect the receiving flask from the apparatus, carefully wash the extension tube and bubble trap, collecting the rinsings in the titration flask. Titrate the excess acid according to the procedure in Method 2.

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

7.4 *Control test*
Before carrying out the analysis, check that the apparatus is working properly and that the correct application of the method is used, using an aliquot part of a freshly prepared solution of sodium nitrate (4.12) containing, according to the variant chosen, 0·050g to 0·150g nitric nitrogen.

8. Expression of Results

Express the results of analysis as a percentage of nitric nitrogen or combined ammoniacal and nitric nitrogen contained in the fertiliser as received for analysis.

4a. Determination of Total Nitrogen in Calcium Cyanamide —in the Absence of Nitrate

1. Scope

This method is for the determination of total nitrogen in nitrate free calcium cyanamide.

2. Field of Application

Exclusively to calcium cyanamide (nitrate free).

3. Principle

After Kjeldahl digestion, the ammoniacal nitrogen formed is displaced by sodium hydroxide, and collected in a standard solution of sulphuric acid. The excess sulphuric acid is titrated with a standard solution of sodium or potassium hydroxide.

4. Reagents

4.1 Sulphuric acid solution 50% (V/V): dilute an appropriate volume of sulphuric acid (d = 1·84g/ml) with an equal volume of water.

4.2 Potassium sulphate.

4.3 Copper oxide (CuO)—0·3 to 0·4g for each determination or an equivalent quantity of copper sulphate pentahydrate, from 0·95 to 1·25g for each determination.

4.4 Sodium hydroxide solution, 30g per 100ml, ammonia free.

4.5 Sulphuric acid, 0·1N solution.
4.6 Sodium or potassium hydroxide, 0·1N solution, carbonate free.
} for variant (a) (page 19)

4.7 Sulphuric acid, 0·2N solution.
4.8 Sodium or potassium hydroxide, 0·2N solution, carbonate free.
} for variant (b) (page 19) (See *Note* on page 18)

4.9 Sulphuric acid, 0·5N solution.
4.10 Sodium or potassium hydroxide, 0·5N solution, carbonate free.
} for variant (c) (page 19) (See *Note* on page 18)

4.11 Indicator solutions:

4.11.1 Mixed indicator:

Solution A: dissolve 1g methyl red in 37ml 0·1N sodium hydroxide solution and make up to 1 litre with water.

Solution B: dissolve 1g methylene blue in water and make up to 1 litre.

Mix 1 volume of A with 2 volumes of B.

This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0·5ml (10 drops).

4.11.2 Methyl red indicator:

dissolve 0·1g methyl red in 50ml 95% ethanol and make up to 100ml with water. Filter if necessary. This indicator (4 to 5 drops) may be used instead of the preceding one.

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

4.13 Potassium thiocyanate.

5. Apparatus

5.1 Distillation apparatus. See Method 2.

6. Preparation of Sample

See Method 1.

7. Procedure

7.1 *Preparation of the solution*
Weigh to the nearest 0·001g, 1g of the prepared sample and place it in the Kjeldahl flask. Add 50ml 50% sulphuric acid (4.1), 10-15g potassium sulphate (4.2), and one of the prescribed catalysts (4.3). Heat slowly to drive off the water, boil gently for two hours, allow to cool, and dilute with 100-150ml water. Cool again, transfer quantitatively the suspension to a 250ml graduated flask, make up to volume with water, shake, and filter through a dry filter into a dry flask.

7.2 *Determination*
According to the variant chosen (see Method 2) transfer with a pipette 50, 100 or 200ml of the solution to the distillation apparatus and add sufficient sodium hydroxide solution (4.4) to ensure a considerable excess. Distil the ammonia and titrate the excess acid as described in Method 2.

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

7.4 *Control Test*
Before carrying out the analysis, check that the apparatus is working properly and that the correct application of the method is used, using

an aliquot part of a standard solution of potassium thiocyanate (4.13), approximating to the concentration of nitrogen in the sample.

8. Expression of the Result

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

Variant (a): $N\% = (50\text{-}A) \times 0{\cdot}7$
Variant (b): $N\% = (50\text{-}A) \times 0{\cdot}7$
Variant (c): $N\% = (35\text{-}A) \times 0{\cdot}875$

Where A = millilitres of sodium or potassium hydroxide used for the titration.

4b. Determination of Total Nitrogen in Calcium Cyanamide—in the Presence of Nitrate

1. Scope

This method is for the determination of total nitrogen in calcium cyanamide.

2. Field of Application

The method is applicable to calcium cyanamide containing nitrates.

3. Principle

The direct application of Kjeldahl's method cannot be applied to calcium cyanamide containing nitrates. For this reason the nitric nitrogen is reduced to ammonia with metallic iron and stannous chloride before Kjeldahl digestion. The ammoniacal nitrogen is that determined as in Method 4a.

4. Reagents

4.1 Sulphuric acid, (d = 1·84g/ml).

4.2 Powdered iron reduced in hydrogen.

4.3 Potassium sulphate, finely pulverised.

4.4 Sulphuric acid, 0·1N solution.
4.5 Sodium or potassium hydroxide, 0·1N solution, carbonate free.
} for variant (a) (page 19)

4.6 Sulphuric acid, 0·2N solution.
4.7 Sodium or potassium hydroxide, 0·2N solution, carbonate free.
} for variant (b) (page 19) (See *Note* on page 18)

4.8 Sulphuric acid, 0·5N solution.
4.9 Sodium or potassium hydroxide, 0·5N solution, carbonate free.
} for variant (c) (page 19) (See *Note* on page 18)

4.10 Indicator solutions:

4.10.1 Mixed indicator:

Solution A: dissolve 1g of methyl red in 37ml of the 0·1N sodium hydroxide solution and make up to 1 litre with water.

Solution B: dissolve 1g of methylene blue in water and make up to 1 litre.

Mix 1 volume of A and 2 volumes of B.

This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0·5ml (10 drops).

4.10.2 Methyl red indicator:

dissolve 0·1g of methyl red in 50ml of 95% ethanol, make up to 100ml with water and filter if necessary. This indicator (4 to 5 drops) may be used instead of the preceding one.

4.11 Solution of stannous chloride:

dissolve 120g of stannous chloride ($SnCl_2.2H_20$), in 400ml concentrated hydrochloric acid (d = 1·18g/ml) and make up to 1 litre with water. The solution must be completely clear and prepared immediately before use.

It is essential to check the reducing power of the stannous chloride.

Dissolve 0·5g of stannous chloride in 2ml concentrated hydrochloric acid (d = 1·18g/ml) and make up to 50ml with water. Then add 5g of Rochelle salt (potassium sodium tartrate) and a sufficient quantity of sodium bicarbonate for the solution to show an alkaline reaction to a litmus paper test.

Titrate with 0·1N iodine solution in the presence of a starch solution as an indicator.

1ml of iodine solution 0·1N corresponds to 0·01128g $SnCl_2.2H_2O$.

At least 80% of the total tin present in the solution thus prepared must be in a bivalent form. For the titration at least 35ml of 0·1N iodine solution should be used.

4.12 Sodium hydroxide solution, 30g per 100ml, ammonia free.

4.13 Standard nitrate-ammoniacal solution:

Weigh out 2·500g of potassium nitrate and 10·160g of ammonium sulphate and place them in a 250ml graduated flask. Dissolve in water and make up to 250ml. 1ml of this solution contains 0·010g of nitrogen.

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

5. Apparatus

5.1 Distillation apparatus. See Method 2.

6. Preparation of the Sample

See Method 1.

7. Procedure

7.1 *Preparation of the solution*

Weigh to the nearest 0·001g, 1g of the prepared sample and place in the Kjeldahl flask. Add 0·5g of powdered iron (4.2) and 50ml of the stannous chloride solution (4.11), stir and leave standing for half an hour. During the time it is left standing, stir again after 10 and 20 minutes. Then add 10g of potassium sulphate (4.3) and 30ml of sulphuric acid (4.1). Boil and carry on the process for an hour after the appearance of white fumes. Leave to cool and dilute with 100-150ml of water. Transfer the suspension quantitatively into a 250ml graduated flask, cool and make up to volume with water, mix and filter through a dry filter into a dry container.

7.2 *Determination*

According to the variant chosen (see Method 2) transfer with a pipette 50, 100 or 200ml of the solution to the distillation apparatus and add

sufficient sodium hydroxide solution (4.12) to ensure a considerable excess. Distil the ammonia and titrate the excess acid as described in Method 2.

7.3 *Blank test*

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

7.4 *Control test*

Before carrying out the analysis, check that the apparatus is working properly and that the correct application of the method is used with a standard solution containing quantities of ammoniacal and nitric nitrogen comparable to the quantities of cyanamide and nitric nitrogen contained in nitrated calcium cyanamide.

For this purpose place 20ml of the standard solution (4.13) in the Kjeldahl flask.

Carry out the analysis according to the method described in paragraph 7.

8. Expression of the Results

The result of the analysis must be expressed as the percentage of total nitrogen (N) contained in the fertiliser as received for analysis.

Variant (a): $N\% = (50\text{-}A) \times 0{\cdot}7$
Variant (b): $N\% = (50\text{-}A) \times 0{\cdot}7$
Variant (c): $N\% = (35\text{-}A) \times 0{\cdot}875$

Where A = millilitres of sodium or potassium hydroxide used for the titration.

5. Determination of Total Nitrogen in Urea

1. Scope

This method is for the determination of total nitrogen in urea.

2. Field of Application

This method is applied exclusively to urea fertilisers which are nitrate free.

3. Principle

Urea is transformed quantitatively into ammonia by boiling in the presence of sulphuric acid. The ammonia thus obtained is distilled from an alkaline medium, and collected in an excess of standard sulphuric acid. The excess acid is titrated by means of a standard alkaline solution.

4. Reagents

4.1 Sulphuric acid, concentrated, (d = 1·84g/ml).

4.2 Sodium hydroxide solution, 30g per 100ml, ammonia free.

4.3 Sulphuric acid, 0·1N solution. } for variant (a)
4.4 Sodium or potassium hydroxide, 0·1N solution, carbonate free. } (page 19)

4.5 Sulphuric acid, 0·2N solution. } for variant (b)
4.6 Sodium or potassium hydroxide, 0·2N solution, carbonate free. } (page 19) (See *Note* on page 18)

4.7 Sulphuric acid, 0·5N solution.
4.8 Sodium or potassium hydroxide, 0·5N solution, carbonate free. } for variant (c) (page 19) (See *Note* on page 18)

4.9 Indicator solutions:

4.9.1 Mixed indicator:

Solution A: dissolve 1g methyl red in 37 ml 0·1N sodium hydroxide solution and make up to 1 litre with water.

Solution B: dissolve 1g methylene blue in water and make up to 1 litre.

Mix 1 volume of solution A with 2 volumes of solution B.

This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0·5ml (10 drops).

4.9.2 Methyl red indicator solution:

dissolve 0·1g methyl red in 50ml 95% ethanol, and make up to 100ml with water. Filter if necessary. This indicator (4 to 5 drops) may be used instead of the preceding one.

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

4.11 Urea.

5. Apparatus

5.1 Distillation apparatus. See Method 2.

6. Preparation of the Sample

See Method 1.

7. Procedure

7.1 *Preparation of the solution*

Weigh to the nearest 0·001g, 2·5g of the prepared sample, place in a 300ml Kjeldahl flask and moisten with 20ml water. Stir in 20ml concentrated sulphuric acid (4.1) and add a few glass beads to prevent bumping. To prevent splashing, place a long-stemmed glass funnel in the neck of the flask. Heat slowly at first, then increase the heat until white fumes are observed (30-40 minutes).

Cool and dilute with 100-150ml water. Quantitatively transfer to a 500ml graduated flask, discarding any sediment. Allow to cool to room temperature. Make up to volume with water, mix and, if necessary, filter through a dry filter into a dry receptacle.

7.2 *Determination*

According to the variant chosen (see Method 2) transfer with a pipette 25, 50 or 100ml of the solution to the distillation apparatus and add sufficient sodium hydroxide solution (4.2) to ensure a considerable excess. Distil the ammonia and titrate the excess acid as described in Method 2.

7.3 *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 result.

7.4 *Control test*

Before carrying out the analysis, check that the apparatus is working properly and that the correct application of the method is used, using an aliquot part of a freshly prepared solution of urea (4.11).

8. Expression of the Result

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

Variant (a): $N\% = (50\text{-}A) \times 1{\cdot}12$
Variant (b): $N\% = (50\text{-}A) \times 1{\cdot}12$
Variant (c): $N\% = (35\text{-}A) \times 1{\cdot}40$

Where A = millilitres of sodium or potassium hydroxide used for the titration.

6. Determination of Cyanamide Nitrogen

1. Scope

This method is for the determination of cyanamide nitrogen.

2. Field of Application

Calcium cyanamide and calcium cyanamide/nitrate mixtures.

3. Principle

Cyanamide nitrogen is precipitated as a silver complex and estimated in the precipitate by Kjeldahl's method.

4. Reagents

4.1 Glacial acetic acid.

4.2 Ammonia solution: dilute one volume of ammonia (d = 0·88g/ml) with 3 volumes of water.

4.3 Ammoniacal silver solution, according to Tollens, freshly prepared: mix 500ml silver nitrate solution (10g per 100ml) with 500ml ammonia solution (4.2).

Do not expose unnecessarily to light, heat or air.

Safety precaution: when handling ammoniacal silver nitrate solution safety goggles must be worn.

4.4 Concentrated sulphuric acid (d = 1·84g/ml).

4.5 Potassium sulphate.

4.6 Copper oxide (CuO), 0·3 – 0·4g for each determination or an equivalent quantity of copper sulphate pentahydrate (0·95 – 1·25g) for each determination.

4.7 Sodium hydroxide solution, 30g per 100ml, ammonia free.

4.8 Sulphuric acid, 0·1N solution.

4.9 Sodium or potassium hydroxide, 0·1N solution.

4.10 Indicator solutions:

4.10.1 Mixed indicator:

Solution A: dissolve 1g methyl red in 37ml 0·1N sodium hydroxide solution and make up to 1 litre with water.

Solution B: dissolve 1g methylene blue in water and make up to 1 litre.

Mix 1 volume of solution A with 2 volumes of solution B.

This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0·5ml (10 drops).

4.10.2 Methyl red indicator solution:

dissolve 0·1g methyl red in 50ml 95% ethanol and make up to 100ml with water. Filter if necessary. This indicator (4 to 5 drops) may be used instead of the preceding one.

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

4.12 Potassium thiocyanate.

5. Apparatus

5.1 Distillation apparatus. See Method 2.

5.2 500ml graduated flask (for example Stohmann).

5.3 Rotary shaker, 35-40 turns per minute.

6. Preparation of the Sample

See Method 1.

7. Procedure

7.1 *Safety precaution*

When handling ammoniacal silver nitrate solution safety goggles must be worn.

7.2 *Preparation of the solution for analysis*

Weigh to the nearest 0·001g, 2·5g of the prepared sample and place in a small glass mortar. Grind the sample three times with water, pouring off the water after each grinding into the 500ml graduated flask (5.2). Transfer quantitatively the sample into the flask, washing the mortar, pestle and funnel with water. Make up with water to approximately 400ml. Add 15ml acetic acid (4.1). Shake on the rotary shaker (5.3) for two hours.

Make up to 500ml with water, mix and filter.

Proceed immediately to 7.3.

7.3 *Determination*

Transfer 50·0ml of the filtrate into a 250ml beaker. Add ammonia solution (4.2) until slightly alkaline and add 30ml warm ammoniacal silver nitrate (4.3) in order to precipitate the yellow silver complex of the cyanamide. Leave overnight, filter and wash the precipitate with cold water until completely free of ammonia.

Place the filter and the precipitate, still moist, in a Kjeldahl flask, add 10-15g potassium sulphate (4.5), the catalyst (4.6) in the prescribed proportion, then 50ml water and 25ml concentrated sulphuric acid (4.4). Warm the flask slowly, whilst shaking it gently until the contents come

to the boil. Increase the heat, boil until the contents of the flask become either colourless or pale green. Continue boiling for one hour, then leave to cool.

Transfer the liquid quantitatively from the Kjeldahl flask to the distilling flask, add a few anti-bump granules of pumice stone (4.11) and make up with water to a total volume of approximately 350ml. Mix and cool. Add sufficient sodium hydroxide solution (4.7) to ensure a considerable excess. Distil the ammonia and titrate the excess acid as described in Method 2 (variant (a)).

7.4 *Blank test*

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

7.5 *Control test*

Before carrying out the analysis, check that the apparatus is working properly and that the correct application of the method is used, using an aliquot part of a standard solution of potassium thiocyanate (4.12), corresponding to 0·05g nitrogen.

8. Expression of Results

Express the result as the percentage of cyanamide nitrogen contained in the fertiliser as received for analysis.

$$N\% = (50 - A) \times 0{\cdot}56$$

Where A = millilitres of sodium or potassium hydroxide used for the titration.

7. Determination of Biuret in Urea

1. Scope

This method is for the determination of biuret in urea.

2. Field of Application

The method is applied exclusively to urea.

3. Principle

In an alkaline medium, in the presence of potassium sodium tartrate, biuret and bivalent copper form a violet cupric compound, the absorbance of which is measured at 546nm.

4. Reagents

4.1 Methanol.

4.2 Sulphuric acid solution, approximately 0·1N.

4.3 Sodium hydroxide solution, approximately 0·1N.

4.4 Alkaline solution of potassium sodium tartrate:

In a 1 litre graduated flask dissolve 40g of sodium hydroxide in 500ml of water and leave to cool. Add 50g of potassium sodium tartrate ($KNaC_4H_4O_6.4H_2O$). Make up to the mark and mix. Leave standing 24 hours before use.

4.5 Copper sulphate solution:

In a 1 litre graduated flask dissolve 15g of copper sulphate ($CuSO_4.5H_2O$) in 500ml of water. Make up to the mark and mix.

4.6 Biuret standard solution:

In a 250ml graduated flask, dissolve 0·250g of pure biuret[a] in water. Make up to the mark and mix. 1 ml of this solution contains 0·001g of biuret. This solution should be freshly prepared.

4.7 Methyl red indicator solution:

Dissolve 0·1g methyl red in 50ml 95% ethanol and make up to 100ml with water. Filter if necessary.

5. Apparatus

5.1 Spectrophotometer.

6. Preparation of Sample

See Method 1.

7. Procedure

7.1 *Preparation of the standard curve*

Transfer 2, 5, 10, 20, 25 and 50ml aliquot parts of biuret standard solution (4.6) into a series of six 100ml graduated flasks. Make up the volumes to about 50ml with water, add one drop of indicator solution (4.7) and neutralise, if necessary, with 0·1N sulphuric acid (4.2). Add with swirling 20·0ml of the alkaline tartrate solution (4.4) and then 20·0ml copper sulphate solution (4.5). Make up to the mark with water, mix and allow to stand at 30 ± 2°C for fifteen minutes.

At the same time prepare a reagent blank as follows. Place 50ml water in a 100ml graduated flask and proceed as described above from "..... ..... add one drop of indicator solution.....".

Measure the absorbance of each solution at 546nm against the reagent blank as reference, using cells of a suitable thickness. Plot the calibration curve, using the absorbances as the ordinates and the corresponding quantities of biuret in milligrams, as the abscissae.

7.2 *Preparation of solution for analysis*

Weigh to the nearest 0·001g, 10g of the prepared sample; dissolve in about 150ml of water in a 250ml graduated flask, and make up to the mark and mix. Filter if necessary.

Note 1: If the sample for analysis contains more than 0·015g of ammoniacal nitrogen, dissolve it in 50ml methanol (4.1) in a 250ml beaker. Reduce by evaporation to a volume of about 25ml. Transfer quantitatively to a graduated 250ml flask. Make up to the mark with water. Filter, if necessary, through a dry fluted filter into a dry receiver.

Note 2: Elimination of the opalescence: if any colloidal substance is present difficulties may arise during filtering. In that case the solution for analysis is prepared as follows:

dissolve the sample in 150ml of water, add 2ml 1N hydrochloric acid, and filter the solution through two flat very fine filters into a 250ml graduated flask. Wash the filters with water and make up to volume. Continue the process according to the method described in 7.3.

[a] Biuret can be purified beforehand by washing with an ammoniacal solution (10%), then with acetone and drying in a vacuum.

7.3 *Determination*

According to the presumed biuret content, transfer with a pipette 25 or 50ml from the solution prepared in 7.2, to a 100ml graduated flask and neutralise if necessary with 0·1N sulphuric acid or sodium hydroxide solution (4.2 or 4.3) as required, using methyl red indicator (4.7). Add 20·0ml of the alkaline solution of potassium sodium tartrate (4.4) and 20·0ml of the copper solution (4.5). Make up to volume, mix thoroughly and leave standing for 15 minutes at 30 ± 2°C. Measure the absorbance of the solution as described in 7.1.

8. Expression of Results

$$\% \text{ biuret} = \frac{C \times 2{\cdot}5}{V}$$

where:

C = weight, in milligrams, of biuret read from the standard curve;

V = volume of the aliquot part used for the determination.

8a Determination of Different Forms of Nitrogen in the same Sample— in the Presence of Cyanamide Nitrogen

1. Scope

This method is for the determination of any one form of nitrogen in the presence of any other form.

2. Field of Application

Any fertiliser in Group 1 (a) of Section A, and Groups 1, 2 and 3 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977 containing nitrogen in various forms.

3. Principle

3.1 *Total soluble and insoluble nitrogen*

According to the list of fertilisers in paragraph 2, this method is applicable to products containing calcium cyanamide.

3.1.1 *In the absence of nitrates,* the sample is subjected to direct Kjeldahl digestion.

3.1.2 *In the presence of nitrates,* the sample is subjected to Kjeldahl digestion after reduction with the aid of metallic iron and stannous chloride.

In both cases, the ammonia is determined according to Method 2.

Note: If analysis shows an insoluble nitrogen content of more than 0·5%, it is presumed that the fertiliser contains other forms of insoluble nitrogen not specified for fertilisers covered by the list in paragraph 2.

3.2 *Forms of soluble nitrogen*

The following are determined from different aliquot parts taken from the same solution of the sample:

3.2.1 *Total soluble nitrogen*

3.2.1.1 *In the absence of nitrates,* by direct Kjeldahl digestion.

3.2.1.2 *In the presence of nitrates,* by Kjeldahl digestion on an aliquot part taken from the solution after reduction according to Ulsch, the ammonia being determined in both cases, as described in Method 2.

3.2.2 *Total soluble nitrogen with the exception of nitric nitrogen* by Kjeldahl digestion after elimination in an acid medium of nitric nitrogen with ferrous sulphate, the ammonia being determined as described in Method 2.

3.2.3 *Nitric nitrogen by difference*

3.2.3.1 *In the absence of calcium cyanamide,* between (3.2.1.2) and (3.2.2) or between total soluble nitrogen (3.2.1.2) and the sum of ammoniacal nitrogen and ureic nitrogen (3.2.4 + 3.2.5).

3.2.3.2 *In the presence of calcium cyanamide,* between (3.2.1.2) and (3.2.2) and between (3.2.1.2) and the sum of (3.2.4 + 3.2.5 + 3.2.6).

3.2.4 *Ammoniacal nitrogen*

3.2.4.1 *Solely in the presence of ammoniacal nitrogen and ammoniacal + nitric nitrogen,* by applying Method 2.

3.2.4.2 *In the presence of ureic nitrogen and/or cyanamide nitrogen,* by cold distillation after making slightly alkaline, the ammonia being absorbed in a standard solution of sulphuric acid and determined as described in Method 2.

3.2.5 *Ureic nitrogen*

Either

3.2.5.1 *By conversion using urease,* into ammonia, which is titrated with a standard solution of hydrochloric acid,

or:

3.2.5.2 *By gravimetry with xanthydrol:* although biuret will also be precipitated by xanthydrol, this should not give rise to a significant error in the determination since its level is generally low in absolute value in compound fertilisers,

or:

3.2.5.3 *By difference,* according to the following table:

Case	Nitric Nitrogen	Ammoniacal Nitrogen	Cyanamide Nitrogen	Difference
1	Absent	Present	Present	(3.2.1.1) – (3.2.4.2 + 3.2.6)
2	Present	Present	Present	(3.2.2) – (3.2.4.2 + 3.2.6)
3	Absent	Present	Absent	(3.2.1.1) – (3.2.4.2)
4	Present	Present	Absent	(3.2.2) – (3.2.4.2)

3.2.6 *Cyanamide nitrogen* by precipitation as a silver compound, the nitrogen being estimated in the precipitate by the Kjeldahl method.

4. Reagents

4.1 Potassium sulphate.

4.2 Iron powder, reduced with hydrogen (the prescribed quantity of iron must be able to reduce at least 50mg of nitric nitrogen).

4.3 Potassium thiocyanate.

4.4 Potassium nitrate.

4.5 Ammonium sulphate.

4.6 Urea.

4.7 Sulphuric acid solution: dilute an appropriate volume of sulphuric acid (d = 1·84g/ml) with an equal volume of water.

4.8 Sulphuric acid, 0·2N solution.

4.9 Sodium hydroxide solution, 30g per 100ml, ammonia free.

4.10 Sodium or potassium hydroxide, 0·2N solution, free from carbonates.

4.11 Stannous chloride solution:

dissolve 120g of stannous chloride ($SnCl_2.2H_2O$) in 400ml of concentrated hydrochloric acid (d = 1·18g/ml) and make up to 1 litre with water. The solution must be perfectly clear and prepared immediately before use.

It is essential to check the reducing power of stannous chloride: dissolve 0·5g of stannous chloride in 2ml of concentrated hydrochloric acid (d = 1·18g/ml) and make up to 50ml with water. Then add 5g of Rochelle salt (potassium sodium tartrate) and a sufficient quantity of sodium bicarbonate for the solution to be alkaline to litmus paper.

Titrate with 0·1N iodine solution in the presence of a starch solution as an indicator.

1ml of 0·1N iodine solution corresponds to 0·01128g of $SnCl_2.2H_2O$.

At least 80% of the total tin present in the solution thus prepared must be in a bivalent form. For the titration, at least 35ml of 0·1N iodine solution must therefore be used.

4.12 Sulphuric acid, concentrated (d = 1·84g/ml).

4.13 Hydrochloric acid solution: dilute an appropriate volume of hydrochloric acid (d = 1·18g/ml) with an equal volume of water.

4.14 Glacial acetic acid.

4.15 Sulphuric acid solution, approximately 30% (W/V) H_2SO_4.

4.16 Ferrous sulphate, crystalline, $FeSO_4.7H_2O$.

4.17 Sulphuric acid, 0·1N solution.

4.18 Octan-1-ol.

4.19 Potassium carbonate, saturated solution.

4.20 Sodium or potassium hydroxide, 0·1N solution, free from carbonate.

4.21 Barium hydroxide, saturated solution.

4.22 Sodium carbonate solution, 10g per 100ml.

4.23 Hydrochloric acid, 2N solution.

4.24 Hydrochloric acid, 0·1N solution.

4.25 Urease solution:

Suspend 0·5g of active urease in 100ml of distilled water. Using 0·1N hydrochloric acid (4.24), adjust the pH to 5·4, measured by a pH meter.

4.26 Xanthydrol solution, 5g per 100ml in ethanol or methanol (4.31) (do not use products giving a high proportion of insoluble matter). The solution may be kept for three months in a well-stoppered bottle, away from the light.

4.27 Copper oxide (CuO): 0·3 to 0·4g per determination or an equivalent quantity of copper sulphate pentahydrate of 0·95 to 1·25g per determination.

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

4.29 Indicator solutions:

4.29.1 Mixed indicator solution:

Solution A: dissolve 1g of methyl red in 37ml of 0·1N sodium hydroxide solution and make up to 1 litre with water.

Solution B: dissolve 1g of methylene blue in water and make up to 1 litre.

Mix one volume of solution A and 2 volumes of solution B.

This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0·5ml (10 drops).

4.29.2 Methyl red indicator solution:

dissolve 0·1g of methyl red in 50ml 95% ethanol, make up to 100ml with water and filter if necessary. This indicator (4 to 5 drops) can be used instead of the previous one.

4.30 Indicator papers:

Litmus, bromothymol blue (or other papers sensitive to pH 6 to 8).

4.31 Ethanol or methanol: solution 95%.

5. Apparatus

5.1 Distillation apparatus. See Method 2.

5.2 Apparatus for the determination of ammoniacal nitrogen according to analytical technique 7.2.5.3. An example of recommended apparatus is reproduced in Figure 6 in the Appendix.

The apparatus is made up of a specially shaped receptacle with a ground glass neck, a side neck, a connecting tube with a splash head and a perpendicular tube for the introduction of air. The tubes can be connected to the receptacle by means of a simple perforated rubber bung. It is important to give a suitable shape to the end of the tubes introducing air, since the bubbles of gas must be evenly distributed throughout the solutions contained in the receptacle and the absorber. The best arrangement consists of small mushroom-shaped pieces with an external diameter of 20mm and six openings of 1mm around the periphery.

5.3 Apparatus for the estimation of ureic nitrogen according to the urease technique (7.2.6.1).

It consists of a 300ml Erlenmeyer flask, with a separating funnel and a small absorber. An example of recommended apparatus is reproduced in Figure 7 in the Appendix.

5.4 Rotary shaker, 35-40 turns per minute.

5.5 pH meter.

5.6 Laboratory oven.

5.7 Sintered glass crucibles, diameter of pores 5 to 15 microns.

6. Preparation of the Sample

See Method 1.

7. Procedure

7.1 *Total soluble and insoluble nitrogen*

7.1.1 *In the absence of nitrates*

7.1.1.1 *Digestion*

Weigh to the nearest 0·001g, a quantity of the prepared sample containing 100mg of nitrogen at the most. Place it in the flask of the distillation apparatus (5.1). Add 10 to 15g of potassium sulphate (4.1), the prescribed quantity of catalyst (4.27), and a few anti-bump granules (4.28). Then add 50ml of dilute sulphuric acid (4.7), and mix thoroughly. First heat gently, mixing from time to time, until foaming ceases. Then heat so that the liquid boils steadily and keep it boiling for one hour after the solution has become clear, preventing any organic matter from sticking to the sides of the flask. Allow to cool. Carefully add about 350 ml of water, with mixing. Ensure that the dissolution is as complete as possible. Allow to cool and connect the flask to the distillation apparatus (5.1).

7.1.1.2 *Distillation of ammonia*

Transfer with a pipette, into the receiver of the apparatus, 50ml standard 0·2N sulphuric acid (4.8). Add the indicator (4.29.1 or 4.29.2). Ensure that the tip of the condenser is at least 1cm below the level of the solution.

Taking the necessary precautions to avoid any loss of ammonia, carefully add to the distillation flask enough of the concentrated sodium hydroxide solution (4.9) to make the liquid strongly alkaline (120ml is generally sufficient; check by adding a few drops of phenolphthalein. At the end of the distillation the solution in the flask must still be clearly alkaline). Adjust the heating of the flask so as to distil 150ml in half an hour. Test with indicator paper (4.30) that the distillation has been completed. If it has not, distil a further 50ml and repeat the test until the supplementary distillate reacts neutrally to the indicator paper (4.30). Then lower the receiver, distil a few ml more and rinse the tip of the condenser. Titrate the excess acid with a standard solution of potassium or sodium hydroxide 0·2N (4.10) to the end point of the indicator.

7.1.1.3 *Blank test*

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

7.1.1.4 *Expression of the result*

$$\% N = \frac{(a - A) \times 0{\cdot}28}{M}$$

where:

a = ml of standard solution of sodium or potassium hydroxide (0·2N) used for the blank, carried out by placing in the receiver of the apparatus (5.1), 50·0ml of standard solution of sulphuric acid (0·2N) (4.8).

A = ml of standard solution of sodium or potassium hydroxide (0.2N) used for the analysis.

M = weight of the sample in grams.

7.1.2 *In the presence of nitrate*

7.1.2.1 *Test sample*

Weigh to the nearest 0·001g, a quantity of the sample containing not more than 40mg of nitric nitrogen.

7.1.2.2 *Reduction of the nitrate*

Mix the sample in a small mortar with 50ml of water. Transfer with the minimum amount of distilled water into a 500ml Kjeldahl flask. Add 5g of reduced iron (4.2) and 50ml of stannous chloride solution (4.11). Shake and leave it to stand for half an hour. During this time shake again after 10 and 20 minutes.

7.1.2.3 *Kjeldahl digestion*

Add 30ml of sulphuric acid (4.12), 5g of potassium sulphate (4.1), the prescribed quantity of catalyst (4.27) and some anti-bump granules (4.28). Heat gently with the flask slightly tilted. Increase the heat slowly and shake the solution frequently to keep the mixture suspended; the liquid darkens and then clears with the formation of a yellow-green anhydrous iron sulphate suspension. Continue heating for one hour after obtaining a clear solution, maintaining it at simmering point. Leave to cool. Cautiously take up the contents of the flask in a little water and add little by little 100ml of water. Mix and transfer the contents of the flask into a 500ml graduated flask. Rinse the flask several times with distilled water. Make up the volume with water and mix. Filter through a dry filter into a dry receiver.

7.1.2.4 *Distillation of ammonia*

Transfer by pipette, into the flask of the distillation apparatus (5.1), an aliquot part containing 100mg of nitrogen at the most. Dilute to about 350ml with distilled water, add a few anti-bump granules (4.28), connect the flask to the distillation apparatus and continue the estimation as described in paragraph 7.1.1.2.

7.1.2.5 *Blank test*

See 7.1.1.3.

7.1.2.6 *Expression of the result*

$$\% N = \frac{(a - A) \times 0{\cdot}28}{M}$$

where:

a = ml of standard solution of sodium or potassium hydroxide (0·2N) used for the blank, carried out by placing in the receiver of the apparatus (5·1), 50·0ml of standard solution of sulphuric acid (0·2 N) (4.8).

A = ml of standard solution of sodium or potassium hydroxide (0·2N) used for the analysis.

M = weight of the sample, expressed in grams, present in the aliquot part taken for analysis.

7.2 *Forms of soluble nitrogen*

7.2.1 *Preparation of the solution to be analysed*

Weigh to the nearest 0·001g, 10g of the sample and place it in a 500ml graduated flask.

7.2.1.1 *In the case of fertilisers not containing cyanamide nitrogen*

Add to the flask 50ml of water and then 20ml of dilute hydrochloric acid (4.13). Shake and leave it to stand until the evolution of carbon dioxide ceases. Then add 400ml of water and shake for half an hour on the rotary shaker (5.4). Make up to volume with water, mix and filter through a dry filter into a dry receiver.

7.2.1.2 *In the case of fertilisers containing cyanamide nitrogen*

Add to the flask 400ml of water and a few drops of methyl red (4.29.2). If necessary make the solution acid by using acetic acid (4.14). Add 15ml of acetic acid (4.14). Shake on the rotary shaker (5.4) for 2 hours. If necessary, re-acidify the solution during the operation, using acetic acid (4.14).

Make up to volume with water, mix, filter immediately through a dry filter into a dry receiver and immediately determine the cyanamide nitrogen.

In both cases, determine the various soluble forms of nitrogen the same day the solution is made up, starting with the cyanamide nitrogen and urea nitrogen, if they are present.

7.2.2 *Total soluble nitrogen*

7.2.2.1 *In the absence of nitrate*

Transfer by pipette into a 300ml Kjeldahl flask, an aliquot part of the filtrate (7.2.1.1 or 7.2.1.2), containing 100mg of nitrogen at the most. Add 15ml of concentrated sulphuric acid (4.12), 0·4g of copper oxide or 1·25g of copper sulphate (4.27) and a few anti-bump granules (4.28). First heat gently to begin the digestion and then at a higher temperature until the liquid becomes colourless or slightly greenish and white fumes are clearly apparent. After cooling, quantitatively transfer the solution into the distillation flask, dilute to about 500ml with water, and add a few anti-bump granules (4.28). Connect the flask to the distillation apparatus (5.1) and continue the determination as described in paragraph 7.1.1.2.

7.2.2.2 *In the presence of nitrate*

Transfer by pipette into a 500ml Erlenmeyer flask, an aliquot part of the filtrate (7.2.1.1. or 7.2.1.2) containing

not more than 40mg of nitric nitrogen. At this stage of the analysis the total quantity of nitrogen is not important. Add 10ml of 30% sulphuric acid (4.15), 5g of reduced iron (4.2), and immediately cover the Erlenmeyer flask with a watch glass. Heat gently until the reaction is steady but not vigorous. At this juncture stop the heating and allow the flask to stand for at least three hours at ambient temperature. With water, quantitatively transfer the liquid into a 250ml graduated flask, leaving behind the undissolved iron, and make up to the mark with the water. Mix thoroughly, and transfer by pipette into a 300ml Kjeldahl flask, an aliquot part containing 100mg of nitrogen at the most. Add 15ml of concentrated sulphuric acid (4.12), 0·4g of copper oxide or 1·25g of copper sulphate (4.27) and some anti-bump granules (4.28). First heat gently to begin the digestion and then at a higher temperature until the liquid becomes colourless or slightly greenish and white fumes are clearly apparent. After cooling, quantitatively transfer the solution into the distillation flask, dilute to approximately 500ml with water and add some anti-bump granules (4.28). Connect the flask to the distillation apparatus (5.1) and continue the determination as described in paragraph 7.1.1.2.

7.2.2.3 *Blank test*

See 7.1.1.3.

7.2.2.4 *Expression of the result*

$$\% \text{ N} = \frac{(a - A) \times 0{\cdot}28}{M}$$

where:

a = ml of standard solution of sodium or potassium hydroxide (0·2N) used for the blank, carried out by placing in the receiver of the apparatus (5.1), 50·0ml of standard solution of sulphuric acid (0·2N) (4.8).

A = ml of standard solution of sodium or potassium hydroxide (0·2N) used for analysis.

M = weight of the sample, expressed in grams, present in the aliquot part taken for analysis.

7.2.3 *Total soluble nitrogen with the exception of nitric nitrogen*

Transfer by pipette into a 300ml Kjeldahl flask, an aliquot part of the filtrate (7.2.1.1 or 7.2.1.2) containing not more than 50mg of nitrogen to be determined. Dilute to 100ml with water, add 5g of ferrous sulphate (4.16), 20ml of concentrated sulphuric acid (4.1) and some anti-bump granules (4.28). First heat gently and then increase the heat until white fumes appear. Continue the digestion for 15 minutes. Stop the heating, introduce the copper oxide (4.27) as a catalyst and keep it at a temperature such that white fumes are emitted for a further 10 to 15 minutes. After cooling, quantitatively transfer the contents of the Kjeldahl flask into the distillation flask of the apparatus (5.1). Dilute to approximately 500ml with water and add a few anti-bump granules (4.28). Connect the flask to the distillation apparatus and continue the determination as described in paragraph 7.1.1.2.

7.2.3.1 *Blank test*

See 7.1.1.3.

7.2.3.2 *Expression of result*

$$\%\,N = \frac{(a - A) \times 0{\cdot}28}{M}$$

where:

a = ml of standard solution of sodium or potassium hydroxide (0·2N) used for the blank, carried out by placing in the receiver of the apparatus (5.1), 50ml of the standard sulphuric acid solution (0·2N) (4.8).

A = ml of standard solution of sodium or potassium hydroxide (0·2N) used for the analysis.

M = weight of the sample, expressed in grams, present in the aliquot part taken for analysis.

7.2.4 *Nitric nitrogen* is obtained:

7.2.4.1 *In the absence of calcium cyanamide*

By the difference between the results obtained in paragraphs 7.2.2.4 and 7.2.3.2 and/or the result obtained in paragraph 7.2.2.4 and the sum of the results obtained in paragraphs (7.2.5.2 or 7.2.5.5) and (7.2.6.3 or 7.2.6.5 or 7.2.6.6).

7.2.4.2 *In the presence of calcium cyanamide*

By the difference between the results obtained in paragraphs 7.2.2.4 and 7.2.3.2 and between the result obtained in paragraph 7.2.2.4 and the sum of the results obtained in paragraphs (7.2.5.5), (7.2.6.3 or 7.2.6.5 or 7.2.6.6) and (7.2.7).

7.2.5 *Ammoniacal nitrogen*

7.2.5.1 *Solely in the presence of ammoniacal nitrogen and ammoniacal + nitric nitrogen*

Transfer by pipette into the flask of the distillation apparatus (5.1) an aliquot part of the filtrate (7.2.1.1) containing 100mg of ammoniacal nitrogen at the most. Add water to obtain a total volume of about 350ml and some anti-bump granules (4.28) to facilitate boiling. Connect the flask to the distillation apparatus, add 20ml of sodium hydroxide solution (4.9) and distil as described in paragraph 7.1.1.2.

7.2.5.2 *Expression of result*

$$\%\,N\ (\text{ammoniacal}) = \frac{(a - A) \times 0{\cdot}28}{M}$$

where:

a = ml of standard solution of sodium or potassium hydroxide (0·2N) used for the blank, carried out by placing in the receiver of the apparatus (5.1), 50·0ml of standard sulphuric acid solution (0·2N) (4.8).

A = ml of standard solution of sodium or potassium hydroxide (0·2N) used for the analysis.

M = weight of the sample, expressed in grams, present in the aliquot part taken for analysis.

7.2.5.3 *In the presence of ureic and/or cyanamide nitrogen*

Transfer by pipette into the dry flask of the apparatus (5.2), an aliquot part of the filtrate (7.2.1.1 or 7.2.1.2) containing 20mg of ammoniacal nitrogen at the most. Then assemble the apparatus. Transfer by pipette into the 300ml Erlenmeyer flask 50ml of the standard sulphuric acid solution (0·1N) (4.17) and enough distilled water for the level of the liquid to be approximately 5cm above the opening of the delivery tube; add the indicator (4.29.1). Introduce, through the side neck of the reaction flask, distilled water to make up the volume to about 50ml and mix. To avoid foaming during aeration, add a few drops of octan-1-ol (4.18). Make the solution alkaline by adding 50ml of saturated potassium carbonate solution (4.19) and immediately begin to expel the ammonia thus liberated from the cold suspension. A strong current of air is necessary (flow of approximately 3 litres per minute) and should be purified beforehand by passing it through washing flasks containing dilute sulphuric acid and dilute sodium hydroxide. Instead of using pressurised air, it is also possible to use a vacuum (water pump) provided that the inflow tube is connected in a sufficiently airtight manner to the receiver used to collect the ammonia. The liberation of the ammonia is generally complete after three hours. It is nevertheless advisable to verify this by changing the receiving flask. When the operation is finished, disconnect the flask from the apparatus, rinse the tip of the tube and the sides of the flask with a little distilled water. Titrate the excess acid with standard sodium hydroxide solution (0·1N) (4.20) to the end point of the indicator (4.29.1).

7.2.5.4 *Blank test*

See 7.1.1.3.

7.2.5.5 *Expression of the result*

$$\% \text{ N (ammoniacal)} = \frac{(a - A) \times 0{\cdot}14}{M}$$

where:

a = ml of standard solution of sodium or potassium hydroxide (0·1N) used for the blank, carried out by placing in the 300ml Erlenmeyer flask of the apparatus (5.2), 50ml of the standard solution of sulphuric acid (0·1N) (4.17).

A = ml of standard solution of sodium or potassium hydroxide (0·1N) used for the analysis.

M = weight of the sample, expressed in grams, present in the aliquot part taken for analysis.

7.2.6 *Ureic nitrogen*

7.2.6.1 *Urease method*

Transfer by pipette into a 500ml graduated flask, an aliquot part of the filtrate (7.2.1.1 or 7.2.1.2) containing not more than 250mg of ureic nitrogen. To remove phosphates add saturated barium hydroxide solution (4.21) until no further precipitation occurs. Eliminate the excess

of barium ions (and any dissolved calcium ions) by adding 10% sodium carbonate solution (4.22). Allow the precipitate to settle and check whether total precipitation has occurred. Make up to the mark, mix and filter through a pleated filter. Transfer by pipette 50ml of the filtrate into the 300ml Erlenmeyer flask of the apparatus (5.3). Acidify the filtrate with 2N hydrochloric acid (4.23), until a pH of 3·0 measured by the pH meter (5.5) is obtained. Then raise the pH to 5·4 with 0·1N sodium hydroxide (4.20).

To avoid losses of ammonia during decomposition by the urease, close the Erlenmeyer flask with a stopper provided with a separating funnel and a small bubble trap containing exactly 2ml of standard 0·1N hydrochloric acid (4.24). Introduce through the separating funnel 20ml of urease solution (4.25), and allow to stand for one hour at 20-25°C. Transfer by pipette 25ml of standard 0·1N hydrochloric acid (4.24) into the separating funnel, allow it to run through into the solution and then rinse with a little water. In the same way quantitatively transfer the contents of the bubble trap into the solution contained in the Erlenmeyer flask. Titrate the excess acid with the standard solution of sodium hydroxide (0·1N) (4.20), until a pH of 5·4 is obtained, measured by the pH meter.

7.2.6.2 *Blank test*

See 7.1.1.3.

7.2.6.3 *Expression of result*

$$\% \text{ N (ureic)} = \frac{(a - A) \times 0{\cdot}14}{M}$$

where:

a = ml of standard solution of sodium or potassium hydroxide (0·1N) used for the blank, carried out exactly under the same conditions as the analysis.

A = ml of standard solution of sodium or potassium hydroxide (0·1N) used for the analysis.

M = weight of the sample, expressed in grams, present in the aliquot part taken for analysis.

Remarks

(1) After precipitation by the solutions of barium hydroxide and sodium carbonate, make up to the mark, filter and neutralise as rapidly as posssible.

(2) The titration may also be carried out with the indicator (4.29.2), but the end point is then more difficult to observe.

7.2.6.4 *Gravimetric method with xanthydrol*

Transfer by pipette into a 250ml beaker, an aliquot part of the filtrate (7.2.1.1 or 7.2.1.2) containing not more than 20mg of urea. Add 40ml of acetic acid (4.14). Stir with a glass rod for one minute, allow any precipitate to settle for five minutes. Filter into a 100ml beaker, wash with several ml of acetic acid (4.14), then add to the filtrate

drop by drop, 10ml of xanthydrol solution (4.26), stirring continuously with a glass rod. Allow to stand until the precipitate appears, then stir again for one or two minutes. Allow to stand for one and a half hours. Filter through a sintered glass crucible (5.7) which has been previously dried and weighed, using a slight reduction in pressure. Wash three times with 5ml ethanol (4.31) without trying to remove all the acetic acid. Place it in the oven (5.6) at a temperature of 130°C for one hour (do not exceed 145°C). Allow to cool in a desiccator and weigh.

7.2.6.5 *Expression of results*

$$\%\,\text{N(ureic)} + \text{biuret} = \frac{6{\cdot}67 \times m}{M}$$

where:

m = weight of the precipitate obtained, in grams.

M = weight of the sample, in grams, present in the aliquot part taken for analysis.

Correct for the blank.

Note: although biuret will also be precipitated by xanthydrol, this should not give rise to a significant error in the determination since its level is generally low.

7.2.6.6 *Method by difference*

Ureic nitrogen may also be calculated according to the following table:—

Case	Nitric Nitrogen	Ammoniacal Nitrogen	Cyanamide Nitrogen	Ureic Nitrogen
1	Absent	Present	Present	(7.2.2.4) – (7.2.5.5 + 7.2.7)
2	Present	Present	Present	(7.2.3.2) – (7.2.5.5 + 7.2.7)
3	Absent	Present	Absent	(7.2.2.4) – (7.2.5.5)
4	Present	Present	Absent	(7.2.3.2) – (7.2.5.5)

7.2.7 *Cyanamide Nitrogen*

Take an aliquot part of the filtrate (7.2.1.2), containing 10 to 30mg of cyanamide nitrogen and place it in a 250ml beaker. Continue the analysis according to Method 6.

8. Verification of the Results

8.1 In certain cases, a difference may be found between the total nitrogen obtained directly from a weighed out sample (paragraph 7.1) and total soluble nitrogen (paragraph 7.2.2). Nevertheless, the difference should not be greater than 0.5%. If this is not the case, the fertiliser contains forms of insoluble nitrogen not specified for fertilisers covered by the list in paragraph 2.

8.2 Before each analysis, check that the apparatus is working properly and that the correct application of the method is used, with a standard solution including the various forms of nitrogen in proportions similar to those of the test sample. This standard solution is prepared from solutions of potassium thiocyanate (4.3), potassium nitrate (4.4), ammonium sulphate (4.5) and urea (4.6).

8b Determination of Different Forms of Nitrogen in the same Sample— in the absence of Cyanamide Nitrogen

1. Scope

This method is for the determination of any one form of nitrogen in the presence of any other form, in the absence of cyanamide nitrogen.

2. Field of Application

This method is applicable to all fertilisers in Group 1(a) of Section A and Groups 1, 2 and 3 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977 which contain exclusively nitric, ammoniacal or ureic nitrogen.

3. Principle

The following determinations are made on different portions of a single sample solution.

3.1 *Total soluble nitrogen*

3.1.1 *In the absence of nitrates,* by direct Kjeldahl digestion of the solution.

3.1.2 *In the presence of nitrates,* by Kjeldahl digestion of a portion of the solution after reduction by the Ulsch method; ammonia is determined in both cases as described in Method 2.

3.2 *Total soluble nitrogen except nitric nitrogen,* by Kjeldahl digestion after elimination of nitric nitrogen in acid medium by means of ferrous sulphate; ammonia is determined as described in Method 2.

3.3 *Nitric nitrogen,* by difference: between 3.1.2 and 3.2 and/or between total soluble nitrogen (3.1.2) and the sum of ammoniacal and ureic nitrogen (3.4 + 3.5).

3.4 *Ammoniacal nitrogen,* by cold distillation of a weak alkaline solution; the ammonia is obtained in a solution of sulphuric acid and determined as described in Method 2.

3.5 *Ureic nitrogen,* either:

3.5.1 *By conversion using urease,* into ammonia, which is determined by titration with a standard solution of hydrochloric acid,

or:

3.5.2 *By gravimetry using xanthydrol:* although biuret will also be precipitated by xanthydrol, this should not give rise to a significant error in the determination since its level is generally low in absolute value in compound fertilisers,

or:

3.5.3 *By difference,* according to the following table:—

Case	Nitric nitrogen	Ammoniacal nitrogen	Difference
1	Absent	Present	(3.1.1)–(3.4)
2	Present	Present	(3.2) –(3.4)

4. Reagents

4.1 Potassium sulphate.

4.2 Iron powder, reduced with hydrogen (the prescribed quantity of iron must be able to reduce at least 50mg nitric nitrogen).

4.3 Potassium nitrate.

4.4 Ammonium sulphate.

4.5 Urea.

4.6 Sulphuric acid, 0·2N solution.

4.7 Sodium hydroxide solution, 30g per 100ml, ammonia free.

4.8 Sodium or potassium hydroxide, 0·2N solution, free of carbonates.

4.9 Sulphuric acid (d = 1·84g/ml).

4.10 Hydrochloric acid solution: dilute an appropriate volume of hydrochloric acid (d = 1·18g/ml) with an equal volume of water.

4.11 Glacial acetic acid.

4.12 Sulphuric acid, solution approximately 30% (W/V) H_2SO_4.

4.13 Ferrous sulphate, crystalline $FeSO_4.7H_2O$.

4.14 Sulphuric acid, 0·1N solution.

4.15 Octan-l-ol.

4.16 Potassium carbonate, saturated solution.

4.17 Sodium or potassium hydroxide, 0·1N solution.

4.18 Barium hydroxide, saturated solution.

4.19 Sodium carbonate solution, 10g per 100ml.

4.20 Hydrochloric acid, 2N solution.

4.21 Hydrochloric acid, 0·1N solution.

4.22 Urease solution: suspend 0·5g active urease in 100ml distilled water. Using 0·1N hydrochloric acid (4.21), adjust pH to 5·4 measured with pH meter.

4.23 Xanthydrol solution, 5g per 100ml in ethanol or methanol (4.28) (do not use products giving a high proportion of insoluble material). The solution can be kept for 3 months in a carefully stoppered bottle in darkness.

4.24 Catalyst: copper oxide (CuO), 0·3 to 0·4g per determination, or an equivalent amount of copper sulphate pentahydrate, 0·95 to 1·25g per determination.

4.25 Anti-bump granules of pumice stone, washed with hydrochloric acid and ignited.

4.26 Indicator solutions:

4.26.1 Mixed indicator:

Solution A: dissolve 1g methyl red in 37ml 0·1N sodium hydroxide solution and make up to 1 litre with water.

Solution B: dissolve 1g methylene blue in water and make up to 1 litre.

Mix 1 volume of solution A and 2 volumes of solution B.

This indicator is violet in acid solution, grey in neutral solution, and green in alkaline soiution. Use 0·5ml (10 drops).

4.26.2 Methyl red indicator solution:

dissolve 0·1g methyl red in 50ml 95% ethanol, make up to 100ml with water and filter if necessary. This indicator (4 to 5 drops) can be used instead of the previous one.

4.27 Indicator papers: litmus, bromothymol blue (or other papers sensitive to pH 6-8).

4.28 Ethanol or methanol, 95% (V/V).

5. Apparatus

5.1 Distillation apparatus. See Method 2.

5.2 Apparatus for determination of ammoniacal nitrogen. An example of recommended apparatus is reproduced in Figure 6 in the Appendix.

5.3 Apparatus for determination of ureic nitrogen by the urease method (7.6.1). An example of recommended apparatus is reproduced in Figure 7 in the Appendix.

5.4 Rotary shaker, 35-40 turns per minute.

5.5 pH meter.

5.6 Sintered glass crucible, diameter of pores 5 to 15 microns.

6. Preparation of Sample

See Method 1.

7. Procedure

7.1 *Preparation of solution for analysis*

Weigh to the nearest 0·001g, 10g of the prepared sample, and transfer to a 500ml graduated flask. Add 50ml water and then 20ml dilute hydrochloric acid (4.10) and shake. Allow to stand until the evolution of carbon dioxide ceases. Add 400ml water; shake for half an hour; make up to volume with water, mix, filter through a dry filter into a dry container.

7.2 *Total nitrogen*

7.2.1 *In the absence of nitrates*

Transfer by pipette into a 300ml Kjeldahl flask a portion of the filtrate (7.1), containing a maximum of 100mg nitrogen. Add 15 ml concentrated sulphuric acid (4.9), 0·4g copper oxide or 1·25g copper sulphate (4.24), and a few glass beads to control boiling. Heat moderately at first in order to initiate the reaction, then more strongly until the liquid becomes colourless or slightly greenish and white fumes appear. After cooling, transfer the solution into the distillation flask, dilute to about 500ml with water and add a few granules of pumice stone (4.25). Connect the flask to the distillation apparatus (5.1) and carry out the determination as described in Method 8a, 7.1.1.2.

7.2.2 *In the presence of nitrates*

Transfer by pipette into a 500ml Erlenmeyer flask a portion of the filtrate (7.1) containing not more than 40mg nitric nitrogen. At this stage of the analysis, the total quantity of nitrogen is unimportant. Add 10ml 30% sulphuric acid (4.12), 5g reduced iron (4.2), and immediately cover the Erlenmeyer flask with a watch glass. Heat gently until the reaction becomes strong but not violent. Stop heating and allow to stand for at least 3 hours at ambient temperature. Transfer the liquid quantitatively to a 250ml graduated flask, ignoring undissolved iron. Make up to the mark with water and mix carefully. Transfer by pipette a portion containing a maximum of 100mg nitrogen into a 300ml Kjeldahl flask. Add 15ml concentrated sulphuric acid (4.9), 0·4g copper oxide or 1·25g copper sulphate (4.24), and a few glass beads.

Heat moderately at first in order to initiate the reaction, then more

strongly until the liquid becomes colourless or slightly greenish and white fumes appear. After cooling, transfer the solution quantitatively to the distillation flask, dilute to about 500ml with water, and add a few granules of pumice stone (4.25). Connect the flask to the distillation apparatus (5.1) and continue the determination as described in Method 8a, 7.1.1.2.

7.2.3 *Blank test*
Make a blank test in the same conditions (omitting only the sample), and use this value in the calculation of the final result.

7.2.4 *Expression of the result*

$$\%N\ (total) = \frac{(a - A) \times 0{\cdot}28}{M}$$

where:

a = ml of standard solution of sodium or potassium hydroxide (0·2N) used for the blank, carried out under the same conditions as the analysis.

A = ml of standard solution of sodium or potassium hydroxide (0·2N) used for the analysis.

M = weight of the sample, in grams, present in the aliquot part taken for analysis.

7.3 *Total nitrogen excluding nitric nitrogen*

7.3.1 Transfer by pipette into a 300ml Kjeldahl flask an aliquot part of filtrate (7.1) containing not more than 50mg nitrogen to be determined. Dilute to 100ml with water, add 5g ferrous sulphate (4.13), 20ml concentrated sulphuric acid (4.9) and a few glass beads to control boiling. Heat moderately at first, then more strongly until white fumes appear. Continue the reaction for 15 minutes. Stop heating, introduce 0·4g copper oxide or 1·25g copper sulphate (4.24) as catalyst, resume heating and maintain production of white fumes for 10-15 minutes. After cooling, transfer the contents of the Kjeldahl flask quantitatively to the distillation flask. Dilute to about 500ml with water, and add a few granules of pumice stone (4.25). Connect the flask to the distillation apparatus (5.1) and continue the determination as in Method 8a, 7.1.1.2.

7.3.2 *Blank test*
See 7.2.3.

7.3.3 *Expression of results*

$$\%\ N\ (total) = \frac{(a - A) \times 0{\cdot}28}{M}$$

where:

a = ml of standard solution of sodium or potassium hydroxide (0·2N) used for the blank, carried out by placing in the receiver of the apparatus (5.1), 50·0ml of standard solution of sulphuric acid (0·2N) (4.6).

A = ml of standard solution of sodium or potassium hydroxide (0·2N) used for analysis.

M = weight of the sample, in grams, present in the aliquot part taken for analysis.

7.4 *Nitric nitrogen* is obtained: by difference between

(7.2.4) — (7.5.3 + 7.6.3)
or (7.2.4) — (7.5.3 + 7.6.5)
or (7.2.4) — (7.5.3 + 7.6.6)

7.5 *Ammoniacal nitrogen*

7.5.1 *In the presence of ureic nitrogen*

Transfer by pipette into the dry flask of the apparatus (5.2) a portion of filtrate (7.1) containing a maximum of 20mg ammoniacal nitrogen. Connect up the apparatus. Place in the 300ml Erlenmeyer flask 50·0ml standard 0·1N sulphuric acid solution (4.14) and an amount of distilled water such that the level of the liquid is about 5cm above the opening of the intake tube. Introduce through the side neck of the reaction flask distilled water so as to bring the volume to about 50ml. Shake. To avoid foaming during aeration add several drops of octan-1-ol (4.15). Add 50ml saturated potassium carbonate solution (4.16), and immediately begin to expel the ammonia thus released from the cold suspension. A strong current of air is necessary (flow rate of about 3 litres per minute) and should be purified by passing it through washing flasks containing dilute sulphuric acid and dilute sodium hydroxide. Instead of using air under pressure, a vacuum may be used (water pump) provided that the connections between the apparatus are air tight. The liberation of ammonia is generally complete after three hours. However, it is desirable to make certain of this by changing the Erlenmeyer flask. When the process is finished, disconnect the Erlenmeyer flask from the apparatus, rinse the end of the intake tube and the walls of the Erlenmeyer flask with a little distilled water, and titrate the excess acid with standard 0·1N sodium hydroxide solution (4.17).

7.5.2 *Blank test*

See 7.2.3.

7.5.3 *Expression of results*

$$\% \text{ N (ammoniacal)} = \frac{(a - A) \times 0{\cdot}14}{M}$$

where:

a = ml of standard solution of sodium or potassium hydroxide (0·1N) (4·17) used for the blank, carried out by placing in the receiver of the apparatus (5.2), 50·0ml of standard solution of sulphuric acid (0·1N) (4·14).

A = ml of standard solution of sodium or potassium hydroxide (0·1N) (4.17) used for analysis.

M = weight of the sample, in grams, present in the aliquot part taken for analysis.

7.6 *Ureic nitrogen*

7.6.1 *Urease method*

Transfer by pipette into a 500ml graduated flask, a portion of filtrate (7.1) containing not more than 250mg ureic nitrogen. To remove phosphates, add a suitable quantity of saturated barium hydroxide solution (4.18) until further addition does not cause the production of more precipitate. Eliminate excess barium ions (and any dissolved calcium ions) by means of 10% sodium carbonate solution (4.19). Allow to settle and check whether

precipitation is complete. Make up to the mark, mix and filter through a fluted filter. Transfer by pipette 50ml of the filtrate into the 300ml Erlenmeyer flask of the apparatus (5.3). Acidify with 2N hydrochloric acid (4.20) to pH 3·0, measured by means of the pH meter (5.5). Raise the pH to 5·4 by the addition of 0·1N sodium hydroxide (4.17). To avoid ammonia losses when hydrolysis by urease occurs, close the Erlenmeyer flask by means of a stopper provided with a dropping funnel and a small bubble trap containing exactly 2ml standard 0·1N hydrochloric acid solution (4.21). Introduce through the separating funnel, 20ml urease solution (4.22). Allow to stand for one hour at 20-25°C. Place 25·0ml of the standard 0·1N hydrochloric acid solution (4.2) in the dropping funnel, allow to run into the solution, then rinse with a little water. Transfer quantitatively the contents of the bubble trap to the solution contained in the Erlenmeyer flask. Titrate the excess acid using the standard 0·1N sodium hydroxide solution (4.17), until a pH of 5·4 is obtained, measured on the pH meter.

Remarks

1. After precipitation by the barium hydroxide and sodium carbonate solutions, make up to the mark, filter, and neutralise as quickly as possible.
2. The titration may also be carried out using an indicator (4.26), although the change of colour is more difficult to observe.

7.6.2 *Blank test*

See 7.2.3.

7.6.3 *Expression of results*

$$\% \text{ N (ureic)} = \frac{(a - A) \times 0{\cdot}14}{M}$$

where:

a = ml of standard solution of sodium or potassium hydroxide (0·1N) (4.17) used for the blank, carried out in exactly the same conditions as the analysis.

A = ml of standard solution of sodium or potassium hydroxide (0·1N) (4.17) used in the analysis.

M = weight of the sample, in grams, present in the aliquot part taken for analysis.

7.6.4 *Gravimetric method using xanthydrol*

Transfer by pipette into a 100ml beaker a portion of the filtrate (7.1) containing not more than 20mg urea. Add 40ml acetic acid (4.11). Stir with a glass rod for one minute. Allow any precipitate to settle for five minutes. Filter, wash with a few ml acetic acid (4.11). Add 10ml xanthydrol solution (4.23) to the filtrate drop by drop, stirring continuously with a glass rod. Allow to stand until the precipitate appears, then stir again for one or two minutes. Allow to stand for one and a half hours. Filter through a sintered glass crucible (5.6) which has been previously dried and weighed, using a slight reduction in pressure. Wash three times with 5ml ethanol (4.28), without trying to remove all the acetic acid. Place in an oven at a temperature of 130°C for one hour (do not exceed 145°C). Allow to cool in a desiccator and weigh.

7.6.5 *Expression of results*

$$\%\ \text{N (ureic)} = \frac{6{\cdot}67 \times m}{M}$$

where:

m = weight of the precipitate in grams.

M = weight of the sample, in grams, present in the aliquot part taken for analysis.

Correct for the blank.

Note: Although biuret will also be precipitated by xanthydrol, this should not give rise to a significant error in the determination since its level is generally low in absolute value in compound fertilisers.

7.6.6 *Method by difference*

Ureic N can also be calculated as indicated in the following table:—

Case	Nitric Nitrogen	Ammoniacal Nitrogen	Ureic Nitrogen
1	Absent	Present	(7.2.4) – (7.5.3)
2	Present	Present	(7.3.3) – (7.5.3)

8. Verification of Results

8.1 Before each analysis, check that the apparatus is working properly and that the correct applications of the methods are used with a standard solution containing the different forms of nitrogen in proportions similar to those in the sample. This standard solution is prepared from solutions of potassium nitrate (4.3), ammonium sulphate (4.4) and urea (4.5).

9a. Extraction of Phosphorus by Mineral Acids

1. Scope

This method is for the determination of phosphorus soluble in mineral acids.

2. Field of Application

Applicable exclusively to the phosphate fertilisers listed in Group 2(a) of Section A, and Groups 1, 2 and 4 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977.

3. Principle

Extraction of the phosphorus in the fertiliser with a mixture of nitric acid and sulphuric acid.

4. Reagents

4.1 Sulphuric acid (d = 1·84g/ml).

4.2 Nitric acid (d = 1·40g/ml).

5. Apparatus

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

6. Preparation of the Sample

See Method 1.

7. Procedure

7.1 *Extraction*

Weigh to the nearest 0·001g, 2·5g of the prepared sample and place it in a dry Kjeldahl flask. Add 15ml water and stir so as to suspend the substance. Add 20ml nitric acid (4.2) and carefully add 30ml sulphuric acid (4.1). 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 and 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.

7.2 *Determination*

Determine the phosphorus according to Method 10 on an aliquot part of the clear filtrate.

9b. Extraction of Phosphorus by 2% Formic Acid

1. Scope

This method is for the determination of phosphorus soluble in 2% formic acid (20g per litre).

2. Field of Application

Soft natural phosphates exclusively.

3. Principle

To differentiate between hard natural phosphates and soft natural phosphates, phosphorus soluble in formic acid is extracted in specific conditions.

4. Reagent

4.1 Formic acid, 2% (20g per litre): dilute 82ml formic acid (concentration 98-100%; d = 1·22g/ml) to 5 litres with distilled water.

5. Apparatus

5.1 500ml graduated flask (for example Stohmann).

5.2 Rotary shaker, 35-40 turns per minute.

6. Preparation of the Sample

See Method 1.

7. Procedure

7.1 *Extraction*

Weigh to the nearest 0·001g, 5g of the prepared sample and place it in a dry 500ml graduated flask (5.1) with a wide neck. While continuously rotating the flask by hand, add the formic acid (4.1) (at 20 ± 1°C) until it is approximately 1cm below the graduation mark and make up to the volume. Close the flask with a rubber stopper and shake for 30 minutes at 20 ± 2°C on the rotary shaker (5.2).

Filter the solution through a dry fluted filter, into a dry receiver, discarding the first portion of the filtrate.

7.2 *Determination*

Determine the phosphorus according to Method 10 on an aliquot part of the clear filtrate.

9c. Extraction of Phosphorus by 2% Citric Acid

1. Scope

This method is for the determination of phosphorus soluble in 2% citric acid (20g per litre).

2. Field of Application

Only applicable to basic slag fertilisers in Group 2(a) of Section A, and Groups 1, 2 and 4 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977.

3. Principle

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

4. Reagent

4.1 2% Citric acid solution (20g per litre), prepared from citric acid monohydrate.

Note: Verify the concentration of this citric acid solution by titrating 10ml of the latter with a sodium hydroxide standard solution 0·1N, using phenolphthalein as an indicator. If the solution is correct, the titre should be 28·55ml.

5. Apparatus

5.1 Rotary shaker, 35-40 turns per minute.

6. 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.

7. Procedure

7.1 *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 500 ± 1ml of the citric acid solution (4.1) at 20 ± 1°C. When adding the first mls of the reagent shake vigorously by hand to stop the formation of lumps and to prevent the substance sticking to the sides. Close the flask with a rubber stopper and shake it on the rotary shaker (5.1) 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.

7.2 *Determination*

Determine the phosphorus according to Method 10 on an aliquot part of the clear filtrate.

9d. Extraction of Phosphorus by Neutral Ammonium Citrate

1. Scope

This method is for the determination of phosphorus soluble in neutral ammonium citrate.

2. Field of Application

All fertilisers in Group 2(a) of Section A, and Groups 1, 2 and 4 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977 in respect of which solubility in neutral ammonium citrate is laid down.

3. Principle

Extraction of phosphorus at a temperature of 65°C using a neutral ammonium citrate solution (pH = 7·0) under specific conditions.

4. Reagents

4.1 Neutral ammonium citrate solution (pH = 7·0).

This solution must contain per litre 185g of citric acid monohydrate and must have a specific gravity of 1·09 at 20°C and a pH of 7·0.

The reagent is prepared as follows:

dissolve 370g citric acid monohydrate in about 1·5 litres of water and make an approximately neutral solution by adding 345ml of ammonia solution (28-29% of NH_3). If the NH_3 concentration is lower than 28% add a correspondingly larger quantity of ammonia solution and dilute the citric acid in correspondingly smaller quantities of water. Cool and make exactly neutral, keeping the electrodes of the pH meter (5.1) immersed in the solution. Add the ammonia solution (28-29% of NH_3) drop by drop, stirring continuously (with a mechanical stirrer) until a pH of exactly 7·0 at 20°C is obtained.

At this point make up the volume to 2 litres and test the pH again.

Keep the reagent in a closed container and check the pH at regular intervals.

5. Apparatus

5.1 pH meter.

5.2 Water-bath which can be set thermostatically at 65°C, equipped with a mechanically operated shaking tray (see Figure 8 in the Appendix).

6. Preparation of the Sample

See Method 1.

7. Procedure

7.1 *Extraction*

Transfer 1[a] or 3[b] grams, as appropriate, of the prepared sample to be analysed into a 200 or 250ml Erlenmeyer flask containing 100ml of ammonium citrate solution previously heated to 65°C. Stopper the Erlenmeyer flask and shake in order to suspend the fertiliser without forming lumps. Remove the stopper for an instant in order to balance the pressure and close the Erlenmeyer flask again. Place the flask in the water-bath (5.2) set to maintain the contents of the flask at exactly 65°C. Shake mechanically for one hour so as to ensure complete suspension of the sample [c].

(a) Where the fertiliser is normal superphosphate or concentrated superphosphate in Group 2(a) of Section A, or NPK fertiliser in Group 1, NP fertiliser in Group 2, or PK fertiliser in Group 4 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977.

(b) Where the fertiliser is triple superphosphate in Group 2(a) of Section A, or NPK fertiliser containing soft ground rock phosphate or partially solubilised rock phosphate in Group 1, or NP fertiliser containing soft ground rock phosphate or partially solubilised rock phosphate in Group 2, or PK fertiliser containing soft ground rock phosphate or partially solubilised rock phosphate in Group 4 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977.

(c) If no mechanical shaker is available, the flask may be shaken by hand every 5 minutes.

The level of suspension in the flask must stay constantly below that of the water in the bath. After exactly one hour remove the Erlenmeyer flask from the water-bath. Cool immediately under running water to ambient temperature and quantitatively transfer the contents from the Erlenmeyer flask into a graduated 500ml flask with a jet of water. Make up to volume with water. Mix thoroughly and filter through a dry fluted filter (medium speed) into a dry container, discarding the first part of the filtrate (about 50ml).

About 100ml of clear filtrate should be collected.

7.2 *Determination*

Determine the phosphorus according to Method 10 on an aliquot part of the clear filtrate.

9e. Extraction of Phosphorus by Alkaline Ammonium Citrate (Petermann's Method) at 65°C

1. Scope

This method is for the determination of phosphorus soluble in alkaline ammonium citrate.

2. Field of Application

Exclusively to precipitated dihydrated dicalcium phosphate ($CaHPO_4 . 2H_2O$).

3. Principle

Extraction of phosphorus at a temperature of 65°C with an alkaline solution of ammonium citrate (Petermann) under specified conditions.

4. Reagents

4.1 *Petermann's solution*
Characteristics:

Citric acid monohydrate, 173g per litre.
Ammonia, 42g per litre ammoniacal nitrogen.
pH, between 9·4 and 9·7.

Preparation from diammonium citrate:
Dissolve 941g diammonium citrate in about 3,500ml water in a 5 litre graduated flask. Stand the flask in a bath of running water, mix and cool. Add, in small amounts, 430ml of ammonia solution (d = 0·880g/ml), *from a freshly opened bottle,* (or an equivalent amount of diluted ammonia, for example if d = 0·906g/ml then 502ml are required). Adjust the temperature to 20°C, make up to volume with water and mix.

Preparation from citric acid and ammonia:

Dissolve 865g citric acid monohydrate in about 2,500ml distilled water in a container of about 5 litres capacity. Place container in an ice bath, and add in small amounts, shaking continually, 966ml of ammonia solution (d = 0·880g/ml), *from a freshly opened bottle*, (or an equivalent amount of diluted ammonia, for example if d = 0·906g/ml, then 1,114ml are required).

Adjust the temperature to 20°C, transfer to a 5 litre graduated flask, make up to the mark with distilled water and mix.

Check the ammoniacal nitrogen content as follows:

Transfer 25ml of the solution into a 250ml graduated flask, make up to volume with distilled water and mix. Determine the ammoniacal nitrogen

content on 25ml of this solution following Method 2. If the solution is correct, 15ml 0·5N H_2SO_4 are consumed. Calculate the concentration of ammoniacal nitrogen in the reagent solution, (1ml 0·5N $H_2SO_4 \equiv$ 0·007g nitrogen).

If the concentration of ammoniacal nitrogen is greater than 42g/litre, ammonia can be expelled by a stream of inert gas or by moderate heating to bring back the pH to 9·7. Carry out a second determination.

If the concentration of ammoniacal nitrogen is less than 42g/litre, calculate the volume of ammonia solution required to achieve this level (1ml ammonia solution, d = 0·880g/ml contains approximately 0·22g ammoniacal nitrogen). For each ml of ammonia solution required add 0·173g of citric acid.

Whenever corrections are made to this reagent solution, it is imperative that the final concentration of both citric acid and ammoniacal nitrogen are as specified.

5. Apparatus

5.1 Water-bath which can be maintained at a temperature of 65±1°C.

5.2 500ml graduated flask (for example Stohmann flask).

6. Preparation of Sample

See Method 1.

7. Procedure

7.1 *Extraction*

Weigh to the nearest 0·001g, 1g of the prepared sample and transfer to the 500ml graduated flask (5.2). Add 200ml alkaline ammonium citrate solution (4.1). Stopper the flask and shake vigorously by hand to avoid the formation of lumps and to prevent any adherence of the substance to the sides.

Place the flask in the water-bath at 65°C and shake every 5 minutes during the first half an hour. After each shaking, raise the stopper to equilibrate the pressure. The level of water in the water-bath should be above the level of solution in the flask. Allow the flask to remain in the water-bath a further hour at 65°C and shake every ten minutes. Remove the flask, cool to a temperature of about 20°C, make up to a volume of 500ml with water. Mix and filter through a dry fluted filter paper, rejecting the first portion of filtrate.

7.2. *Determination*

Determine the phosphate according to Method 10 on an aliquot part of the clear filtrate.

9f. Extraction of Phosphorus by Alkaline Ammonium Citrate (Petermann's Method) at Ambient Temperature

1. Scope

This method is for the determination of phosphorus soluble in cold alkaline ammonium citrate.

2. Field of Application

Disintegrated phosphates exclusively.

3. Principle

Extraction of phosphorus at a temperature about 20°C with an alkaline solution of ammonium citrate (Petermann's solution) in specific conditions.

4. Reagent

See Method 9e.

5. Apparatus

5.1 250ml graduated flask (for example Stohmann).

5.2 Rotary shaker, 35 – 40 turns per minute.

6. Preparation of the Sample

See Method 1.

7. Procedure

7.1 *Extraction*

Weigh to the nearest 0·001g, 2·5g of the prepared sample and put it in a 250ml graduated flask (5.1). Add a little of Petermann's solution (4) at 20°C, shake very hard in order to stop the formation of lumps and to prevent any of the substance adhering to the side of the flask. Make up to the mark with Petermann's solution and close the flask with a rubber stopper.

Shake for two hours on the rotary shaker (5.2). Filter immediately through a dry fluted filter, into a dry container, discarding the first portion of the filtrate.

7.2 *Determination*

Determine the phosphorus according to Method 10 on an aliquot part of clear filtrate.

9g. Extraction of Phosphorus by Joulie's Alkaline Ammonium Citrate

1. Scope

This method is for the determination of phosphorus soluble in Joulie's alkaline ammonium citrate.

2. Field of Application

All the straight and compound phosphate fertilisers in Group 2(a) of Section A and Groups 1 to 4 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977 in which the phosphate occurs in an alumino-calcic form.

3. Principle

Extraction by shaking vigorously with an alkaline solution of ammonium citrate of defined specification (and where appropriate in the presence of oxine), at about 20°C.

4. Reagents

4.1 *Joulie's alkaline solution of ammonium citrate:*

this solution contains 400g of citric acid monohydrate and 153g of NH_3 per litre. Its free ammonia content is approximately 55g per litre. It can be prepared by one of the methods described below:

4.1.1 In a 1 litre graduated flask, dissolve 400g of citric acid monohydrate in approximately 600ml ammonia solution (d = 0·925g/ml), containing 200g NH_3 per litre; this may be prepared by diluting 760ml ammonia solution (d = 0·880g/ml) *from a freshly opened bottle* with water to 1 litre. The citric acid is added successively in quantities of 50 to 80g maintaining the temperature below 50°C. Make up the volume to 1 litre with ammonia.

4.1.2 In a 1 litre graduated flask, dissolve 432g of diammonium citrate in 300ml of water. Add 440ml of ammonia solution (d = 0·925g/ml) (see 4.1.1 above). Make up the volume to 1 litre with water.

Verification of the total ammonia content:

take a 10ml sample of the citrate solution and place it in a 250ml flask. Make up the volume with distilled water. Determine the ammoniacal nitrogen content on 25ml of this solution according to Method 2. In these conditions the reagent is considered to be correct when the volume of 0·5N sulphuric acid consumed is between 17·7 and 18·0ml (1ml 0·5N $H_2SO_4 \equiv 0{\cdot}008516g$ NH_3). If this is not so add 4·25ml of ammonia (d = 0·925g/ml) per 0·1ml below the 18ml indicated above.

4.2 8 - Hydroxyquinoline (oxine), powdered.

5. Apparatus

5.1 Rotary shaker, 35 – 40 turns per minute.

6. Preparation of the Sample

See Method 1.

7. Procedure

7.1 *Extraction*

Weigh to the nearest 0·001g, 1g of the prepared sample and place in a small mortar (glass or porcelain). Add about ten drops of ammonium citrate solution (4.1) to moisten it and break it up very carefully with a pestle. Add 20ml ammonium citrate solution (4.1) mix to a paste and leave it to settle for about 1 minute.

Decant the liquid into a 500ml graduated flask straining off particles which might have escaped the preceding moist disintegration. Add 20ml ammonium citrate solution (4.1) to the residue, grind as above and decant the liquid into the graduated flask. Repeat the process four times, so that by the end of the fifth time all the product can be poured into the flask. The total quantity of ammonium citrate solution used for these processes must be approximately 100ml.

Rinse the pestle and mortar above the graduated flask with 40ml of distilled water. Stopper the flask and shake for three hours on the rotary shaker (5.1).

Leave the flask standing for fifteen to sixteen hours, and then shake it again under the same conditions for three hours. The temperature during the whole process should be kept at $20 \pm 2°C$.

Make up to volume with distilled water and mix. Filter through a dry filter, discard the first portion of the filtrate and collect the clear filtrate in a dry flask.

7.2 *Determination*

Determine the phosphorus according to Method 10 on an aliquot part of the clear filtrate.

8. Remark

The use of oxine makes it possible to apply this method to fertilisers containing magnesium. This is recommended when the ratio of magnesium and phosphoric anhydride contents is higher than 0·03 ($Mg/P_2O_5 > 0{\cdot}03$). If this is the case, add 3g of oxine to the moistened sample for analysis. The use of oxine in the absence of magnesium is not, moreover, likely to interfere subsequently with the determination. In the known absence of magnesium, oxine may be omitted.

9h. Extraction of Phosphorus by Water

1. Scope

This method is for the determination of water-soluble phosphorus.

2. Field of Application

All fertilisers, including compound fertilisers, where water-soluble phosphorus is to be determined.

3. Principle

Extraction in water by shaking under specific conditions.

4. Apparatus

4.1 500ml graduated flask (for example Stohmann).

4.2 Rotary shaker, 35-40 turns per minute.

5. Preparation of the Sample

See Method 1.

6. Procedure

6.1 *Extraction*

Weigh to the nearest 0·001g, 5g of the prepared sample and place it in a 500ml graduated flask (4.1). Add to the flask 450ml of water, the temperature of which must be between 20 and 25°C. Shake on the rotary shaker (4.2) 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.

6.2 *Determination*

Determine the phosphorus according to Method 10, on an aliquot part of the clear filtrate.

10. Determination of Extracted Phosphorus

(Gravimetric method using quinoline phosphomolybdate)

1. Scope

This method is for the determination of phosphorus in the extracts from fertilisers.

2. Field of Application

The method is applicable to all extracts of fertilisers[a], for the determination of the different forms of phosphorus.

3. Principle

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.

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.

(a) Phosphorus soluble in mineral acids, water-soluble phosphorus, phosphorus soluble in solutions of ammonium citrate, phosphorus soluble in 2% citric acid and phosphorus soluble in 2% formic acid.

4. Reagents

4.1 Concentrated nitric acid (d = 1·40g/ml).

4.2 Molybdate reagent:

4.2.1 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 (4.1).

Solution C : stir solution A into solution B to obtain solution C.

Solution D: to 50ml water and 35ml concentrated nitric acid (4.1) add 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 (5.3).

4.2.2 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 (4.1).

Solution C: add 10ml freshly distilled quinoline to 70ml of concentrated nitric acid (4.1).

Solution D : slowly pour, stirring well, 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 (5.3).

The reagents 4.2.1 and 4.2.2 can be used in the same way; both must be kept in the dark in stoppered polyethylene bottles.

5. Apparatus

5.1 Filter crucible with porosity of 5 to 20 microns.

5.2 Drying oven regulated at 250 ± 10°C.

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

6. Procedure

6.1 *Treatment of the solution*

With a pipette take an aliquot part of fertiliser extract (see Table on page 65) containing about 0·01g of P_2O_5 and put it in a 500ml Erlenmeyer flask. Add 15ml concentrated nitric acid [a] (4.1) and dilute with water to about 100ml.

6.2 *Hydrolysis*

Bring the contents of the Erlenmeyer flask to the boil slowly and keep at this temperature until hydrolysis is completed (this usually takes 1 hour). 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.

[a] 21ml when the solution to be precipitated contains more than 15ml of citrate solution neutral citrate, Petermann or Joulie alkaline citrate).

6.3 *Weighing the crucible*

Dry the filter crucible (5.1) for at least 15 minutes in the drying oven (5.2). Cool the crucible in a desiccator and weigh.

6.4 *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 (4.2.1 or 4.2.2) [a] 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.

6.5 *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.

6.6 *Drying and weighing*

Wipe the outside of the crucible with a filter paper. Place the crucible in the drying oven (5.5) 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 rapidly.

6.7 *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.

6.8 *Control test*

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

7. Expression of the Results

If the samples for analysis and dilutions shown in the Table are used the following formulae apply:

$$\%P = (A - a) \times F'$$

$$\%P_2O_5 = (A - a) \times F$$

where:

A = weight in grams of the quinoline phosphomolybdate.

a = weight in grams of the quinoline phosphomolybdate obtained in the blank test.

F and F′ = factors given in the last two columns of the Table.

With samples for analysis and dilutions which differ from those of the Table the following formulae apply:

$$\%P_2O_5 = \frac{(A-a) \times f \times D \times 100}{M}$$

$$\%P = \frac{(A-a) \times f' \times D \times 100}{M}$$

[a] To precipitate phosphate solutions containing more than 15ml citrate solution (neutral, Petermann or Joulie) which have been acidified with 21ml concentrated nitric acid (see footnote to paragraph 6.1) use 80ml of the precipitating reagent.

TABLE FOR METHOD 10

% P_2O_5 in the fertiliser	% P in the fertiliser	Sample for analysis (g)	Dilution to (ml)	Sample (ml)	Dilution to (ml)	Sample to be precipitated (ml)	Quinoline phospho-molybdate conversion factor (F) in percentage P_2O_5	Quinoline phospho-molybdate conversion factor (F') in percentage P
5–10	2·2–4·4	1	500	—	—	50	32·074	13·984
		5	500	—	—	10	32·074	13·984
10–25	4·4–11·0	1	500	—	—	25	64·148	27·968
		5	500	50	500	50	64·148	27·968
more than 25	more than 11	1	500	—	—	10	160·370	69·921
		5	500	50	500	25	128·296	55·937

where:

f = conversion factor, quinoline phosphomolybdate into P_2O_5 = 0·032074

f′ = conversion factor, quinoline phosphomolybdate into P = 0·013984

D = dilution factor

M = weight in g of the sample analysed.

11. Determination of Water-Soluble Potassium

1. Scope

This method is for the determination of water-soluble potassium.

2. Field of Application

All the potassium fertilisers listed in Group 3(a) of Section A and Groups 1, 3 and 4 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977.

3. Principle

The potassium is extracted with water and after the removal of interfering substances, the potassium is precipitated in a slightly alkaline medium in the form of potassium tetraphenylborate (KTPB).

4. Reagents

4.1 Formaldehyde, 25 – 35% solution, filter if necessary before use.

4.2 Potassium chloride.

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

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

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

4.6 STPB solution: dissolve 32·5g sodium tetraphenylborate in 480ml of water, add 2ml sodium hydroxide solution (4.3) 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.

4.7 Liquid for washing: dilute 20ml of the STPB solution (4.6) to 1 litre with water.

4.8 Bromine water: saturated bromine solution in water.

5. Apparatus

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

5.2 Oven regulated at 120±10°C.

6. Preparation of the Sample

See Method 1.

In the case of potassium salts the sample must be ground fine enough in order that a representative sample is obtained for analysis. For these products, Method 1, paragraph 6(a) must be used.

7. Procedure

7.1 *Extraction*

Weigh to the nearest 0·001g, 10g of the prepared sample (5g for potassium salts containing more than 50% of potassium oxide) and place in a 600ml beaker with approximately 400ml of water. Bring to the boil and allow it to boil for 30 minutes. Cool, transfer quantitatively into a 1 litre graduated flask, make up to volume, mix and filter into a dry receiver. Discard the first 50ml of the filtrate.

Note: If the filtrate is dark in colour, transfer by pipette, an aliquot part containing at the most 100mg of K_2O and place in a 100ml graduated flask, add bromine water and bring to the boil to eliminate any surplus bromine. After cooling make up to volume, filter and quantitatively determine the potassium in an aliquot part of the filtrate.

7.2 *Determination*

Transfer by pipette an aliquot part of the filtrate containing 25-50mg of potassium (see Table on page 68) into a 250ml beaker; make up to 50ml with water.

To remove interferences, add 10ml of the EDTA solution (4.5), several drops of the phenolphthalein solution (4.4) and stir in, drop by drop, sodium hydroxide solution (4.3) 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).

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 (4·1). Add several drops of phenolphthalein solution (4.4) 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.

7.3 *Weighing the crucible*

Dry the filter crucible (5.1) to constant weight in the oven at 120°C (5.2) (about 15 minutes).

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

7.4 *Precipitation*

Remove the beaker from the steam bath, stir in *drop by drop* 10ml of the STPB solution (4.6). This addition should take about 2 minutes; allow to stand for at least 10 minutes before filtering.

7.5 *Filtering and washing*

Filter under vacuum into the weighed crucible, rinse the beaker with the liquid for washing (4.7), 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.

7.6 *Drying and weighing*

Wipe the outside of the crucible with a filter paper and place in the oven (5.2) 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.

TABLE FOR METHOD 11

% K_2O in the fertiliser	% K in the fertiliser	Sample for analysis (g)	Aliquot part to be taken as a sample for precipitation (ml)	Conversion factor F $\frac{\%\ K_2O}{g\ KTPB}$	Conversion factor F' $\frac{\%\ K}{g\ KTPB}$
5–10	4·2–8·3	10	50	26·280	21·812
10–20	8·3–16·6	10	25	52·560	43·624
20–50	16·6–41·5	10	10	131·400	109·060
more than 50	more than 41·5	5	10	262·800	218·120

7.7 *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.

7.9 *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.

8. Expression of Results

8.1 *Method of calculation and formulae*

If the quantities and the dilutions shown in the Table on page 68 are used, the following formulae apply:

$$\%K_2O = (A - a) \times F$$

or

$$\%K = (A - a) \times F'$$

where:

A = weight in grams of the precipitate from the sample
a = weight in grams of the precipitate from the blank
F and F′ = factors—see table.

With samples and dilutions which differ from those shown in the table use the following formulae:

$$\%K_2O = \frac{(A - a) \times f \times D \times 100}{M}$$

or

$$\%K = \frac{(A - a) \times f' \times D \times 100}{M}$$

where:

f = conversion factor, KTPB into K_2O = 0·1314
f′ = conversion factor, KTPB into K = 0·109
D = dilution factor
M = weight in grams of sample for analysis.

12a Determination of Water-Soluble Magnesium—Atomic Absorption Spectrophotometric Method

1. Scope

This method is for the determination of water-soluble magnesium.

2. Field of Application

Exclusively to fertilisers in Groups 1(a) and 3(a) of Section A of the table in Schedule 1 of the Fertilisers Regulations 1977, in respect of which the declaration of water-soluble magnesium is required.

3. Principle

Solution of magnesium by boiling the test sample in water, and determination by atomic absorption spectrophotometry.

4. Reagents

4.1 Hydrochloric acid, N solution (approximately).

4.2 Hydrochloric acid, 0·5N solution.

4.3 Magnesium standard solution: dissolve 1·013g magnesium sulphate ($MgSO_4.7H_2O$) in 0·5N hydrochloric acid solution (4.2) 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 (4.1). After dissolution, transfer quantitatively into a one litre graduated flask, make up to volume with water and mix.
1ml of this solution contains 1mg of magnesium (Mg).

4.4 Strontium chloride solution: dissolve 15g strontium chloride ($SrCl_2.6H_2O$) in 0·5N hydrochloric acid solution (4.2) and dilute to 100ml with the same solvent.

5. Apparatus

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

6. Preparation of Sample

See Method 1.

7. Procedure

7.1 *Extraction*

Weigh to the nearest 0·001g, 5g of the prepared sample and place in a 500ml graduated flask. Add about 300ml water, and boil for half an hour. Allow to cool, dilute to the mark with water, mix and filter.

7.2 *Preparation of the sample solution*

7.2.1 If the fertiliser has a declared magnesium oxide (MgO) content greater than 10%, transfer by pipette 25ml of the filtrate (7.1) into a 100ml graduated flask, make up to the mark with water and mix.

7.2.2 Transfer by pipette 10ml of the filtrate (7.1) or the diluted filtrate (7.2.1) into a 200ml graduated flask and make up to the mark with 0·5N hydrochloric acid solution (4.2).

7.2.3 Dilute solution (7.2.2) with 0·5N hydrochloric acid solution (4.2) to a concentration within the working range of the spectrophotometer.

The final solution must contain 10% (V/V) of the strontium chloride solution (4.4).

7.3 *Blank solution*

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

7.4 *Standard solutions for calibration*

By diluting the standard solution (4.3) with 0·5N hydrochloric acid solution (4.2), 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 strontium chloride solution (4.4).

7.5 *Measurement*

Set up the spectrophotometer (5.1), at a wavelength of 285·2nm using an oxidising air-acetylene flame. Spray successively, in triplicate, the standard solutions (7.4), the sample solution (7.2) and the blank solution (7.3), 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 by reference to the calibration curve.

8. 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.

12b Determination of Water-Soluble Magnesium—EDTA Method

1. Scope

This method is for the determination of water-soluble magnesium.

2. Field of Application

Exclusively to straight fertilisers in Groups 1(a) and 3(a) of Section A of the table in Schedule 1 of the Fertilisers Regulations 1977 in respect of which the indication of water-soluble magnesium, expressed as magnesium oxide, is required.

3. Principle

Solution of magnesium by boiling a test sample in water. Titration with EDTA of calcium and magnesium in the presence of eriochrome black-T, followed by titration with EDTA of calcium in the presence of calcein or of calcon carbonic acid. Determination of magnesium by difference.

4. Reagents

4.1 Magnesium solution, 0·05M: weigh out 2·016g magnesium oxide, previously calcined at 600°C for 2 hours, place in a beaker with 100ml water and stir in 120ml of approximately N hydrochloric acid. After dissolution, transfer quantitatively into a 1 litre graduated flask, make up to volume with water and mix. Check the strength of the solution gravimetrically by precipitation as magnesium ammonium phosphate.

1ml of the solution should contain 1·216mg of Mg (=2·016mg of MgO).

4.2 EDTA solution, 0·05M: dissolve 18·61g of the dihydrated disodium salt of ethylenediaminetetra-acetic acid in 600-800ml water contained in a 1 litre beaker. Transfer the solution quantitatively to a 1 litre graduated flask, make up to volume with water and mix. Check this solution (4.1) by taking a sample of 20ml of the latter and titrating as described under 7.3.1.

1ml of the EDTA solution should correspond to 1·216mg of Mg or 2·016mg of MgO and to 2·004mg of Ca or 2·804mg of CaO.

4.3 Calcium solution, 0·05M: weigh out 5·004g of dry calcium carbonate and place in a beaker with 100ml water. Progressively stir in 120ml approximately N hydrochloric acid. Bring to the boil in order to drive off the carbon dioxide, cool, transfer quantitatively into a 1 litre graduated flask, make up to volume with water and mix. Check this solution against the EDTA solution (4.2) following analytical procedure 7.3.2. One ml of this solution should contain 2·004mg of Ca (=2·804mg of CaO) and should correspond to 1ml of the 0.05 molar EDTA solution.

4.4 Calcein indicator: carefully mix in a mortar 1g calcein with 100g sodium chloride. Use 10mg of this mixture. The indicator changes from green to orange. Titration must be carried out until an orange colour is obtained which is free from green tinges.

4.5 Calcon carbonic acid indicator: dissolve 400mg calcon carbonic acid in 100ml methanol. Use three drops of this solution. The indicator changes from red to blue. Titration must be carried out until a blue colour is obtained which is free from red tinges.

4.6 Eriochrome black-T indicator: dissolve 300mg eriochrome black-T in a mixture of 25ml propan-1-ol and 15ml triethanolamine. Use three drops of this solution. This indicator turns from red to blue and titration must be carried out until a blue colour is obtained which is free from red tinges. It changes colour only when magnesium is present. If necessary add 0·1ml of standard solution (4.1).

4.7 Potassium cyanide solution, 2g per 100ml.

4.8 Solution of potassium hydroxide and potassium cyanide: dissolve 280g potassium hydroxide and 66g potassium cyanide in water, make up the volume to 1 litre and mix.

4.9 pH 10 buffer solution: dissolve 33g ammonium chloride in 200ml water, add 207ml ammonia solution (d=0·880g/ml) *from a freshly opened bottle,* (or an equivalent amount of diluted ammonia, for example if d=0·91g/ml, use 250ml). Make up the volume to 500ml with water and mix. Check the pH of this solution regularly.

5. Apparatus

5.1 Magnetic or mechanical stirrer.

5.2 pH meter.

6. Preparation of the Sample

See Method 1.

7. Procedure

7.1 *Extraction*

Weigh to the nearest 0·001g, 5g of the prepared sample and place in a 500ml graduated flask. Add about 300ml water and boil for half an hour. Cool, make up to volume, mix and filter.

7.2 *Control test*

Carry out a determination on aliquot parts of solutions (4.1) and (4.3) such that the Ca/Mg ratio is equal to that expected from the sample. For this purpose take (a) ml of standard solution (4.3) and (b — a) ml standard solution (4.1), where (a) and (b) are the numbers of ml EDTA solution used in the two titrations when analysing the sample. This procedure is correct only if the standard solutions of EDTA, calcium and magnesium are exactly equivalent. If this is not the case, it is necessary to make the appropriate corrections.

7.3 *Determination*

7.3.1 *Titration in the presence of eriochrome black-T*

Place an aliquot part of the solution to be analysed (see Table on page 73) in a 300ml beaker and dilute with water to about 100ml. Add 5ml buffer solution (4.9). The pH measured by the meter (5.2) must be 10·5±0·1. Add 2ml potassium cyanide solution (4.7)

and 3 drops of the eriochrome black-T indicator (4.6). Stir gently and titrate with the EDTA solution (4.2). Let "b" be the number of ml of 0·05 molar EDTA solution.

Note: For titration with eriochrome black-T, the titration must not exceed 25ml of EDTA, otherwise the volume of the aliquot part must be reduced.

7.3.2 *Titration in the presence of calcein or of calcon carbonic acid*

Place an aliquot part of the solution to be analysed equal to that taken for the above titration in a beaker. Dilute with water to about 100ml. Add 10ml potassium hydroxide-potassium cyanide solution (4.8) and the indicator (4.4) or (4.5). Stir gently and titrate with the EDTA solution (4.2). Let "a" be the number of ml of 0·05 molar EDTA solution.

TABLE FOR METHOD 12b

Type of fertiliser	Aliquot part to be taken as sample for each titration (ml)	Quantity of sample present in one aliquot part (g)
Nitrate of calcium and of magnesium	20	0·200
Magnesium ammonium sulphate-nitrate	50	0·500
Crude potassium salts	25	0·250
Potassium magnesium chloride	25	0·250
Sulphate of potassium and magnesium	25	0·250

8. Expression of the Results

$$\%MgO = \frac{(b-a) \times 0{\cdot}2016}{M}$$

or

$$\%Mg = \frac{(b-a) \times 0{\cdot}1216}{M}$$

M = weight of the sample, expressed in grams, present in the aliquot part.

13a Determination of Total Magnesium—Atomic Absorption Spectrophotometric Method

1. Scope

This method is for the determination of total magnesium.

2. Field of Application

Exclusively to the fertiliser magnesium ammonium nitrate in Group 1(a) of Section A of the table in Schedule 1 of the Fertilisers Regulations 1977 in respect of which the declaration of total magnesium is required.

3. Principle

Solution of magnesium by boiling the test sample in dilute acid, and determination by atomic absorption spectrophotometry.

4. Reagents

4.1 Hydrochloric acid solution 50% (V/V): dilute an appropriate volume of hydrochloric acid (d = 1·18g/ml) with an equal volume of water.

4.2 Hydrochloric acid, N solution (approximately).

4.3 Hydrochloric acid, 0·5N solution.

4.4 Magnesium solution: dissolve 1·013g magnesium sulphate ($MgSO_4.7H_2O$) in 0·5N hydrochloric acid solution (4.3) 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 (4.2). After dissolution, transfer quantitatively into a one litre graduated flask, make up to volume with water and mix.
1ml of this solution contains 1mg of magnesium (Mg).

4.5 Strontium chloride solution: dissolve 75g strontium chloride ($SrCl_2.6H_2O$) in 0·5N hydrochloric acid solution (4.3) and dilute to 500ml with this acid.

5. Apparatus

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

6. Preparation of Sample

See Method 1.

7. Procedure

7.1 *Extraction*

Weigh to the nearest 0·001g, 5g of the prepared sample and place in a 500ml graduated flask. Add about 200ml water, 20ml hydrochloric acid solution (4.1) and boil for half an hour. Allow to cool, dilute to the mark with water, mix and filter.

7.2 *Preparation of the sample solution*

7.2.1 If the fertiliser has a declared magnesium oxide (MgO) content greater than 10%, transfer by pipette 25ml of the filtrate (7.1) into a 100ml graduated flask, make up to the mark with water and mix.

7.2.2 Transfer by pipette 10ml of the filtrate (7.1) or the diluted filtrate (7.2.1), into a 200ml graduated flask and make up to the mark with 0·5N hydrochloric acid solution (4.3).

7.2.3 Dilute solution (7.2.2) with 0·5N hydrochloric acid solution (4.3) to a concentration within the working range of the spectrophotometer. The final solution must contain 10% (V/V) strontium chloride solution (4.5).

7.3 *Blank solution*

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

7.4 *Standard solutions for calibration*

By diluting the standard solution (4.4) with 0·5N hydrochloric acid solution (4.3), prepare at least 5 standard solutions of increasing concentration corresponding to the optimal measuring range of the spectro-

photometer. The final solutions must contain 10% (V/V) of the strontium chloride solution (4.5).

7.5 *Measurement*

Set up the spectrophotometer (5.1), at a wavelength of 285·2nm using an oxidising air-acetylene flame. Spray successively, in triplicate, the standard solutions (7.4), the sample solution (7.2) and the blank solution (7.3), 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 by reference to the calibration curve.

8. 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.

13b. Determination of Total Magnesium—EDTA Method

1. Scope

This method is for the determination of total magnesium.

2. Field of Application

Exclusively to the fertiliser magnesium ammonium nitrate in Group 1 (a) of Section A of the table in Schedule 1 of the Fertilisers Regulations 1977 in respect of which the indication of total magnesium is required.

3. Principle

Solution of magnesium by boiling a test sample in dilute acid. Titration of calcium and magnesium with EDTA in the presence of eriochrome black-T, followed by titration with EDTA of calcium in the presence of calcein or of calcon carbonic acid. Determination of magnesium by difference.

4. Reagents

4.1 Magnesium solution, 0·05M: weigh out 2·016g of magnesium oxide previously calcined at 600°C for 2 hours, place in a beaker with 100ml of water and stir in 120ml of approximately 1N hydrochloric acid. After dissolution, transfer quantitatively into a 1 litre graduated flask, make up to volume with water and mix. Check the strength of the solution gravimetrically by precipitation as ammonium-magnesium phosphate.

1ml of the solution should contain 1·216mg of magnesium (Mg) (=2·016 mg of magnesium oxide (MgO)).

4.2 EDTA solution, 0·05M: dissolve 18·61g of the dihydrated disodium salt of ethylenediaminetetra-acetic acid in 600-800ml water contained in a 1 litre beaker. Transfer the solution quantitatively into a 1 litre graduated flask, make up to volume with water and mix. Check this solution with solution (4.1) by taking a sample of 20ml of the latter and titrating following analytical procedure 7.3.1.

1ml of the EDTA solution should correspond to 1·216mg of Mg or 2·016mg of MgO and to 2·004mg of Ca or 2·804mg of CaO.

4.3 Calcium solution, 0·05M: weigh out 5·004g of dry calcium carbonate and place in a beaker with 100ml of water. Progressively stir in 120ml of approximately N hydrochloric acid. Bring to the boil in order to drive

off the carbon dioxide, cool, transfer quantitatively into a 1 litre graduated flask, make up to volume with water and mix. Check this solution against the EDTA solution (4.2) following analytical procedure 7.3.2.

One ml of this solution should contain 2·004mg of Ca (= 2·804mg of CaO) and should correspond to 1ml of the 0·05 molar EDTA solution.

4.4 Calcein indicator: carefully mix in a mortar 1g of calcein with 100g of sodium chloride. Use 10mg of this mixture. The indicator changes from green to orange. Titration must be carried out until an orange colour is obtained which is free from green tinges.

4.5 Calcon carbonic acid indicator: dissolve 400mg of calcon carbonic acid in 100ml of methanol. Use three drops of this solution. The indicator changes from red to blue. Titration must be carried out until a blue colour is obtained which is free from red tinges.

4.6 Eriochrome black-T indicator: dissolve 300mg of eriochrome black-T in a mixture of 25ml of propan-1-ol and 15ml of triethanolamine. Use three drops of this solution. This indicator turns from red to blue and titration must be carried out until a blue colour is obtained which is free from red tinges. It changes colour only when magnesium is present. If necessary add 0·1ml of standard solution (4.1).

4.7 Potassium cyanide solution, 2g per 100ml.

4.8 Solution of potassium hydroxide and potassium cyanide: dissolve 280g potassium hydroxide and 66g potassium cyanide in water, make up the volume to one litre and mix.

4.9 pH 10·5 buffer solution: dissolve 33g ammonium chloride in 200ml of water, add 207ml ammonia solution (d = 0·880g/ml) *from a freshly opened bottle* (or an equivalent amount of diluted ammonia, for example if d = 0·91g/ml, use 250ml). Make up the volume to 500ml with water and mix. Check the pH of this solution regularly.

4.10 Hydrochloric acid solution, 50% (V/V): dilute an appropriate volume of hydrochloric acid (d = 1·18g/ml) with an equal volume of water.

4.11 Sodium hydroxide solution, 5N.

5. Apparatus

5.1 Magnetic or mechanical stirrer.

5.2 pH meter.

6. Preparation of the Sample

See Method 1.

7. Procedure

7.1 *Extraction*

Weigh to the nearest 0·001g, 5g of the prepared sample and place in a 500ml graduated flask. Add about 200ml water and 20ml hydrochloric acid (4.10) and boil for half an hour. Cool, make up to volume with water, mix and filter.

7.2 *Control test*

Carry out a determination on aliquot parts of solutions (4.1) and (4.3) such that the Ca/Mg ratio is equal to that expected from the sample. For this purpose take (a) ml of standard solution (4.3) and (b – a) ml standard solution (4.1), where (a) and (b) are the numbers of ml EDTA

solution used in the two titrations when analysing the sample. This procedure is correct only if the standard solutions of EDTA, calcium and magnesium are exactly equivalent. If this is not the case, it is necessary to make the appropriate corrections.

7.3 *Determination*

7.3.1 *Titration in the presence of eriochrome black-T*
Transfer by pipette 50ml of the solution to be analysed into a 300ml beaker. Neutralise the excess acid with the 5N sodium hydroxide solution (4.11) using the pH meter (5.2). Dilute with water to 100ml. Add 5ml buffer solution (4.9). The pH measured by the meter must be 10·5 ± 0·1. Add 2ml potassium cyanide solution (4.7) and three drops eriochrome black-T indicator (4.6). Titrate with the EDTA solution (4.2), stirring gently with the stirrer (5.1). Let "b" be the number of ml of 0.05 molar EDTA solution.

Note: For titration with eriochrome black-T, the titration must not exceed 25ml of EDTA otherwise the volume of the aliquot part must be reduced.

7.3.2 *Titration in the presence of calcein or of calcon carbonic acid*
Place an aliquot part of the solution to be analysed equal to that taken for the above titration in a 300ml beaker.
Neutralise the excess acid with 5N sodium hydroxide solution (4.11) using the pH meter (5.2).

Dilute with water to about 100ml. Add 10ml potassium hydroxide —potassium cyanide solution (4.8) and the indicator (4.4) or (4.5). Stir gently and titrate with the EDTA solution. Let "a" be the number of ml of 0·05 molar EDTA solution.

8. Expression of the Results

$$\%MgO = \frac{(b-a) \times 0{\cdot}2016}{M}$$

$$\%Mg = \frac{(b-a) \times 0{\cdot}1216}{M}$$

M = weight of the sample, expressed in grams, present in the aliquot part.

14. Determination of Chlorides in the Absence of Organic Material

1. Scope

This method is for the determination of chloride, in the absence of organic material.

2. Field of Application

All fertilisers which are free from organic material.

3. Principle

The chlorides, dissolved in water, are precipitated in an acid medium by an excess of standard solution of silver nitrate. The excess is titrated with a solution of ammonium thiocyanate in the presence of ferric ammonium sulphate (Volhard's method).

4. Reagents

4.1 Nitrobenzene or diethyl ether.

4.2 Nitric acid, 10N solution.

4.3 Indicator solution: dissolve 40g of ferric ammonium sulphate $[Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O]$ in water and make up to 1 litre.

4.4 Silver nitrate, 0·1N solution.

4.5 Ammonium thiocyanate, 0·1N solution.

Preparation: since this salt is hygroscopic and cannot be dried without risk of decomposition, it is advisable to weigh out approximately 9g, dissolve in water and make up the volume to one litre. Standardise by titration against 0·1N silver nitrate solution.

5. Apparatus

5.1 Rotary shaker, 35–40 turns per minute.

6. Preparation of Sample

See Method 1.

7. Procedure

7.1 *Extraction*

Weigh to the nearest 0·001g, 5g of the prepared sample and place in a 500ml graduated flask and add 450ml water. Mix for half an hour on the shaker (5.1); make up to 500ml with distilled water, mix and filter into a beaker.

7.2 *Determination*

Take an aliquot part of the filtrate containing not more than 0·150g of chloride. If the sample taken is smaller than 50ml it is necessary to make up the volume to 50ml with distilled water. Add 5ml 10N nitric acid (4.2), 20ml indicator solution (4.3), and two drops ammonium thiocyanate standard solution (taken from a burette adjusted to zero). From a burette then add silver nitrate solution (4.4) until there is an excess of 2 to 5ml. Add 5ml nitrobenzene or 5ml diethyl ether (4.1) and shake well to agglomerate the precipitate. Titrate the excess silver nitrate with 0·1N ammonium thiocyanate (4.5) until a red-brown colour appears which remains after the flask has been shaken slightly.

Note: Nitrobenzene or diethyl ether (especially the former) prevents the silver chloride from reacting with thiocyanate ions, thus a clear colour change is obtained.

7.3 *Blank test*

Make a blank test under the same conditions (omitting only the sample) and allow for it when calculating the final result.

7.4 *Control test*

Carry out the determination on an aliquot part of a freshly prepared solution of potassium chloride, containing 0·100g as chloride.

8. Expression of the Result

Express the result of the analysis as a percentage of chloride contained in the sample as it has been received for analysis.

Calculation: calculate the percentage of chloride (Cl) with the formula:

$$\%Cl = \frac{0{\cdot}003546 \times (V_z - V_{cz}) - (V_a - V_{ca}) \times 100}{M}$$

Where:

V_z = number of millilitres of silver nitrate added
V_{cz} = number of millilitres of silver nitrate used in the blank test
V_a = number of millilitres of ammonium thiocyanate used for the titration of the sample
V_{ca} = number of millilitres of ammonium thiocyanate used for the titration of the blank
M = weight in grams of the sample in aliquot volume taken for titration.

15a. Determination of Fineness of Grinding—Dry Method

1. Scope

This method is for the determination of the fineness of grinding by the dry method.

2. Field of Application

All fertilisers in Group 2(a) of Section A, and Groups 1, 2 and 4 of Section B of the table in Schedule 1 of the Fertilisers Regulations 1977 for which requirements are given of fineness of grinding using 0·630mm and 0·160mm sieves.

3. Principle

By mechanical sieve shaking, the quantities of product with a granule size greater than 0·63mm and those with a granule size between 0·16mm and 0·63mm are determined, and the percentages of fineness of grinding are calculated.

4. Apparatus

4.1 Mechanical sieve shaker.

4.2 Sieves with apertures of 0·160mm and 0·630mm respectively of standard ranges (diameter 20cm, height 5cm).

5. Procedure

Weigh to the nearest 0·05g, 50g of the sample. Assemble the two sieves and the collecting container on the shaker (4.1), the sieve with the larger apertures being placed on top. Place the sample for analysis on the top. Sieve for ten minutes and remove the part collected on the bottom. Sieve again for one minute and check that the amount collected on the bottom during this time is not more than 250mg. Repeat the process (for one minute each time) until the amount collected is less than 250mg. Weigh the residual material on both sieves separately.

6. Expression of the Results

Percentage of material passing sieve of 0·630mm apertures $= (50–M_1) \times 2$

Percentage of material passing sieve of 0·160mm apertures $= [50–(M_1+M_2)] \times 2$

M_1 = weight in grams of residue on the sieve with 0·630mm apertures
M_2 = weight in grams of residue on the sieve with 0·160mm apertures

The results are to be rounded up to the nearest unit.

15b. Determination of the Fineness of Grinding of Soft Natural Phosphates

1. Scope

This method is for determining the fineness of grinding of soft natural phosphates.

2. Field of Application

Soft natural phosphates.

3. Principle

For samples of fine particle size, agglomeration may occur thus making dry sieving difficult. For this reason, wet sieving is normally used.

4. Reagents

Sodium hexametaphosphate solution, 1g per 100ml.

5. Apparatus

5.1 Sieves with apertures of 0·063mm and 0·125mm respectively of standard ranges (diameter 20cm, height 5cm) and collecting containers.

5.2 Glass funnel of 20cm diameter mounted on a stand.

5.3 Laboratory oven.

6. Procedure

Wash both sides of the sieves with water and place the sieve with 0·125mm apertures above the 0·063mm sieve.

Weigh to the nearest 0·05g, 50g of the prepared sample and place on the top sieve. Sieve under a small jet of cold water (tap water can be used) until the water is practically clear when it passes through. Care should be taken to ensure that the flow of water is such that the lower sieve never fills with water. When the residue on the top sieve seems to remain more or less constant, remove this sieve, and place in the meanwhile on a collecting container.

Continue the wet sieving through the lower sieve for a few minutes, until the water passing through is nearly clear. Replace the 0·125mm sieve over the 0·063mm sieve. Transfer any deposit from the collecting container to the top sieve and begin sieving again under a small jet of water until this water becomes almost clear once more.

Quantitatively transfer each of the residues into a separate 250ml beaker by means of the funnel. Suspend each residue by filling the beakers with water. Allow to stand for about 1 minute and then decant as much water as possible. Place the beakers in the oven (5.3) at 150°C for two hours. Allow them to cool, detach the residues with a brush and weigh them.

7. Expression of the Results

Percentage of material passing sieve of 0·125mm apertures $= (50-M_1) \times 2$

Percentage of material passing sieve of 0·063mm apertures
$= [50-(M_1+M_2)] \times 2$

M_1 = weight in grams of the residue on the 0·125mm sieve

M_2 = weight in grams of the residue on the 0·063mm sieve

The results are to be rounded up to the nearest unit.

8. Remark

If the presence of lumps is observed after sieving the analysis should be carried out again in the following way:

slowly pour 50g of the sample into a 1 litre flask containing 500ml of the sodium hexametaphosphate solution, stirring continuously. Stopper the flask and shake vigorously by hand to break up the lumps. Transfer the whole suspension into the top sieve and wash the flask thoroughly. Continue the analysis as described under paragraph 6.

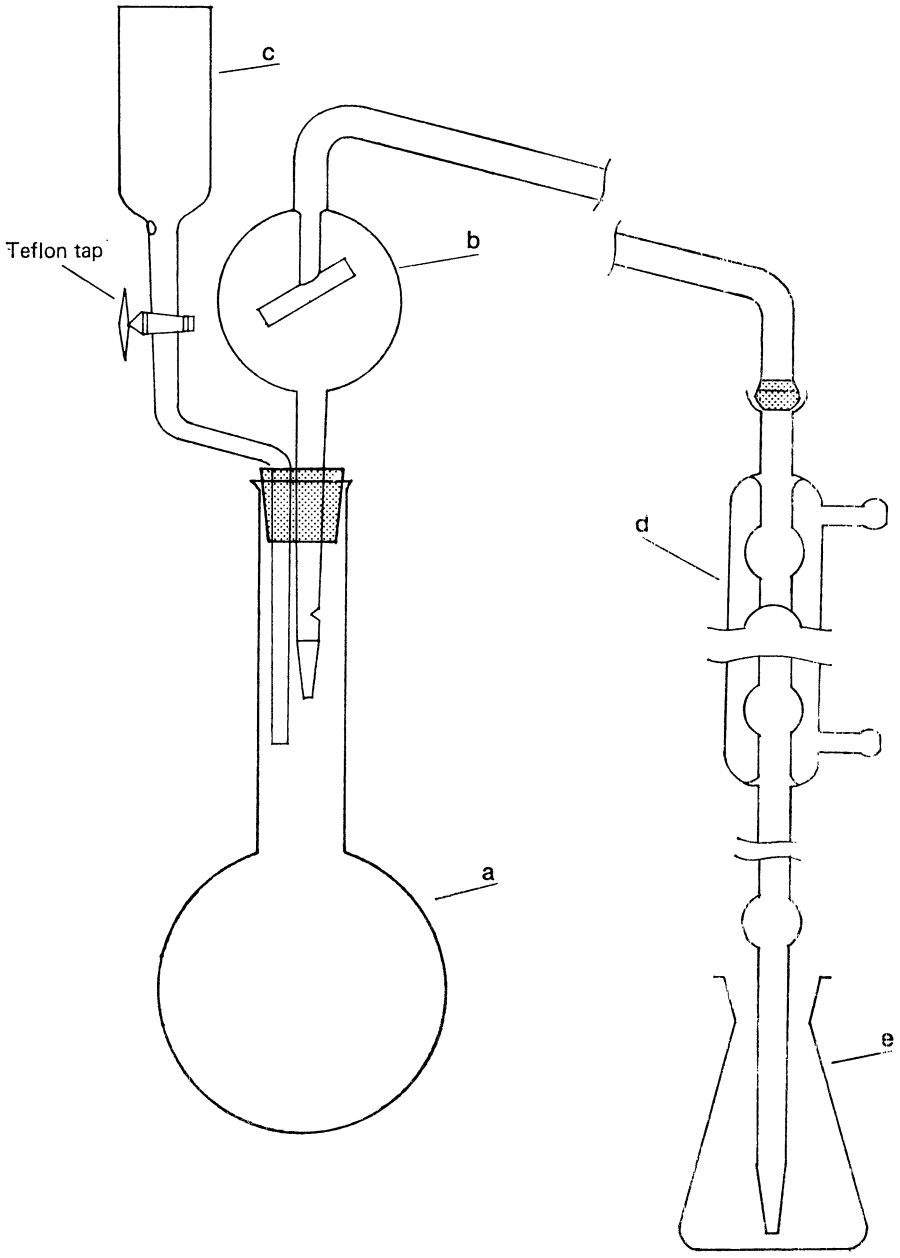

Figure 1

KEY TO FIGURE 1

(a) A round-bottomed, long-necked flask of 1,000ml capacity.

(b) Distillation tube with a splash head, connected to the condenser by means of a spherical joint (the spherical joint for the connection to the condenser may be replaced by an appropriate rubber connection).

(c) Funnel with a teflon tap for the addition of sodium hydroxide (the tap may likewise be replaced by a rubber connection with a clip).

(d) A six-bulb condenser with a spherical joint, fitted with a glass extension tube. (The connection to the distillation tube may be effected by means of a rubber bung instead of a spherical joint.)

(e) A 500ml flask in which the distillate is collected.

The equipment is made of borosilicate glass.

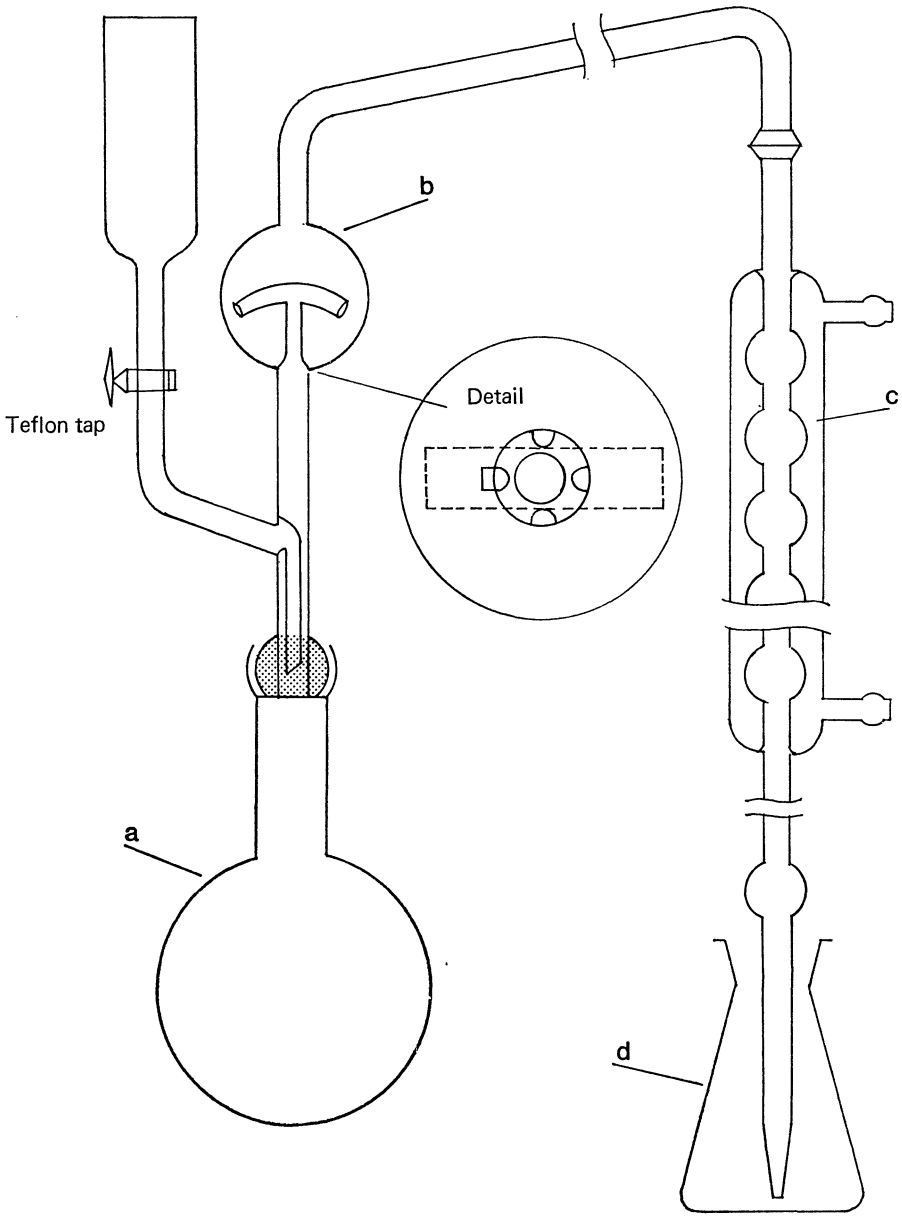

Figure 2

KEY TO FIGURE 2

(a) A round-bottomed, short-necked flask of 1,000ml capacity with a spherical joint.

(b) Distillation tube with a splash head, fitted with spherical joints, connected at the side to a funnel with a teflon tap for the addition of sodium hydroxide.

(c) A six-bulb condenser with a spherical joint, fitted with a glass extension tube.

(d) A 500ml flask in which the distillate is collected.

The equipment is made of borosilicate glass.

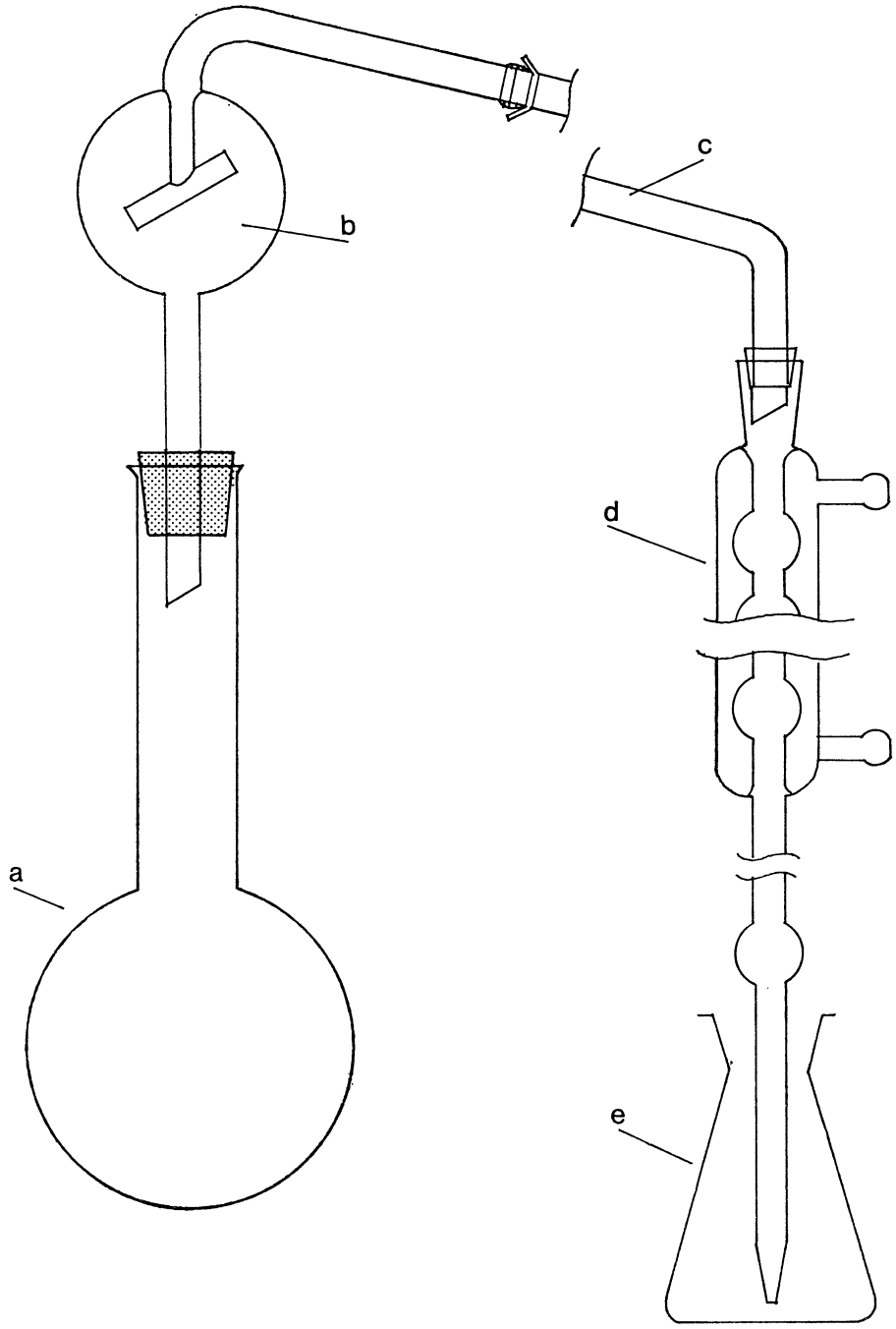

Figure 3

KEY TO FIGURE 3

(a) A round-bottomed, long-necked flask of 750 or 1,000ml capacity with a bell mouth.

(b) Distillation tube with a splash head and a spherical joint.

(c) An elbow tube with a spherical joint and a drip cone. (The connection to the distillation tube may be effected by means of a rubber tube instead of a spherical joint.)

(d) A six-bulb condenser with a glass extension tube.

(e) A 500ml flask in which the distillate is collected.

The equipment is made of borosilicate glass.

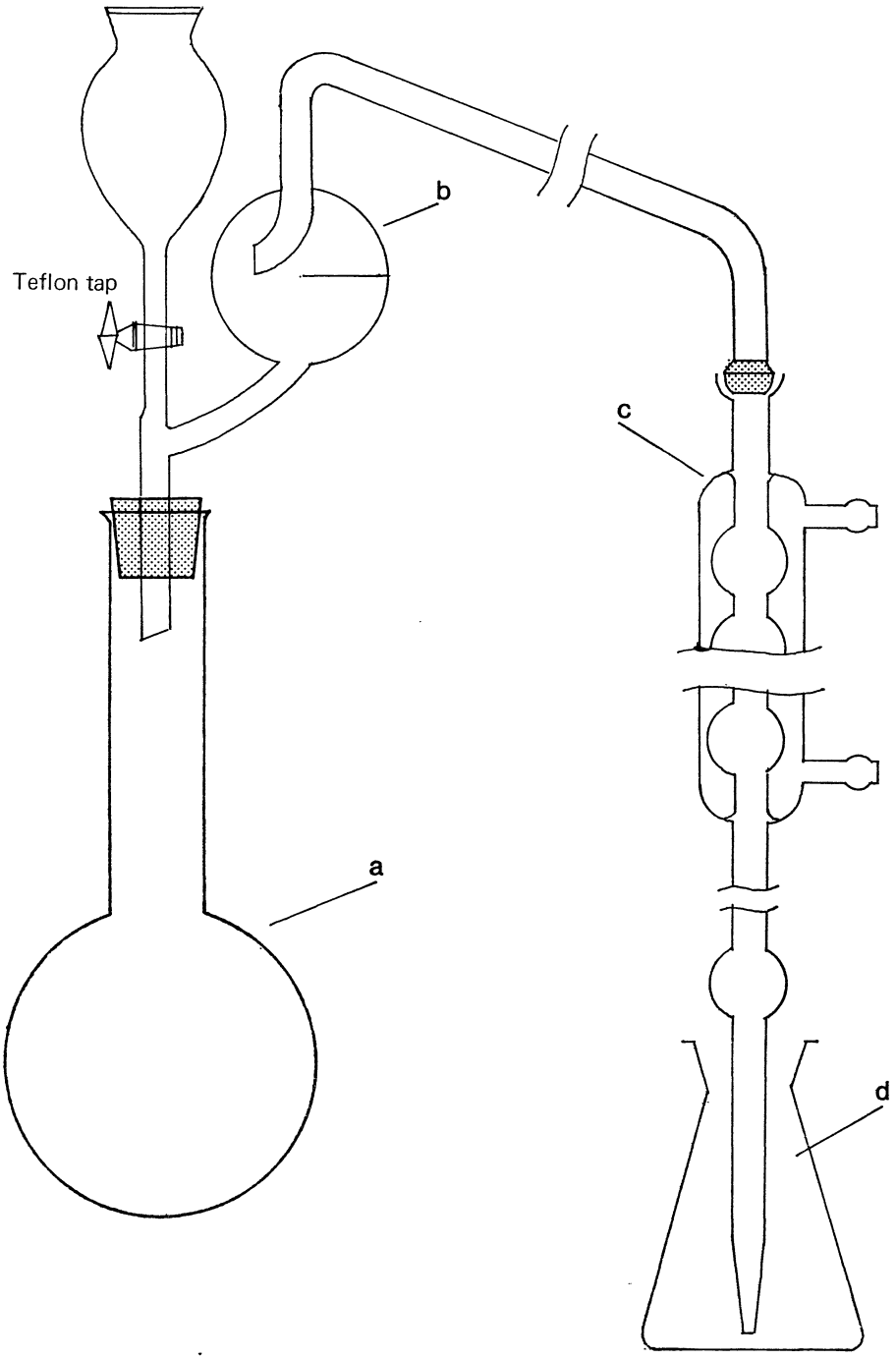

Figure 4

KEY TO FIGURE 4

(a) A round-bottomed, long-necked flask of 1,000ml capacity with a bell mouth.

(b) Distillation tube with a splash head and a spherical joint, connected at the side to a funnel with a teflon tap for the addition of sodium hydroxide. (A suitable rubber bung may be used instead of the spherical joint; the tap may be replaced by a rubber connection with an appropriate clip.)

(c) A six-bulb condenser with a spherical joint, fitted with a glass extension tube. (The connection to the distillation tube may be effected by means of a rubber bung instead of a spherical joint.)

(d) A 500ml flask for the collection of the distillate.

The equipment is made of borosilicate glass.

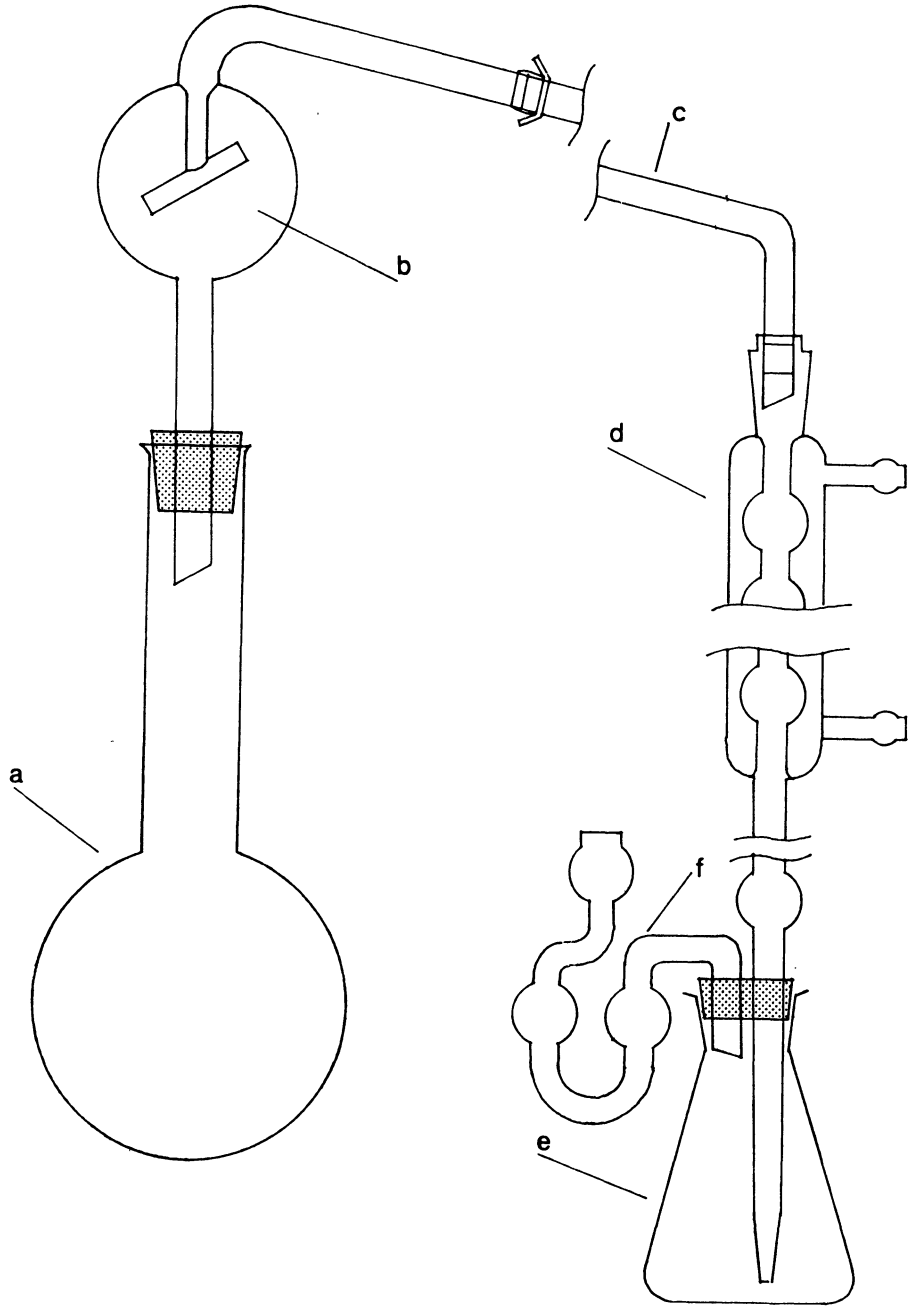

Figure 5

KEY TO FIGURE 5

(a) A round-bottomed, long-necked flask of 750 or 1,000ml capacity with a bell mouth.

(b) Distillation tube with a splash head and a spherical joint.

(c) Elbow tube with a spherical joint and a drip cone. (A suitable rubber connection may be used instead of the spherical joint.)

(d) A six-bulb condenser with an extension tube mounted on a rubber bung holding a bubble trap.

(e) A 750ml receiving flask.

(f) A bubble trap to prevent loss of ammonia.

The equipment is made of borosilicate glass.

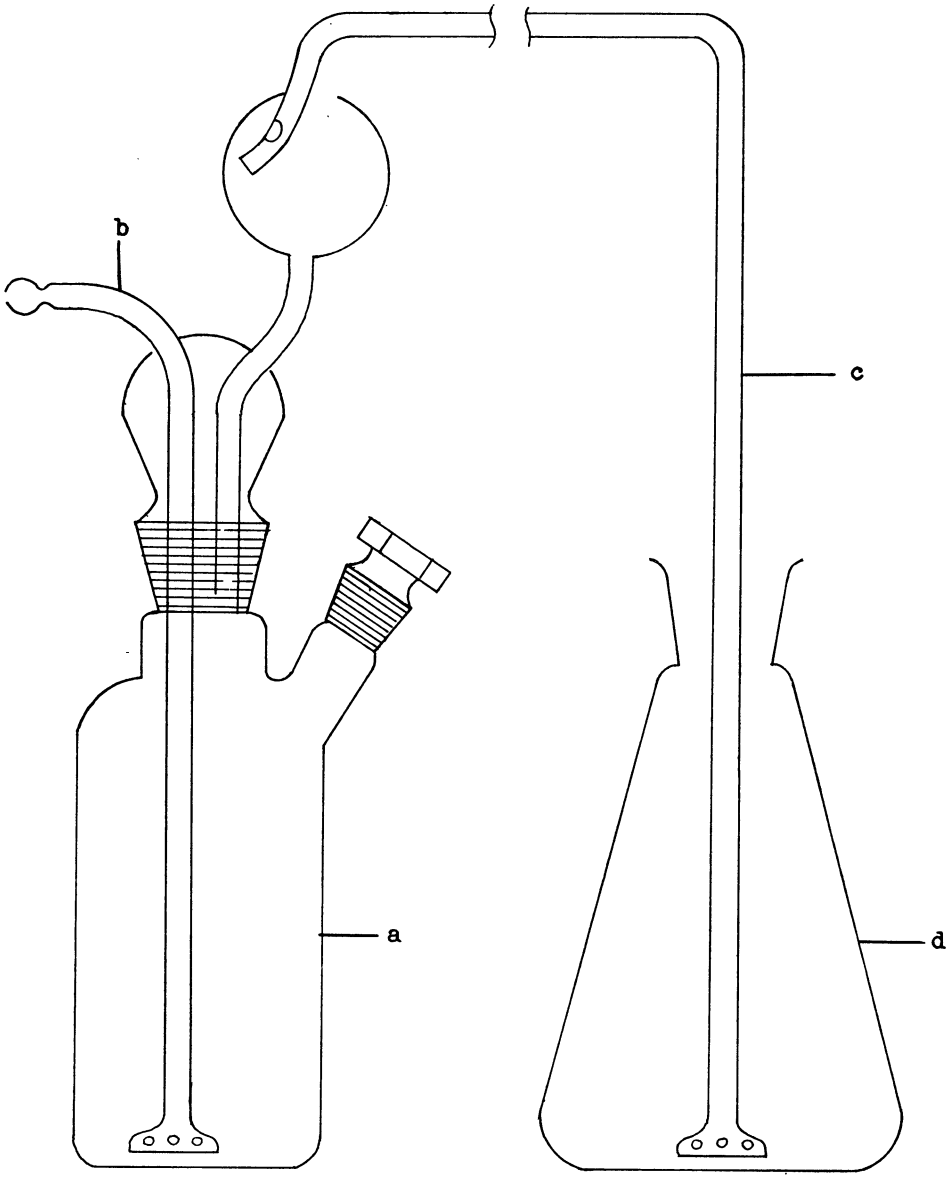

Figure 6

KEY TO FIGURE 6

(a) Reaction vessel, 350-400ml capacity.

(b) Tube for introduction of air.

(c) Delivery tube with splash head.

(d) Conical flask, 300ml capacity.

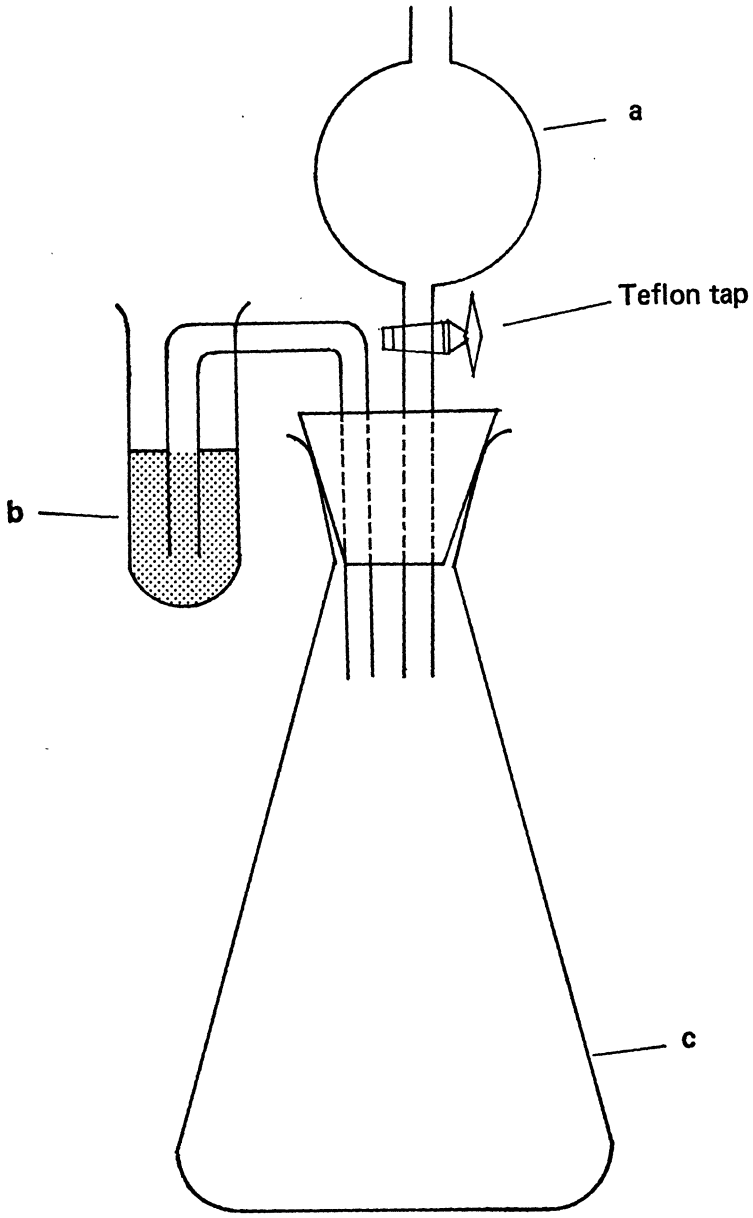

Figure 7

KEY TO FIGURE 7

(a) Separating funnel.

(b) Bubble trap.

(c) Conical flask, 300ml capacity.

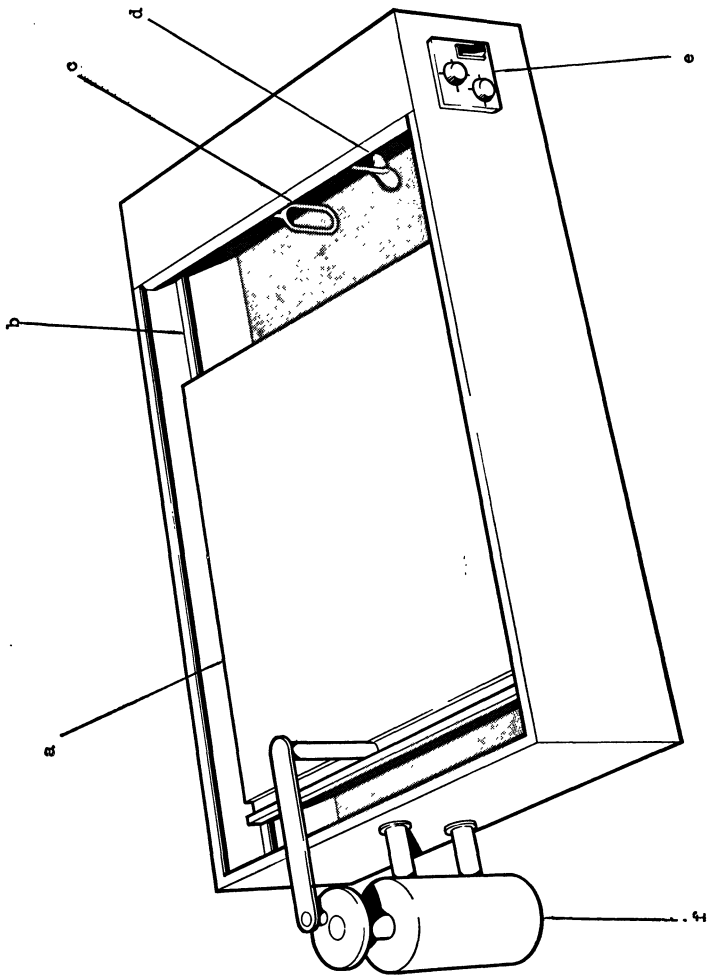

Figure 8

KEY TO FIGURE 8

(a) Tray for flasks.

(b) Tray support.

(c) Heater.

(d) Stirrer.

(e) Controls for heater, stirrer and electric motor.

(f) Electric motor.

SCHEDULE 3

FORM OF CERTIFICATE OF ANALYSIS

(Sections 74A, 77(4), 78(3) and 79(5), (6), (7) and (8) and Regulation 7)

CERTIFICATE OF ANALYSIS OF FERTILISER[1]

in the form prescribed by Schedule 3 of the Fertilisers (Sampling and Analysis) Regulations 1978.

I, the undersigned, agricultural analyst for the[2] , in pursuance of the provisions of section 79 of the Agriculture Act 1970, Part IV and regulation 7 of the Fertilisers (Sampling and Analysis) Regulations 1978, hereby certify that I received on the day of , 19 , from [3] one part of a sample of [4] for analysis; which was duly sealed and fastened up and marked [5] and was accompanied by a [6] , as follows:—[7]

and also by a signed statement that the sample was taken in the prescribed manner; and that the said part has been analysed by me, or under my direction, and I declare the results of analysis to be as follows:—[8]

	%
Nitrogen (N) Total	
Nitric nitrogen	
Ammoniacal nitrogen	
Ureic nitrogen	
Cyanamide nitrogen	
Phosphorus pentoxide (P_2O_5) Total	
Soluble in water	
Insoluble in water	
Soluble in alkaline ammonium citrate[9]	
Soluble in 2% citric acid ...	
Soluble in 2% formic acid ...	
Soluble in neutral ammonium citrate	
Soluble in neutral ammonium citrate and in water	
Soluble in mineral acids	
Soluble in mineral acids (after deduction of amount soluble in water)	
Soluble only in mineral acids ...	
Potassium oxide (K_2O) Total ...	
Soluble in water	
Magnesium oxide (MgO) Total ...	
Soluble in water	
Chlorine (Cl)	

	%	mg/kg
Trace elements		
Boron (B)		
Cobalt (Co) ...		
Copper (Cu) ...		
Iron (Fe)		
Magnesium (Mg)		
Manganese (Mn) ...		
Molybdenum (Mo)		

Neutralising value expressed in terms of Calcium oxide (CaO).....%

Amount that will pass through the prescribed sieve[10].....%

Names of pesticides and herbicides found.....
(11)

and I am of the opinion that(12)

The analysis was made in accordance with the Fertilisers (Sampling and Analysis) Regulations 1978.

As witness my hand this day of , 19 .

(Signature and address of analyst)

(1) Statements made in certificates are to be confined to matters which are necessary to verify compliance with the Act.

(2) Here insert the name of the local authority.

(3) Here insert the name of the inspector who submitted the sample for analysis; and also the mode of transit, for example "by hand", "by registered post", "by rail", as the case may be.

(4) Here insert the name or description applied to the material.

(5) Here insert the distinguishing mark on the sample.

(6) Here insert either "statutory statement", "copy of statutory statement", "copy of particulars marked on the material" or "copy of particulars indicated by a mark applied to the material", or as the case may be.

(7) Here insert the analytical particulars contained in the statutory statement, or particulars marked on or indicated by a mark applied to the material, or as the case may be.

(8) Insert relevant results under the appropriate headings, ie percentage or milligrams per kilogram.

(9) Here insert "Petermann" or "Joulie" according to the method used for the determination.

(10) Insert the size of sieve used.

(11) In the case of analysis of substances for which no analytical method is prescribed in regulation 6 and Schedule 2 here indicate the method used. If analysis cannot be carried out because no suitable method exists then the certificate should be noted accordingly.

(12) Here enter information as follows:—

(a) whether the material was correctly named in accordance with the requirements of the Fertilisers Regulations 1977 and whether it accords with the meaning corresponding to that name; and if not, in what respect.

(b) If the composition of the material agrees with or differs by no more than the limits of variation specified in the Fertilisers Regulations 1977 from the statement of particulars contained in the statutory statement, or the particulars marked on or indicated by a mark associated with the material, state that the particulars are correct within the limits of variation.

(c) If the composition of the material differs by more than the limits of variation specified in the Fertilisers Regulations 1977 from the particulars contained in the statutory statement, or the particulars marked on or indicated by a mark associated with the material, state the difference between the amount found and the amount stated and that the difference is outside the limits of variation; and that the difference is to the prejudice of the purchaser, if such is believed to be the case.

(These notes and the numbers referring to them are for guidance only and do not form part of, and need not appear on, the certificate.)

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), supersede, insofar as they apply to fertilisers, Regulations 3, 4, 5, 15, 16 and 17 and Parts I, II and IV of Schedule 1 and Part I of Schedule 8 of the Fertilisers and Feeding Stuffs Regulations 1973, and Regulations 2(1), (2), (7), (8), (9), (16) and (18) and 3(2) and Schedule 8 of the Fertilisers and Feeding Stuffs (Amendment) Regulations 1976, also made under Part IV of the Act. They apply throughout Great Britain and are made after consultation with persons and organisations representing the interests concerned.

The Regulations prescribe a number of matters required by the Act of 1970 to be prescribed for the purposes of Part IV of that Act and include provisions implementing Directive 77/535/EEC of the Commission (O.J. No. L.213, 22.8.77) as respects the sampling and analysis of fertilisers. These matters include:—

(a) the amounts of fertilisers from which samples are to be taken (regulation 2);

(b) the manner of taking, dividing, marking, sealing and fastening of samples (regulation 3 and Schedule 1);

(c) the methods of sending part of a sample (regulation 4);

(d) the required qualifications of agricultural analysts and deputy agricultural analysts (regulation 5);

(e) the methods by which analyses are to be carried out (regulation 6 and Schedule 2), and the form of certificate of analysis (regulation 7 and Schedule 3);

(f) a modification of the Act to provide for metrication (regulation 8);

(g) an amendment to the Fertilisers Regulations 1977 to provide for new operative dates as respects fertilisers in packages or containers not exceeding 25 kilograms or 10 litres, as appropriate, and to exempt containers of liquid fertilisers of a capacity not exceeding 10 litres from the sealing requirements of those regulations (regulation 9);

(h) the revocation with effect from 1st June 1983 of the Fertilisers and Feeding Stuffs Regulations 1973, as amended, insofar as they apply to the sampling and analysis of fertilisers (regulation 10).

The principal changes from the Regulations which have been superseded are:—

(i) the Regulations introduce a new sampling procedure for solid fertilisers, with more detailed sampling tables;

(ii) there are additional methods of analysis;

(iii) more information is required in the certificate of analysis and provision is made in the certificate for cases where no method of analysis is prescribed in the Regulations.

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