FERTILISERS AND FEEDING STUFFS (JERSEY) ORDER 1972

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Jersey

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Arrangement

Article

Supporting Documents

Jersey

FERTILISERS AND FEEDING STUFFS (JERSEY) ORDER 1972

THE ECONOMIC DEVELOPMENT COMMITTEE, in pursuance of Article 20 of the Fertilisers and Feeding Stuffs (Jersey) Law 1950,[1] orders as follows –

Commencement [see endnotes]

1 Interpretation

In this Order, unless the context otherwise requires –

"feeding stuff" means any article intended for use as food for cattle or poultry;

"fertiliser" means any article intended for use as a fertiliser of the soil;

"Law" means the Fertilisers and Feeding Stuffs (Jersey) Law 1950.[2]

2 Manner of marking particulars on sales of small quantities

(Article 2(1)(ii) of the Law)

The label of a parcel to which sub-paragraph (ii) of the proviso to Article 2(1) of the Law relates shall bear the particulars required by the said Article 2 to be contained in the statutory statement in block capital letters and figures not less than half an inch in height.

3 Manner of marking parcels

(Article 5(1) of the Law)

A parcel required by Article 5(1) of the Law to be marked shall be marked in writing –

(a) on the article itself;

(b) where the parcel consists of a single package, on the wrapper or container of, or on a label securely attached to or placed inside, the package;

(c) where the parcel consists of a number of separate packages, either –

(i) on the wrapper or container of, or on a label securely attached to or placed inside, each of the packages, or

(ii) otherwise in such manner that the mark shall be readily apparent and unequivocally associated with the parcel;

(d) where the parcel consists of a number of packages themselves enclosed in a larger package or packages, on the wrapper or container of, or on a label securely attached to or placed inside –

(i) each of the packages,

(ii) such larger package, or

(iii) each of such larger packages; or

(e) where the parcel is in a bulk container or tanker, either –

(i) on the bulk container or tanker, or on a label securely attached thereto, or

(ii) otherwise in such a manner that the mark shall be readily apparent and unmistakably associated with the parcel:

Provided that –

(a) the marking shall be legible; and

(b) every parcel shall be marked in such a manner that it shall remain marked so long as it is on the premises where it has been marked.

4 Form of register of marks

(Article 5(2) of the Law)

A register of marks kept in accordance with Article 5(2) of the Law, specifying the particulars which the several marks entered in the register are used as indicating, shall be kept in such a form that the particulars required by the said Article 5, relating to each separate parcel, shall be readily ascertainable by an inspector.

5 Form of register of articles delivered or consigned ex ship or quay

(Article 6(2) of the Law)

The register of articles delivered or consigned direct from a ship or quay to a purchaser, required to be kept in accordance with Article 6(2) of the Law, shall be kept in such a form that the particulars required, relating to each separate article, shall be readily ascertainable by an inspector.

6 Period for which registers and statutory statements are to be preserved

(Article 10(1) of the Law)

The period for which a register or statutory statement is to be preserved in accordance with Article 10(1) of the Law shall be 4 months.

7 Manner of taking and dividing samples

(Articles 4(1) and (2), 5(3), 6(3), 7, 8(1) and 11(1) of the Law)

The manner in which samples are to be taken and dealt with in cases where under the Law they are to be taken in the prescribed manner shall be as set forth in Schedule 1 to this Order.

8 Method of dealing with third part of sample

(Article 12(1) of the Law)

Where a sample has been taken by an inspector and divided by the person into 3 parts in accordance with Article 12(1) of the Law and Article 7 of this Order, the third part shall be delivered or sent by registered post to the last seller or the seller's agent.

9 Period for which one part of sample is to be retained by official analyst

(Article 12(2) of the Law)

The period for which the Official Analyst shall, in accordance with Article 12(2) of the Law, retain one part of a sample sent to the Official Analyst shall be 6 months from the date of the Official Analyst's certificate of analysis of the sample unless in the meantime such part of the sample has been submitted to the Government Chemist in pursuance of Article 12(7) or Article 18(3) of the Law.

10 Methods of analysis of fertilisers

The methods in which analyses of fertilisers shall be made for the purposes of the Law are as set forth in Schedule 2 to this Order.

11 Methods of analysis of feeding stuffs

The methods in which analyses of feeding stuffs shall be made for the purposes of the Law are as set forth in Schedule 3 to this Order.

12 Limits of variation

(Articles 1(6) and 3(5) of the Law)

The limits of variation in relation to the particulars of the nature, substance or quality of an article or as to the amount of any ingredient, for the purposes of Article 1(6) and Article 3(5) of the Law, shall be as set out in Schedule 4 to this Order.

13 Forms of certificate of analysis

The certificates of the Official Analyst –

(a) of the analysis of a fertiliser; and

(b) of the analysis of a feeding stuff,

shall be in forms respectively set forth in Parts 1 and 2 of Schedule 5 to this Order.

14 Citation

This Order may be cited as the Fertilisers and Feeding Stuffs (Jersey) Order 1972.

SCHEDULE 1

(ARTICLES 4, 5(3), 6(3), AND 11(1) OF THE LAW)

MANNER OF TAKING AND DIVIDING SAMPLES

PART 1

PROVISIONS APPLICABLE TO BOTH FERTILISERS AND FEEDING STUFFS

A. General Provisions.

1. In the case of articles in packages, bottles, drums or kegs, only unopened containers shall be selected for the purpose of the sample.

2. Samples shall not be drawn from part of any quantity where such part bears the appearance of having received damage.

3. In every case the sampling shall be done as quickly as is possible, consistent with due care, and the material shall not be exposed any longer than is absolutely necessary.

B. Provisions applicable where the fertiliser or feeding stuff is in solid condition.

4. Where the weight of the whole quantity does not exceed 2 cwt., or the whole quantity is in one container, the sample may consist of such a portion of the quantity as is fairly representative of the whole, and the sample shall be of not less than 1½ 1bs. in weight.

5. In each case it shall be assumed that the quantity is composed of separate approximately equal parts and that the number of such parts is equivalent to –

   (a) the number of packages to be selected in accordance with paragraph 1(a) of Part 2; or

   (b) the number of portions where the quantity is in bulk, to be taken in accordance with paragraph 1(b) of Part 2.

   The packages or portions shall be selected on the basis of at least one from each assumed approximately equal part, and shall be drawn at random.

6. Notwithstanding anything in this Order a sampling spear shall not be used if objection is raised thereto, prior to the taking of a sample, on the ground that the material is unsuitable.

C. Provisions applicable where the fertiliser or feeding stuff is in a liquid or semi liquid condition.

7.

(a) *In bottles or containers each containing not more than one quart.*

The number of bottles or containers to be selected shall be in accordance with the appropriate scale for solid fertilisers in paragraph 1(a) of Part 2. The entire contents of the selected bottles or containers shall be emptied into a clean, dry vessel of glass or other suitable material and well mixed by stirring or shaking. From this mixture a sample of between about one quart and about half-a-gallon shall be drawn, the mixture being stirred or shaken until immediately before the sample is drawn

(b) *In drums, kegs, or other containers each containing more than one quart and not more than 40 gallons.*

The number of containers to be selected shall be in accordance with the appropriate scale for solid fertilisers in paragraph 1(a) of Part 2. 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, emptied into a clean, dry vessel of glass or other suitable material and well mixed by stirring or shaking. From this mixture a sample of between about one quart and about half-a-gallon shall be drawn, the mixture being stirred or shaken until immediately before the sample is drawn.

(c) In a bulk container or containers containing more than 40 gallons.

(i) When a consignment is being withdrawn from the bulk container, and there is a tap in the outlet pipe from which it is suitable to draw a sample, a quantity in accordance with the table below shall be drawn from the tap (after first withdrawing sufficient to remove any residues in the pipe), into a clean, dry vessel of glass or other suitable material, made up of portions of not less than one pint and of approximately equal size taken at regular intervals, otherwise

(ii) if the liquid is homogeneous, about one quart 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 glass or other 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), 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 to a clean, dry vessel of glass or other 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 representative of the whole. The appropriate process shall be repeated until a quantity in accordance with the table below has been withdrawn,

(v) Where a parcel consists of 2 or more containers, a sample from each, drawn in the manner described in sub-paragraphs (i) to (iv), as appropriate, shall be placed in a clean, dry vessel of glass or other suitable material,

(vi) The quantity taken as described in sub-paragraphs (i), (iv) and (v) shall be thoroughly mixed and a sample of about one quart transferred into a clean, dry vessel of glass or other suitable material.

TABLE

*Quantities of liquid fertilisers and feeding stuffs to be withdrawn in accordance with sub-paragraphs (*c)(i) *and* (iv) *above*

Where the quantity to be sampled –	Quantity to be withdrawn
does not exceed 1,000 gallons	not less than 2 pints
exceeds 1,000 gallons but does not exceed 5,000 gallons	„ „ „ 3 pints
exceeds 5,000 gallons but does not exceed 10,000 gallons	„ „ „ 4 pints
exceeds 10,000 gallons but does not exceed 15,000 gallons	„ „ „ 5 pints
exceeds 15,000 gallons but does not exceed 20,000 gallons	„ „ „ 6 pints
exceeds 20,000 gallons but does not exceed 50,000 gallons	„ „ „ 7 pints
exceeds 50,000 gallons but does not exceed 100,000 gallons	„ „ „ 10 pints
exceeds 100,000 gallons	„ „ „ 20 pints

PART 2

PROVISIONS APPLICABLE TO SOLID FERTILISERS

1. Where the fertiliser is in a state of fine division.

(a) In packages.

Where the fertiliser is in packages and the quantity exceeds 2 cwt, a number of packages shall be selected as follows, viz: –

	If the sample is drawn by an inspector under Article 11(1) of the Law.		If the sample is drawn by an official sampler after delivery of the article, under Article 4 of the Law.	
	Quantity taken for sampling	But not fewer packages than	Quantity taken for sampling	But not fewer packages than
	%		%	
Where the quantity exceeds one package and does not exceed 20 packages	20	2	10	2
Where the quantity exceeds 20 packages and does not exceed 60 packages	10	4	5	2
Where the quantity exceeds 60 packages and does not exceed 200 packages	7	6	4	3
Where the quantity exceeds 200 packages and does not exceed 500 packages	5	15	3	8
Where the quantity exceeds 500 packages and does not exceed 1,000 packages	4	25	2	13
Where the quantity exceeds 1,000 packages	3	40	1	20

When the number of packages to be selected according to either of the above percentage scales contains a fraction, this fraction shall be counted as a whole number.

Either

(i) the selected packages shall be emptied separately on a clean dry surface and worked up with a shovel and one shovelful taken from each. The shovelfuls so taken shall then be thoroughly mixed together and any lumps broken up, or

(ii) when the material is of a suitable nature, a portion shall be taken for each selected package by means of a closed sampling spear. The separate portions thus taken shall be thoroughly mixed together.

From the mixture so obtained, the sample shall be drawn in the following manner: –

Heap the material to form a "cone"; flatten the cone and quarter it. Reject 2 diagonally opposite quarters, mix the remainder and continue the quartering and rejection until the remainder is from about 2 1b. to 4 1b. in weight. Alternatively the reduction of the gross sample by the quartering method may be effected by the use of a mechanical quartering device known as a sample divider or riffle.

(b) In bulk

Where the fertiliser is in bulk, a number of portions shall be taken by a shovel or a closed sampling spear as follows –

	Portions
Where the quantity exceeds 2 cwt. and does not exceed 1 ton	4
Where the quantity exceeds 1 ton and does not exceed 2 tons	6
Where the quantity exceeds 2 tons and does not exceed 5 tons	10
Where the quantity exceeds 5 tons and does not exceed 10 tons	15
Where the quantity exceeds 10 tons and does not exceed 25 tons	25
Where the quantity exceeds 25 tons and does not exceed 50 tons	40
Where the quantity exceeds 50 tons and does not exceed 100 tons	60
Where the quantity exceeds 100 tons for each additional 10 tons or part thereof	2

The portions, according to whether they have been taken by a shovel or spear, shall be treated in the manner described in paragraph 1(a) and the sample drawn in the manner also described in that paragraph.

2. *Where the fertiliser is in a coarse or lump condition (as in the case of burnt lime not ground*)

(a) In packages

The packages, selected according to the appropriate scale in paragraph 1(a), shall be emptied separately on a clean dry surface and worked up with a shovel and one shovelful taken from each. The shovelfuls so taken shall be crushed immediately and the whole passed through a sieve with meshes one and a quarter inch square. It shall be mixed thoroughly and rapidly and a sample of about 4 1b. to 6 1b. in weight drawn in the manner described in paragraph 1(a).

(b) In bulk

Shovelfuls shall be taken according to the appropriate scale in paragraph 1(b). The shovelfuls so taken shall be treated, and a sample shall be drawn, in the manner described in paragraph 1(a).

3. *Where the fertiliser consists of bulky material, uneven in character and likely to get matted together (such as shoddy, wool refuse, hair, etc.*)

(a) In packages

The packages, selected according to the appropriate scale in paragraph 1(a) shall be emptied separately on a clean dry surface and the matted portions torn up.

One shovelful shall be taken from each and the shovelfuls so taken shall be thoroughly mixed together. The sample shall be drawn from the mixture and shall be from about 2 1b. to 4 1b. in weight. If the material separates into a fibrous part and a powdery part, the sample drawn shall consist of these 2 parts in approximately their relative proportions as they exist in the material.

(b) In bulk

Shovelfuls shall be taken according to the appropriate scale prescribed in paragraph 1(b). The shovelfuls thus taken shall be treated, and a sample shall be drawn, in the manner described in paragraph 3(a).

4. When the fertiliser consists of materials such as burnt lime or slaked lime (calcium hydroxide) which are liable to undergo change on exposure to air and moisture, or when the fertiliser consists of materials such as calcium nitrate, or ammonium nitrate, which are liable to absorb moisture, or when the material is sulphate of ammonia, the sampling shall be carried out rapidly in a dry place and the sample divided into parts and packed immediately.

5. 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. If they cannot be broken up 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 shall be ascertained and reported to the analyst.

PART 3

PROVISIONS APPLICABLE TO SOLID FEEDING STUFFS

1. *Where the feeding stuff is in the state of small lumps or meal*

The sample shall be taken in the manner prescribed for a fertiliser in paragraphs 1(a) or 1(b) of Part 2.

2. *Where the feeding stuff is in the form of cake, whether in bags or in bulk*

A number of cakes shall be selected from the different parts of the whole quantity as follows: –

	Cakes
Where the quantity exceeds 2 cwt. and does not exceed 2 tons	5
Where the quantity exceeds 2 tons and does not exceed 5 tons	10
Where the quantity exceeds 5 tons and does not exceed 50 tons	15
Where the quantity exceeds 50 tons and does not exceed 100 tons...	25
Where the quantity exceeds 100 tons for each additional 20 tons or part thereof	2

The selected cakes shall be broken by a cakebreaker or in some other manner so that the whole will pass through a sieve with meshes one and a quarter inch square and then shall be thoroughly mixed. From the mixture so obtained, a sample of not less than 6 1b. in weight shall be drawn in the manner described in paragraph 1(a) of Part 2.

3. Where any appreciable portion of the feeding stuff appears to be mouldy, or is otherwise apparently unsuitable for feeding purposes, separate samples shall be drawn of the unsuitable portion and of the residue of the feeding stuff respectively, and in the case of unsuitable cakes, the sample may consist of several large pieces representative thereof.

4. *Where the feeding stuff consists of particles of grossly differing sizes*

(a) In packages

The packages shall be selected according to the appropriate scale in paragraph 1(a) of Part 2. The selected packages shall be emptied separately on a clean surface, worked up with a shovel and one shovelful from each set aside. The shovelfuls so set aside shall then be thoroughly mixed together and reduced if necessary by the cone and quartering method described in paragraph 1(a) of Part 2 to a quantity of not less than 15 1bs. Any lumps in the said quantity shall be crushed (and for this purpose may be separated from other material) and the whole then thoroughly re-mixed. From the mixture a sample of 2 1bs. to 4 1bs. weight shall be drawn.

(b) In bulk

Shovelfuls shall be taken according to the appropriate scale prescribed in paragraph 1(b) of Part 2. The shovelfuls thus taken shall be treated, and a sample drawn in the manner described in paragraph (a) above.

PART 4

DIVISION OF SAMPLE

1. Where the sample has been taken in the prescribed manner the person taking the sample shall divide it into 3 parts, as nearly as possible equal, in the following manner –

   (a) In the case of dry or powdered substances

   The sample, drawn as prescribed in the foregoing paragraphs, shall be thoroughly mixed on a floor covering which will adequately protect the sample from accidental contamination, and divided into 3 similar and approximately equal parts. Each of these parts shall be placed in a clean, dry bottle or jar with a close-fitting stopper or lid or (except in the case of a fertiliser) a clean, dry tin with a close-fitting lid (such as a lever lid), so that the original composition of the fertiliser or feeding stuff may be preserved. In the case of burnt lime, slaked lime (calcium hydroxide), calcium nitrate, ammonium sulphate and other substances likely to undergo change if not kept in an air-tight receptacle, the bottle or jar used shall have a ground-in or rubber stopper or a metal cap with inner pad or a closure of the kind used on preserving jars. Each of the said parts shall be so secured and sealed that the bottle, jar or tin containing it cannot be opened without breaking the seal; or alternatively, the bottle, jar or tin containing the part may be placed in a stout envelope or in a linen or cotton bag, and the envelope or bag then secured and sealed in such a manner that the part of the sample cannot be removed without breaking the seal or the envelope or the bag.

   (b) In the case of substances in a fluid or semi-fluid condition

   The sample, drawn as prescribed in the foregoing paragraphs, shall be thoroughly mixed and at once divided into similar and approximately equal parts by pouring successive portions into each of 3 clear glass bottles or jars, preferably with wide mouths. The bottles or jars used shall be provided with air-tight stoppers or with lids which shall be so fastened that spillage or evaporation of the contents is prevented.

2. Each of the said parts shall be sealed and initialled by the person taking the sample. It may also be sealed or initialled by the person on whose premises the sample is taken, or the person's representative. Each part shall be marked with the name of the article, any mark applied to the article in compliance with the Law, the date and place of the sampling and some distinguishing number, in such a manner that the particulars so marked can be seen without breaking the seal or seals.

SCHEDULE 2

(ARTICLES 1(5), 4(1), 5(3), 6(3), 7, 8(1) AND 12(2) OF THE LAW)

METHODS OF ANALYSIS OF FERTILISERS

(In this Schedule a "decimal" system has been adopted for the numbering of divisions and sub-divisions. Main divisions are given numbers which precede a decimal point. Each sub-division into which a main division is first divided is distinguished by a digit immediately following the decimal point. For example, the main division 5 is divided into 3 sub-divisions numbered 5.1, 5.2 and 5.3 respectively. Succeeding digits indicate further sub-division with the result that, for example, the sub-division numbered 5.1 may itself be divided into sub-divisions numbered 5.11, 5.12, 5.13 etc., and those sub-divisions may be further divided in the same way (thus, 5.111, 5.112, 5.113, etc.), and so on.)

The main divisions in this Schedule are as follows –

1. Preparation of the Sample for Analysis.
2. Determination of Moisture.
3. Determination of Nitrogen.
4. Determination of Phosphoric Acid.
5. Determination of Potash.
6. Determination of Neutralising Value in Liming Materials.
7. Determination of Magnesium in Lime and Ground Limestone.
8. Determination of Thiocyanate in Ammoniacal gas liquor; Nitrogenous gas liquor; Gas liquor.
9. Determination of Biuret.
10. Determination of Boron.
11. Determination of Cobalt.
12. Determination of Copper.
13. Determination of Iron.
14. Determination of Magnesium.
15. Determination of Manganese.
16. Determination of Molybdenum.
17. Determination of Fineness.

NOTE. References to "water" mean purified water as defined in the British Pharmacopoeia. All reagents used should be of analytical quality.

1. PREPARATION OF THE SAMPLE FOR ANALYSIS.

With some materials, fine grinding may lead to loss or gain of moisture, and allowance for this must be made. Grinding should be as rapid as possible and unnecessary exposure to the atmosphere avoided. Grinding in a laboratory mill is usually quicker than grinding in a mortar although the latter is permissible.

1.1 Procedure

For solid fertilisers, weigh the whole sample and then empty on to a smooth dry surface. Remove, and allow for in the calculation of results, any obvious extraneous matter e.g. metallic particles which may be present in samples of basic slag.

1.11 Dry powered and granular fertilisers.

Grind the sample as rapidly as possible to pass through a sieve having apertures of about 1 mm square.[1] Mix thoroughly and take a representative portion of about 250 g. Grind this portion to pass through the appropriate sieve[2] prescribed in paragraph 1.18 and transfer to a non-corrodible container provided with an air-tight closure.

1.12 Crystalline fertilisers, *e.g.* sulphate of potash and nitrate of soda.

Grind the sample as rapidly as possible to pass through the appropriate sieve prescribed in paragraph 1.18. Mix, withdraw a portion for analysis and grind to a fine condition in a mortar. (If the sample is in a damp condition, grind thoroughly in a mortar until a uniformly fine texture is obtained.) Transfer to a non-corrodible container provided with an air-tight closure.

1.13 Basic slag.

Grind the sample to pass through the appropriate sieve prescribed in paragraph 1.18. Mix thoroughly and transfer to a non-corrodible container provided with an air-tight closure.

1.14 Wool, hair, shoddy, etc.

Prepare coarse organic fertilisers by tearing apart and cutting into a fine condition; some organic fertilisers, e.g. shoddy, may be prepared by a mincing or shredding machine. Prepare for analysis by pulling out or teazing out small

[1]British Standard Test Sieve, Mesh No. 16 is suitable (British Standards for Test Sieves 410 : 1962).
Where an analysis for copper has to be carried out a stainless steel sieve shall be used.
[2] Where an analysis for copper has to be carried out a stainless steel sieve shall be used.

portions of approximately equal size from throughout the bulk prepared as above, mix thoroughly and transfer to a non-corrodible container provided with an air-tight closure.

1.15 Hoof meal.

In the case of hard samples of hoof meal which cannot be ground in the "as received" condition, determine the moisture in the sample by the method described in paragraph 2. Then grind the dried portion in a mill to pass through the appropriate sieve prescribed in paragraph 1.18 and transfer to a non-corrodible container provided with an air-tight closure. Determine the moisture in this prepared sample and calculate the result of analysis of this sample to the "as received" condition.

1.16 Fertilisers in a moist condition.

Mix the sample well and withdraw a portion for moisture determination. Determine the moisture in this portion by the method described in paragraph 2. (In the case of fertilisers in which ammonia is lost on heating or of fertilisers containing soluble phosphoric acid, the sample should be dried either by placing it in a desiccator over calcium chloride or silica gel, or alternatively by passing dry air at room temperature over the sample until it is in a suitable condition for grinding and sieving.) For subsequent analysis, dry a further portion under similar conditions and grind this dried portion in a mortar or mill until the sample passes through the appropriate sieve prescribed in paragraph 1.18. Mix thoroughly and transfer to a non-corrodible container provided with an air-tight closure. Determine the moisture in a portion of this prepared sample. Calculate the results of analysis of the sample to the "as received" condition.

1.17 Liquid fertilisers.

Shake to mix thoroughly, ensuring that any insoluble matter is thoroughly dispersed immediately before drawing a portion of the sample for analysis.

1.18 Sieve

Type of fertiliser	*Sieve apertures*
Basic slag	About 0.15 mm. square[3]
Ground mineral phosphate and granular fertilisers	About 0.25 mm. square[4]
Other dry powdered fertilisers...	About 0.5 mm. square[5]

[3] British Standard Test Sieve, Mesh No. 100 is suitable British Standards for Test Sieves 410 : 1962.
[4] British Standard Test Sieve, Mesh No. 60 is suitable British Standards for Test Sieves 410 : 1962.
[5] British Standard Test Sieve, Mesh No. 30 is suitable British Standards for Test Sieves 410 : 1962.

Crystalline fertilisers and fertilisers containing organic matter	About 1.0 mm. square[6]

2. DETERMINATION OF MOISTURE

Weight to the nearest mg. about 5 g. of the sample, heat at 100°C for 2 to 3 hours, cool in a desiccator and weigh. Reheat for another hour, cool and reweigh. If the difference in weight exceeds 10 mg., continue the heating and cooling procedure until a weight constant within 2 mg. is attained. Calculate the total loss of weight as a percentage of the original weight and regard as moisture.

3. DETERMINATION OF NITROGEN

The relevant methods of analysis are described in the following paragraphs –

3.3 Total nitrogen (organic and ammoniacal) in the absence of nitrates.

3.4 Total nitrogen (organic, ammoniacal and nitrate) in the presence of nitrates.

3.5 Nitrogen in the form of ammonium salts, and nitrogen in nitrogenous gas liquor, ammoniacal gas liquor and gas liquor.

3.6 Nitrogen in nitrates.

3.7 Nitrate nitrogen in the presence of ammoniacal and urea nitrogen.

3.1 Reagents

Aluminium ammonium sulphate.

Devarda alloy – finely powdered – not less than 80% to pass through a sieve having apertures of about 0.25 mm. square.[7]

p-Dimethylaminobenzaldehyde solution – Dissolve 0.4 g. p-dimethylamino-benzaldehyde in 10 ml. concentrated hydrochloric acid and dilute to 100 ml. with propan-2-ol.

Indigo carmine standard solution – Cautiously add 40 ml. concentrated sulphuric acid to 1 g. indigo carmine (B.P. quality) and stir until dissolved. Pour the solution into 800 ml. water, cool and dilute to 1 litre. Adjust the strength of the solution to comply with the following test –

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

Light magnesium oxide.

Mercury or mercuric oxide.

[6] British Standard Test Sieve, Mesh No. 16 is suitable British Standards for Test Sieves 410 : 1962.
[7] British Standard Test Sieve, Mesh No. 60 is suitable (British Standards for Test Sieves 410:1962.)

Methyl red-methylene blue mixed indicator solution –

Mix 2 volumes of methyl red solution and 1 volume of methylene blue solution prepared as follows:

Methyl red solution – Dissolve 0.05 g. methyl red in ethanol and dilute to 100 ml with ethanol.

Methylene blue solution – Dissolve 0.05 g. methylene blue in ethanol and dilute to 100 ml. with ethanol.

Paraffin wax.

Sodium sulphate or potassium sulphate – anhydrous.

Sodium hydroxide solution, 5% w/v – Dissolve 50 g. sodium hydroxide in water and dilute to 1 litre.

Sodium hydroxide solution, 50% w/v – Dissolve 500 g. sodium hydroxide in water and dilute to 1 litre.

Sodium hydroxide, 0.2 N – carbonate free.

Sodium thiosulphate.

Sodium tungstate solution, 10% w/v – Dissolve 10 g. sodium tungstate $Na_2WO_42H_20$ in water and dilute to 100 ml.

Sulphuric acid, concentrated (d=1.84) – nitrogen free.

Sulphuric acid, 5% v/v – To 50 ml. water cautiously add 5 ml. concentrated sulphuric acid (d=1.84). Cool and dilute to 100 ml.

Sulphuric acid, 10% v/v – To 500 ml. water cautiously add 100 ml. concentrated sulphuric acid. Cool and dilute to 1 litre.

Sulphuric acid, 50% v/v – To 500 ml. water cautiously add 500 ml. concentrated sulphuric acid. Cool and dilute to 1 litre.

Sulphuric acid (or hydrochloric acid), 0.2 N.

Urease tablets – of known activity.

3.2 Test for absence of Nitrates.

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

3.3 Total Nitrogen (Organic and Ammoniacal) in the absence of Nitrates.

3.31 Weigh to the nearest mg. about 2 g. of the sample (or such an amount as shall contain not more than 250 mg. nitrogen) and transfer to a Kjeldahl flask. Add 25 ml. concentrated sulphuric acid, 2 small globules of mercury (approximately 400 mg.) or approximately 0.5 g. mercuric oxide, and 10 g. anhydrous sodium sulphate or potassium sulphate. Heat gently over a small flame until frothing ceases and the liquid is

practically colourless. Continue to heat for a further 2 hours. Avoid local overheating. If frothing is excessive, add about 0.5g. paraffin wax.

Dissolve the cooled digest in water, and make up to a total volume of about 250 ml. Taking precautions against loss of ammonia, add sufficient 50% sodium hydroxide solution to neutralise the acid and 10 ml. in excess; then add 5 g. sodium thiosulphate, mix well and connect immediately to a distillation apparatus. Distil into an appropriate volume of 0.2 N acid, controlling the rate of distillation so that not less than 150 ml. distil in 30 minutes. Titrate the excess of acid with 0.2 N sodium hydroxide solution using methyl red-methylene blue mixed indicator solution. Carry out a similar determination using all the reagents omitting only the sample. Calculate the total nitrogen content of the sample. 1 ml. 0.2 N acid ≡ 0.0028g. nitrogen.

3.4 Total Nitrogen (Organic, Ammoniacal and Nitrate) in the presence of Nitrates.

Weigh to the nearest mg. about 2 g. of the sample (or such an amount as shall contain not more than 250 mg. nitrogen), transfer to a 500 ml. Kjeldahl flask, add 3 g. Devarda alloy and wash down the inside wall of the flask with 50 ml. water. Close the flask with a rubber stopper provided with a tap funnel and a delivery tube connected with 2 'U'-tubes (with bulbs) in series, each containing 10 ml. 10% sulphuric acid. Add 5 ml. 50% sodium hydroxide solution through the tap funnel, allow to stand for 30 minutes, and then heat just below boiling point for 60 minutes. Cool, add 20 ml. 50% sulphuric acid through the tap funnel, such that the sides of the flask are washed down by the acid. Remove the rubber stopper, wash the contents of the 'U'-tubes into the Kjeldahl flask, add 30 ml. concentrated sulphuric acid and heat until all the water has boiled off. Heat gently over a small flame until the solution is clear and then heat for a further 2 hours. If frothing is excessive add 0.5 g. paraffin wax. Cool, carefully dilute with water, cool and transfer quantitatively to a 250 ml. volumetric flask. Dilute to 250 ml., mix well and transfer an aliquot of 100 ml. to a 500 ml. distillation flask. Add 200 ml. water and 50% sodium hydroxide solution, until the solution is neutral, cooling during the addition. Add an additional 10 ml. 50% sodium hydroxide, quickly close the distillation flask and distil about 150 ml. into 50 ml. 0.2 N hydrochloric acid. Titrate the excess acid using 0.2 N sodium hydroxide solution and methyl redmethylene blue mixed indicator. Carry out a similar determination using all the reagents omitting only the sample. Calculate the total nitrogen content of the sample. 1 ml. 0.2 N acid ≡ 0.0028 g. nitrogen.

3.5 Nitrogen in the form of Ammonium Salts and Nitrogen in Nitrogenous Gas Liquor, Ammoniacal Gas Liquor or Gas Liquor.

3.51 *In the absence of organic matter.*

Weigh to the nearest mg. about 5 g. of the sample, transfer to a 250 ml. volumetric flask, dissolve in about 200 ml. water and dilute with water to 250 ml. Transfer 50 ml. of the solution (or such a volume as shall contain not more than 250 mg. nitrogen) to a distillation flask, add approximately 300 ml. water and 20 ml. 50% sodium hydroxide solution. Distil into an

appropriate volume of 0.2 N acid at the rate of 250-300 ml. in 30 minutes. Titrate the excess of acid with 0.2 N sodium hydroxide solution using methyl red-methylene blue mixed indicator solution. Carry out a blank test on the reagents and water used omitting only the sample. Calculate the nitrogen content. 1 ml. 0.2 N acid ≡ 0.0028 g. nitrogen.

3.52 *In the presence of organic matter other than urea.*

Weigh to the nearest mg. about 5 g. of the sample, transfer to a 250 ml. volumetric flask, add 200 ml. water and shake well to ensure solution of all the water-soluble matter. Dilute to 250 ml., filter, and complete the determination with 50 ml. of the filtrate by the method described in paragraph 3.51.

3.53 *In the presence of urea.*

Weigh to the nearest mg. about 5 g. of the sample (or such an amount as shall contain not more than 1 g. ammoniacal nitrogen), and transfer to a 250 ml. volumetric flask. Add 200 ml. water, shake well to dissolve soluble salts, dilute to 250 ml. and mix well. Filter a portion through a suitable dry filter paper, rejecting the first 25 ml. and transfer an aliquot of 25 ml. to a thick walled, 1 litre, round bottom flask. Fit a tap funnel, thermometer and an "air-bleed" terminating in a capillary tube reaching to the bottom of the flask as used in distillations under reduced pressure, an efficient spray trap, a double surface condenser and a 750 ml. Buchner flask as receiver. The condenser should reach almost to the bottom of the Buchner flask. Connect the sidearm of the Buchner flask to a vacuum pump and fit a mercury manometer into the system. Control the flow of air through the capillary in the distillation flask by means of a screw clip or similar device, on a thick walled rubber tube fixed to the open end of the capillary tube. Place 50 ml. 0.2 N acid in the Buchner flask and connect to the condenser. Add 250 ml. water and 20 ml. 50% sodium hydroxide solution through the tap funnel to the contents of the distillation flask. Start the vacuum pump, adjust the "air-bleed" to a pressure of approximately 55 mm. of mercury. Heat to a temperature of not greater than 40°C. Distil for 20 minutes. At the end of the distillation, admit air to the apparatus via the tap funnel and disconnect the vacuum pump. Titrate excess acid with 0.2 N sodium hydroxide solution using methyl red-methylene blue mixed indicator. Carry out a similar determination using all the reagents omitting only the sample. Calculate the nitrogen content. 1 ml. 0.2 N acid ≡ 0.0028 g. nitrogen.

3.6 Nitrogen in Nitrates.

Weigh to the nearest mg. about 3 g. of the sample, transfer to a 250 ml. volumetric flask, add 200 ml. water, shake well to ensure complete solution, dilute to 250 ml. and, if necessary, filter. Transfer 50 ml. of the solution or filtrate (or such a volume as shall contain not more than 250 mg. nitrogen) to a distillation flask. Add 10 g. Devarda alloy, 250 ml. water and 15 ml. 50% sodium hydroxide solution. Connect the flask immediately to the distillation apparatus and allow to stand in the cold for 15 minutes. Warm gently for a further 30 minutes, slowly increasing the temperature, and then distil into an appropriate volume of 0.2 N acid at the rate of not less than 150 ml. in 30

minutes (the residual bulk should be small). Titrate the excess acid with 0.2 N sodium hydroxide solution using methyl red-methylene blue mixed indicator solution. Carry out a blank test on the reagents omitting the water solution of the sample. Calculate the nitrogen content. 1 ml. 0.2 N acid ≡ 0.0028 g. nitrogen.

NOTE: If nitrogen in other forms is also present, the method described in paragraph 3.7 should be used.

3.7 Nitrate Nitrogen in the presence of Ammoniacal and Urea Nitrogen.

Weigh to the nearest mg. about 5 g. of the sample (or such an amount as shall contain not more than 2.5 g. nitrate nitrogen), and transfer to a 500 ml. volumetric flask. Add 400 ml. water, shake well to ensure dissolution of all soluble salts, dilute to 500 ml. with water and shake well. Transfer 100 ml. to a 250 ml. beaker, and adjust to pH 6–7 with 5% sodium hydroxide or 5% sulphuric acid solution. Transfer quantitatively to a 250 ml. volumetric flask, dilute to 200 ml. and add sufficient crushed urease tablets to hydrolyse all the urea present, and add 25% in excess. Stopper the flask and allow to stand in a constant temperature bath at 37°C for 3 hours.

Dilute the solution to 250 ml. and mix well. Filter a portion through a suitable dry filter paper and test for absence of urea. (see Note 1). If free from urea, filter the remainder, transfer a 100 ml. aliquot of the urea-free filtrate to a 250 ml. volumetric flask, add 10 ml. sodium tungstate solution or sufficient to precipitate all the protein matter, dilute to 250 ml. with water and mix well. Filter a portion through a suitable dry filter paper, and transfer a 100 ml. aliquot to a 500 ml. distillation flask. Add 200 ml. water, 15 ml. 50% sodium hydroxide solution and distil until 150 ml. is collected. Discard the distillate. Cool the flask, dilute the contents to 300 ml., add 3 g. Devarda alloy and 15 ml. 50% sodium hydroxide solution and immediately connect the flask to the distillation apparatus with the condenser outlet below the surface of 50 ml. 0.2 N acid in the receiver. Allow to stand in the cold for 15 minutes, warm for 30 minutes, slowly increasing the temperature, and then distil 150 ml. into the receiver. Titrate the excess acid with 0.2 N sodium hydroxide using methyl red-methylene blue mixed indicator. Calculate the nitrate nitrogen content of the sample after making allowance for the reagent blank. (see Note 2).

NOTE 1.

The test for urea is carried out as described in (i) and (ii) below.

(i) Instrumental Method.

Transfer a 50 ml. aliquot of the solution after urease treatment to a 100 ml. stoppered cylinder, adjust to pH 5, add 1 g. of activated charcoal and 5 ml. each of Carrez solutions 1 and 2 (see method for determination of urea – paragraph 5 of Schedule 3). Dilute to 70 ml., mix well and filter a portion through a suitable dry filter paper. Transfer 35 ml. of the filtrate to a 50 ml. flask add 10 ml. p-dimethylaminobenzaldehyde solution, dilute to 50 ml. and mix well. Allow to stand 10 minutes and compare the extinction at 435 nm. in a 1 cm. cell with that of a blank test carried through the method described, omitting only the sample. The amount of urea

present should not exceed 0.5 mg., determined from a previously prepared calibration curve.

(ii) Visual Method.

Transfer a 50 ml. aliquot of the solution after urease treatment to a 100 ml. stoppered cylinder, adjust to pH 5, add 1 g. activated charcoal and 5 ml. each of Carrez solutions 1 and 2 (see method for determination of urea – paragraph 5 of Schedule 3).

Dilute to 70 ml., mix well and filter a portion through a suitable dry filter paper. Transfer 35 ml. of the filtrate to a Nessler tube, add 10 ml. of p-dimethylaminobenzaldehyde solution, dilute to 50 ml. with water and mix well. To a 50 ml. aliquot of the blank solution prepared for the determination of nitrate, add 1 mg. of urea and treat exactly as described above. This is the control solution. The depth of colour of the sample solution should not exceed that of the control solution.

NOTE 2.

Carry out a similar determination using all the reagents as in the method described, omitting only the sample. The reagent blank is required at 2 stages in the determination, namely in the test for absence of urea, and in the determination of the nitrate nitrogen.

4. DETERMINATION OF PHOSPHORIC ACID.

For the purposes of the Law "phosphoric acid" means P_2O_5 (molecular weight 142.04).

Phosphoric acid may be determined by the quinolinium phosphomolybdate method or, alternatively, by the spectrophotometric (vanadium phosphomolybdate) method.

The quinolinium phosphomolybdate method depends on the precipitation of quinolinium phosphomolybdate under carefully controlled conditions; citric acid is added in appropriate amounts to prevent interference by soluble silica or ammonium salts in the amounts present in the materials to be analysed. The spectrophotometric method compares the amount of light transmitted by the solution to that by a solution of known phosphoric acid content. The determination is carried out differentially in order to increase the accuracy. Preferably an instrument with a monochromator giving a source of light with a wavelength of 420 mm. is required; alternatively a filter instrument can be used.

Phosphoric acid in materials other than basic slag, dicalcium phosphate, precipitated bone phosphate and dicalcium bone phosphate may be required to be determined as water-soluble and water-insoluble and as total phosphoric acid. In the analysis of basic slag, dicalcium phosphate, precipitated bone phosphate and dicalcium bone phosphate, solubility in a 2% solution of citric acid is substituted for solubility in water. Because of the chemical composition of basic slag, the methods of analysis differ in several respects from the methods for other fertilisers when the quinolinium phosphomolybdate method is used; these modified methods are given separately in paragraphs 4.16 and 4.17. When phosphoric acid soluble in citric acid is being determined by the

spectrophotometric method, certain modifications in the procedure for the standardisation of the spectrophotometer are necessary and these are given separately in paragraphs 4.26 and 4.27.

The relevant methods of analysis are described in the following paragraphs –

4.12 and 4.22 Total phosphoric acid in fertilisers other than basic slag.

4.13 and 4.23 Water-soluble phosphoric acid.

4.14 and 4.24 Water-insoluble phosphoric acid.

4.15 and 4.25 Citric acid-soluble phosphoric acid in fertilisers other than basic slag.

4.16 and 4.26 Total phosphoric acid in basic slag.

4.17 and 4.27 Citric acid-soluble phosphoric acid in basic slag.

4.1 Quinolinium Phosphomolybdate method

4.11 Reagents.

Calcium oxide – finely ground.

Calcium carbonate.

Citric acid – monohydrate.

Citric-molybdic acid solution (A), for use in the determination of water-soluble, citric acid-soluble and total phosphoric acid in fertilisers other than basic slag – Stir 54 g. *molybdenum trioxide* ($Mo0_3$) with 200 ml. water, add 11 g. *sodium hydroxide* and stir the mixture, whilst heating to boiling point until the *molybdenum trioxide* dissolves. Dissolve 60 g. citric acid in about 250 to 300 ml. water and add 140 ml. concentrated hydrochloric acid. Pour the *molybdate* solution into the acid solution, which is stirred throughout the addition. Then cool and, if necessary, filter the solution through a paper pulp pad. Dilute the solution to 1 litre. If the solution is slightly green or blue in colour, add dropwise a dilute (0.5 or 1.0%) solution of *potassium bromate* until the colour is discharged. This reagent should be kept in the dark.

Citric-molybdic acid solution (B), for use in the determination of citric acid-soluble and total phosphoric acid in basic slag – Stir 54 g. *molybdenum trioxide* ($Mo0_3$) with 200 ml. water, add 11 g. *sodium hydroxide* and stir the mixture, whilst heating to boiling point until the *molybdenum trioxide* dissolves. Dissolve 120 g. citric acid in about 250 to 300 ml. water and add 140 ml. concentrated hydrochloric acid. Pour the *molybdate* solution into the acid solution, which is stirred throughout the addition. Then cool and, if necessary, filter the solution through a paper pulp pad. Dilute the solution to 1 litre. If the solution is slightly green or blue in colour, add dropwise a dilute (0.5 or 1.0%) solution of potassium bromate until the colour is discharged. This reagent should be kept in the dark.

Hydrochloric acid, concentrated (d =1.18).

Hydrochloric acid, 25% *v/v* – Dilute 25 ml. concentrated hydrochloric acid with water to 100 ml.

Hydrochloric acid, 0.1 N.

Hydrochloric acid, 0.5 N.

Indicator solution – Mix 3 volumes of thymol blue solution and 2 volumes of *phenolphthalein* solution prepared as follows –

Thymol blue solution – Dissolve 0.25 g. thymol blue in 5.5 ml. 0.1 N sodium hydroxide solution and 125 ml. industrial methylated spirit. Dilute with water to 250 ml.

Phenolphthalein solution – Dissolve 0.25 g. *phenolphthalein* in 150 ml. industrial methylated spirit and dilute with water to 250 ml.

Nitric acid, concentrated (d =1.42).

Quinoline solution – Measure 60 ml. concentrated hydrochloric acid and 300 to 400 ml. water into a 1 litre beaker and warm to 70–80°C. Pour 50 ml. quinoline in a thin stream into the diluted acid, whilst stirring. When the quinoline has dissolved, cool the solution, dilute to 1 litre and, if necessary, filter through a paper pulp filter.

Sodium hydroxide, 5 N.

Sodium hydroxide, 0.1 *N* – carbonate free.

Sodium hydroxide, 0.5 *N* – carbonate free.

Surface active agent – 0.5% solution of sodium dodecylbenzene-sulphonate is suitable.

4.12 Total phosphoric acid in fertilisers other than basic slag.

4.121 DISSOLUTION OF THE SAMPLE.

4.1211 In the absence of organic matter

Weigh to the nearest mg. about 5 g. of the sample into a 400 ml. beaker, add 100 ml. water and stir thoroughly. Boil the mixture, add slowly to the boiling solution 10 ml. concentrated hydrochloric acid in a thin stream, and then 10 ml. concentrated nitric acid; boil gently for 10 minutes, cool, transfer to a 500 ml. volumetric flask and dilute to the mark with water. Mix well and filter the solution through a dry filter paper into a dry flask, discarding the first 10 or 20 ml. Retain the rest of the filtrate.

4.1212 In the presence of organic matter.

Weigh to the nearest mg. about 5 g. of the sample into a capsule or dish of about 5 cm. in diameter; add 1 g. calcium oxide and mix well with a stout platinum wire or thin glass rod. Calcine the mixture at a temperature not exceeding 500°C to destroy the organic matter. Allow the capsule or dish to cool and transfer the contents to a 400 ml. beaker; add 100 ml. water, stir thoroughly and heat to boiling point.

Add slowly to the boiling solution 10 ml. concentrated hydrochloric acid, and then 10 ml. concentrated nitric acid, and boil gently.

If the solution is clear, continue to boil gently for 10 minutes, then cool, transfer to a 500 ml. volumetric flask and dilute to the mark.

If the solution shows the presence of carbonaceous matter, filter the solution, wash the insoluble matter with a little water and then transfer the filter paper containing the insoluble matter to the capsule or dish and calcine until all the carbon is destroyed. Allow to cool and transfer the contents to the filtrate; heat to boiling point and gently boil for 10 minutes. Then cool, transfer to a 500 ml. volumetric flask and dilute to the mark. Filter.

4.122 PROCEDURE.

Transfer a volume of the solution prepared according to paragraph 4.1211 or paragraph 4.1212 containing less than 70 mg. phosphoric acid and preferably about 50 mg. to a 500 ml. stoppered conical flask marked at 150 ml. Dilute the solution with water to 100 ml. If the sample does not contain calcium add 100 to 200 mg. calcium carbonate. Then add 5 N sodium hydroxide solution dropwise until a faint permanent turbidity or precipitate is formed. Dissolve the precipitate by the dropwise addition of 25% hydrochloric acid, but avoid an excess.

Dilute to 150 ml. add 50 ml. of the citric-molybdic acid reagent (A), heat the solution to incipient ebullition, maintain it at this temperature for 3 minutes and then bring it to the boiling point. From a burette slowly add 25 ml. of the quinoline solution, with constant swirling throughout, the first few ml. being added dropwise, the rest in a slow stream. Keep the solution gently boiling during the addition. Immerse the flask in boiling water for 5 minutes, then cool it to 15°C in running water.

Filter with suction the contents of the flask on a paper pad and wash the flask, precipitate and filter with successive small washes of cold water until they are free from acid. Transfer the filter pad and precipitate to the original flask, rinse the funnel with water and collect the rinsings in the flask. If necessary, wipe the funnel with a small piece of damp filter paper to ensure complete removal of the precipitate, and place the paper in the flask. Add water to a total of about but not exceeding 100 ml. Stopper the flask and shake it vigorously until the pulp and precipitate are completely dispersed.

Remove the stopper and wash it with water, returning the washings to the flask. Add a measured volume of 0.5 N sodium hydroxide solution sufficient to dissolve the precipitate and leave a few ml. in excess. Shake the flask vigorously until all the precipitate dissolves. (To facilitate the dispersal of the precipitate, after addition of 0.5 N sodium hydroxide solution, a few drops of the surface active agent may be added if necessary.) Add 0.5–1.0 ml. of the indicator solution and titrate the excess of sodium hydroxide with the 0.5 N hydrochloric acid until the indicator changes from violet to green-blue and then very sharply to yellow at the end point. Deduct the number of ml. of 0.5 N hydrochloric

acid used from the number of ml. 0.5 N sodium hydroxide, to ascertain the volume of 0.5 N sodium hydroxide equivalent to the phosphoric acid.

Carry out a blank determination on all the reagents, omitting only the sample, and using 0.1 N standard alkali and acid instead of 0.5 N for the titration. Calculate the blank in terms of 0.5 N alkali and subtract it from the original result.

Calculate the amount of phosphoric acid in the portion taken for analysis from the factor 1.0 ml. 0.5 N sodium hydroxide ≡ 1.366 mg. P_2O_5.

4.13 Water soluble phosphoric acid.

4.131 EXTRACTION OF THE SAMPLE.

Weigh to the nearest centigram about 10 g. of the sample and transfer to a 500 ml. volumetric flask; add 400 ml. water at 20°C and shake the flask continuously for 30 minutes. Dilute the contents to the mark, mix well and filter.

4.132 PROCEDURE.

Transfer a volume of the aqueous extract containing less than 70 mg. of phosphoric acid and preferably about 50 mg. to a 500 ml. stoppered conical flask marked at 150 ml. Dilute with water to 150 ml. add 50 ml. of the citric-molybdic acid reagent (A), heat the solution to incipient ebullition, maintain it at this temperature for 3 minutes, and then bring it to the boiling point. From a burette slowly add 25 ml. of the quinoline solution with constant swirling throughout, the first few ml. being added dropwise, the rest in a slow stream. Keep the solution gently boiling during the addition. Immerse the flask in boiling water for 5 minutes, then cool it to 15°C in running water.

Filter with suction the contents of the flask on a paper pulp pad, and wash the flask, precipitate and filter with successive small washes of cold water until they are free from acid. Transfer the filter pad and precipitate to the original flask, rinse the funnel with water and collect the rinsings in the flask. If necessary, wipe the funnel with a small piece of damp filter paper to ensure complete removal of the precipitate, and place the paper in the flask. Add water to a total of about but not exceeding 100 ml. Stopper the flask and shake it vigorously until the pulp and precipitate are completely dispersed.

Remove the stopper and wash it with water, returning the washings to the flask. Add a measured volume of 0.5 N sodium hydroxide solution sufficient to dissolve the precipitate and leave a few ml. in excess. Shake the flask vigorously until all the precipitate dissolves. (To facilitate the dispersal of the precipitate, after addition of 0.5 N sodium hydroxide solution, a few drops of the surface active agent may be added if necessary.) Add 0.5–1.0 ml. of the indicator solution, and titrate the excess of sodium hydroxide with the 0.5 N hydrochloric acid until the indicator changes from violet to green-blue and then very sharply to yellow at the end point. Deduct the number of ml. of 0.5 N hydrochloric

acid used from the number of ml. 0.5 N sodium hydroxide, to ascertain the volume of 0.5 N sodium hydroxide equivalent to the phosphoric acid.

Carry out a blank determination on all the reagents, omitting only the sample and using 0.1 N standard alkali and acid instead of 0.5 N for the titration. Calculate the blank in terms of 0.5 N alkali and subtract it from the original result.

Calculate the amount of phosphoric acid in the portion taken for analysis from the factor 1.0 ml. 0.5 N sodium hydroxide ≡ 1.366 mg. P_2O_5.

4.14 Water-insoluble phosphoric acid.

Determine the water-insoluble phosphoric acid as the difference between the total phosphoric acid determined by the method described in paragraph 4.12 and the water-soluble phosphoric acid determined by the method described in paragraph 4.13.

4.15 Citric acid-soluble phosphoric acid in fertilisers other than basic slag.

4.151 PREPARATION OF THE SOLUTION.

Weigh to the nearest mg. about 5 g. of the sample and transfer to a stoppered bottle of about 1 litre capacity. Dissolve 10 g. citric acid monohydrate in water, dilute to 500 ml. and adjust the temperature to 20°C. Add the solution to the sample in the bottle, shaking so as to avoid the possibility of caking. Shake the bottle continuously for 30 minutes. Pour the whole of the liquid at once on to a large medium-fine filter and collect the filtrate. If the filtrate is not clear, pass it again through the same filter.

4.152 PROCEDURE.

Transfer a volume of the solution prepared according to paragraph 4.151 containing less than 70 mg. phosphoric acid and preferably about 50 mg. to a 500 ml. stoppered conical flask marked at 150 ml. Dilute the solution with water to 100 ml. If the sample does not contain calcium add 100 to 200 mg. calcium carbonate. Then add 5 N. sodium hydroxide solution dropwise until a faint permanent turbidity or precipitate is formed. Dissolve the precipitate by the dropwise addition of 25% hydrochloric acid, but avoid an excess.

Dilute to 150 ml. and add 50 ml. of the citric-molybdic acid reagent (A); heat the solution to incipient ebullition, maintain it at this temperature for 3 minutes and then bring it to the boiling point. From a burette slowly add 25 ml. of the quinoline solution with constant swirling throughout, the first few ml being added dropwise, the rest in a slow stream. Keep the solution gently boiling during the addition. Immerse the flask in boiling water for 5 minutes, then cool it to 15°C in running water.

Filter with suction the contents of the flask on a paper pulp pad, and wash the flask, precipitate and filter with successive small washes of cold water until they are free from acid. Transfer the filter pad and precipitate to the original flask, rinse the funnel with water and collect the rinsings in the flask. If necessary, wipe the funnel with a small piece of damp filter

paper to ensure complete removal of the precipitate, and place the paper in the flask. Add water to a total of about but not exceeding 100 ml. Stopper the flask and shake it vigorously until the pulp and precipitate are completely dispersed.

Remove the stopper and wash it with water, returning the washings to the flask. Add a measured volume of 0.5 N sodium hydroxide solution sufficient to dissolve the precipitate and leave a few ml. in excess. Shake the flask vigorously until all the precipitate dissolves. (To facilitate the dispersal of the precipitate, after addition of 0.5 N sodium hydroxide solution, a few drops of the surface active agent may be added if necessary.) Add 0.5–1.0 ml. of the indicator solution, and titrate the excess of sodium hydroxide with the 0.5 N hydrochloric acid until the indicator changes from violet to green-blue and then very sharply to yellow at the end point. Deduct the number of ml. of 0.5 N hydrochloric acid used from the number of ml. 0.5 N sodium hydroxide, to ascertain the volume of 0.5 N sodium hydroxide equivalent to the phosphoric acid.

Carry out a blank determination on all the reagents, omitting only the sample, and using 0.1 N standard alkali and acid instead of 0.5 N for the titration. Calculate the blank in terms of 0.5 N alkali and subtract it from the original result.

Calculate the amount of phosphoric acid in the portion taken for analysis from the factor 1.0 ml. 0.5 N sodium hydroxide ≡ 1.366 mg. P_2O_5.

4.16 Total phosphoric acid in basic slag.

4.161 PREPARATION OF THE SOLUTION.

Weigh to the nearest mg. about 2.5 g of the sample into a 400 ml. beaker, wet the solid thoroughly with 20 to 30 ml. water and then add a further 70 ml. water with continuous stirring. Warm the mixture and add dropwise with stirring, 10 ml. concentrated hydrochloric acid, then 5 ml. concentrated nitric acid. Gently boil the solution for 10 minutes, cool, and dilute to 250 ml. in a volumetric flask. Mix well. Filter the solution through a dry medium-fine filter paper into a dry beaker, rejecting the first 20 to 30 ml. of the filtrate.

4.162 PROCEDURE.

Transfer a volume of the solution prepared according to paragraph 4.161, containing less than 70 mg. phosphoric acid and preferably about 50 mg. to a 500 ml. stoppered conical flask marked at 150 ml. Dilute the solution with water to about 100 ml., heat almost to boiling and then add 5 N sodium hydroxide solution dropwise until a faint permanent turbidity or precipitate is formed. Add a few drops of concentrated hydrochloric acid to clear the solution while it is still boiling. Dilute to 150 ml. and add 1 g. citric acid and then 50 ml. of the citric-molybdic acid reagent (B). Boil the solution gently for 3 minutes. From a burette slowly add 25 ml. of the quinoline solution with constant swirling throughout, the first few ml. being added dropwise, the rest in a slow stream. Again heat to boiling and boil gently for 1 to 2 minutes. Immerse the flask in boiling water for 5 minutes and then cool the flask and its contents to 15°C in running water.

Filter with suction the contents of the flask on a paper pulp pad and wash the flask, precipitate and filter with successive small washes of cold water until they are free from acid. Transfer the filter pad and precipitate to the original flask, rinse the funnel with water and collect the rinsings in the flask. If necessary, wipe the funnel with a small piece of damp filter paper to ensure complete removal of the precipitate and place the paper in the flask. Add water to about but not exceeding 100 ml., stopper the flask and shake it vigorously until the pulp and precipitate are completely dispersed.

Remove the stopper and wash it with water, returning the washings to the flask. Add a measured volume of 0.5 N sodium hydroxide solution sufficient to dissolve the precipitate and leave a few ml. in excess. Shake the flask vigorously until all the precipitate dissolves. (To facilitate the dispersal of the precipitate, after addition of 0.5 N sodium hydroxide solution, a few drops of the surface active agent may be added if necessary.) Add 0.5–1.0 ml. of the indicator solution and titrate the excess of sodium hydroxide with the 0.5 N hydrochloric acid until the indicator changes from violet to green-blue and then very sharply to yellow at the end point. Deduct the number of ml. of 0.5 N hydrochloric acid used from the number of ml. 0.5 N sodium hydroxide to ascertain the volume of 0.5 N sodium hydroxide equivalent to the phosphoric acid.

Carry out a blank determination on all the reagents, omitting only the sample, and using 0.1 N standard alkali and acid instead of 0.5 N for the titration. Calculate the blank in terms of 0.5 N alkali and subtract it from the original result.

Calculate the amount of phosphoric acid in the portion taken for analysis from the factor 1 ml. 0.5 N sodium hydroxide solution ≡ 1.366 mg. P_2O_5.

4.17 Citric acid-soluble phosphoric acid in basic slag.

4.171 PREPARATION OF THE SOLUTION.

Weigh to the nearest mg. about 5 g. of the sample and transfer to a stoppered bottle of about 1 litre capacity. Dissolve 10 g. citric acid monohydrate in water, dilute to 500 ml. and adjust the temperature to 20°C. Add the solution to the sample in the bottle, shaking so as to avoid the possibility of caking. Shake the bottle continuously for 30 minutes. Pour the whole of the liquid at once on to a large medium-fine filter and collect the filtrate. If the filtrate is not clear, pass it again through the same filter.

4.172 PROCEDURE.

Transfer a volume of the solution prepared according to paragraph 4.171 containing less than 70 mg. phosphoric acid and preferably about 50 mg. to a 500 ml. stoppered conical flask marked at 150 ml. Dilute the solution with water to 150 ml., heat almost to boiling and then add 50 ml. of the citric-molybdic acid reagent (B). Boil the solution gently for 3 minutes. From a burette slowly add 25 ml. of the quinoline solution with constant swirling throughout, the first few ml. being added dropwise, the rest in a slow stream. Again heat to boiling and boil gently for 1 to 2 minutes.

Immerse the flask in boiling water for 5 minutes and then cool the flask and its contents to 15°C in running water.

Filter with suction the contents of the flask on a paper pulp pad and wash the flask, precipitate and filter with successive small washes of cold water until they are free from acid. Transfer the filter pad and precipitate to the original flask, rinse the funnel with water and collect the rinsings in the flask. If necessary wipe the funnel with a small piece of damp filter paper to ensure complete removal of the precipitate, and place the paper in the flask. Add water to about but not exceeding 100 ml., stopper the flask and shake it vigorously until the pulp and precipitate are completely dispersed.

Add a measured volume of 0.5 N sodium hydroxide solution sufficient to dissolve the precipitate and leave a few ml. in excess. Shake the flask vigorously until all the precipitate dissolves. (To facilitate the dispersal of the precipitate after addition of 0.5 N sodium hydroxide solution, a few drops of the surface active agent may be added if necessary.) Add 0.5–1.0 ml. of the indicator solution and titrate the excess of sodium hydroxide with the 0.5 N hydrochloric acid until the indicator changes from violet to green-blue and then very sharply to yellow at the end point. Deduct the number of ml. of 0.5 N hydrochloric acid used from the number of ml. 0.5 N sodium hydroxide to ascertain the volume of 0.5 N sodium hydroxide equivalent to the phosphoric acid.

Carry out a blank determination on all the reagents, omitting only the sample, and using 0.1 N standard alkali and acid instead of 0.5 N for the titration. Calculate the blank in terms of 0.5 N alkali and subtract it from the original result.

Calculate the amount of phosphoric acid in the portion taken for analysis from the factor 1 ml. 0.5 N sodium hydroxide solution ≡ 1.366 mg. P_2O_5.

4.2 Spectrophotometric (Vanadium Phosphomolybdate) method

4.21 Reagents

Calcium oxide – finely ground.

Citric acid – monohydrate.

Hydrochloric acid, concentrated (d=1.18).

Nitric acid, concentrated (d=1.42).

Potassium dihydrogen phosphate solution (*stock phosphate solution*) – Dissolve in water 1.917 g. potassium dihydrogen phosphate previously dried at 105°C for 1 hour and dilute to 1 litre.

Potassium dihydrogen phosphate solution (*standard phosphate solution*) – Dilute 50 ml. stock solution to 250 ml. with water. (1 ml. ≡ 0.2 mg. phosphoric acid (P_2O_5)).

Sodium hydroxide, N.

Vanado-molybdate reagent – Dissolve separately 20 g. ammonium molybdate and 1 g. ammonium vanadate in water, mix, acidify with 140 ml. concentrated nitric acid and dilute to 1 litre.

4.22 Total phosphoric acid in fertilisers other than basic slag.

4.221 DISSOLUTION OF THE SAMPLE.

4.2211 In the absence of organic matter.

Weigh to the nearest mg. about 5 g. of the sample into a 400 ml. beaker, add 100 ml. water and stir thoroughly. Boil the mixture, add slowly to the boiling solution 10 ml. concentrated hydrochloric acid in a thin stream, and then 10 ml. concentrated nitric acid; boil gently for 10 minutes, cool, transfer to a 500 ml. volumetric flask and dilute to the mark with water. Mix well and filter the solution through a dry filter paper into a dry flask, discarding the first 10 or 20 ml. Retain the rest of the filtrate.

4.2212 In the presence of organic matter.

Weigh to the nearest mg. about 5 g. of the sample into a capsule or dish of about 5 cm. in diameter; add 1 g. calcium oxide and mix well with a stout platinum wire or thin glass rod. Calcine the mixture at a temperature not exceeding 500°C to destroy the organic matter. Allow the capsule or dish to cool and transfer the contents to a 400 ml. beaker; add 100 ml. water, stir thoroughly and heat to boiling point. Add slowly to the boiling solution 10 ml. concentrated hydrochloric acid, and then 10 ml. concentrated nitric acid, and boil gently.

If the solution is clear, continue to boil gently for 10 minutes, then cool, transfer to a 500 ml. volumetric flask, and dilute to the mark.

If the solution shows the presence of carbonaceous matter, filter the solution, wash the insoluble matter with a little water, and then transfer the filter paper containing the insoluble matter to the capsule or dish and calcine until all the carbon is destroyed. Allow to cool and transfer the contents to the filtrate; heat to boiling point and gently boil for 10 minutes. Then cool, transfer to a 500 ml. volumetric flask and dilute to the mark. Filter.

4.222 PROCEDURE.

4.2221 *Standardisation of instrument.*

From a burette, measure into a series of 100 ml. volumetric flasks 25.0, 26.0, 27.0, 28.0, 29.0, 30.0 and 31.0 ml. of the standard phosphate solution (i.e. 5.0, 5.2, 5.4, 5.6, 5.8, 6.0 and 6.2 mg. phosphoric acid). Add 25 ml. of the vanado-molybdate reagent to each flask and dilute to 100 ml. with water, making sure that the temperature of the reagent and the dilution water is 20°C. Shake and allow to stand for 10 minutes.

Set the spectrophotometer to the correct wavelength, *circa* 420 nm., fill two 1 cm. cells with the 5.0 mg. solution and check the extinction of the cells. If there is a small difference, select the cell with the smaller reading as the standard reference cell.

Determine the apparent extinction at 20°C (corrected for cell differences) of the 5.2, 5.4, 5.6, 5.8, 6.0 and 6.2 mg. phosphoric acid solutions referred to the 5.0 mg. phosphoric acid solution as standard.

Plot a calibration graph of scale readings against known phosphoric acid content.

4.2222 *Analysis of sample.*

Successively dilute a portion of the solution prepared according to paragraph 4.2211 or paragraph 4.2212 so that the final volume of about 25 mls. contain between 5.5 and 6.2 mg. phosphoric acid, taking care that the dilution water is at a temperature of 20°C.

Transfer this final volume to a 100 ml. volumetric flask, add 25 ml. of the vanado-molybdate reagent (at a temperature of 20°C), dilute to the mark, mix, and allow to stand for 10 minutes. At the same time transfer 25 ml. of the standard phosphate solution (at 20°C) into a second 100 ml. volumetric flask. Add 25 ml. of the vanado-molybdate reagent (at 20°C), dilute to the mark, mix, and allow to stand for 10 minutes.

Measure the difference in extinction at 20°C between the two solutions and estimate the phosphoric acid content of the volume of the unknown solution from the calibration graph.

Calculate the phosphoric acid content of the sample from dilution factors and the weight of the sample.

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

4.23 Water-soluble phosphoric acid.

4.231 EXTRACTION OF THE SAMPLE.

Weigh to the nearest centigram about 10 g. of the sample and transfer to a 500 ml. volumetric flask; add 400 ml. water at 20°C, and shake the flask continuously for 30 minutes. Dilute the contents to the mark, mix well and filter.

4.232 PROCEDURE.

4.2321 *Standardisation of instrument.*

From a burette measure into a series of 100 ml. volumetric flasks 25.0, 26.0, 27.0, 28.0, 29.0, 30.0 and 31.0 ml. of the standard phosphate solution (i.e. 5.0, 5.2, 5.4, 5.6, 5.8, 6.0 and 6.2 mg. phosphoric acid). Add 25 ml. of the vanado-molybdate reagent to each flask and dilute to 100 ml. with water, making sure that the temperature of the reagent and the dilution water is 20°C. Shake and allow to stand for 10 minutes.

Set the spectrophotometer to the correct wavelength, *circa* 420 nm., fill 2 1 cm. cells with the 5.0 mg. solution and check the extinction of the cells. If there is a small difference, select the cell with the smaller reading as the standard reference cell.

Determine the apparent extinction at 20°C (corrected for cell differences) of the 5.2, 5.4, 5.6, 5.8, 6.0 and 6.2 mg. phosphoric acid solutions referred to the 5.0 mg. phosphoric acid solution as standard.

Plot a calibration graph of scale readings against known phosphoric acid content.

4.2322 *Analysis of sample.*

To 25 ml of the solution prepared according to paragraph 4.231, add 1 ml. concentrated nitric acid; heat to incipient ebullition on a hotplate and maintain it at this temperature for 10 minutes. Cool, neutralise with N sodium hydroxide solution and then successively dilute until a final volume of about 25 ml. contains between 5.5 and 6.2 mg. phosphoric acid, taking care that the dilution water is at a temperature of 20°C.

Transfer this final volume to a 100 ml. volumetric flask, add 25 ml. of the vanado-molybdate reagent (at a temperature of 20°C), dilute to the mark, mix, and allow to stand for 10 minutes. At the same time, transfer 25 ml. of the standard phosphate solution (at 20°C) into a second 100 ml. volumetric flask. Add 25 ml. of the vanado-molybdate reagent (at 20°C), dilute to the mark, mix, and allow to stand for 10 minutes.

Measure the difference in extinction at 20°C between the 2 solutions and estimate the phosphoric acid content of the volume of the unknown solution from the calibration graph.

Calculate the phosphoric acid content of the sample from known dilution factors and the weight of the sample.

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

4.24 Water-insoluble phosphoric acid.

Determine the water-insoluble phosphoric acid as the difference between the total phosphoric acid determined by the method described in paragraph 4.22 and the water-soluble phosphoric acid determined by the method described in paragraph 4.23.

4.25 Citric acid-soluble phosphoric acid in fertilisers other than basic slag.

4.251 PREPARATION OF THE SOLUTION.

Weigh to the nearest mg. about 5 g. of the sample and transfer to a stoppered bottle of about 1 litre capacity. Dissolve 10 g. citric acid monohydrate in water, dilute to 500 ml. and adjust the temperature to 20°C. Add the solution to the sample in the bottle, shaking so as to avoid the possibility of caking. Shake the bottle continuously for 30 minutes. Pour the whole of the liquid at once on to a large medium-fine filter and collect the filtrate. If the filtrate is not clear, pass it again through the same filter.

4.252 PROCEDURE.

4.2521 Standardisation of instrument.

From a burette measure into a series of 100 ml. volumetric flasks 25.0, 26.0, 27.0, 28.0, 29.0, 30.0, and 31.0 ml. of the standard phosphate solution (i.e. 5.0, 5.2, 5.4, 5.6, 5.8, 6.0 and 6.2 mg. phosphoric acid). Add to each flask a quantity of citric acid equal to that in the "final volume of about 25 ml." of the sample under examination quoted in paragraph 4.2522. Add 25 ml. of the vanado-molybdate reagent to each flask and dilute to 100 ml. with water, making sure that the temperature of the reagent and the dilution water is 20°C. Shake and allow to stand for 10 minutes.

Set the spectrophotometer to the correct wavelength, say 420 nm., fill 2 1 cm. cells with the 5.0 mg. solution and check the extinction of the cells. If there is a small difference, select the cell with the smaller reading as the standard reference cell.

Determine the apparent extinction at 20°C (corrected for cell differences) of the 5.2, 5.4, 5.6, 5.8, 6.0 and 6.2 mg. phosphoric acid solutions referred to the 5.0 mg. phosphoric acid solution as standard. Plot a calibration graph of scale readings against known phosphoric acid content.

4.2522 Analysis of sample.

Successively dilute a portion of the solution prepared according to paragraph 4.251 so that the final volume of about 25 ml. contains between 5.5 and 6.2 mg. phosphoric acid, taking care that the dilution water is at a temperature of 20°C.

Transfer this final volume to a 100 ml. volumetric flask, add 25 ml. of the vanado-molybdate reagent (at a temperature of 20°C), dilute to the mark, mix, and allow to stand for 10 minutes. At the same time, transfer 25 ml. of the standard phosphate solution (at 20°C) into a second 100 ml. volumetric flask, add sufficient citric acid to obtain a concentration in the final 100 ml. equal to that of the sample solution. Then add 25 ml. of the vanado-molybdate reagent (at 20°C), dilute to the mark, mix, and allow to stand for 10 minutes.

Measure the difference in extinction at 20°C between the 2 solutions and estimate the phosphoric acid content of the volume of the unknown solution from the calibration graph.

Calculate the phosphoric acid content of the sample from known dilution factors and the weight of the sample.

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

4.26 Total phosphoric acid in basic slag.

4.261 PREPARATION OF THE SOLUTION.

Weigh to the nearest mg. about 2.5 g. of the sample into a 400 ml. beaker, wet the solid thoroughly with 20 to 30 ml. water and then add a further 70 ml. water with continuous stirring. Warm the mixture and add dropwise

with stirring, 10 ml. concentrated hydrochloric acid, then 5 ml. concentrated nitric acid. Gently boil the solution for 10 minutes, cool, transfer to a 250 ml. volumetric flask, and dilute to the mark with water. Mix well. Filter the solution through a dry medium-fine filter paper into a dry beaker, rejecting the first 20 to 30 ml. of the filtrate.

4.262 PROCEDURE.

4.2621 Standardisation of instrument.

From a burette, measure into a series of 100 ml. volumetric flasks 25.0, 26.0, 27.0, 28.0, 29.0, 30.0 and 31.0 ml. of the standard phosphate solution (i.e. 5.0, 5.2, 5.4, 5.6, 5.8, 6.0 and 6.2 mg. phosphoric acid). Add 25 ml. of the vanado-molybdate reagent to each flask and dilute to 100 ml. with water, making sure that the temperature of the reagent and the dilution water is 20° C. Shake and allow to stand for 10 minutes.

Set the spectrophotometer to the correct wavelength, *circa* 420 nm., fill 2 1 cm. cells with the 5.0 mg. solution and check the extinction of the cells. If there is a small difference, select the cell with the smaller reading as the standard reference cell.

Determine the apparent extinction at 20°C (corrected for cell differences) of the 5.2, 5.4, 5.6, 5.8, 6.0 and 6.2 mg. phosphoric acid solutions referred to the 5.0 mg. phosphoric acid solution as standard.

Plot a calibration graph of scale readings against known phosphoric acid content.

4.2622 Analysis of sample.

Successively dilute a portion of the solution prepared according to paragraph 4.261 so that the final volume of about 25 ml. contains between 5.5 and 6.2 mg. phosphoric acid, taking care that the dilution water is at a temperature of 20°C.

Transfer this final volume to a 100 ml. volumetric flask, add 25 ml. of the vanado-molybdate reagent (at a temperature of 20°C), dilute to the mark, mix, and allow to stand for 10 minutes. At the same time, transfer 25 ml. of the standard phosphate solution (at 20°C) into a second 100 ml. volumetric flask. Add 25 ml. of the vanado-molybdate reagent (at 20°C), dilute to the mark, mix, and allow to stand for 10 minutes.

Measure the difference in extinction at 20°C between the 2 solutions and estimate the phosphoric acid content of the volume of the unknown solution from the calibration graph.

Calculate the phosphoric acid content of the sample from known dilution factors and the weight of the sample.

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

4.27 Citric acid-soluble phosphoric acid in basic slag.

4.271 PREPARATION OF THE SOLUTION.

Weigh to the nearest mg. about 5 g. of the sample and transfer to a stoppered bottle of about 1 litre capacity. Dissolve 10 g. citric acid monohydrate in water, dilute to 500 ml. and adjust the temperature to 20°C. Add the solution to the sample in the bottle, shaking so as to avoid the possibility of caking. Shake the bottle continuously for 30 minutes. Pour the whole of the liquid at once on to a large medium-fine filter and collect the filtrate. If the filtrate is not clear, pass it again through the same filter.

4.272 PROCEDURE.

4.2721 Standardisation of instrument.

From a burette measure into a series of 100 ml. volumetric flasks 25.0, 26.0, 27.0, 28.0, 29.0, 30.0 and 31.0 ml. of the standard phosphate solution (i.e. 5.0, 5.2, 5.4, 5.6, 5.8, 6.0 and 6.2 mg. phosphoric acid). Add to each flask a quantity of citric acid equal to that in the "final volume of about 25 ml." of the sample under examination quoted in paragraph 4.2722. Add 25 ml. of the vanado-molybdate reagent to each flask and dilute to 100 ml. with water, making sure that the temperature of the reagent and the dilution water is 20°C. Shake and allow to stand for 10 minutes.

Set the spectrophotometer to the correct wavelength, *circa* 420 nm., fill 2 1 cm. cells with the 5.0 mg. solution and check the extinction of the cells. If there is a small difference, select the cell with the smaller reading as the standard reference cell.

Determine the apparent extinction at 20°C (corrected for cell differences) of the 5.2, 5.4, 5.6, 5.8, 6.0 and 6.2 mg. phosphoric acid solutions referred to the 5.0 mg. phosphoric acid solution as standard.

Plot a calibration graph of scale readings against known phosphoric acid content.

4.2722 Analysis of sample.

Successively dilute a portion of the solution prepared according to paragraph 4.271 so that the final volume of about 25 ml. contains between 5.5 and 6.2 mg. phosphoric acid, taking care that the dilution water is at a temperature of 20°C.

Transfer this final volume to a 100 ml. volumetric flask, add 25 ml. of the vanado-molybdate reagent (at a temperature of 20°C), dilute to the mark, mix, and allow to stand for 10 minutes. At the same time, transfer 25 ml. of the standard phosphate solution (at 20°C) into a second 100 ml. volumetric flask, add sufficient citric acid to obtain a concentration in the final 100 ml. equal to that of the sample solution. Then add 25 ml. of the vanado-molybdate reagent (at 20°C), dilute to the mark, mix, and allow to stand for 10 minutes.

Measure the difference in extinction at 20°C between the 2 solutions and estimate the phosphoric acid content of the volume of the unknown solution from the calibration graph.

Calculate the phosphoric acid content of the sample from known dilution factors and the weight of the sample.

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

5. DETERMINATION OF POTASH.

For the purposes of the Law "potash" means potassium oxide(K_2O).

Potash in all kinds of fertilisers may be determined by the perchloric acid method, or by the potassium chloroplatinate method or, in fertilisers containing not more than 20% of potash, by the flame photometric method.

5.1 Perchloric Acid method.

This method depends on the insolubility of potassium perchlorate and the solubility of sodium perchlorate in alcohol, and is applicable in the presence of alkali metals, chlorides and nitrates. Sulphates and ammonium salts must be absent on account of the low solubility of sodium sulphate and of ammonium perchlorate in alcohol. Phosphates must be removed. Methods are given for the elimination of the effect of interfering substances.

5.11 Reagents.

Alcohol – industrial methylated spirit.

Ammonium carbonate solution – saturated aqueous solution.

Ammonia solution, (d=0.88).

Ammonium oxalate solution – saturated aqueous solution.

Barium chloride solution – Dissolve 100 g barium chloride in water, filter the solution and dilute to 1 litre.

Calcium oxide – finely ground.

Hydrochloric acid, concentrated (d=1.18).

Hydrochloric acid, 25% *v/v* – Dilute 25 ml. concentrated hydrochloric acid with water to 100 ml.

Perchloric acid, 20% w/w.

Wash solution – Add potassium perchlorate to alcohol and shake until a saturated solution is obtained. Keep the solution over solid potassium perchlorate and filter *immediately* before use.

5.12 Potassium salts free from sulphates and other interfering substances.

Dissolve in water a portion of the sample weighed to the nearest mg. equivalent in potassium content to 1.5 to 2.0 g. potash. Cool the solution to 20°C, dilute to 500 ml. in a volumetric flask, mix well and filter through a dry filter. Determine the potash in 50 ml. of the solution by precipitating with perchloric acid as described in paragraph 5.15.

5.13 Potassium salts containing sulphates or other interfering substances.

A method is given in paragraph 5.131 for eliminating the interference caused by the presence of sulphate. If the salts contain phosphates, iron, manganese or substances other than sulphate that interfere with the determination of potash, the method described in paragraph 5.14 should be used.

5.131 Weigh to the nearest mg. a portion of the sample, equivalent in potassium content to 1.5 to 2.0 g. potash, into a 500 ml. beaker, add about 300 ml. water and 20 ml. concentrated hydrochloric acid and heat the solution to boiling. To the boiling solution cautiously add, drop by drop, barium chloride solution in an amount slightly in excess of that previously determined as necessary to ensure the complete precipitation of sulphate. Cool the liquid to 20°C, transfer to a 500 ml. volumetric flask, dilute to 500 ml., mix, and filter through a dry filter. Take 50 ml. of the filtrate and evaporate to dryness in a basin; moisten the residue with concentrated hydrochloric acid, again evaporate to dryness, dissolve the residue with 5–10 ml. 25% hydrochloric acid and filter if necessary. Determine the potash in the solution by the method described in paragraph 5.15.

5.14 Potash in guanos and mixed fertilisers.

Weigh to the nearest centigram about 10 g. of the sample and, if organic matter is present, gently incinerate at a temperature not exceeding 500°C. Transfer the weighed portion of the sample or the incinerated residue to a 500 ml. beaker with a little water and 10 ml. concentrated hydrochloric acid and then warm for 10 minutes. Dilute with water to about 300 ml. and bring gradually to the boiling point. Add 10 g. calcium oxide made into a paste with water. Bring the contents again gently to the boiling point, and keep so heated for about half an hour with frequent stirring. Cool to 20°C, transfer to a 500 ml. volumetric flask, dilute to 500 ml. and, after thoroughly shaking, filter through a dry filter paper. Transfer 250 ml. of the filtrate to another 500 ml. volumetric flask, make just acid with hydrochloric acid and heat to boiling point. To the boiling solution cautiously add, drop by drop, barium chloride solution until there is no further precipitation of barium sulphate. Render the contents of the flask alkaline with ammonia solution, and precipitate the calcium and any excess of barium by adding ammonium carbonate solution until no further visible precipitation occurs, followed by the addition of about 1 ml. ammonium oxalate solution. Cool to 20°C, dilute with water to 500 ml. and, after thoroughly shaking, filter through a dry paper filter. Measure 100 ml. of the filtrate and evaporate to dryness in a basin. Expel the ammonium salts from the residue by gently heating the basin over a low flame, being careful to keep the temperature below that of faint redness. Cool the residue, moisten with concentrated hydrochloric acid and again evaporate to dryness. Take up the residue with water and filter if necessary. Determine the potash in the solution by precipitation with perchloric acid as described in paragraph 5.15.

5.15 Precipitation of potash as potassium perchlorate.

Transfer the solution obtained as described in paragraph 5.12, 5.131 or 5.14 into a basin and add about 7 ml. perchloric acid solution. Place the

basin on a hot plate or sand bath and evaporate the contents until white fumes are copiously evolved. Cool, and dissolve the precipitate in a little hot water. Add about 1 ml. perchloric acid solution and again concentrate to the fuming stage. Thoroughly cool the residue in the basin and stir in 20 ml. alcohol. Allow the precipitate to cool and settle; then pour the clear liquid through a dry filter paper, draining the precipitate in the basin as completely as possible. Re-dissolve the precipitate on the paper and that remaining in the basin with hot water, add 2 ml. perchloric acid solution to the combined solution and evaporate the whole down to the fuming stage. Cool the residue in the basin and thoroughly stir the contents with 20 ml. alcohol. Allow the precipitate to cool and settle and pour the clear liquid through a weighed Gooch or sintered glass crucible, draining the precipitate as completely as possible from the liquid before adding 5 ml. of the wash solution. Wash the precipitate by decantation with several similar small portions of the wash solution, pouring the washings through the crucible. Transfer the precipitate to the crucible and wash it well with the wash solution until free from acid. Dry the precipitate at 100°C and weigh. Regard the precipitate as potassium perchlorate ($KC10_4$) and calculate its equivalent as potash (K_2O) by multiplying its weight by 0.34.

5.2 Potassium Chloroplatinate method.

This method depends on the insolubility of potassium chloroplatinate in alcohol. Preliminary treatment is necessary for the removal of calcium, iron and aluminium which are precipitated by ammonium hydroxide and ammonium oxalate. Ammonium salts are then removed by boiling with aqua regia, and potassium chloroplatinate precipitated from the resultant solution.

5.21 Reagents.

Alcohol – industrial methylated spirit.

Ammonia solution (d=0.88).

Ammonium oxalate solution – saturated aqueous solution.

Chloroplatinic acid solution – Dissolve a weighed quantity of platinum by gentle heating in a mixture of 4 volumes concentrated hydrochloric acid, 1 volume concentrated nitric acid and 1 volume water in a covered beaker or flask. When the platinum is dissolved, transfer the solution to a basin and evaporate to a syrupy consistency. Add 10 ml. 50% hydrochloric acid and evaporate again to a syrup. Repeat the evaporation with 50% hydrochloric acid twice. Dilute the residue with water and filter the solution, thoroughly washing the filter. Combine the filtrate and washings and dilute with water to give a solution containing 0.5 g. platinum in 10 ml.

Hydrochloric acid, concentrated (d=1.18).

Hydrochloric acid, 50% v/v – Dilute 50 ml. concentrated hydrochloric acid with water to 100 ml.

Nitric acid, concentrated (d=1.42).

Wash solution – Dissolve 200 g. ammonium chloride in 1 litre of water, add 10 to 20 g. pulverised potassium chloroplatinate and shake the mixture at intervals for 6 to 8 hours. Allow the mixture to settle and filter before use.

5.22 Potassium salts.

If the salts contain calcium, iron, aluminium or other substances that interfere with the potassium chloroplatinate method, the procedure described in paragraph 5.23 should be used instead of the following procedure.

Weigh to the nearest mg. about 2.5 g. of the sample and transfer to a beaker. Add 10 ml. concentrated hydrochloric acid and 50 ml. water and bring the contents to the boiling point, breaking down with a stirring rod any crystals or lumps. Dilute the solution with water to about 100 ml. and boil gently for a few minutes. Cool the solution to 20°C and dilute in a volumetric flask to 250 ml. or to such larger volume that 50 ml. of the solution contains from 30 to 100 mg. potash (K_2O). Mix the solution and filter through a dry filter. Determine the potash in the filtrate by the method described in paragraph 5.25.

5.23 Potash in mixed fertilisers containing little or no organic matter.

Weigh to the nearest mg. about 2.5 g. of the sample and transfer to a 250 ml. beaker. Add 125 ml. water and 50 ml. ammonium oxalate solution. Boil the contents for 30 minutes. If necessary a small quantity of potassium-free anti-foaming agent may be added. Cool the liquid, add a slight excess of ammonia solution and cool to 20°C; dilute to 250 ml. or to such larger volume that 50 ml. shall contain from 30 to 100 mg. potash (K_2O). Mix the solution and filter through a dry filter. Determine the potash in the filtrate by the method described in paragraph 5.25.

5.24 Potash in mixed fertilisers containing organic matter.

Weigh to the nearest centigram about 10 g. of the sample and gently incinerate at a temperature not exceeding 500°C in order to destroy the organic matter. Grind the residue to eliminate any lumps and boil the residue for 30 minutes with 125 ml. water and 50 ml ammonium oxalate solution. Cool the solution, add a slight excess of ammonia solution, cool to 20°C and dilute to 500 ml. or to such larger volume that 50 ml. shall contain from 30 to 100 mg. potash (K_2O). Mix the solution and filter through a dry filter. Determine the potash in the filtrate by the method described in paragraph 5.25.

5.25 Precipitation of potash as potassium chloroplatinate.

From the solution obtained as described in paragraph 5.22, 5.23 or 5.24, take 50 ml. and place in a digestion flask of capacity about 300 to 500 ml. together with 10 ml. concentrated nitric acid. A small silica bead or granule weighing about 0.25 g. may be added to prevent bumping. (This bead or granule should have been previously tared with a prepared Gooch crucible or sintered glass crucible having an average pore diameter of 5 to 15 microns.) Boil the mixture for 2

minutes, then add 10 ml. concentrated hydrochloric acid. Boil the liquid down to approximately 25 ml. and add 5 ml. concentrated hydrochloric acid followed by chloroplatinic acid solution in excess over that required by the total alkalis present. Boil the mixture down to 10 to 15 ml., rotating the flask occasionally, and then add 5 ml. concentrated hydrochloric acid. Reduce the heat and gently boil the mixture down to 3 to 5 ml. (depending on the amount of precipitate), rotating the flask frequently near the end of the evaporation. Remove the flask from the heat and swirl to dissolve any soluble residue of the salts on the walls of the flask. Cool and immediately add 25 ml. alcohol so that it washes completely the neck of the flask. Chill the flask by swirling under running water and then allow to stand for at least 5 minutes. Filter the clear liquid through the prepared Gooch crucible or sintered glass crucible, using gentle suction, and draining the liquid as completely as possible from the precipitate. Wash the precipitate several times by decantation with alcohol until the washings are free from platinum; then, with the aid of alcohol, transfer the precipitate, together with the silica bead or granule, if used, to the crucible. Cut off the suction, add 10 ml. of the wash solution to the precipitate and allow to stand for 5 minutes; then operate the suction at a low pressure and drain. Wash with a further 5 consecutive portions of 10 ml. each of the wash solution; finally increase the suction and wash the precipitate with alcohol until the filtrate is free from ammonium salts. Dry the crucible and contents at 100°C, weigh, and calculate the weight of the precipitate to its equivalent of potash (K_2O) by multiplying its weight by 0.1938.

5.3 Flame Photometric method.

The determination of potash by this method depends on the measurement of the characteristic radiation emitted from a flame into which a solution of the sample is sprayed. The chosen radiations lie in the spectral range 766–770 nm. These radiations may be isolated by either a monochromator or the use of a suitable filter.

This method must not be used where the potash content of the material being analysed exceeds 20% by weight.

5.31 Reagents.

Ammonia solution, 30% *v/v* – Dilute 30 ml. concentrated ammonia solution (d=0.88) with water to 100 ml.

Ammonium oxalate solution – saturated aqueous solution.

Hydrochloric acid, concentrated (d=1.18).

Potassium dihydrogen phosphate solution (*stock potash solution*) – Dissolve in water 5.779 g. potassium dihydrogen phosphate previously dried for 1 hour at 105°C and dilute to 1 litre.

Potassium dihydrogen phosphate solution (*standard potash solution*) – Dilute 50 ml. stock solution to 1 litre with water. This solution contains 100 ppm. potash (K_2O).

5.32 Potassium salts.

If the salts contain calcium, iron, aluminium or other interfering substances, the procedure described in paragraph 5.33 should be used instead of the following procedure.

Weigh to the nearest mg. about 2.5 g. of the sample and transfer to a 400 ml. beaker. Add 10 ml. concentrated hydrochloric acid and 50 ml. water and bring the contents to the boiling point, breaking down with a stirring rod any crystals or lumps. Dilute the solution with water to about 100 ml. and boil gently for a few minutes. Cool the solution to 20°C, transfer to a 250 ml. volumetric flask, and dilute to the mark. Mix and filter through a dry filter. Successively dilute so that the final solution contains approximately 16 ppm. potash and determine the potash in the filtrate by the method described in paragraph 5.35.

5.33 Potash in mixed fertilisers containing little or no organic matter.

Weigh to the nearest mg. about 2.5 g. of the sample and transfer to a 400 ml. beaker. Add 125 ml. water and 50 ml. ammonium oxalate solution. Boil the contents for 30 minutes. If necessary, a small quantity of a potassium-free anti-foaming agent may be added. Cool the liquid, add a slight excess of ammonia solution and cool to 20°C. Transfer to a 250 ml. volumetric flask, and dilute to the mark. Mix the solution and filter through a dry filter. Successively dilute so that the final solution contains approximately 16 ppm. potash and determine the potash in the filtrate by the method described in paragraph 5.35.

5.34 Potash in mixed fertilisers containing organic matter.

Weigh to the nearest centigram about 10 g. of the sample and gently incinerate at a temperature not exceeding 500°C in order to destroy the organic matter. Grind the residue to eliminate any lumps and boil the residue for 30 minutes with 125 ml. water and 50 ml. ammonium oxalate solution. Cool the solution, add a slight excess of ammonia solution, cool to 20°C, transfer to a 500 ml. volumetric flask and dilute to the mark. Mix the solution and filter through a dry filter. Successively dilute so that the final solution contains approximately 16 ppm. potash and determine the potash in the filtrate by the method described in paragraph 5.35.

5.35 Determination of potash by flame photometry.

5.351 CALIBRATION OF INSTRUMENT.

From the standard potash solution, prepare a set of accurate dilutions containing 10, 12, 14, 16, 18 and 20 ppm. potash. Set the sensitivity of the flame photometer so that 100 scale divisions (full scale deflection) is equivalent to 20 ppm. potash solution. Spray the 10, 12, 14, 16 and 18 ppm. potash solutions 3 times. Take the median reading (*not* the mean), and construct a calibration graph. After spraying each different strength solution, again spray the 20 ppm. solution to ensure that the sensitivity of the flame photometer has not changed.

5.352 ANALYSIS OF SAMPLE.

Reset the instrument at 100 scale divisions (full scale deflection) with 20 ppm. potash solution. Spray the diluted fertiliser solution prepared in accordance with paragraph 5.32, 5.33 or 5.34 and read from the graph the approximate potash content of the solution.

Prepare 2 further dilutions of the standard potash solution to contain respectively 1 ppm. more and 1 ppm. less potash than the estimated potash content of the diluted solution of the sample. Successively spray the low standard solution, the diluted solution of the sample, and the high standard solution. Repeat this operation twice more. Take the median result of each set of 3 readings and calculate the potash content of the sample solution and hence of the fertiliser from the proportionality of the radiation given by the sample solution and that given by the 2 standard solutions containing respectively 1 ppm. more and 1 ppm. less potash than the predicted potash content.

NOTE: It is essential that the flame photometer should be set up in a vibration-free position and in a dust-free atmosphere.

Dilute standard solutions should be freshly prepared.

6.0 DETERMINATION OF NEUTRALISING VALUE IN LIMING MATERIALS.

6.1 Reagents.

Hydrochloric acid, 0.5 *N*.

Phenolphthalein indicator solution – Dissolve 0.25 g. phenolphthalein in 150 ml. industrial methylated spirit and dilute with water to 250 ml.

Sodium hydroxide, 0.5 *N* – carbonate free.

6.2 Preparation of the sample.

Prepare a portion of at least 50 g. of the sample for analysis as described in paragraph 1.11. When a small part of the sample has been used for a sieving test as described in paragraph 17, grind the remainder of the dried portion to pass through a sieve of approximately 1/8 in. square apertures, and quarter down until about 100 g. remains. Grind this portion for analysis as described in paragraph 1.11. Where the greater part of the sample has been used for the sieving test, mix the various fractions obtained in the test together and grind until the whole passes a sieve of approximately 1/8 in. square apertures, quarter down until about 100 g. remains. Grind this portion for analysis as described in 1.11.

6.3 Procedure.

Weigh to the nearest mg. about 500 mg. of the sample prepared according to paragraph 6.2 and transfer to a 300 ml. flask. Add 50 ml. 0.5 N hydrochloric acid, cover the flask with a glass and boil the contents gently for 5 minutes. Cool the mixture, add 2 or 3 drops of the phenolphthalein indicator solution and titrate with 0.5 N sodium hydroxide solution. Calculate by difference the

volume of 0.5 N hydrochloric acid required to neutralise the sample. Express the result as percentage by weight of calcium oxide (CaO). 1 ml. 0.5 N hydrochloric acid ≡ 0.01402 g. calcium oxide (CaO). Correct the neutralising value for the moisture lost if the sample has been dried for sieving purposes. Express the neutralising value as a percentage of the original.

7. DETERMINATION OF MAGNESIUM IN LIME AND GROUND LIMESTONE.

7.1 Reagents.

Ammonia solution, 25% *v/v* – Dilute 25 ml. concentrated ammonia solution (d=0.88) with water to 100 ml.

Ammonium chloride solution – Dissolve 330 g. ammonium chloride in water and dilute to 1 litre.

Ammonium persulphate solution – Dissolve 10 g. ammonium persulphate in water and dilute to 100 ml. Store in a cool dark place for not more than one week.

Buffer solution – Dissolve 6.75 g. ammonium chloride, 62 mg. magnesium sulphate ($MgSO_4$, $7H_2O$), 93 mg. disodium ethylenediamine-tetra-acetate dihydrate and 57 ml. ammonia solution (d=0.88) in water and dilute to 100 ml.

Calcium standard solution – Dissolve 2.5 g. calcium carbonate in 120 ml. 0.5 N hydrochloric acid and dilute to 1 litre.

EDTA solution, 0.026 *M* – Dissolve 10 g. disodium ethylenediamine-tetra-acetate dihydrate in 800 ml. water containing 55 ml. N sodium hydroxide solution. Dilute 20 ml. standard calcium solution with 30 ml. water. Add 1 ml. buffer solution and 200 mg. Mordant Black 11; titrate with the EDTA solution to a blue end point and adjust the strength of this solution so that 1 ml. is equivalent to 2.5 mg. calcium carbonate ($CaCO_3$).

Hydrochloric acid, 0.5 N.

Hydrogen peroxide solution, 6% w/v (20 volumes).

Mordant Black 11 (colour index No. 14645) – Mix 200 mg. Mordant Black 11 and 50 g. sodium chloride uniformly together and grind to pass through a sieve having apertures of about 0.3 mm. square.[8]

Murexide indicator – Mix 200 mg. Murexide and 100 g. sodium chloride uniformly together and grind to pass through a sieve having apertures of about 0.3 mm. square.12 Protect this mixture from light.

Sodium hydroxide, N.

[8] British Standard Test Sieve, Mesh No. 52 is suitable (British Standards for Test Sieves 410 : 1962).

7.2 Procedure.

Weigh to the nearest mg. about 1 g. of finely ground sample and add 50 ml. 0.5 N hydrochloric acid. Transfer to a conical flask, cover with a glass and boil for 3 minutes. Add 2 ml hydrogen peroxide solution, reboil, cool, add 1 ml. ammonium chloride solution, a slight excess of 25% ammonia solution and 1 ml. ammonium persulphate solution. Remove the excess ammonia by boiling and filter the precipitate, if any, on a small paper and wash with 2 portions each of 10 ml. hot water. Wash the precipitate off the paper with not more than 50 ml. water, and boil with 50 ml. 0.5 N hydrochloric acid. Cool the solution, add 1 ml. ammonium chloride solution, a slight excess of dilute ammonia and 1 ml. ammonium persulphate solution and remove the excess of ammonia by boiling. Filter and wash with hot water. Add the filtrate and washings to the filtrate and washings from the first precipitation, cool, and dilute the whole to 200 ml.

If no precipitate forms on the addition of the ammonia and persulphate solutions, remove the excess of ammonia by boiling, add 6 ml. ammonium chloride solution, cool, and dilute to 200 ml.

If the amount of the precipitate is small, omit the second precipitation but add 6 ml. ammonium chloride solution to the filtrate and washings before cooling and diluting to 200 ml.

Dilute 20 ml. of the solution to 50 ml. and add 3 ml. 25% ammonia solution. Then add 200 mg. Mordant Black 11 and titrate with EDTA solution to a blue end point.

Dilute a further 20 ml. of the solution to 50 ml. and add 7 ml. N sodium hydroxide. Then add 200 mg. Murexide indicator and titrate with EDTA solution to a violet end point.

Calculate the magnesium content from the difference between the 2 titrations. 1 ml. EDTA solution ≡ 0.608 mg. magnesium.

8. DETERMINATION OF THIOCYANATE IN AMMONIACAL GAS LIQUOR; NITROGENOUS GAS LIQUOR; GAS LIQUOR.

8.1 Reagents.

Ammonium ferric sulphate solution – Saturated aqueous solution of ammonium ferric sulphate.

Copper sulphate solution – Dissolve 10 g. copper sulphate in water and dilute to 100 ml.

Lead carbonate.

Nitric acid, 50% *v/v* – Dilute 50 ml. concentrated nitric acid (d=1.42) with water to 100 ml.

Potassium thiocyanate, 0.1 N.

Silver nitrate, 0.1 N.

Sodium hydroxide solution – Dissolve 4 g. sodium hydroxide (free from chloride) in water and dilute to 100 ml.

Sodium metabisulphite (or *potassium metabisulphite*) *solution* – Saturated aqueous solution.

Sulphuric acid, 10% *v/v* – To 50 ml. water cautiously add 10 ml. concentrated sulphuric acid. Cool and dilute to 100 ml.

8.2 Procedure.

Place 25 or 50 ml. of the liquor in a 100ml. beaker and add 2 g. lead carbonate. Stir well and allow to stand for 10 minutes (in order to remove sulphide.) Filter the solution into a 150 ml. beaker, washing the beaker and the filter twice with distilled water. Slightly acidify the filtrate with sulphuric acid solution, warm to about 40°C and add a few drops of ammonium ferric sulphate solution to clarify the liquor and remove any ferrocyanide which may be present. Filter the solution through paper pulp with the aid of a suction pump and wash the beaker and the filter with water. To the filtrate contained in a 250 ml. flask add 10 drops of sodium metabisulphite (or potassium metabisulphite) solution, and heat the mixture to about 60°C. Add an excess of copper sulphate solution and continue the heating to incipient boiling. Allow to stand from 5 to 10 minutes with occasional agitation. Filter and well wash the beaker and the filter with hot water until the washings remain colourless upon the addition of a drop of ferrocyanide solution. Pierce the filter paper and wash the residue back into the original flask, and finally wash with 25 ml. sodium hydroxide solution. Warm the solution to about 50°C to decompose the cuprous salt and add a few drops of ammonium ferric sulphate solution to promote coagulation. Filter the solution through paper pulp, well wash the flask and the filter with water. Acidify the filtrate with 5 ml. nitric acid solution, add 2 drops of ammonium ferric sulphate solution and titrate with 0.1 N silver nitrate.

$$\textit{Thiocyanate} \text{ as CNS in g. per 100 ml.} = \frac{0.58 \text{ x ml. } 0.1 \text{ N } AgNO_3}{\text{mls. liquor taken}}$$

9. DETERMINATION OF BIURET.

9.1 Reagents.

Alkaline tartrate solution – Dissolve 40 g. sodium hydroxide in 500 ml. water, cool and add 50 g. potassium sodium tartrate. Dilute to 1 litre and allow to stand for 24 hours before use.

Biuret standard solution – Dissolve 0.100 g. biuret in carbon dioxide-free water and dilute to 100 ml. 1ml.≡ 1 mg. biuret. The sample of biuret, when taken through the procedure for the preparation of the standard curve, should have an E (1% 1 cm) not less than 2.5.

Copper sulphate solution – Dissolve 15 g. copper sulphate $CuSO_4.5H_2O$ in carbon dioxide-free water and make up to 1 litre.

Methanol.

Methyl red indicator solution – Dissolve 0.025 g. methyl red in 5 ml. 90% industrial methylated spirit with the aid of 0.5 ml. 0.1 N sodium

hydroxide solution. Dilute to 250 ml. with 50% industrial methylated spirit. If desired, a screened methyl red indicator may be used.

Sulphuric acid, 0.1 N.

9.2 Procedure.

Place 10g. of the sample in a small glass evaporating dish, add 30 ml. methanol and evaporate to dryness on a water bath. Treat the residue with 50 ml. water and digest at 50°C for half an hour. Filter and wash into a 250 ml. flask and dilute to volume with carbon dioxide-free water. Transfer a 50 ml. aliquot to a 100 ml. volumetric flask, add 1 drop methyl red indicator solution and neutralise with 0.1 N sulphuric acid to a pink colour. Add with swirling 20 ml. alkaline tartrate solution and then 20 ml. copper sulphate solution. Dilute to volume, shake for 10 seconds and place in a water bath at 30±5°C for 15 minutes. Prepare a reagent blank solution. Determine the extinction of each solution against the blank at 555 nm. using 4 cm. cells.

Calculate the biuret content of the sample by reference to a calibration graph prepared at the same time as the test sample.

Establish the calibration graph as follows: –

Transfer 5, 10, 20, 30, 40, 50 ml. aliquots of standard biuret solution to 100 ml. volumetric flasks. Adjust the volumes to about 50 ml. with carbon dioxide-free water, and proceed as described above commencing at "add one drop methyl red indicator solution .....". Construct a graph relating the extinctions of the solutions to the milligrams of biuret.

10. DETERMINATION OF BORON.

For levels above 1000 ppm., boron is determined by titration as boric acid and for levels up to 1000 ppm. by the carmine spectrophotometric method.

10.1 Titrimetric Method.

10.11 Reagents.

Calcium oxide.

Hydrochloric acid, 50% v/v – Dilute 50 ml. concentrated hydrochloric acid (d=1.18) with water to 100 ml.

Hydrochloric acid, 0.5 N.

Lead nitrate solution – Dissolve 10 g. lead nitrate in water and dilute to 100 ml.

Mannitol.

Methyl red indicator solution – Dissolve 0.025 g. methyl red in 5 ml. 90% industrial methylated spirit with the aid of 0.5 ml. 0.1 N sodium hydroxide. Dilute to 250 ml. with 50% industrial methylated spirit.

Phenolphthalein indicator solution – Dissolve 0.25 g. phenolphthalein in 150 ml. industrial methylated spirit and dilute with water to 250 ml.

Sodium carbonate.

Sodium hydroxide, 0.5 N.

Sodium hydroxide, 0.05 N. Prepare from a 50% solution which has been allowed to settle. Use boiled and cooled water for dilution. Store in a polythene bottle protected from the atmosphere by a guard tube and fitted with a syphon for withdrawing the solution.

10.12 Dissolution of the sample.

10.121 In the absence of organic matter.

Weigh to the nearest mg. about 2 g. of the sample, if it contains 0.5% or less of boron, and 1 g. if it contains from 0.5-1.0% of boron. Transfer to a 400 ml. beaker. Add 100 ml. water and some phenolphthalein indicator. Add sodium carbonate to make the solution slightly alkaline and boil gently. Keep the boiling solution just alkaline by further additions of sodium carbonate until all the ammonia which may be present has been evolved. Cool the solution, add 12 ml. 50% hydrocholoric acid.

10.122 In the presence of organic matter.

Weigh to the nearest mg. about 2 g. of the sample, if it contains 0.5% or less of boron, and 1 g. if it contains from 0.5-1.0% of boron. Place in a silica dish, add 0.2 calcium oxide for each 1 g. of the sample, moisten with water, mix thoroughly, evaporate the mixture to dryness and ignite gently in a muffle furnace at 450°C. Allow the ashing to proceed for about 3 hours. Cool. Moisten with 10 ml. 50% hydrochloric acid, warm on a water bath for 15 minutes, covering the dish with a watch glass. Transfer to a 400 ml. beaker, add a few drops of phenolphthalein indicator and dilute to about 120 ml. with water.

10.13 Procedure.

To the solution prepared in accordance with paragraph 10.121 or 10.122, add 20 ml. lead nitrate solution for each 12% P_2O_5 in the sample if 2 g. of the sample have been used and 10 ml. lead nitrate solution for each 12% P_2O_5 in the sample if 1 g. of the sample has been used. Heat just to boiling, remove from source of heat and make just alkaline by adding solid sodium carbonate. Stand on a water bath for 5 minutes. Cool, transfer to a 200 ml. volumetric flask and dilute to the mark with water. Mix and filter through a 24 cm. Whatman No. 42 (or equivalent) filter paper, rejecting the first 10–20 ml. of the filtrate. Transfer 100 ml. of the filtrate to a 250 ml. beaker. Add a few drops of methyl red indicator and acidify the solution with 0.5 N hydrochloric acid. Heat almost to boiling and stir vigorously to remove carbon dioxide, adding a little more 0.5 N hydrochloric acid if the colour changes to orange or to yellow. Neutralise to methyl red with 0.5 N sodium hydroxide solution and then make just acid with 0.5 N hydrochloric acid. Cover with a watch glass and boil gently for 5 minutes to expel any remaining carbon dioxide. Cool rapidly.

Place the electrodes of a potentiometric titration apparatus in the beaker and adjust the pH to 6.3 by adding 0.05 N sodium hydroxide solution. Add 10 g. mannitol and titrate with 0.05 N sodium hydroxide solution to a final pH of 6.3. Add a further quantity of mannitol and continue the titration to a pH of 6.3. Further additions of mannitol should not alter the pH. Let x ml. of 0.05 N sodium hydroxide be used for the titration after the addition of the mannitol.

Allow a standard value of 0.1 ml 0.05 N sodium hydroxide solution as a "blank" value.

Calculate Boron: % Boron in sample = $\frac{0.1082\ (x - 0.1)}{\text{Weight of sample taken}}$

10.2 Spectrophotometric (Carmine) Method

10.21 Reagents.

Boric acid (*stock boron solution*) – Dissolve 1.905 g. boric acid in water and dilute to 1000 ml. at 20°C. 1 ml. = 0.333 mg. boron.

Boric acid (*standard boron solutions*) – Dilute 10 ml. stock solution with water to 100 ml. at 20°C. Transfer 5, 10, 15, 20 and 25 ml. of this dilute solution to 100 ml. volumetric flasks and dilute to the marks with water. These standards will contain 5, 10, 15, 20, 25 μg. of boron per 3 ml.

Calcium oxide.

Carminic acid solution – Dissolve 0.025 g. carminic acid in concentrated sulphuric acid and dilute to 100 ml. with concentrated sulphuric acid.

Hydrochloric acid, 20% *v/v* – Dilute 20 ml concentrated hydrochloric acid (d=1.18) with water to 100 ml.

Sulphuric acid, concentrated, (d=1.84).

10.22 Dissolution of sample.

This procedure should be followed even in the absence of organic matter in the fertiliser. Weigh to the nearest mg. about 5 g. of the sample. Transfer to a silica dish and add 1 g. calcium oxide, moisten with water, mix thoroughly, evaporate the sample to dryness, and ignite gently in a muffle furnace at 450°C. Allow ashing to proceed for about 3 hours. Cool and add 20% hydrochloric acid solution until the mixture is just acid. Add 5 ml. 20% hydrochloric acid in excess and digest the mixture at 70°C for 15 minutes. Cool and filter the contents of the dish into a suitable volumetric flask, making up to the mark with washings. Dilute an aliquot of this solution so that 3 ml. contain between 5 and 25 μg of boron.

10.23 Procedure.

Transfer 3 ml. to a small flask. Add cautiously 15 ml. concentrated sulphuric acid. Swirl the flask and add 10 ml. carminic acid solution. Cool the flask rapidly to room temperature, mix well and allow to stand for exactly 2 hours. Measure the extinction of the coloured complex at 625 nm. using a 1 cm. cell,

and against a blank which has been taken through all the stages of the determination. Read from a previously prepared calibration graph the number of micrograms of boron corresponding to the observed extinction, and calculate the boron content of the sample.

Establish the calibration graph as follows: –

Pipette 3 ml. of each standard solution into a series of small flasks and proceed as described above commencing at "Add cautiously 15 ml.....". Measure the extinctions of the solutions, and construct a graph relating the extinctions to the number of micrograms of boron.

11. DETERMINATION OF COBALT.

11.1 Reagents.

Ammonium cobaltous sulphate, $(NH_4)_2\ Co(SO_4)_2.\ 6H_2O$, (*stock cobalt solution*) – Dissolve 0.670 g. ammonium cobaltous sulphate in water and dilute to 100 ml. at 20°C.

Ammonium cobaltous sulphate, (*standard cobalt solution*) – Dilute 1 ml. stock solution to 1000 ml. with water at 20°C immediately before use. 1 ml.≡ 1 µg. cobalt.

Hydrochloric acid, 50% *v/v* – Dilute 50 ml. concentrated hydrochloric acid (d=1.18) with water to 100 ml.

Hydrochloric acid, 2 N.

Hydrogen peroxide solution, 3% w/v (10 volumes).

Nitric acid, 30*% v/v* – Dilute 30 ml concentrated nitric acid (d=1.42) with water to 100 ml.

2-*Nitroso* -1-*naphthol reagent* – Dissolve 1 g. 2-nitroso-1 napthol in 100 ml. glacial acetic acid, and add 1g. activated carbon. Shake the solution before use, and filter the required amount.

Sodium citrate solution – Dissolve 40 g. sodium citrate in water and dilute to 100 ml.

Sodium hydroxide, 2 N.

Sodium sulphate, anhydrous.

Toluene, redistilled.

11.2 Dissolution of the sample.

11.21 In the absence of organic matter.

Weigh to the nearest mg. about 5 g. of the sample, and transfer into a 100 ml. beaker, add 10 ml 50% v/v hydrochloric acid, and evaporate to dryness on a water-bath. Extract the soluble salts with 3 successive 10 ml. portions of boiling 2 N hydrochloric acid, decanting the solution each time through the same

Whatman No. 541 (or equivalent) filter paper into a 50 ml. volumetric flask. Dilute the combined extracts to the mark with distilled water, washing the filter paper in the process.

11.22 In the presence of organic matter.

Weigh to the nearest mg. about 5 g. of the sample, and transfer into a silica basin, cover with a silica clock glass, and replace in a cool muffle furnace. Raise the temperature to 450 ± 10°C, and allow to ash overnight; a slow movement of air through the furnace during the initial stages of ashing is desirable. In the case of high-fat materials, care must be taken to avoid ignition of the sample.

When all the organic matter has been destroyed, cool, add 10 ml 50% v/v hydrochloric acid, and evaporate to dryness on a water bath. Extract the soluble salts from the residue with 2 successive 10 ml. portions of boiling 2 N hydrochloric acid, decanting the solution each time through the same Whatman No. 541 (or equivalent) filter paper into a 50 ml. volumetric flask. Then add 5 ml. 50% v/v hydrochloric acid and about 5 ml. 30% v/v nitric acid to the residue in the basin, and take the mixture to dryness on a hot-plate at low heat. Finally, add a further 10 ml. of boiling 2 N hydrochloric acid to the residue and filter the solution through the same paper into the flask. Dilute the combined extracts to the mark with distilled water, washing the filter paper in the process.

11.3 Procedure.

Transfer a suitable aliquot of the solution prepared in accordance with paragraph 11.2 to a 100 ml. beaker, add 15 ml. sodium citrate solution, and dilute to approximately 50 ml. with distilled water. Adjust the pH to between 3 and 4 by the addition of 2 N hydrochloric acid and 2 N sodium hydroxide, using pH test paper (a precipitate of ferric hydroxide may form, but this can be dissolved by heating the solution), and cool to room temperature. Add 10 ml. 3% hydrogen peroxide solution and, after 5 minutes, 1 ml. of 2-nitroso-1-naphthol reagent, heat to about 90°C, and then allow to stand for 30 minutes at room temperature.

Transfer the solution to a 125 ml. separating funnel, add exactly 10 ml. toluene, shake vigorously for 2 minutes, and discard the lower aqueous phase. To the toluene extract add 20 ml. 2 N hydrochloric acid, shake for 1 minute, and run off and discard the lower aqueous phase. Add 20 ml. 2 N sodium hydroxide, shake for 1 minute, and again run off and discard the lower aqueous phase. Repeat the treatment of the toluene extract with a further 20 ml. 2 N sodium hydroxide. Finally run off the toluene solution through a little anhydrous sodium sulphate and a cotton-wool plug into a glass-stoppered tube.

Carry out a blank determination by repeating the procedure, omitting only the sample.

Measure the extinctions of the test and blank solutions at a wavelength of 367 nm., using a 1 cm. cell and toluene in the comparison cell. Read the number of micrograms of cobalt equivalent to the observed extinctions of the test and blank solutions from a previously prepared calibration graph. Determine the amount of cobalt in the sample from the difference between the test and blank solutions.

Establish the calibration graph as follows –

Measure amounts of standard cobalt solution corresponding to 0, 3, 6, 9, 12, 15 µg of cobalt into a series of 100 ml. beakers and proceed as described above commencing at "add 15 ml. sodium citrate solution.....". Measure the extinctions of the solutions, and construct a graph relating the extinctions to the number of micrograms of cobalt.

12. DETERMINATION OF COPPER.

Copper may be determined by the diethyldithiocarbamate spectrophotometric method or, alternatively, by the atomic absorption spectrophotometric method.

12.1 Diethyldithiocarbamate Spectrophotometric Method.

12.11 Reagents.

Ammonia solution, approximately 6 *N* – This may be prepared by passing gaseous ammonia into distilled water, or by purifying ammonia solution as described for EDTA-citrate solution below.

Carbon tetrachloride, redistilled.

Copper sulphate, stock solution – Dissolve 0.393 g. copper sulphate, $CuSO_4$. $5H_2O$, in 100 ml. 2 N sulphuric acid and dilute to 1 litre at 20°C with distilled water.

Copper sulphate standard solution – Dilute 5 ml. stock solution to 250 ml. with 2 N sulphuric acid at 20°C immediately before use. 1 ml. ≡ 2 µg copper.

EDTA-citrate solution – Dissolve 20 g. ammonium citrate and 5 g. of the disodium salt of ethylenediaminetetra-acetic acid (EDTA) in distilled water and dilute to 100 ml. To purify, add 0.1 ml. sodium diethyldithiocarbamate solution and extract with carbon tetrachloride. Add a further quantity of sodium diethyldithiocarbamate solution to ensure that it is in excess.

Sodium diethyldithiocarbamate solution – Dissolve 1 g. sodium diethyldithiocarbamate in distilled water and dilute to 100 ml. Filter the solution if it is not clear. Store the solution in the dark in a refrigerator and discard after 7 days.

Sodium hydroxide, 0.1 N.

Sulphuric acid, 2 N.

Thymol blue indicator solution – Dissolve 0.1 g. thymol blue in 2.15 ml. 0.1 N sodium hydroxide and dilute to 100 ml. with water.

12.12 Dissolution of the Sample.

Prepare a solution of the sample as described in paragraph 11.2.

12.13 Procedure.

Transfer to a separating funnel a suitable aliquot (containing not more than 50 µg. of copper) of the solution prepared in accordance with paragraph 11.2. Add 10 ml. EDTA-citrate solution, 2 drops of thymol blue indicator solution and ammonia solution until the mixture is coloured green or bluish-green. Cool the mixture, add 1 ml. sodium diethyldithiocarbamate solution and, from a burette, 15 ml. carbon tetrachloride. Stopper the funnel, shake vigorously for 2 minutes and allow the layers to separate. Place a piece of cotton-wool in the stem of the funnel and run off the carbon tetrachloride layer into a dry spectrophotometer cell. Avoid undue exposure of the solution to light.

Simultaneously with the test determination, carry out a blank determination on all the reagents used.

Measure immediately the extinctions of the test and blank solutions at a wavelength of 436 nm., using carbon tetrachloride in the comparison cell. Read from a previously prepared calibration graph the number of micrograms of copper corresponding to the observed extinctions of the test and blank solutions, and so obtain by difference the net measure of copper in the sample.

Establish the calibration graph as follows: –

To a series of separating funnels transfer 10 ml. ECTA-citrate solution and the following amounts of standard copper solution and 2 N sulphuric acid: –

Copper solution	0	1	2.5	5	10	15	20	25ml
2 N sulphuric acid	25	24	22.5	20	15	10	5	0 ml

Proceed as for the test solution, as described above, commencing at "2 drops of thymol blue....". Measure the extinctions of the solutions and construct a graph relating the extinctions to the number of micrograms of copper.

12.2 ATOMIC ABSORPTION SPECTROPHOTOMETRIC METHOD.

12.21 Apparatus.

Atomic absorption spectrophometer.

Copper hollow– cathode lamp.

12.22 Reagents.

Copper sulphate standard solution – Dissolve 0.393 g. copper sulphate, $CuSO_4.5H_2O$, in 0.5 N hydrochloric acid and dilute to 100 ml. with 0.5 N hydrochloric acid, 1 ml .≡ 1 mg. copper. Dilute this solution as required.

Hydrochloric acid, 0.5 N.

12.23 Procedure.

Set up the instrument using the line at 324.7 nm. Prepare from the standard copper solution a series of solutions, in 0.5 N hydrochloric acid, containing between 0 and 10 ppm. copper. Dilute a suitable aliquot of the sample solution, prepared in accordance with paragraph 11.2, with 0.5 N hydrochloric acid to produce a standard volume of solution containing between 0 and 10 ppm.

copper. Prepare a blank solution from which only the sample has been omitted. Spray distilled water into the flame and zero the instrument. Spray successively, in triplicate, the standard solutions, sample and blank, washing the instrument through with distilled water between each spraying. Record the galvanometer deflection or the peak height on the recorder if a recording instrument is used. Plot the mean reading obtained for each standard solution against its copper content. Determine the copper content of the sample and blank solutions from the graph and from the difference between them calculate the copper content of the sample.

If a large number of samples is being examined one or more standard solutions must be resprayed at intervals during the course of the analyses.

13. DETERMINATION OF IRON.

For levels up to 1%, iron is determined by the o-phenanthroline spectrophotometric method and for levels above 1% by the titrimetric method with potassium dichromate.

13.1 O-Phenanthroline Method.

13.11 Reagents.

Ammonium ferric sulphate solution (*stock iron solution*) – Dissolve 0.863 g. ammonium ferric sulphate, $Fe_2 (SO_4)_3 . (NH_4)_2 SO_4 . 24 H_2O$, in water containing 2 ml. perchloric acid, and dilute to 100 ml. at 20°C.

Ammonium ferric sulphate solution (*standard iron solution*) – Dilute 10 ml. stock solution to 100 ml. with water at 20°C immediately before use. 1 ml. ≡ 100 µg. iron.

Bromophenol blue indicator solution – Dissolve 0.4 g. bromophenol blue in 95% ethanol and dilute to 100 ml.

Hydrochloric acid, 50% v/v – Dilute 50 ml. concentrated hydrochloric acid (d=1.18) with water to 100 ml.

Hydrochloric acid, 20% v/v – Dilute 20 ml. concentrated hydrochloric acid (d=1.18) with water to 100 ml.

Nitric acid, 30% v/v – Dilute 30 ml. concentrated nitric acid (d=1.42) with water to 100 ml.

o-Phenanthroline solution – Dissolve 0.25 g. o-phenanthroline in 25% ethanol and dilute to 100 ml.

Quinol solution – Dissolve 1 g. quinol in water and dilute to 100 ml.

Sodium citrate solution – Dissolve 25 g. sodium citrate in water and dilute to 100 ml.

13.12 Dissolution of the Sample.

Prepare a solution of the sample as described in paragraph 11.2.

13.13 Procedure.

Transfer a suitable aliquot of the solution, prepared in accordance with paragraph 11.2, to a small flask, add a few drops of the bromophenol blue indicator solution, and titrate with sodium citrate solution until the colour changes from yellow to blue. Transfer another aliquot to a 25 ml. volumetric flask, add 1 ml. quinol solution, 3 ml. o-phenanthroline solution and an amount of sodium citrate solution equal to the above titration, and then dilute with water to 25 ml. Allow the solution to stand for 1 hour.

Carry out a blank determination on all the reagents used.

Measure the extinctions of the test and blank solutions at a wavelength of 510 nm., using 4 cm. or 1 cm. cells according to the depth of colour, with water in the comparison cell. Read the number of micrograms of iron equivalent to the observed extinctions of the test and blank solutions from a previously prepared calibration graph, and so obtain the net measure of iron in the sample.

Establish the calibration graph as follows: –

Measure amounts of standard iron solution corresponding to 0, 200, 300, 400, 500, 600 µg. of iron into a series of 100 ml. volumetric flasks. To each add 50 ml. 20% v/v hydrochloric acid, and dilute to 100 ml. with water. Using 5 ml. aliquots, proceed as for the test solution, as described above commencing at "Transfer a suitable aliquot of the solution...".

Measure the extinctions of the solutions and construct a graph relating the extinctions to the number of micrograms of iron.

13.2 Titrimetric Method.

13.21 Reagents.

Hydrochloric acid, concentrated (d=1.18).

Hydrochloric acid, 30% *v/v* – Dilute 30 ml. concentrated hydrochloric acid (d=1.18) with water to 100 ml.

Mercuric chloride solution – Dissolve 5 g. mercuric chloride in water and dilute to 100 ml.

Orthophosphoric acid, concentrated (d=1.75).

Potassium dichromate, 0.1 N.

Sodium diphenylamine-4-sulphonate indicator solution – Dissolve 0.2 g. sodium diphenylamine-4-sulphonate in water and dilute to 100 ml.

Stannous chloride solution – Dissolve 15 g. stannous chloride dihydrate in 30% v/v hydrochloric acid and dilute to 100 ml, with 30% v/v hydrochloric acid. This solution should be prepared immediately before use.

Stannous chloride solution dilute – Dilute 5 ml. stannous chloride solution with 30% v/v hydrochloric acid to 50 ml.

Sulphuric acid, 16% v/v – To 50 ml. water cautiously add 16 ml. concentrated sulphuric acid (d=1.84). Cool and dilute to 10 ml.

13.22 Dissolution of the Sample.

Prepare a solution of the sample as described in paragraph 11.2.

13.23 Procedure.

Transfer a suitable aliquot of the solution, prepared in accordance with paragraph 11.2, to a 500 ml. flask and dilute or concentrate the solution to about 20 ml. Add concentrated hydrochloric acid so that the total amount of acid present is equivalent to about 5 ml. concentrated hydrochloric acid.

Heat the solution to 70–90°C and add the stannous chloride solution dropwise until the yellow colour has almost disappeared. Continue the addition using diluted stannous chloride solution until the solution becomes colourless or slightly green and add 1 or 2 drops more. Cool the solution rapidly to room temperature, and add 10 ml. mercuric chloride solution. A small, white, 'silky' looking precipitate should form. (If no precipitate forms, insufficient stannous chloride has been added; on the other hand if the precipitate is grey or black too much stannous chloride has been added. In either case the solution must be discarded). Add 200 ml. water, 10 ml. 16% v/v sulphuric acid, 5ml. orthophosphoric acid and 6.8 drops of indicator. Titrate with 0.1 N potassium dichromate until the indicator changes from green to violet-blue. Calculate the amount of iron in the sample using the factor 1 ml. 0.1 N potassium dichromate ≡ 0.00559 g. iron.

14. DETERMINATION OF MAGNESIUM.

Magnesium may be determined by the pyrophosphate method or, alternatively, by the atomic absorption spectrophotometric method.

14.1 Pyrophosphate Method.

14.11 Reagents.

Ammonia solution, (d=0.88).

Ammonia solution, 5% v/v – Dilute 5 ml. concentrated ammonia solution (d=0.88) with water to 100 ml.

Ammonium oxalate solution – saturated aqueous solution.

Ammonium phosphate solution – Dissolve 20 g. diammonium hydrogen phosphate, $(NH_4)_2\ HPO_4$, in water and dilute to 100 ml.

Calcium wash solution – Dissolve 1 g. oxalic acid, $(COOH)_2.2H_2O$ and 2 g. ammonium oxalate, in water and dilute to 1000 ml.

Citric acid, monohydrate.

Hydrochloric acid, concentrated (d=1.18).

Hydrochloric acid, 20% v/v – Dilute 20 ml. concentrated hydrochloric acid (d=1.18) with water to 100 ml.

Methyl red indicator solution – Dissolve 0.025 g. methyl red in 5 ml. 90% industrial methylated spirit with the aid of 0.5 ml. 0.1 N sodium hydroxide. Dilute to 250 ml. with 50% industrial methylated spirit.

Oxalic acid solution – Dissolve 10 g. oxalic acid, $(COOH)_2$ $2H_2O$, in water and dilute to 100 ml.

14.12 Dissolution of the Sample.

Prepare a solution of the sample as described in paragraph 11.2.

14.13 Procedure.

Transfer a suitable aliquot (containing approximately 50 mg. magnesium) of the solution, prepared in accordance with paragraph 11.2, to a 500 ml. beaker, and add 5% v/v ammonia solution until a slight precipitate is formed. Add citric acid, in small portions, until the precipitate just dissolves, and then 1 g. in excess. Heat the solution to 50°C, add 0.2 ml. (4 drops) of methyl red indicator solution. Neutralise with 5% v/v ammonia solution, and add 1 ml. in excess. Add oxalic acid solution until the mixture is just acid, and then 10 ml. in excess. Boil the solution for 1 to 2 minutes, add 50 ml. saturated ammonium oxalate solution, dilute, if necessary, to about 200 ml. with distilled water, boil for a further minute, and heat on a water bath for at least an hour. Filter through a Whatman No. 40 (or equivalent) filter paper; wash the residue thoroughly with calcium wash solution. Combine the filtrate and washings, measure the volume, transfer to a beaker, and add, while stirring with a glass rod (avoid touching the sides of the beaker with the rod), 20 ml. of ammonium phosphate solution. While stirring continuously throughout, neutralise the solution with ammonia solution, added drop by drop from a burette, and add 20 ml. in excess, together with a further 10 ml of ammonia solution for each 100 ml. of solution in the beaker. Set the beaker aside for at least 4 hours or, preferably, overnight. Filter through a No. 4 sintered-silica crucible, and wash the residue with cold 5% v/v ammonia solution, ensuring that any precipitate adhering to the sides of the beaker and the glass rod is transferred to the crucible. Dry the crucible and residue, transfer to a cool muffle furnace, slowly raise the temperature to 950°C, and heat at this temperature for ½ to 1 hour. Allow the crucible to cool in a desiccator, and weigh. Calculate the weight of the precipitate to its equivalent of magnesium by multiplying its weight by 0.2184.

14.2 Atomic Absorption Spectrophotometric Method.

14.21 Apparatus.

Atomic absorption spectrophotometer.

Magnesium hollow-cathode lamp.

14.22 Reagents.

Hydrochloric acid, 0.5 *N*.

Magnesium sulphate standard solution – Dissolve 1.013 g. magnesium sulphate, Mg SO_4. $7H_2O$, in 0.5 N hydrochloric acid and dilute to 100 ml. with 0.5 N hydrochloric acid. 1 ml. ≡ 1 mg. magnesium. Dilute this solution as required.

Strontium chloride solution – Dissolve 15 g. strontium chloride, $SrCl_2$. $6H_2O$, in 0.5 N hydrochloric acid and dilute to 100 ml. with 0.5 N hydrochloric acid.

14.23 Procedure.

Set up the instrument using the line at 285.2 nm. Prepare from the standard magnesium solution a series of solutions, in 0.5 N hydrochloric acid, containing between 0 and 3 ppm. magnesium (see Note). Dilute a suitable aliquot of the sample solution, prepared in accordance with paragraph 11.2, with 0.5 N hydrochloric acid to produce a standard volume of solution containing between 0 and 3 ppm. magnesium (see Note). Prepare a blank solution from which only the sample has been omitted (see Note).

Spray distilled water into the flame and zero the instrument.

Spray successively, in triplicate, the standard solutions, sample and blank, washing the instrument through with distilled water between each spraying. Record the galvanometer deflection, or the peak height on the recorder if a recording instrument is used. Plot the mean reading obtained for each standard solution against its magnesium content. Determine the magnesium content of the sample and blank solutions from the graph and from the difference between them calculate the magnesium content of the sample. If a large number of samples is being examined one or more standard solutions must be resprayed at intervals during the course of the analyses.

NOTE: If the sample contains phosphate add strontium chloride solution at the rate of 5 ml. for each 50 ml. of diluted sample solution, before adjusting to standard volume.

15. DETERMINATION OF MANGANESE.

15.1 Reagents.

Orthophosphoric acid, concentrated (d=1.75).

Potassium periodate.

Potassium permanganate (*stock manganese solution*) – Dissolve 0.288 g. potassium permanganate in 100 to 200 ml. water, add 5 ml. 25% v/v sulphuric acid and dilute with water to 1 litre at 20°C.

Potassium permanganate (*standard manganese solution*) – Dilute 10 ml. stock solution to 100 ml. with water at 20°C immediately before use. 1 ml. ≡ 10 µg. manganese.

Sulphuric acid, concentrated (d=1.84).

Sulphuric acid, 25% v/v – To 50 ml. water cautiously add 25 ml. concentrated sulphuric acid (d=1.84). Cool and dilute to 100 ml.

15.2 Dissolution of the sample.

Prepare a solution of the sample as described in paragraph 11.2.

15.3 Procedure.

Transfer to a small beaker a suitable aliquot (containing not more than 70 µg. of manganese) of the solution prepared in accordance with paragraph 11.2. Evaporate just to dryness at a low heat on a hot plate, cool, add 10 ml. water, 1.5 ml. orthophosphoric acid and 1.5 ml. concentrated sulphuric acid. Warm until the residue is dissolved and evaporate on the hot plate at a low heat until the solution just fumes. Cool, add 3 ml. water, warm again and transfer the solution to a glass-stoppered tube calibrated at 10 ml. Wash the beaker with 2 further 3 ml. quantities of water, adding these to the contents of the tube. (If there is a precipitate, allow the solution to stand and withdraw an aliquot of the clear supernatant liquid). Add 0.5 g. potassium periodate, adjust the volume of the solution to just above the 10 ml. mark with water and heat the loosely stoppered tube in a boiling waterbath for 30 minutes. Cool, and adjust the volume to the mark with water. Carry out a blank determination on all the reagents used.

Measure the extinctions of the test and blank solutions at a wavelength of 526 nm., using 1 cm. cells, with water in the comparison cell. Read from a previously prepared calibration graph the number of micrograms of manganese corresponding to the observed extinctions of the test and blank solutions, and so obtain by difference the net measure of manganese in the sample.

Establish the calibration graph as follows: –

Measure amounts of the standard manganese solution corresponding to 0, 10, 20, 30, 40, 50, 60, 70 µg. manganese into a series of glass-stoppered tubes calibrated at 10 ml. To each add 1.5 ml. orthophosphoric acid and 1.5 ml. concentrated sulphuric acid, and proceed as described above for the test solution, commencing at "Add 0.5 g. potassium periodate ...". Measure the extinctions of the solutions, and construct a graph relating the extinctions to the number of micrograms of manganese.

16. DETERMINATION OF MOLYBDENUM.

16.1 Reagents.

Ammonium molybdate (*stock molybdenum solution*) – Dissolve 1.840 g. ammonium molybdate, $(NH_4)_6\ Mo_7O_{24}.\ 4H_2O$, in water and dilute to 1000 ml. at 20°C.

Ammonium molybdate (*standard molybdenum solution*) – Dilute 1 ml. stock solution to 1000 ml. with water at 20°C immediately before use. 1 ml. ≡ 1 µg. molybdenum.

Ammonium ferrous sulphate solution – Dissolve 4 g. ammonium ferrous sulphate in water and dilute to 1000 ml.

Hydrochloric acid, N.

Hydrochloric acid, 2 N.

Potassium thiocyanate solution – Dissolve 40 g. potassium thiocyanate in water and dilute to 100 ml.

Sodium sulphate, anhydrous.

Solvent mixture – Mix equal volumes of carbon tetrachloride and 3-methylbutan-1-o1.

Stannous chloride solution. Suspend 40 g. stannous chloride dihydrate in 20 ml. 6.5 N hydrochloric acid, add water to dissolve and dilute to 100 ml. Filter if turbid.

16.2 Dissolution of the sample.

Prepare a solution of the sample as described in paragraph 11.2.

16.3 Procedure.

Transfer a suitable aliquot of the solution prepared in accordance with paragraph 11.2 to a 125 ml. separating funnel, add 1 ml. ammonium ferrous sulphate solution and sufficient N hydrochloric acid to bring the volume to 50 ml. (see Note), then add 1 ml. potassium thiocyanate solution and mix. Add 1 ml. stannous chloride solution, and mix again. Add exactly 7 ml. solvent mixture, shake vigorously for 2 minutes and allow to separate for 15 minutes. Filter the lower layer through a 7 cm. paper into a small stoppered tube.

If the lower layer is not bright or if filtration is difficult, filter through a small suitable column packed with anhydrous sodium sulphate, solid stannous chloride and plugged with cotton wool.

Carry out a blank determination on all the reagents used.

Measure the extinction of the test and blank solutions at a wavelength of 470 nm., using 1 cm. cells with water in the comparison cell.

Read the number of micrograms of molybdenum equivalent to the observed extinctions of the test and blank solutions from a previously prepared calibration graph, and so obtain the net measure of molybdenum in the sample.

Establish the calibration graph as follows: –

Measure amounts of the standard molybdenum solution corresponding to 0, 5, 10, 15, 20, 25 µg. molybdenum into a series of 125 ml. separating funnels. Add to each funnel 1 ml. ammonium ferrous sulphate and 25 ml. 2 N hydrochloric acid, dilute to 50 ml. and proceed as for the test solution, as described above beginning at "then add 1 ml. potassium thiocyanate solution and mix". Measure the extinctions of the solutions at a wave-length of 470 nm. and construct a graph relating extinction to the number of micrograms of molybdenum.

NOTE. The acidity of the final solution must not exceed 1.5 N with respect to hydrochloric acid; with more strongly acid conditions, fading of the colour will occur.

17. DETERMINATION OF FINENESS.

17.1 Method of sieving.

Use the method appropriate to the size of the sieve which is prescribed or declared or referred to in the implied definition.

17.11 Sieves having apertures of less than 1/8″ square.

Thoroughly mix the sample and quarter down until a portion of about 100 g. is obtained. Heat this portion at 100°C until dry, and thoroughly mix. Weigh to the nearest centigram about 20 g. and transfer to the sieve with the lower receiver attached. Continue as in 17.2.

17.12 Sieves having apertures of 1/8″ square or more but less than ¼″ square.

Oven dry the sample, at 100°C for 24 hours, and thoroughly mix. Weigh to the nearest centigram about 200 g. and transfer to the sieve with the lower receiver attached. Continue as in 17.2.

17.13 Sieves having apertures of ¼″ square or more.

If the sample appears moist or damp, oven dry at 100°C for 24 hours, but if the sample appears dry, heating is not necessary. Thoroughly mix the sample and weigh to the nearest centigram about 500 g. and transfer to the sieve with the lower receiver attached. Continue as in 17.2.

17.2

Shake the sieve for 5 mins., frequently tapping the side. Disintegrate soft lumps such as can be caused to crumble by the application of the fibres of a soft brush, taking care that the hard part of the brush does not make contact with the sieve, and that the brush is not used to brush particles through the sieve. Brush out the powder in the lower receiver and weigh. Replace the receiver and repeat the shaking and tapping procedure for 2 mins. Add the powder in the receiver to the first portion and weigh. Repeat the process until not more than 40 mg. passes through the sieve during 2 minutes.

17.3 Calculation.

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

NOTE: Where a neutralising value is to be determined, the loss in weight on drying at 100°C must be determined and due allowance for the moisture made after the determination of neutralising value.

SCHEDULE 3

(ARTICLES 1(5), 4(1), 5(3), 6(3), 7, 8(1) AND 12(2) OF THE LAW).

METHODS OF ANALYSIS OF FEEDING STUFFS

(A "decimal" system has been adopted for the numbering of divisions and sub-divisions in this Schedule. It is explained at the beginning of Schedule 2).

The main divisions in this Schedule are as follows: –

1. Preparation of the Sample for Analysis.
2. Determination of Moisture.
3. Determination of Oil.
4. Determination of Protein.
5. Determination of Urea nitrogen.
6. Determination of Phosphoric Acid.
7. Determination of Fibre.
8. Determination of Sugar.
9. Determination of Salt.
10. Determination of Ash.
11. Determination of Sand, Silicious Matter or Other Insoluble Mineral Matter.
12. Determination of Copper.
13. Determination of Magnesium.
14. Determination of Acinitrazole.
15. Determination of Amprolium.
16. Determination of Nitrofurazone.
17. Determination of Sulphaquinoxaline.
18. Determination of Ethopabate.
19. Determination of Furazolidone.
20. Determination of Dinitolinide.
21. Determination of Calcium.

NOTE. References to "water" mean purified water as defined in the British Pharmacopoeia. All reagents used should be of analytical quality.

1. PREPARATION OF SAMPLE FOR ANALYSIS.

With some materials, fine grinding may lead to loss or gain of moisture, and allowance for this must be made. Grinding should be as rapid as possible and unnecessary exposure to the atmosphere avoided. Grinding in a laboratory mill is usually quicker than grinding in a mortar although the latter is permissible.

1.1 If the sample is in a fine condition and passes through a sieve having apertures of about 1 mm. square[9] mix thoroughly and transfer a portion of not less than 100 g. to a non-corrodible container with an air-tight closure.

1.2 If the sample does not wholly pass through a sieve having apertures of about 1 mm. square,[10] and wholly passes through a sieve having apertures from 2 to 3 mm. square,[11] mix thoroughly and further grind a portion of not less than 100 g. to pass through a sieve having apertures of about 1 mm. square.[12] Transfer the portion so prepared to a non-corrodible container provided with an air-tight closure.

1.3 If the sample is in coarse condition as, for example, pieces of broken cake, carefully grind until the whole passes through a sieve having apertures of from 2 to 3 mm. square.[13] Mix thoroughly and further grind a portion of not less than 100 g. to pass through a sieve having apertures of about 1 mm. square.[14] Transfer the portion so prepared to a non-corrodible container provided with an air-tight closure.

1.4 If the sample is appreciably moist or if for any reason the processes of grinding and mixing are likely to result in loss or gain of moisture, take a sample immediately after the preliminary mixing procedure described in paragraph 1.2 or the preliminary grinding and mixing procedure described in paragraph 1.3 for the determination of moisture by the method described in paragraph 2. Determine also the moisture content in the finally prepared sample so that the results of the analysis may be corrected to correspond with the sample in its original condition as regards moisture.

1.5 If, because of its physical condition, grinding is difficult, take a portion immediately after the preliminary mixing procedure described in

[9] British Standard Test Sieve, Mesh No. 16 is suitable (British Standards for Test Sieves 410 : 1962.

[10] British Standard Test Sieve, Mesh No. 16 is suitable British Standards for Test Sieves 410 : 1962

[11] British Standard Test Sieve, Mesh No. 8,7 or 6 is suitable British Standards for Test Sieves 410 : 1962

Where an analysis for copper has to be carried out a stainless steel sieve should be used. (See para 12.12)

[12] British Standard Test Sieve, Mesh No. 16 is suitable British Standards for Test Sieves 410 : 1962

[13] British Standard Test Sieve, Mesh No. 8,7 or 6 is suitable British Standards for Test Sieves 410 : 1962

Where an analysis for copper has to be carried out a stainless steel sieve should be used. (See para 12.12)

[14]British Standard Test Sieve, Mesh No. 16 is suitable (British Standards for Test Sieves 410 : 1962. Where an analysis for copper has to be carried out a stainless steel sieve should be used. (See para 12.12)

paragraph 1.2 or the preliminary grinding and mixing procedure described in paragraph 1.3 for the determination of moisture by the method described in paragraph 2. Dry the sample until grinding with an iron mortar and pestle, or by other means, enables the sample to be passed completely through a sieve having apertures of about 1 mm. square.[14] Determine also the moisture content in the finally prepared sample so that the results of the analysis may be corrected to correspond with the sample in its original condition as regards moisture.

1.6 Treat by any other suitable means materials which cannot conveniently be ground or passed through a sieve.

2. DETERMINATION OF MOISTURE.

Weigh to the nearest mg. about 5 g. of the sample, heat at 100°C for 2 to 3 hours, cool in a desiccator and weigh. Reheat for another hour, cool and reweigh. If the difference in weight exceeds 10 mg., continue the heating and cooling procedure until a weight constant within 2 mg. is attained. Calculate the total loss of weight as a percentage of the original weight and regard as moisture.

3. DETERMINATION OF OIL.

For the purposes of the Law "oil" means the extract obtained as a result of treatment of a feeding stuff according to the method described in paragraph 3.21 or 3.22.

3.1 REAGENT.

Petroleum spirit – light petroleum – boiling point 40°–60°C.

3.2 PROCEDURE.

3.21. For feeding stuffs not containing full cream dried milk.

Weigh to the nearest mg. about 3–5 g. of the sample; transfer to an extraction apparatus and extract with petroleum spirit for a period of at least 4 hours. Transfer the residue of the feeding stuff from the extraction apparatus to a small mortar, grind lightly and return it to the extraction apparatus. Wash out the mortar with a small quantity of petroleum spirit and add the washings to the contents of the extraction flask. Continue the extraction for at least another hour. The extract should be clear but if seen to include insoluble matter, pour it through a filter paper or cotton wool plug into another weighed flask; wash the extraction flask and the filter twice with petroleum spirit and add the washings to the contents of the second weighed flask. Remove the bulk of the solvent from the flask, dry at 100°C for 2 hours, cool and weigh. Reheat at 100°C for 30 minutes, cool and again weigh. This second weight should not differ by more than 1 or 2 mg. from the first weight. Regard this petroleum spirit as oil.

Where a sample is presumed to have an oil content in excess of 10% or where there is reason to believe that the whole of the oil will not be removed from the

feeding stuff in a 5 hours extraction, place a fresh flask on the extraction apparatus and continue the extraction with a fresh quantity of petroleum spirit for at least a further hour. Filter and wash into a second weighed flask; dry and weigh as described in the preceding paragraph.

3.22 For feeding stuffs containing full cream dried milk.

The procedure described in paragraph 3.21 above may give an incomplete extraction of oil from full cream dried milk and feeding stuffs containing full cream dried milk, and for these products the following modified procedure is prescribed. This modified procedure involves equilibration of the material with water vapour under conditions such that the moisture content is suitably increased but does not become excessive.

Weigh to the nearest mg. about 3–5 g. of the sample. Spread the weighed portion in a thin layer and place it in a suitable closed receptacle over a layer of water. Maintain at room temperature until the moisture content of the portion reaches approximately 10% and thereafter for a period of not less than 12 hours. The moisture content of the portion must not exceed 18% at the end of this time. Examine the portion so treated by the procedure described in paragraph 3.21.

4. DETERMINATION OF PROTEIN.

Ascertain the percentage of nitrogen by the method described in paragraph 4.3, and calculate the percentage of protein by multiplying the result by 6.25.

4.1 NITROGEN.

4.2 REAGENTS.

Methyl red indicator solution – Dissolve 0.025 g. methyl red in 5 ml. 90% industrial methylated spirit with the aid of 0.5 ml. 0.1 N sodium hydroxide solution. Dilute to 250 ml. with 50% industrial methylated spirit. If desired a screened methyl red indicator may be used.

Mercury or mercuric oxide.

Paraffin wax.

Sodium hydroxide, 0.2 *N* – carbonate free.

Sodium hydroxide solution, 50% *w/v* – Dissolve 500 g. sodium hydroxide in water and dilute to 1 litre.

Sodium sulphate or potassium sulphate – anhydrous.

Sodium thiosulphate.

Sucrose.

Sulphuric acid, concentrated (d=1.84) – nitrogen free.

Sulphuric acid, (or hydrochloric acid), 0.2 N.

4.3 PROCEDURE.

Weigh to the nearest mg. about 2 g. of the sample (or such an amount as shall contain not more than 250 mg. nitrogen) and transfer to a Kjeldahl flask. Add 25 ml. concentrated sulphuric acid, 2 small globules of mercury (approximately 400 mg.) or approximately 0.5 g. mercuric oxide, and 10 g. anhydrous sodium sulphate or potassium sulphate. Heat gently over a small flame until frothing ceases and the liquid is practically colourless. Continue to heat for a further 2 hours. Avoid local overheating. If frothing is excessive, add about 0.5 g. paraffin wax.

Dissolve the cooled digest in water, and make up to a total volume of about 250 ml. Taking precautions against loss of ammonia, add sufficient 50% sodium hydroxide solution to neutralise the acid and 10 ml. in excess; then add 5 g. sodium thiosulphate, mix well and connect immediately to a distillation apparatus. Distil into an appropriate volume of 0.2 N acid, controlling the rate of distillation so that not less than 150 ml. distil in 30 minutes. Titrate the excess of acid with 0.2 N sodium hydroxide solution, using methyl red solution as an indicator. Carry out a blank test on the reagents using 2 g. sucrose in place of the sample. Express the result in terms of nitrogen. 1 ml. 0.2 N acid ≡ 0.0028 g. nitrogen.

NOTE: Where there is reason to suspect that the sample contains nitrogen in the form of ammoniacal, nitrate or urea nitrogen, the appropriate determination should be made as described in paragraph 3.52, 3.53, 3.6 or 3.7 (Methods of Analysis of Fertilisers) or paragraph 5 (Methods of Analysis of Feeding Stuffs), and the amount so obtained deducted from the total nitrogen content. In the case of compound cakes or meals containing urea, the deduction of the nitrogen content of urea is unnecessary for the calculation of the protein content.

5. DETERMINATION OF UREA NITROGEN.

5.1 REAGENTS.

Activated charcoal.

Carrez solution 1 – Dissolve 21.9 g. zinc acetate dihydrate in water, and 3 ml. glacial acetic acid and dilute to 100 ml. with water.

Carrez solution 2 – Dissolve 10.6 g. potassium ferrocyanide in water and dilute to 100 ml.

p-Dimethylaminobenzaldehyde – Dissolve 2 g. p-dimethylaminobenzaldehyde in 10 ml. concentrated hydrochloric acid and dilute to 100 ml. with propan-2-ol.

Hydrochloric acid, 0.02 N.

Sodium acetate solution – Dissolve 136 g. sodium acetate ($CH_3COONa.3H_2O$) in water and dilute to 1 litre.

Urea standard solution – Dissolve 1 g. urea in water and dilute to 100 ml.

5.2 PROCEDURE.

Weigh to the nearest mg. about 5 g. of the sample (or such an amount as shall contain not more than 250 mg. urea) and transfer to a 250 ml. volumetric flask. Add 150 ml. 0.02 N hydrochloric acid, shake for 30 minutes then add 10 ml. sodium acetate solution and mix well. Add 1 g. activated charcoal (see Note) to the flask and shake well, and stand for a further 15 minutes. Add 5 ml. Carrez solution 1, followed by 5 ml. Carrez solution 2, mixing well between additions. Dilute to volume with water and mix well. Filter a portion through a suitable dry filter paper into a clean dry 250 ml. beaker. Transfer a 10 ml. aliquot of the filtrate to a 50 ml. flask, add 10.0 ml. p-dimethylaminobenzaldehyde solution, dilute to 50 ml. with water, mix well and allow to stand for 10 minutes. Determine the extinction of the solution at 435 nm. using a 1 cm. cell against a blank of 10 ml. p-dimethylaminobenzaldehyde reagent diluted to 50 ml. with water. Calculate the urea content of the sample by reference to a calibration graph prepared at the same time as the test sample. (mg. urea x 0.4665=mg. urea nitrogen).

Establish the calibration graph as follows: –

Measure amounts of standard urea solution corresponding to 50, 100, 150, 200 and 250 mg. of urea into a series of 250 ml. volumetric flasks and proceed as described above commencing at "Add 150 ml. 0.02 N hydrochloric acid, ..." Measure the extinctions of the solutions, and construct a graph relating the extinctions to the milligrams of urea.

NOTE: If the sample is highly coloured due to the presence of molasses the proportion of activated charcoal must be increased up to 5 g. The final solution after filtering should be colourless.

6. DETERMINATION OF PHOSPHORIC ACID.

For the purposes of the Law "phosphoric acid" means P_2O_5 (molecular weight 142.04).

Phosphoric acid may be determined by the quinolinium phosphomolybdate method or, alternatively, by the spectrophotometric (vanadium phosphomolybdate) method.

The quinolinium phosphomolybdate method depends on the precipitation of quinolinium phosphomolybdate under carefully controlled conditions. The spectrophotometric method compares the amount of light transmitted by the solution to that by a solution of known phosphoric acid content.

6.1 QUINOLINIUM PHOSPHOMOLYBDATE METHOD.

6.11 Reagents.

Calcium oxide – finely ground.

Citric-molybdate acid solution – Stir 54 g. molybdenum trioxide ($Mo0_3$) with 200 ml. water; add 11 g. sodium hydroxide and stir the mixture whilst heating to boiling point until the molybdenum trioxide dissolves.

Dissolve 60 g. citric acid in about 250 to 300 ml. water and add 140 ml. concentrated hydrochloric acid. Pour the molybdate solution into the acid solution, which is stirred throughout the addition. Then cool and, if necessary, filter the solution through a paper pulp pad. Dilute the solution to 1 litre. If the solution is slightly green or blue in colour, add dropwise a dilute (0.5 or 1.0%) solution of potassium bromate until the colour is discharged. This reagent should be kept in the dark.

Hydrochloric acid, concentrated (d=1.18).

Hydrochloric acid, 25% v/v – Dilute 25 ml. concentrated hydrochloric acid with water to 100 ml.

Hydrochloric acid, 0.5 N.

Hydrochloric acid, 0.1 N.

Indicator solution – Mix 3 volumes of thymol blue solution and 2 volumes of phenolphthalein solution prepared as follows: –

Thymol blue solution – Dissolve 0.25 g. thymol blue in 5.5 ml. 0.1 N sodium hydroxide solution and 125 ml. industrial methylated spirit. Dilute with water to 250 ml.

Phenolphthalein solution – Dissolve 0.25 g. phenolphthalein in 150 ml. industrial methylated spirit and dilute with water to 250 ml.

Nitric acid, concentrated (d=1.42).

Quinoline solution – Measure 60 ml. concentrated hydrochloric acid and 300 to 400 ml. water into a 1 litre beaker and warm to 70°–80°C. Pour 50 ml. quinoline in a thin stream into the diluted acid, whilst stirring. When the quinoline has dissolved, cool the solution, dilute to 1 litre and, if necessary, filter through a paper pulp filter.

Sodium hydroxide, 5 N.

Sodium hydroxide, 0.5 *N* – carbonate free.

Sodium hydroxide, 0.1 *N* – carbonate free.

Surface active agent – 0.5% solution of sodium dodecylbenzenesulphonate is suitable.

6.12 Dissolution of the sample.

Weigh to the nearest mg. about 5 g. of the sample into a capsule or dish; add 1 g. calcium oxide, mix well and thoroughly wet with a little water. Dry the mixture and incinerate at a temperature not exceeding 500°C until completely charred. Cool, transfer the contents of the capsule or dish to a 250 ml. beaker and add 10 ml. water; then add slowly 12 ml. concentrated hydrochloric acid, taking suitable precautions to avoid loss by effervescence, and finally 5 ml. concentrated nitric acid. Heat to incipient boiling and keep at this temperature for 10 minutes. Dilute with about 10 ml. water, filter, transfer the insoluble matter to the filter paper with a minimum amount of water and wash twice with small volumes of water. Then transfer the filter paper and insoluble matter to the original capsule or dish and incinerate until all the carbon is destroyed. Combine the ash with the filtrate and heat to boiling point. Cool, transfer to a

250 ml. volumetric flask, dilute to the mark, mix well and filter. Discard the first 10 or 20 ml. of the filtrate.

6.13 Procedure.

Transfer a volume of the filtrate prepared according to paragraph 6.12 containing less than 70 mg. phosphoric acid and preferably about 50 mg., to a 500 ml. stoppered conical flask marked at 150 ml. Dilute the solution with water to 100 ml. and add 5 N sodium hydroxide solution until a faint permanent turbidity or precipitate is formed. Dissolve the precipitate by the dropwise addition of 25% hydrochloric acid, but avoid an excess.

Dilute to 150 ml., add 50 ml. of the citric-molybdic acid solution, heat the solution to incipient ebullition, maintain it at this temperature for 3 minutes and then bring it to the boiling point. From a burette slowly add 25 ml. of the quinoline solution with constant swirling throughout, the first few ml. being added dropwise, the rest in a slow stream. Keep the solution gently boiling during the addition. Immerse the flask in boiling water for 5 minutes, then cool it to 15°C in running water.

Filter with suction the contents of the flask on a paper pulp pad, and wash the flask, precipitate and filter with successive small washes of cold water until they are free from acid. Transfer the filter pad and precipitate to the original flask, rinse the funnel with water and collect the rinsings in the flask. If necessary, wipe the funnel with a small piece of damp filter paper to ensure completely removal of the precipitate, and place the paper in the flask. Add water to a total of about but not exceeding 100 ml. Stopper the flask and shake it vigorously until the pulp and precipitate are completely dispersed.

Remove the stopper and wash it with water, returning the washings to the flask. Add a measured volume of 0.5 N sodium hydroxide solution sufficient to dissolve the precipitate and leave a few ml. in excess. Shake the flask vigorously until all the precipitate dissolves. (To facilitate the dispersal of the precipitate after addition of 0.5 N sodium hydroxide solution, a few drops of the surface active agent may be added if necessary.) Add 0.5–1.0 ml. of the indicator solution, and titrate the excess of sodium hydroxide with the 0.5 N hydrochloric acid until the indicator changes from violet to green-blue and then very sharply to yellow at the end point. Deduct the number of ml. of 0.5 N hydrochloric acid used from the number of ml. 0.5 N sodium hydroxide to ascertain the volume of 0.5 N sodium hydroxide equivalent to the phosphoric acid.

Carry out a blank determination on all the reagents, omitting only the sample, and using 0.1 N standard alkali and acid instead of 0.5 N for the titration. Calculate the blank terms of 0.5 N alkali and subtract it from the original result.

Calculate the amount of phosphoric acid in the portion taken for analysis from the factor 1.0 ml. 0.5 N sodium hydroxide ≡ 1.366 mg. P_2O_5.

6.2 SPECTROPHOTOMETRIC (VANADIUM PHOSPHOMOLYBDATE) METHOD.

6.21 Reagents.

Calcium oxide – finely ground.

Hydrochloric acid, concentrated (d=1.18).

Nitric acid, concentrated (d=1.42).

Potassium dihydrogen phosphate solution (stock phosphate solution) – Dissolve in water 1.917 g. potassium dihydrogen phosphate previously dried at 105°C for 1 hour and dilute to 1 litre.

Potassium dihydrogen phosphate solution (standard phosphate solution) – Dilute 50 ml. stock solution to 250 ml. with water. 1 ml. ≡ 0.2 mg. phosphoric acid (P_2O_5).

Vanado-molybdate reagent – Dissolve separately 20 g. ammonium molybdate and 1 g. ammonium vanadate in water, mix, acidify with 140 ml. concentrated nitric acid and dilute to 1 litre.

6.22 Dissolution of the sample.

Weigh to the nearest mg. about 5 g. of the sample into a capsule or dish; add 1 g. calcium oxide, mix well and thoroughly wet with a little water. Dry the mixture and incinerate at a temperature not exceeding 500°C until completely charred. Cool, transfer the contents of the capsule or dish to a 250 ml. beaker and add 10 ml. water; then add slowly 12 ml. concentrated hydrochloric acid, taking suitable precautions to avoid loss by effervescence, and finally 5 ml. of concentrated nitric acid. Heat to incipient boiling and keep at this temperature for 10 minutes. Dilute with about 10 ml. of water, filter, transfer the insoluble matter to the filter paper with a minimum amount of water and wash twice with small volumes of water. Then transfer the filter paper and insoluble matter to the original capsule or dish and incinerate until all the carbon is destroyed. Combine the ash with the filtrate and heat to boiling point. Cool, transfer to a 250 ml. volumetric flask, dilute to the mark, mix well and filter. Discard the first 10 or 20 ml. of the filtrate.

6.23 Procedure.

6.231 Standardisation of instrument.

From a burette measure into a series of 100 ml, volumetric flasks 25.0, 26.0, 27.0, 28.0, 29.0, 30.0 and 31.0 ml. of the standard phosphate solution (i.e. 5.0, 5.2, 5.4, 5.6, 5.8, 6.0 and 6.2 mg. phosphoric acid). Add 25 ml. of the vanado-molybdate reagent to each flask and dilute to 100 ml. with water making sure that the temperature of the reagent and the dilution water is 20°C. Shake and allow to stand for 10 minutes.

Set the spectrophotometer to the correct wavelength, *circa* 420 nm, fill two 1 cm. cells with the 5.0 mg. solution and check the extinction of the cells. If there

is a small difference, select the cell with the smaller readings as the standard reference cell.

Determine the apparent extinction at 20°C (corrected for cell differences) of the 5.2, 5.4, 5.6, 5.8, 6.0 and 6.2 mg. phosphoric acid solutions referred to the 5.0 mg. phosphoric acid solution as standard.

Plot a calibration graph of scale readings against known phosphoric acid content.

6.232 Analysis of sample.

Successively dilute a portion of the solution prepared according to paragraph 6.22 so that the final volume of about 25 ml. contains between 5.5 and 6.2 mg. phosphoric acid, taking care that the dilution water is at a temperature of 20°C.

Transfer this final volume to a 100 ml. volumetric flask, add 25 ml. of the vanado-molybdate reagent (at a temperature of 20°C.), dilute to the mark, mix, and allow to stand for 10 minutes. At the same time transfer 25 ml. of the standard phosphate solution (at 20°C) into a second 100 ml. volumetric flask. Add 25 ml. of the vanado-molybdate reagent (at 20°C), dilute to the mark, mix, and allow to stand for 10 minutes.

Measure the difference in extinction at 20°C between the 2 solutions and estimate the phosphoric acid content of the volume of the unknown solution from the calibration graph.

Calculate the phosphoric acid content of the sample from known dilution factors and the weight of the sample.

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

7. DETERMINATION OF FIBRE.

For the purposes of the Law "fibre" means the organic matter calculated as the result of treatment of the feeding stuff according to the method described in paragraph 7.2.

7.1 REAGENTS.

Alcohol – industrial methylated spirit.

Diethyl ether.

Hydrochloric acid, 1% *v/v* – Dilute 10 ml. concentrated hydrochloric acid with water to 1 litre.

Petroleum spirit – light petroleum – boiling point 40–60°C.

Sodium hydroxide, 0.313 *N* – This solution must be free or nearly free from sodium carbonate.

Sulphuric acid, 0.255 *N*.

7.2 PROCEDURE.

Weigh to the nearest mg. about 2.7 to 3.0 g. of the sample, transfer to an extraction apparatus and extract with petroleum spirit. Alternatively, extract with petroleum spirit by stirring, settling and decanting 3 times. Air dry the extracted sample and transfer to a dry 1000 ml. conical flask.* Add 200 ml. 0.255 N sulphuric acid measured at ordinary temperature and brought to boiling point within 1 minute. An appropriate amount of anti-foaming agent may be added if necessary. Boil gently for exactly 30 minutes, maintaining a constant volume and rotating the flask every few minutes in order to mix the contents and remove particles from the sides.

Meantime prepare a Buchner funnel fitted with a perforated plate by adjusting a piece of cut cotton cloth or filter paper to cover the holes in the plate so as to serve as a support for a circular piece of suitable filter paper. Pour boiling water into the funnel, allow to remain until the funnel is hot and then drain by applying suction. Care should be taken to ensure that the filter paper used is of such quality that it does not release any paper fibre during this and subsequent washings.

At the end of the 30 minutes boiling period, allow the acid mixture to stand for 1 minute and then pour immediately into a shallow layer of hot water under gentle suction in the prepared funnel. Adjust the suction so that the filtration of the bulk of the 200 ml. is completed within 10 minutes. Repeat the determination if this time is exceeded.

Wash the insoluble matter with boiling water until the washings are free from acid; then wash back into the original flask by means of a wash bottle containing 200 ml. 0.313 N sodium hydroxide solution measured at ordinary temperature and brought to boiling point. Boil for 30 minutes with the same precautions as those used in the earlier boiling and treatment. Allow to stand for 1 minute and then filter immediately through a suitable filter paper. Transfer the whole of the insoluble material to the filter paper by means of boiling water, wash first with boiling water then with 1% hydrochloric acid, and finally with boiling water until free from acid. Then wash twice with alcohol and 3 times with ether. Transfer the insoluble matter to a dried weighed ashless filter paper and dry at 100°C to a constant weight. Incinerate the paper and contents to an ash at a dull red heat. Subtract the weight of the ash from the increase of weight on the paper due to the insoluble material, and report the difference as fibre.

*NOTE: In the event of the sample containing 3% or more of calcium carbonate (chalk or limestone flour), it will be necessary to remove the calcium carbonate before digesting the sample with acid. This can be done at the stage in the procedure when the portion taken for analysis has been extracted with petroleum spirit. The original weight taken for the determination should be such that the actual amount of feeding stuff free from calcium carbonate is between 2.7 and 3.0 g.

Transfer the air-dried extracted sample to a 1000 ml. conical flask, add a quantity of 1% hydrochloric acid more than sufficient to neutralise the calcium carbonate present and stir well. Allow to settle, decant off the supernatant liquid through a filter and wash the residue twice by decantation with water, passing the washings through the filter. Allow the residue and the filter to drain thoroughly. Bring 200 ml. 0.255 N sulphuric acid (measured at ordinary temperature) to boiling point and use a portion of this to wash any particles on

the filter back into the flask. Add the remainder of the acid to the flask and heat to boiling point within 1 minute. Continue the determination as described in paragraph 7.2.

8. DETERMINATION OF SUGAR.

For the purposes of the Law "sugar" means total reducing sugars after inversion expressed as sucrose.

Sugar is included in the Schedules to the Law only as molasses or treacle, or as the sweetening constituent of molassed beet pulp and molasses feeds. It is necessary, therefore, as the first procedure, to "clean" the sugar from impurities, or from its absorbent body. The total reducing sugar content is then determined after inversion of the sucrose.

8.1 REAGENTS.

Fehling's solution – Mix equal volumes of a solution of copper sulphate and a solution of sodium potassium tartrate prepared as follows: –

Copper sulphate solution – Dissolve 69.28 g. copper sulphate ($CuSO_4$. $5H_2O$) in water and dilute to 1 litre.

Sodium potassium tartrate solution – Dissolve 346 g. sodium potassium tartrate and 100 g. sodium hydroxide in water and dilute to 1 litre.

NOTE: The strength of the Fehling's solution should be such that 10 ml. is equivalent to 0.0525 g. invert sugar. It should be checked by titrating with a solution of pure sucrose (inverted by the procedure described in the Note following paragraph 8.223) using the procedure described in paragraph 8.223.

Hydrochloric acid, N.

Methylene blue solution – Dissolve 2.5 g. methylene blue in water and dilute to 250 ml.

Phenolphthalein indicator solution – Dissolve 0.25 g. phenolphthalein in 150 ml. industrial methylated spirit and dilute with water to 250 ml.

Potassium ferrocyanide solution – Dissolve 106 g. potassium ferrocyanide solution in water and dilute to 1 litre.

Potassium oxalate solution – Dissolve 50 g. potassium oxalate in water and dilute to 1 litre.

Sodium hydroxide, 10% *w/v* – Dissolve 100 g. sodium hydroxide in water and dilute to 1 litre.

Zinc acetate solution – Dissolve 219 g. zinc acetate and 30 ml. glacial acetic acid in water and dilute to 1 litre.

8.2 PROCEDURE.

8.21 Preparation of the sample.

8.211 When the substance is in solid form.

Weigh to the nearest centigram about 10 g. of the sample or a sufficient quantity to contain about 2 g. sugar. Grind in a mortar with hot water (temperature not to exceed 60°C) and transfer to a 500 ml. volumetric flask using in all about 400 ml. water. Shake the flask at intervals during 30 minutes. Add 5 ml. potassium oxalate solution to the contents of the flask, followed by 5 ml. zinc acetate solution; mix well and then add 5 ml. potassium ferrocyanide solution, make up with water to 500 ml. at the correct temperature, mix well and filter. Determine the sugar in 100 ml. of the filtrate by the method described in paragraph 8.22.

8.212 When the substance is in liquid form.

Weigh to the nearest mg. about 5 g. of the sample and wash with water into a 250 ml. volumetric flask using about 200 ml. water. To clear the solution add 5 ml. zinc acetate solution. Mix, then add 5 ml. potassium ferrocyanide solution, again mix, dilute to 250 ml., mix and filter. Determine the sugar in 25 ml. of the filtrate by the method described in paragraph 8.22.

8.22 Determination of the sugar content.

8.221 Transfer the measured volume of filtrate obtained as described in paragraph 8.211 or paragraph 8.212 to a 300 ml. beaker, add 15 ml. N hydrochloric acid, dilute to 150 ml. with water, cover with a watch glass and heat to boiling point. Continue to boil for 2 minutes, cool, add 2 or 3 drops of phenolphthalein indicator solution, just neutralise with 10% sodium hydroxide solution, transfer to a 200 ml. volumetric flask and dilute to 200 ml. Filter if necessary.

8.222 Preliminary estimation.

(This estimation is usually necessary where the percentage of sugar is unknown.) – Transfer exactly 10 ml. Fehling's solution to a 250 ml. conical flask and add 20 ml. water. Add from a burette approximately 10 ml. of the filtrate prepared as described in paragraph 8.221, heat to boiling point and boil briskly for 1 minute. Add 3 drops of methylene blue solution and titrate from the burette at the rate of 1 ml. per 15 seconds until the blue colour is discharged, the contents of the flask being kept boiling throughout the titration. Note the total number of ml. required and call this X ml. This titration should not be outside the range of 15–40 ml. otherwise the determination should be repeated using a more appropriate volume of the filtrate.

8.223 Extract determination.

To 10 ml. Fehling's solution in a 250 ml. conical flask add from a burette (X-1) ml of the filtrate prepared as described in paragraph 8.221, together with sufficient water to make a total volume of 60 ml. Heat to boiling point, boil briskly for 1½ minutes and add 3 drops of methylene blue solution. Titrate from the burette at the rate of approximately 0.25 ml. per 15 seconds until the blue colour is discharged, the contents of the flask being kept boiling briskly throughout the titration which must not take more than 1½ minutes. Then the total number of ml. used in the determination equals the sugar equivalent of 10 ml. Fehling's solution.

10 ml Fehling's solution ≡ 0.0525 g. invert sugar.

Not more than 1 ml. of filtrate should be required for the completion of the titration. If more than 1 ml. is required, then the determination should be repeated using a more closely calculated volume of filtrate for the original addition. The time taken from the initial boiling point until the end of the titration should be about 3 minutes. If this time is exceeded by more than about 20 seconds, the titration should be repeated.

The total copper reducing power should be calculated as invert sugar and diminished by 1/20 to give the sugar.

NOTE. The Fehling's solution may be standardised as follows –

Dissolve 2.375 g. sucrose (dried at 100°C) in about 100 ml. water in a 300 ml. beaker, add 15 ml. N hydrochloric acid and sufficient water to give a volume of 150 ml. Heat to boiling point, boil for 2 minutes, cool, add 2 or 3 drops of phenolphthalein solution, just neutralise with 10% sodium hydroxide solution, transfer to a 500 ml. volumetric flask and dilute to 500 ml. Then follow the procedure described in paragraph 8.223.

1 ml. of this solution ≡ 0.00475 g. sucrose ≡ 0.005 g. invert sugar, i.e. 10 ml. Fehling's solution ≡ 10.5 ml. of this standard invert sugar solution.

9. DETERMINATION OF SALT.

9.1 REAGENT.

Calcium oxide – finely ground – This reagent must be free from chloride.

9.2 PROCEDURE.

Weigh to the nearest mg. about 5 g. of the sample, mix with 1 g. calcium oxide and wet with water to a thick paste. Dry the mixture, grind to a fine powder and heat to a temperature not exceeding 500°C until all the organic matter has been thoroughly charred. Extract the residue with repeated portions of hot water, filter, cool the filtrate and dilute to 250 ml. in a volumetric flask. Determine the chloride in an aliquot part of the filtrate and express the result in terms of sodium chloride (NaCl).

10. DETERMINATION OF ASH.

Weigh to the nearest mg. from 2 to 5 g. of the sample, incinerate at a temperature not exceeding 500°C until the carbon has been destroyed. Cool, weigh and regard as ash.

11. DETERMINATION OF SAND, SILICIOUS MATTER OR OTHER INSOLUBLE MINERAL MATTER.

11.1 REAGENTS.

Hydrochloric acid, concentrated (d=1.18).

Hydrochloric acid, 25% *v/v* – Dilute 25 ml. concentrated hydrochloric acid with water to 100 ml.

11.2 PROCEDURE.

Weigh to the nearest mg. from 2 to 5 g. of the sample and incinerate until all the carbon has been destroyed.* Moisten with concentrated hydrochloric acid, evaporate to dryness, bake to render the silica insoluble, and then extract repeatedly with hot 25% hydrochloric acid. Filter, wash the insoluble matter with hot water, incinerate the insoluble matter and weigh. Regard the quantity obtained as sand and silicious matter.

* The ash obtained from the procedure described in paragraph 10 may be used for this determination.

12. DETERMINATION OF COPPER.

Copper may be determined by the diethyldithiocarbamate spectrophotometric method or, alternatively by the atomic absorption spectrophotometric method.

12.1 DIETHYLDITHIOCARBAMATE SPECTROPHOTOMETRIC METHOD.

12.11 Reagents.

Ammonia solution, approximately 6 *N* – This may be prepared by passing gaseous ammonia into distilled water, or by purifying ammonia solution as described for EDTA-citrate solution below.

Carbon tetrachloride, redistilled.

Copper sulphate, stock solution – Dissolve 0.393 g. copper sulphate, $CuSO_4$. $5H_2O$, in 100 ml. 2 N sulphuric acid and dilute to 1 litre at 20°C with distilled water.

Copper sulphate standard solution – Dilute 5 ml. stock solution to 250 ml. with 2 N sulphuric acid at 20°C immediately before use. 1 ml ≡ 2µg copper.

EDTA-citrate solution – Dissolve 20 g. ammonium citrate and 5 g. of the disodium salt of ethylenediaminetetra-acetic acid (EDTA) in distilled water and dilute to 100 ml. To purify, add 0.1 ml. sodium diethyldithiocarbamate solution and extract with carbon tetrachloride. Add a further quantity of sodium diethyldithiocarbamate solution to ensure that it is in excess.

Sodium diethyldithiocarbamate solution – Dissolve 1 g. sodium diethyldithiocarbamate in distilled water and dilute to 100 ml. Filter the solution if it is not clear. Store the solution in the dark in a refrigerator and discard after 7 days.

Sodium hydroxide, 0.1 N.

Sulphuric acid, 2 N.

Thymol blue indicator solution – Dissolve 0.1 g thymol blue in 2.15 ml. 0.1 N sodium hydroxide and dilute to 100 ml. with water.

12.12 Preparation of sample.

Grind the sample to pass a stainless steel sieve having apertures about 1 mm. square. With some materials, fine grinding may lead to loss or gain of moisture, and allowance for this must be made. Grinding should be as rapid as possible and unnecessary exposure to the atmosphere avoided.

A moisture determination should be carried out on the sample "as received" and again on the sample after grinding, before analysis.

12.13 Dissolution of the sample.

Weigh to the nearest mg. about 10 g. of the sample into a silica basin, cover with a silica clock glass, and place in a cool muffle furnace. Raise the temperature to 450±10°C, and allow to ash overnight; a slow movement of air through the furnace during the initial stages of ashing is desirable. In the case of high-fat materials, care must be taken to avoid ignition of the sample.

When all the organic matter has been destroyed, cool, add 10 ml. 50% v/v hydrochloric acid, and evaporate to dryness on a water bath. Extract the soluble salts from the residue with 2 successive 10 ml. portions of boiling 2 N hydrochloric acid, decanting the solution each time through the same Whatman No. 541 (or equivalent) filter paper into a 50 ml. volumetric flask. Then add 5 ml. 50% v/v hydrochloric acid and about 5 ml. 30% v/v nitric acid to the residue in the basin, and take the mixture to dryness on a hot-plate at low heat. Finally, add a further 10 ml. boiling 2 N hydrochloric acid to the residue and filter the solution through the same paper into the flask. Dilute the combined extracts to the mark with distilled water, washing the filter paper in the process.

12.14 Procedure.

Transfer to a separating funnel a suitable aliquot (containing not more than 50µg. of copper) of the solution prepared in accordance with paragraph 12.13. Add 10 ml. EDTA-citrate solution, 2 drops thymol blue indicator solution and

ammonia solution until the mixture is coloured green or bluish-green. Cool the mixture, add 1 ml. sodium diethyldithiocarbamate solution and, from a burette, 15 ml. carbon tetrachloride. Stopper the funnel, shake vigorously for 2 minutes and allow the layers to separate. Place a piece of cotton-wool in the stem of the funnel and run off the carbon tetrachloride layer into a dry spectrophotometer cell. Avoid undue exposure of the solution to light.

Simultaneously with the test determination, carry out a blank determination on all the reagents used.

Measure immediately the extinctions of the test and blank solutions at a wavelength of 436 nm., using carbon tetrachloride in the comparison cell. Read from a previously prepared calibration graph the number of micrograms of copper corresponding to the observed extinctions of the test and blank solutions, and so obtain by difference the net measure of copper in the sample.

Establish the calibration graph as follows: –

To a series of separating funnels transfer 10 ml. EDTA-citrate solution and the following amounts of standard copper solution and 2 N sulphuric acid: –

Copper solution	0	1	2.5	5	10	15	20	25 ml
2 N sulphuric acid	25	24	22.5	20	15	10	5	0 ml

Proceed as for the test solution, as described above, commencing at "2 drops thymol blue ...". Measure the extinctions of the solutions and construct a graph relating the extinctions to the number of micrograms of copper.

12.2 ATOMIC ABSORPTION SPECTROPHOTOMETRIC METHOD.

12.21 Apparatus.

Atomic absorption spectrophotometer.

Copper hollow-cathode lamp.

12.22 Reagents.

Copper sulphate standard solution – Dissolve 0.393 g. copper sulphate, $CuSO_4.5H_2O$, in 0.5 N hydrochloric acid and dilute to 100 ml. with 0.5 N hydrochloric acid. 1 ml. ≡ 1 mg. copper. Dilute this solution as required.

Hydrochloric acid, 0.5 N.

12.23 Procedure.

Set up the instrument using the line at 324.7 nm. Prepare from the standard copper solution a series of solutions, in 0.5 N hydrochloric acid, containing between 0 and 10 ppm. copper. Dilute a suitable aliquot of the sample solution, prepared in accordance with para. 12.13, with 0.5 N hydrochloric acid to produce a standard volume of solution containing between 0 and 10 ppm. copper. Prepare a blank solution from which only the sample has been omitted.

Spray distilled water into the flame and zero the instrument. Spray successively, in triplicate, the standard solutions, sample and blank, washing the instrument

through with distilled water between each spraying. Record the galvanometer deflection, or the peak height on the recorder if a recording instrument is used. Plot the mean reading obtained for each standard solution against its copper content. Determine the copper content of the sample and blank solutions from the graph and from the difference between them calculate the copper content of the sample.

If a large number of samples is being examined one or more standard solutions must be resprayed at intervals during the course of the analyses.

13. DETERMINATION OF MAGNESIUM

Magnesium may be determined by the pyrophosphate method or, alternatively, by the atomic absorption spectrophometric method.

13.1 PYROPHOSPHATE METHOD.

13.11 Reagents.

Ammonia solution, (d=0.88)

Ammonia solution, 5% *v/v* – Dilute 5 ml. concentrated ammonia solution (d=0.88) with water to 100 ml.

Ammonium oxalate solution – saturated aqueous solution.

Ammonium phosphate solution – Dissolve 20 g. di-ammonium hydrogen phosphate, $(NH_4)_2HPO_4$, in water and dilute to 100 ml.

Calcium wash solution – Dissolve 1 g. oxalic acid, $(COOH)_2.2H_2O$ and 2 g. ammonium oxalate in water and dilute to 1000 ml.

Citric acid – monohydrate.

Hydrochloric acid, *concentrated* (d=1.18).

Hydrochloric acid, 20% *v/v* – Dilute 20 ml. concentrated hydrochloric acid (d=1.18) with water to 100 ml.

Methyl red indicator solution – Dissolve 0.025 g. methyl red in 5 ml. 90% industrial methylated spirit with the aid of 0.5 ml. 0.1 N sodium hydroxide. Dilute to 250 ml. with 50% industrial methylated spirit.

Oxalic acid solution – Dissolve 10 g. oxalic acid, $(COOH)_2.2H_2O$ in water and dilute to 100 ml.

13.12 Dissolution of the sample.

Prepare a solution of the sample as described in paragraph 12.13.

13.13 Procedure.

Transfer a suitable aliquot (containing approximately 50 mg. magnesium) of the solution, prepared in accordance with paragraph 12.13, to a 500 ml. beaker, and

add 5% v/v ammonia solution until a slight precipitate is formed. Add citric acid, in small portions, until the precipitate just dissolves, and then 1 g in excess. Heat the solution to 50°C, add 0.2 ml. (4 drops) methyl red indicator solution. Neutralise with 5% v/v ammonia solution, and add 1 ml. in excess. Add oxalic acid solution until the mixture is just acid, and then 10 ml. in excess. Boil the solution for 1 to 2 minutes, add 50 ml. saturated ammonium oxalate solution, dilute, if necessary, to about 200 ml. with distilled water, boil for a further minute, and heat on a water bath for at least 1 hour. Filter through a Whatman No. 40 (or equivalent) filter paper, wash the residue thoroughly with calcium wash solution.

Combine the filtrate and washings, measure the volume, transfer to a beaker, and add, while stirring with a glass rod (avoid touching the sides of the beaker with the rod), 20 ml. ammonium phosphate solution. While stirring continuously throughout, neutralise the solution with ammonia solution added drop by drop from a burette and add 20 ml. in excess, together with a further 10 ml. ammonia solution for each 100 ml. of solution in the beaker. Set the beaker aside for at least 4 hours or, preferably, overnight.

Filter through a No. 4 sintered-silica crucible and wash the residue with cold 5% v/v ammonia solution, ensuring that any precipitate adhering to the sides of the beaker and the glass rod is transferred to the crucible. Dry the crucible and residue, transfer to a cool muffle furnace, slowly raise the temperature to 950°C, and heat at this temperature for ½ to 1 hour. Allow the crucible to cool in a desiccator and weigh. Calculate the weight of the precipitate to its equivalent of magnesium by multiplying its weight by 0.2184.

13.2 ATOMIC ABSORPTION SPECTROPHOTOMETRIC METHOD.

13.21 Apparatus.

Atomic absorption spectrophotometer.

Magnesium hollow-cathode lamp.

13.22 Reagents.

Hydrochloric acid, 0.5. *N*

Magnesium sulphate standard solution – Dissolve 1.013 g. magnesium sulphate, $MgSO_4.7H_2O$, in 0.5 N hydrochloric acid and dilute to 100 ml. with 0.5 N hydrochloric acid. 1 ml. ≡ 1 mg. magnesium. Dilute this solution as required.

Strontium chloride solution – Dissolve 15 g. strontium chloride, $SrCl_2.6H_2O$, in 0.5 N hydrochloric acid and dilute to 100 ml. with 0.5 N hydrochloric acid.

13.23 Procedure.

Set up the instrument using the line 285.2 nm. Prepare from the standard magnesium solution a series of solutions, in 0.5 N hydrochloric acid, containing between 0 and 3 ppm. magnesium (see Note). Dilute a suitable aliquot of the

sample solution, prepared in accordance with para. 12.13, with 0.5 N hydrochloric acid to produce a standard volume of solution containing 0 and 3 ppm. magnesium (see Note). Prepare a blank solution from which only the sample has been omitted (see Note). Spray distilled water into the flame and zero the instrument. Spray successively, in triplicate, the standard solutions, sample and blank, washing the instrument through with distilled water between each spraying. Record the galvanometer deflection, or the peak height on the recorder if a recording instrument is used. Plot the mean reading obtained for each standard solution against its magnesium content. Determine the magnesium content of the sample and blank solutions from the graph and from the difference between them calculate the magnesium content of the sample. If a large number of samples is being examined one or more standard solutions must be resprayed at intervals during the course of the analyses.

NOTE. If the sample contains phosphate add strontium chloride solution, at the rate of 5 ml. for each 50 ml. diluted sample solution, before adjusting to standard.

14. DETERMINATION OF ACINITRAZOLE.

(2-acetamido-5-nitrothiazole.)

14.1 REAGENTS.

Acinitrazole standard solution – Dissolve 0.10 g. acinitrazole in dimethylformamide and dilute to 100 ml. with dimethylformamide. Dilute 5 ml. of this solution to 200 ml. with dimethylformamide. 1 ml. ≡ 25µg acinitrazole.

Aluminium oxide – suitable for chromatography. Transfer 100 g. aluminium oxide to a suitable container, add 250 ml. 1% v/v hydrochloric acid and stir mechanically for 15 minutes. Collect the slurry on filter paper in a Buchner funnel. Wash the aluminium oxide on the filter with 10 50 ml. portions of water and suck it dry. Dry it for at least 4 hours at 100°C.

Dimethylformamide.

Hydrochloric acid, 5 N.

Methanol, acidified – Add 2 ml. 5 N hydrochloric acid to 100 ml. methanol.

Sodium, hydroxide, alcoholic solution – Dilute 2.5 ml. 10 N sodium hydroxide to 100 ml. with ethanol. Stand for 2 days to allow carbonates to settle.

14.2 PROCEDURE.

Weigh about 20 g of the sample and transfer to a 250 ml. beaker. Add 60 ml. of boiling dimethylformamide, boil for 2 minutes stirring continuously and then cool to room temperature. Filter the liquid through a sintered-glass funnel (porosity 3) using gentle suction. Repeat the extraction with 60 ml. of boiling

dimethylformamide and filter through the funnel. Rinse the beaker with 2 30 ml. portions of cold dimethylformamide and filter through the funnel. Cool the filtrate to room temperature, transfer to a 200 ml. volumetric flask and dilute to volume with dimethylformamide.

Preparation of chromatographic columns: –

Glass column: – 9 mm. internal diameter glass tubing, 40 to 50 cm. long with an opening 4 to 5 mm. in diameter at the lower end. Insert a small plug of glass-wool in the lower end of the clean dry tube and compress the plug firmly with a glass rod so that a thickness of about 2 to 3 mm. is obtained. Prepare a slurry of the aluminium oxide using 3 volumes of dimethylformamide to 1 volume of aluminium oxide. Heat the slurry on a hot plate (do not boil) and then cool to room temperature. Pour the slurry into the glass column and allow it to settle to produce a column of aluminium oxide about 27 cm. high. Prepare a separate column for each sample.

Chromatography of feed extract – Run a 10 ml. aliquot of the dimethyl-formamide extract on to the top of the column and allow the liquid to pass through under gravity. Wash with 3 successive 10 ml. portions of dimethylformamide ensuring that the surface of the aluminium oxide is completely covered throughout.

Discard all dimethylformamide eluates.

Run 4 successive 10 ml. portions of acidified methanol through the column into a 50 ml. volumetric flask ensuring that the whole of the yellow band of acinitrazole is eluted. Leave about 2 ml. of the last acidified methanol portion on top of the column. Add 0.5 ml. 5 N hydrochloric acid to the flask and mix. Dilute to the mark with methanol.

Pipette 20 ml. aliquots of this solution into each of 2 25 ml. volumetric flasks. Dilute the first (1) to the mark with methanol and the second (II) with alcoholic sodium hydroxide. Prepare a reagent blank by adding 5 ml. alcoholic sodium hydroxide to a third 25 ml. volumetric flask and dilute to the mark with methanol. Measure the extinction of the solutions I and II at 410 nm. in 1 cm. cells against the reagent blank. Read the extinctions immediately after the solutions have been prepared.

Repeat the procedure using a 10 ml. aliquot of the dilute standard solution and a new aluminium oxide column commencing at "Run a 10 ml. aliquot of the dimethylformamide extract ...".

Calculate the amount of acinitrazole in the sample from the difference in extinction between solutions I and II compared with the extinction of the standard solution.

15. DETERMINATION OF AMPROLIUM.

[1-(4-amino-2-propylpyrimidin-5-yl-methyl)-2-methyl-pyridinium chloride hydrochloride.]

15.1 REAGENTS.

Amprolium standard solution – Dissolve 0.025 g. amprolium (B.Vet.C.grade) in aqueous methanol and dilute to 50 ml. with aqueous

methanol. Dilute 5 ml. of this solution to 100 ml. with aqueous methanol. (1 ml. ≡ 25µg. amprolium). The solution is stable for one week.

Methanol, aqueous – Mix 2 volumes of methanol with one volume of water. Cool to room temperature before use.

2,7-*Dihydroxynaphthalene solution* – Dissolve 0.025 g. 2,7-dihydroxynaphthalene in anhydrous methanol and dilute to 1000 ml. with anhydrous methanol.

Potassium ferricyanide solution – Dissolve 0.20 g. potassium ferricyanide in water and dilute to 100 ml.

Potassium cyanide solution – Dissolve 1 g. potassium cyanide in water and dilute to 100 ml.

Sodium hydroxide solution – Dissolve 2.25 g. sodium hydroxide in water and dilute to 200 ml.

Sodium hydroxide, methanolic solution – Dilute 15 ml. sodium hydroxide solution with methanol to 200 ml.

Colour developing reagent – Transfer 90 ml. of the dihydroxynaphthalene solution into a 250 ml. glass-stoppered flask, add 5 ml. potassium ferricyanide solution, and mix well. Then add 5 ml. of the potassium cyanide solution, stopper the flask, and mix well. Set aside for 30 to 35 minutes, and then add 100 ml. of the methanolic sodium hydroxide solution. Mix well. Use within 75 minutes, filtering through a medium-porosity sintered-glass filter just before use.

Aluminium oxide – neutral, suitable for chromatography. This material should pass the following test. Shake vigorously for at least 2 minutes 10 g. of the aluminium oxide with 100 ml. water in a glass-stoppered 250 ml. flask. Allow the slurry to settle, decant off the liquid, and determine its pH electrometrically. The pH should be 9.5 to 10.5.

To prepare the aluminium oxide for use, transfer 100 g. to a suitable container, add 500 ml. distilled water, and stir mechanically for 30 minutes. Collect the slurry on filter paper in a Buchner funnel. Wash the aluminium oxide on the filter with 3 50 ml. portions of methanol, and suck it dry. Dry it for 2 hours at 100°C in a vacuum oven. Then aluminium oxide thus prepared should be free-flowing. Store it in a stoppered bottle.

15.2 PROCEDURE.

Weigh a sufficient amount of the ground feed equivalent to 3.0 to 5.0 mg. amprolium. Transfer to a glass-stoppered 250 ml. flask, and add 200 ml. aqueous methanol. Stopper the flask, and continuously stir the contents magnetically or shake on a mechanical shaker for 60 minutes. Filter the liquid through a Whatman No. 42 (or equivalent) filter paper, and collect 25 to 40 ml. of clear filtrate, rejecting the first 10 to 15 ml. If necessary transfer the filtrate to a centrifuge tube and spin until clear.

Preparation of chromatographic columns – Glass column; 9 mm. internal diameter glass tubing, 40 to 50 cm. long with an opening 4 to 5 mm. in diameter

at the lower end. Insert a small plug of glass-wool in the lower end of the clean dry tube, and compress the plug firmly with a glass rod so that a thickness of about 2 to 3 mm. is obtained. Weigh 5 g. of the prepared aluminium oxide, and transfer it to the dry column. Pack by gentle tapping against the side of the tube. Prepare a separate column for each sample.

Chromatography of feed extract – Transfer approximately 10 ml. of the clear extract to the column, and allow the liquid to pass through the column bed by gravity. Reject the first 1.0 ml. of eluate and collect the next 5.0 ml. for subsequent colour development.

The exact volumes specified must be collected.

Mark separate centrifuge tubes X, S and B. In tube X place 4.00 ml. of the clear eluate from the column, in tube S place 4.00 ml. of the dilute amprolium standard solution and in tube B place 3.00 ml. of aqueous methanol. Add 10.0 ml. of the colour-developing reagent to the contents of each tube, stopper the tubes, and mix well. Set the stoppered tubes aside for 20 minutes, then clarify the coloured solution by spinning in a centrifuge for 2 to 3 minutes at 1500 rpm.

Decant the clear solutions into 1 cm. cells, and insert covers. If the solutions are not clear and free from suspended particles after centrifuging, decant them into the cells through a small plug of dry glass-wool. Measure the extinctions of the solutions in tubes X and S at 530 nm., using the solution in tube B as reference. Read the extinctions within 20 to 45 minutes of adding the colour-developing reagent.

Calculate the amount of amprolium in the sample from the extinctions of the sample and standard solutions.

16. DETERMINATION OF NITROFURAZONE.

(5-nitrofurfuraldehyde semicarbazone)

16.1 REAGENTS.

Acetone.

Dimethylformamide – Test the suitability of the reagent by developing the colour from nitrofurazone with solutions of phenol and sodium hydroxide (see "Procedure" below); the colour should remain stable for at least 2 hours.

Nitrofurazone standard solution – Dissolve 0.10 g. nitrofurazone (B. Vet. C. grade) in dimethylformamide and dilute to 100 ml. with dimethylformamide. Dilute 10 ml. of this solution to 100 ml. with dimethylformamide. 1 ml. ≡ 100 µg. nitrofurazone. Prepare this solution immediately before use.

Petroleum ether, boiling range 40° to 60°C.

Phenol solution – Dissolve 5 g. phenol in dimethylformamide and dilute to 100 ml. with dimethylformamide.

Potassium permanganate, 0.1 N.

Sodium dithionite solution – Dissolve 1 g dithionite, $Na_2S_2O_4$ (sodium hydrosulphite), B.P. quality, in N sodium hydroxide and dilute to 100 ml. with N sodium hydroxide. Prepare this solution immediately before use.

Sodium hydroxide, N.

16.2 PROCEDURE.

Weigh accurately an amount of sample containing about 1 mg. of nitrofurazone, and transfer it to an extraction thimble; cover the sample with a small pad of cotton-wool. Insert the packed thimble into an extraction apparatus with ground glass joints, assemble the extraction apparatus and extract the sample with petroleum ether; use an electric pad as the source of heat, so adjusted that the solvent cycles 20 times in about 45 minutes, and sufficient solvent so that the volume in the flask throughout the operation is not less than 25 ml.

Remove the packed thimble, allow the solvent to drain, and carefully remove any residual solvent in a current of warm air at a temperature not exceeding 60°C.

Transfer the packed thimble to a clean extraction apparatus, and extract the sample with acetone; use a water-bath as the source of heat so that the solvent cycles 20 times in about 1 hour, and sufficient solvent so that the volume in the flask throughout the operation is not less than 25 ml.

During the extraction shield the apparatus from light with a cardboard cylinder containing a small inspection window, or by any other suitable means. When the extraction is complete, rapidly cool the flask containing the extract to 20°C, and add 0.1 N potassium permanganate, drop by drop, until a faint pink colour is obtained that is persistent for about 2 seconds (about 4 drops are required). Evaporate the extract on a water-bath to a volume of about 5 ml., shielding the extract from light. It is important at this stage to avoid evaporating to dryness.

Remove the flask from the water-bath, place an externally ribbed conical filter funnel into the neck of the flask, and evaporate off the residual acetone under vacuum or by blowing a current of warm air (temperature not exceeding 60°C) across the top of the funnel in such a way that a slight turbulence is produced on the surface of the liquid in the flask.

Dissolve the residue in dimethylformamide, transfer the solution quantitatively to a 50 ml. volumetric flask, suitably shielded from light, and dilute to the mark at 20°C with dimethylformamide. Transfer a suitable portion containing about 200 µg. of nitrofurazone to each of 2 50 ml. volumetric flasks containing 5 ml. phenol solution.

To the contents of one flask add 2.5 ml. N sodium hydroxide, and dilute to the mark at 20°C with dimethylformamide; this is the sample solution. To the contents of the other flask add 2.5 ml. sodium dithionite solution, and dilute to the mark at 20°C with dimethylformamide; this is the blank solution and it should be a pale lemon-yellow colour free from any red or purplish tinge. Spin the solutions in a centrifuge, with a radius of 6 cm, at a speed of not less than 4000 rmp. for 2 minutes.

Measure the extinction of the clear sample solution against the blank solution in 1 cm. cells at 530 nm.

Obtain the amount of nitrofurazone present in the sample solution by reference to a previously prepared calibration graph.

Establish the calibration graph as follows: –

Measure amounts of dilute nitrofurazone standard solution, corresponding to 100, 150, 200, 250, 300 µg. of nitrofurazone into a series of 50 ml. volumetric flasks containing 5 ml. phenol solution and proceed as described above commencing at "To the contents of ...". Measure the extinctions of the solutions, and construct a graph relating the extinctions to the number of micrograms of nitrofurazone.

16.21 Nitrofurazone in the presence of furazolidone.

Carry out the determination of furazolidone according to 19.2.

Correct the extinction obtained in the determination of nitrofurazone at 530 nm. by means of the following expression:

Corrected extinction, $E_{cor} = E_{obs} - \frac{34\,Wxy}{2500}$

Where E_{obs} = extinction observed in 16.2

W = weight of sample in grams taken for nitrofurazone method

x = content per cent of furazolidone found by determination of 19.2

y = number of ml. taken from original dimethylformamide extract of 50 ml. at point "transfer a suitable portion containing about 200 µg".

17. DETERMINATION OF SULPHAQUINOXALINE.

(2-p-aminobenzenesulphonamidoquinoxaline)

17.1 REAGENTS.

Ammonium sulphamate solution – Dissolve 0.5 g. ammonium sulphamate in water and dilute to 100 ml.

Alkaline brine – Dissolve 2 g. sodium hydroxide and 5 g. sodium chloride in water and dilute to 100 ml.

Chloroform.

Dimethylformamide.

Hydrochloric acid, concentrated (d=1.18).

N -1-*Naphthylethylenediamine dihydrochloride solution*, (*coupling agent*) – Dissolve 0.1 g. N-1-naphthylethylenediamine dihydrochloride in 0.1% v/v hydrochloric acid and dilute to 100 ml. with 0.1% v/v hydrochloric acid. Store the solution in a brown-glass bottle, but discard if not colourless.

Sodium nitrate solution – Dissolve 0.10 g. sodium nitrite in water and dilute to 100 ml. Prepare immediately before use.

Sulphaquinoxaline standard solution – Dissolve 0.25 g. sulphaquinoxaline (B.Vet.C.grade) in a mixture of 25 ml. 0.1 N sodium hydroxide and 25 ml. water and dilute to 500 ml. with water. Dilute 5 ml. of this solution to 100 ml. with water. 1 ml. ≡ 25 µg. sulphaquinoxaline.

17.2 PROCEDURE.

Transfer 10 ± 0.1 g. of a representative sample of the feed to a 250 ml. conical flask, and add 20 ml. dimethylformamide. Heat the flask on a bath of boiling water for 20 minutes. Cool the flask and contents, add 60 ml. chloroform, stopper the flask, and shake it for 30 minutes. Filter the liquid through an 8 cm. sintered-glass funnel (porosity 3) under mild suction, wash the flask with 4 5 ml. portions of chloroform, and pass the washings through the funnel. Transfer the filtrate to a separating funnel, rinse the filter flask with about 15 ml. chloroform, and transfer the rinsings to the funnel. Add 50 ml. alkaline brine and 5 ml. ethanol. Thoroughly mix the layers, either by slow inversion of the funnel about 20 times or by rotating it above the horizontal axis of the stem and the stopper. Allow the layers to separate (separation is usually complete in about 15 minutes). Transfer the upper aqueous layer to a 250 ml. volumetric flask. Repeat the extraction of the chloroform layer with 3 further 50 ml. portions of alkaline brine, and add each aqueous extract to the contents of the volumetric flask.

Dilute the solution in the flask to the mark with water. Transfer 25 ml. of the solution to a 50 ml. volumetric flask, add 5 ml hydrochloric acid, and dilute to volume with water. Normally, a clear solution is obtained, but if insoluble material is present filtration is necessary, the first 15 ml. of filtrate being discarded.

Transfer 10 ml. of the acidified solution to a 150 mm. x 25 mm. boiling tube, add 2.0 ml. sodium nitrite solution, shake well to mix, and set the tube aside for 3 minutes; then add 2.0 ml ammonium sulphamate solution, mix and set the tube aside for 2 minutes. Add 1.0 ml. of the coupling agent. By means of a water-pump, apply a vacuum to the tube through rubber connections in order to remove dissolved nitrogen. Transfer the coloured solution to a 2 cm. cell, and measure the extinction of the solution at 545 nm. about 10 minutes after the coupling agent has been added. Obtain the amount of sulphaquinoxaline present in the sample solution by reference to a previously prepared calibration graph.

Establish the calibration graph as follows: –

Measure amounts of dilute sulphaquinoxaline standard solution, corresponding to 50, 100, 150, 200, 250 µg of sulphaquinoxaline into a series of 100 ml. volumetric flasks. Add 8 ml. hydrochloric acid to each flask and dilute to volume with water.

Pipette 10 ml. of each of the standard solutions into 150 mm. x 25 mm. boiling-tubes, and proceed as described above commencing at "add 2 ml. sodium nitrite solution".

18. DETERMINATION OF ETHOPABATE.

(methyl 4-acetamido-2-ethoxybenzoate)

18.1 REAGENTS.

Ammonium sulphate solution – Dissolve 1.00 g. ammonium sulphamate in water and dilute to 100 ml.

Butan -1-ol.

Chloroform.

Ethopabate, stock solution – Dissolve 40.0 mg pure ethopabate in methanol, and dilute to 100 ml. with methanol.

Ethopabate, standard solution – Dilute 10 ml. ethopabate stock solution with 50% methanol to 100 ml.

Ethopabate, working standard solution – Dilute 5.00 ml. ethopabate standard solution to 250 ml. with 50% methanol and mix well. 20 ml. of this solution contains 16.0 µg ethopabate.

Hydrochloric acid, dilute solution A – Dilute 10 ml. concentrated hydrochloric acid (d=1.18) with water to 100 ml.

Hydrochloric acid, dilute solution B – Dilute 25 ml. concentrated hydrochloric acid (d=1.18) with water to 1 litre.

Methanol, 50% *v/v* – Dilute one volume methanol to 2 volumes with water.

N -1-*Naphthylethylenediamine dihydrochloride solution*, (*coupling agent*) – Dissolve 50 mg N- 1-naphthylethylene-diamine dihydrochloride in 25 ml. water. Prepare freshly as required.

Sodium carbonate solution – Dissolve 40 g. anhydrous sodium carbonate in water and dilute to 1 litre.

Sodium chloride.

Sodium nitrite solution – Dissolve 0.20 g. sodium nitrite in water and dilute to 100 ml. Prepare immediately before use.

18.2 PROCEDURE

Weigh out a portion of the prepared sample between 5 g. and 20 g. (ideally the portion should contain about 80 µg ethopabate) and transfer it to a glass stoppered 250 ml. flask. Add 100 ml. 50% methanol and agitate the mixture for one hour. Collect sufficient clear extract for a test by passing the mixture through a fast filter paper or by centrifuging a suitable portion. This extract can be stored overnight at room temperature in a tightly stoppered flask.

Transfer 20.0 ml of the clear extract into a 50 ml. centrifuge tube, and add 5 ml. dilute hydrochloric acid, solution A. Then add 10 ml. chloroform, close the tube with a polythene stopper and shake vigorously for 3 minutes. Separate into 2 phases by centrifuging and carefully transfer the lower chloroform layer to a second 50 ml. centrifuge tube. (This is conveniently accomplished by the use of a syringe fitted with a capillary tube). Re-extract the aqueous portion in the first centrifuge tube with a second 10 ml. chloroform by mixing, centrifuging, and transferring the chloroform phase to the second centrifuge tube as before. Repeat this extraction procedure with a third 10 ml. chloroform and combine the chloroform extracts in the second centrifuge tube. Add 10 ml. sodium

carbonate solution to the combined chloroform extracts and shake vigorously for 3 minutes. Centrifuge and, without disturbing the interface, draw off most of the upper layer and discard it. Repeat the washing with another 10 ml. sodium carbonate solution and discard the aqueous layer. Wash the chloroform with 10 ml. water by closing the tube and shaking vigorously for 1 minute. Centrifuge and draw off and discard the aqueous layer. Repeat this washing with a further 10 ml. water. (Note: it is important that the chloroform interface should not be disturbed as loss of drug may occur. Also the extraction and washings should be completed in as short a time as possible, as prolonged contact with hydrochloric acid or sodium carbonate may cause partial hydrolysis of the ethopabate.)

Prepare a reagent blank and a standard in the following way:

Into separate 50 ml. centrifuge tubes transfer by pipette 20.0 ml. 50% methanol (reagent blank) and 20.0 ml. (16 µg.) ethopabate working standard solution. Add 5.0 ml. hydrochloric acid, dilute solution A to the contents of each tube and carry out the extraction procedure described above, commencing at "Then add 10 ml. chloroform, close the tube with a polythene stopper and ...".

Transfer the washed chloroform extracts obtained from the sample, the reagent blank, and the standard to 3 100 ml. beakers. Rinse the centrifuge tubes with 2 3 ml. portions of 50% methanol and add the rinsings to the respective beakers. Evaporate the contents of the beakers on a steam bath to about 2 ml. Add 5.0 ml. 50% methanol to each beaker and redissolve any solid material which has separated out.

Transfer these solutions quantitatively to 3 centrifuge tubes and rinse each beaker successively with 10, 10 and 5 ml. portions of hydrochloric acid, dilute solution B, adding the rinsings to the centrifuge tube. Immerse the tubes in a boiling water bath, so that the level of the liquid in the tubes is just below the level of the water in the bath, for 45 minutes. Remove the tubes and cool to 10–15°C.

To each tube add 1.0 ml. sodium nitrite solution, mix, and allow to stand for 2 minutes. Add 1.0 ml. ammonium sulphamate solution, mix, and set aside for 2 minutes. Add 1.0 ml. of N-1-naphthylethylenediamine dihydrochloride coupling agent solution, mix and allow to stand for 10 minutes. Then add 5.0 g. sodium chloride and 5.0 ml. butan-1-ol, stopper the tube and shake it vigorously until the sodium chloride has dissolved. Remove the stoppers and spin the tubes in a centrifuge. Measure the extinction of the butan-1-ol layer from each tube in a 10 mm. cell at 555 nm. against a cell containing pure butan-1-ol.

Calculate the quantity of ethopabate in the feed from the ratios of the extinctions of the sample and standard solutions correcting each reading for the extinction of the blank.

Calculation:

$$\text{Ethopabate in feed, per cent.} = \frac{0.008\ (A_x - A_b) \times W}{(A_s - A_b)}$$

Where A_x = optical density of sample solution

A_b = optical density of reagent blank solution

A_s = optical density of standard solution

W = weight in grams of original sample.

19. DETERMINATION OF FURAZOLIDONE.

[3-(5-nitrofurfurylideneamino)-oxazolidin-2-one]

19.1 REAGENTS.

Acetone.

Aluminium oxide – neutral aluminium oxide suitable for chromatography; activity grade 1; 100–240 mesh. Prepare the aluminium oxide as follows: Slurry 500 g. aluminium oxide with 1 litre of hot distilled water, and decant the supernatant liquid. Repeat this procedure twice more. Dry the aluminium oxide at 105°C to constant weight before use.

Amyl alcohol.

Amyl acetate.

Petroleum spirit – light petroleum – boiling range 40–60°C or 60–80°C.

Urea solution – Dissolve 90 g. urea in 100 ml. water.

19.2 PROCEDURE.

Weigh a quantity of the feed sample expected to contain between 0.9 and 1.1 mg. furazolidone into a 25 x 80 mm. extraction thimble and transfer it to a suitable extraction apparatus. Extract with petroleum spirit for half an hour, ensuring 13 to 17 cycles of solvent. Remove the extraction thimble from the apparatus, drain off residual solvent and dry the thimble and the extracted feed in a current of warm air. Place the dried thimble and contents in a clean extraction apparatus and extract with acetone for 1 hour, ensuring not less than 25 cycles of solvent. Protect the apparatus from light. Evaporate the acetone extract to 5–10 ml. on a steam bath and cool to room temperature.

Prepare a chromatographic column as follows – Glass column; 10 mm. internal diameter 300 mm. long with a constriction of 5 mm. at the lower end. Insert a plug of glass wool in the lower end and tamp it down with a suitable rod to a thickness of 2 to 3 mm. Prepare a slurry of aluminium oxide with acetone, pour the slurry into the column and allow to settle. The prepared column should be about 200 mm. high. Allow the acetone layer to drain down to the top of the aluminium oxide column.

Chromatography of feed extract – Transfer the acetone extract of the feed to the prepared chromatographic column, and elute with acetone until the furazolidone band has passed through the column and collect the eluate. Evaporate the acetone eluate just to dryness on a steam bath. Dissolve the residue in 10 ml. amyl alcohol and transfer the solution to an amber-glass 100 ml. separating funnel. Complete the transfer using 10 ml. amyl acetate as a rinse liquid. Extract the solution with 5 separate 10 ml. portions urea solution and transfer each separate aqueous extract to an amber-glass 100 ml. volumetric flask. Dilute to 100 ml. with urea solution and mix.

Measure the extinction of the solution at 375 nm. against urea solution as a blank and calculate the furazolidone content of the feed from the relationship:

$E^{1\%}_{1cm.}$ of furazolidone in urea solution = 643.

Note: Solutions of furazolidone should be protected from light at all times.

20. DETERMINATION OF DINITOLMIDE.

(3, 5-dinitro-o -toluamide)

20.1 REAGENTS.

Acetone, 95% – Add 5 ml. water to 95 ml. acetone.

Acetonitrile, 85% – Add 850 ml. acetonitrile to 150 ml. water.

Aluminium oxide – Dry a suitable grade of aluminium oxide prepared for chromatography at 105°C for 30 minutes before use.

Diaminoethane – Fresh undiscoloured diaminoethane is imperative.

Dimethylformamide, 95% – Add 5 ml. water to 95 ml. dimethylformamide.

Dinitolmide standard solution – Weigh 40.0 mg. pure dinitolmide and transfer to a 100 ml. volumetric flask. Add acetonitrile, 85%, and shake until all the dinitolmide has dissolved. Dilute to 100 ml. with acetonitrile, 85%. Dilute 10 ml. of this solution to 100 ml. with acetonitrile, 85%, to give a solution containing 0.04 mg. per ml.

20.2 PROCEDURE.

Weigh 10.0 g. of the sample and transfer to a 250 ml. conical flask. Add 65 ml. 85% acetonitrile and heat to 50±5°C. (Caution: all operations involving acetonitrile should be carried out in an efficient fume hood.) Maintain at this temperature for 30 minutes, swirling occasionally. Allow the flask to cool to room temperature and add 20 g. activated aluminium oxide, gently mixing for 3 minutes. (Note: the addition of aluminium oxide is unnecessary where the content of dinitolmide is in excess of 1%.)

Filter the solution with suction through a 40 mm. sintered glass funnel (porosity 3), transferring as much of the solids as possible. Transfer the remaining solids to the sintered glass funnel with 85% acetonitrile, using as little as possible, and suck the residue dry. Suspend the filter cake in the sintered glass funnel by the addition of a little 85% acetonitrile with gentle stirring but without suction. Remove the liquid by applying suction, then repeat the suspension and filtration. Keep the volume of the filtrate below 100 ml. Transfer the filtrate to a 100 ml. volumetric flask, dilute to volume with 85% acetonitrile and mix.

Having regard to the expected concentration of dinitolmide in the sample, dilute the filtrate with 95% acetone by reference to the following table.

Dinitolmide %	Further dilution	Aliquot ml.	Factor M
0.004– 0.012	none	4	1
0.012– 0.025	none	2	2
0.025– 0.050	x 10	10	4
0.050– 0.100	x 10	5	8
0.100– 0.250	x 10	2	20
0.25 – 0.50	x 100	10	40
0.50 – 1.00	x 100	5	80
1.00 – 2.50	x 100	2	200
2.50 – 5.00	x 1000	10	400
5.00 –10.00	x 1000	5	800
10.00 –25.00	x 1000	2	2000

Transfer the appropriate aliquot indicated in the table to each of 3 beakers, A, B and C. (Omit beaker A for samples containing dinitolmide in excess of 0.25%.) Add 1 ml. standard dinitolmide solution to beaker C and evaporate each of the solutions in beakers A, B and C at a temperature not exceeding 60°C in a current of air. Transfer 10 ml. 95% dimethylformamide to beaker A and 2 ml. 95% dimethylformamide to each of beakers B and C. Swirl the beakers intermittently for 5 minutes to dissolve the dinitolmide. Add 8 ml. diaminoethane to each of beakers B and C and mix. Filter the solution through a suitable filter paper if a persistent turbidity is formed.

Measure the extinctions, E, at 560 nm. in a 10 mm. stoppered cell, of each solution 5 minutes after the addition of diaminoethane. Keep the temperature of the cell compartment below 30°C to avoid rapid fading of colour. Calculate the dinitolmide content of the sample from the expression:

$$\text{Dinitolmide per cent} = \frac{(E_b - E_a) \times M}{100\ (E_c - E_b)}$$

21. DETERMINATION OF CALCIUM.

Calcium may be determined by the oxalate method or, alternatively, by the atomic absorption spectrophotometric method.

21.1 OXALATE METHOD.

21.11 Reagents.

Ammonia solution, 2% v/v – Dilute 20 ml. concentrated ammonia solution (d=0.88) with water to 1 litre.

Ammonium acetate solution – Dissolve 500 g. ammonium acetate in 500 ml. water.

Ammonium oxalate solution – saturated aqueous solution.

Bromocresol green indicator solution – Dissolve 0.05 g. bromocresol green in 20 ml. ethanol and dilute with water to 100 ml.

Citric acid – monohydrate.

Hydrochloric acid, 50% v/v – Dilute 50 ml. concentrated hydrochloric acid (d=1.18) with water to 100 ml.

Potassium permanganate, 0.1 N.

Sulphuric acid, 20% *v/v* – Cautiously add 100 ml. concentrated sulphuric acid (d.=1.84) to 400 ml. water, and, while hot, add 0.1 N potassium permanganate drop by drop until a faint pink colour persists.

21.12 Dissolution of the sample.

Weigh to the nearest mg., 5 g. of the sample into a platinum or silica basin and incinerate at a temperature not exceeding 500°C until all the organic matter has been destroyed. Allow to cool, moisten the ash with water and cautiously add 10 ml. 50% v/v hydrochloric acid, avoiding loss by use of a cover glass. Wash the cover glass with water, adding the washings to the basin and evaporate to dryness. Continue heating for at least one hour to dehydrate any silica which may be present. Cool, add 20 ml. water and 10 ml. 50% v/v hydrochloric acid, bring to the boil and filter into a 250 ml. volumetric flask. Wash the basin and filter with hot water collecting the washings in the flask. Cool, make up to volume and mix.

21.13 Procedure.

Transfer an aliquot of the filtrate, containing about 40 mg. Ca., to a 400 ml. beaker and add water to make the volume approximately 150 ml. Add sufficient bromocresol green indicator, 1–2 g. citric acid, and ammonium acetate solution drop by drop until the colour changes to yellow-green (pH 4.0). Bring the solution to the boil and while boiling, slowly add with stirring 20 ml. boiling ammonium oxalate solution. Digest the mixture at boiling point for 15 minutes, allow to cool and stand for at least 4 hours. Decant the supernatant liquid through a sintered glass crucible (porosity 4). Wash down the sides of the beaker with hot water, stir up the calcium oxalate precipitate and allow to settle. Decant the supernatant liquid through the sintered glass crucible. Transfer the precipitate to the sintered glass crucible with 2% v/v ammonia solution and wash the beaker and crucible with 2% v/v ammonia solution until the washings are free from chloride. Remove the crucible and carefully rinse the outside with water, discarding the rinsings. Transfer the bulk of the precipitate to the original beaker and wash the remainder through with hot 20% v/v sulphuric acid, adding the washings to the beaker. Add 70–80 ml. boiling water and mix to dissolve the precipitate. Heat the contents to 75–80°C and titrate with 0.1 N potassium permanganate until a faint pink colour persists for 30 seconds, transferring the crucible to the beaker towards the end of the titration.

1 ml. 0.1 N $KMnO_4 \equiv$ 2.0 mg. calcium.

21.2 ATOMIC ABSORPTION SPECTROPHOTOMETRIC METHOD.

21.21 Apparatus.

Atomic absorption spectrophotometer.

Calcium hollow-cathode lamp.

21.22 Reagents.

Calcium stock solution – Dry calcium carbonate at 105°C for 1 hour. Transfer 2.497 g. into a 1 litre volumetric flask using approximately 100 ml. water. Add slowly with swirling 60 ml. N hydrochloric acid. When all the calcium carbonate has dissolved, dilute to 1 litre with water.

1 ml. ≡ 1 mg. calcium.

Calcium dilute solution – Dilute 20 ml. calcium stock solution to 200 ml.

1 ml. ≡ 100 µg. calcium.

Calcium working standard solutions – Add 10 ml. releasing agent to each of 6 100 ml. volumetric flasks. Measure 0, 3, 6, 9, 12, 15 ml. dilute calcium solution (1 ml. ≡ 100 µg. calcium) into the flasks and dilute to 100 ml. with water. The flasks contain 0, 3, 6, 9, 12, 15 µg. Ca. per ml. respectively.

Lanthanum oxide solution (releasing agent) – Wet 117.3 g. lanthanum oxide, La_2O_3, low in calcium with water. Add 350 ml. concentrated hydrochloric acid (d=1.18) slowly, and shake until all the lanthanum oxide is dissolved. Allow to cool and dilute to 1 litre with water.

21.23 Procedure.

Set up the instrument using the line at 422.7 nm. Use a fuel rich flame. Add releasing agent and water to a suitable aliquot of the sample solution, prepared in accordance with para. 21.12 to produce a standard volume of solution to contain between 5 and 10 µg. of calcium per ml. and 10% v/v releasing agent. Prepare a blank solution from which only the sample has been omitted. Spray water into the flame and zero the instrument. Spray successively, in triplicate, the standard solutions, sample and blank, washing the instrument through with water between each spraying. Plot the mean reading obtained for each standard solution against its calcium content. Determine the calcium content of the sample and blank solutions from the graph and from the difference between them calculate the calcium content of the sample. If a number of samples is being examined, one or more standard solutions must be resprayed at intervals during the course of the analyses.

SCHEDULE 4

(ARTICLES 1(5) AND 3(5) OF THE LAW)

LIMITS OF VARIATION

PART 1

LIMITS OF VARIATION FOR FERTILISERS

Article	Limits of Variation (expressed as percentages of the *whole bulk*				
	Nitrogen	Phosphoric acid soluble in water	Phosphoric acid insoluble in water	Phosphoric acid	Potash
1. Calcium cyanamide	0.5	–	–	–	–
2. Dissolved or vitriolised bone: -					
(i) When the total of the percentages of phosphoric acid (soluble and insoluble) stated amounts to 14 or more, then:					
(a) If the excess of the actual percentage of insoluble phosphoric acid over that stated is 1.5 or more	0.3	2.0	–	–	–
(b) If such excess is not less than 1, but is less than 1.5	0.3	1.5	–	–	–
(c) If such excess is not less than 0.5 but is less than 1	0.3	1.0	–	–	–
(ii) In all other cases ...	0.3	0.5	0.5	–	–
3 Dried blood for fertilising purposes	0.5	–	–	–	
4. Hoofs	0.5	–	–	–	–
5. Hoofs and horns	0.5	–	–	–	–
6. Horns	0.5	–	–	–	–
7. Nitrate of lime	0.5	–	–	–	–
8. Nitrate of potash	0.5	–	–	–	2.0
9. Nitrate of soda	0.5	–	–	–	–
10. Oil seed fertiliser as described in Schedule 1 of the Law	0.5	–	–	–	–

11. Potassic nitrate of soda	0.5	–	–	–	0.75
12. Potassium salts used as fertilisers, as described in Schedule 1 of the Law: -					
(a) If the percentage of potash stated does not exceed 15	–	–	–	–	1.0
(b) If such percentage exceeds 15	–	–	–	–	2.0

Article	Limits of Variation (percentages are percentages of the *whole bulk)*
13. A product not otherwise mentioned in Part 1 of Schedule 1 of the Law obtained by mixing one or more of the articles mentioned in Part 1 of Schedule 1 of the Law with any other such article or with any other substance or substances.	Nitrogen, potash, phosphoric acid soluble in water, and phosphoric acid insoluble in water respectively, (a) 0.5%, where the amount stated does not exceed 5%; (b) 0.75%, where the amount stated exceeds 5% but does not exceed 8%; (c) One eighth of the amount stated, where the amount stated exceeds 8% and the quantity sampled does not exceed one ton; (d) One tenth of the amount stated, where the amount stated exceeds 8% and the quantity sampled exceeds one ton: Provided that the variation from each amount stated shall not exceed 1.75% and where the total of the amounts stated is 25% or over, the amount of all variations taken together after setting off deficiencies against excesses shall not exceed 1/20 of the aforesaid total.
14. Ammonium nitrate and mixtures of ammonium nitrate with any article not mentioned elsewhere in Schedule 1 of the Law.	Nitrogen, 1/20 of the amount stated.
15. Ammonium sulphate nitrate ...	Nitrogen, 1/20 of the amount stated.
16. Basic slag	Total phosphoric acid, 1%; phosphoric acid soluble in citric acid, 1%; amount that will pass through a British Standard Test Sieve Mesh No. 100, 1/20 of the amount stated.
17. Bone meal or other bone product as described in Part 1 of Schedule 1 of the Law.	Nitrogen, 0.5%; phosphoric acid, 1.5%.
18. Dicalcium phosphate	Phosphoric acid soluble in citric acid, 1%.
19. Fish residues or other fish product as described in Part 1 of Schedule 1 of the Law.	Nitrogen, 0.5% and phosphoric acid, 1%; provided that the aforesaid limits may be extended if (a) an excess of one of the said

20. Meat and bone residues as described in Part 1 of Schedule 1 of the Law.	constituents is offset by a deficiency of the other in the proportion of 0.25% nitrogen to 1% phosphoric acid, and (b) the extension of the aforesaid limits does not exceed for nitrogen 0.75% and for phosphoric acid 3%.
21. Guano as described in Schedule 1 of the Law.	Nitrogen, 1/5 of the amount stated, with a minimum of 0.25% and a maximum of 1.5%; phosphoric acid, 1/10 of the amount stated, with a maximum of 2%; and potash, 1/5 of the amount stated.
22. Phosphate rock, ground or otherwise.	Phosphoric acid, 1/20 of the amount stated; amount that will pass through a British Standard Test Sieve Mesh No. 100 1/20 of the amount stated.
23. Precipitated bone phosphate; dicalcium bone phosphate.	Phosphoric acid soluble in citric acid, 1%.
24. Sulphate of ammonia	Nitrogen, 0.3%.
25. Superphosphate ... ... 26. Triple superphosphate 27. Concentrated super-phosphate	Phosphoric acid soluble in water, 1/20th of the amount stated.
28. Burnt or quick lime, ground or otherwise. 29. Burnt magnesian lime, ground or otherwise. 30. Calcium hydroxide; hydrated lime; slaked lime; slaked magnesian lime. 31. Mixed lime	Neutralising value, 1/10 of the amount stated.
32. Chalk, ground	Neutralising value, 1/20 of the amount stated.
33. Chalk, screened	Neutralising value, 1/8 of the amount stated; amount that will pass through a declared British Standard Test Sieve, 1/10 of the amount stated.
34. Limestone, ground; magnesian limestone, ground.	Neutralising value, 1/20 of the amount stated; amount that will pass through a British Standard Test Sieve Mesh No. 100, 1/20 of the amount stated.
35. Nitrogenous gas liquor; ammoniacal gas liquor; gas liquor.	Nitrogen, 0.3%.
36. Urea	Nitrogen, 0.3%.
37. Any article mentioned in this Part of this Schedule containing boron, cobalt, copper, magnesium, manganese or molybdenum.	(a) Where the amount of boron, cobalt, copper, magnesium, manganese or molybdenum stated does not exceed 250 parts per million, one half of the amount stated, and

	(b) Where the amount of boron, cobalt, copper, magnesium, manganese or molybdenum stated exceeds 250 parts per million, 3/10 of the amount stated.
38. Any article mentioned in this Part of this Schedule containing iron.	(a) Where the amount of iron stated does not exceed 250 parts per million, in the case of a deficiency, one half of the amount stated; in the case of an excess, no limit. (b) Where the amount of iron stated exceeds 250 parts per million, in the case of a deficiency, 3/10 of the amount stated; in the case of an excess, no limit.

PART 2

LIMITS OF VARIATION FOR FEEDING STUFFS

Article	Limits of Variation (percentages are percentages of the *whole bulk*)
1. Alfalfa meal; lucerne meal ... ... 2. Clover meal	Protein, 1/10 of the amount stated; fibre, 1/8 of the amount stated.
3. Coconut or copra cake or meal ... ... 4. Cotton cakes or meals not decorticated. 5. Oil cakes or meals not otherwise specifically mentioned in Schedule 1 of the Law which are the product of any one undecorticated substance or seed from which oil has been removed. 6. Palm kernel cake or meal.	Oil, 0.75%, or 1/10 of the amount stated, whichever is the greater; protein, 1/10 of the amount stated.
7. Compound cakes or meals, that is to say, a product, not otherwise mentioned in this Part of this Schedule, obtained by mixing one or more of the articles mentioned in this Part of this Schedule or in Part 2 of	Oil, 0.75%, or 1/10 of the amount stated, whichever is the greater; protein, 1/10 of the amount stated; protein equivalent of urea, 1.25% or 1/5 of the amount stated, whichever is the greater; fibre, if the actual amount exceeds that stated, 1/8 of

Schedule 2 of the Law any other such article or with any other substance or substances.	the amount stated; if the actual amount is less than that stated, one-half of the amount stated.
8. Cotton cakes or meals from decorticated or partly decorticated cotton seed. 9. Maize by-products, not otherwise specifically mentioned in Schedule 1 of the Law. 10. Oil cakes or meals not otherwise specifically mentioned in which are the product of any one decorticated or partly decorticated substance or seed from which oil has been removed. 11. Rice bran or rice meal, or the by-product produced in milling shelled rice.	Oil, 0.75%, or 1/10 of the amount stated whichever is the greater; protein, 1/10 of the amount stated; fibre, 1/8 of the amount stated.
12. Dried brewery grains	Oil, 0.75%, or 1/5 of the amount stated, whichever is the greater; protein, 1/5 of the amount stated.
12a. Dried distillery by-products (other than malt culms and dried yeast).	Oil, 0.75% or 1/5 of the amount stated, whichever is the greater; protein, 1/5 of the amount stated; fibre, if present in excess of 2%, if the actual amount exceeds that stated, 1/8 of the amount stated; if the actual amount is less than that stated, one half of the amount stated; lime (expressed as calcium (Ca)), if present in excess of 2%, 1/5 of the amount stated.
13. Dried Grass ... ... 14. Dried Grass (maintenance quality). 15. Dried green fodder crops. 16. Dried green roughage	Protein, 1/10 of the amount stated, provided that this limit of variation shall not operate so as to permit the application of the name "dried grass" to any article containing less than 13% protein or the names "dried grass (maintenance quality)" or "dried green fodder crops" to any article containing less than 10% protein.
17. Dried plain beet pulp	Fibre, 1/8 of the amount stated.
18. Dried molassed beet pulp. 19. Molasses feeds, as	Sugar, 1/10 of the amount stated; fibre, 1/8 of the amount stated.

described in Schedule 1 of the Law.	
20. Mixtures of molasses and urea.	Sugar, 1/10 of the amount stated; protein equivalent of urea, 1/5 of the amount stated.
21. Dried yeast ... ... 22. Feeding dried blood	Protein, 1/20 of the amount stated.
23. Feeding bone flour	Phosphoric acid, one-twentieth of the amount stated; protein, 1/5 of the amount stated.
24. Feeding bone meal, ground bone, or any other bone product for feeding purposes.	Phosphoric acid and protein, 1/10 of the respective amounts stated.
25. Feeding meat meal or any other product of meat for feeding purposes. 26. Feeding meat and bone meal or any other product of meat and bone for feeding purposes.	Oil, 0.75%, or 1/10 of the amount stated whichever is the greater; protein and phosphoric acid, 1/10 of the respective amounts stated; provided that these limits of variation shall not operate so as to permit the application of the names "feeding meat meal" and "feeding meat and bone meal" to articles containing less than 55% and less than 40% of protein respectively.
27. Fish meal, white fish meal, or other product obtained by drying or grinding or otherwise treating fish or fish waste.	Oil, 0.75%, or 1/10 of the amount stated whichever is the greater; protein, 1/10 of the amount stated; phosphoric acid, 1/6 of the amount stated; salt 0.75%; provided that these limits of variation shall not operate so as to permit the application of the name "white fish meal" to an article containing more than 6% of oil or 4% of salt.
28. Linseed cakes and the meals of such cakes; extracted linseed meal. 29. Maize, flaked... ... ... 30. Maize germ cake or meal ... ... 31. Maize gluten feed 32. Rape cake or meal 33. Soya cake or meal	Oil, 0.75%, or 1/8 of the amount stated whichever is the greater; protein, 1/8 of the amount stated.
34. Linseed meal	Oil, 0.75%, or 1/10 of the amount stated whichever is the greater.
35. Malt culms	Protein, 1/5 of the amount stated; fibre, 1/8 of the amount stated.
36. Oatmeal by-products	Fibre, 1/8 of the amount stated;

	provided that this limit of variation shall not operate so as to permit the application of the name "oatfeed" to any article containing more than 27% of fibre.
37. Treacle or molasses	Sugar, 1/20 of the amount stated.
38. Wheat offals or millers' offals.	Fibre, if the actual amount exceeds that stated, 1/8 of the amount stated; if the actual amount is less than that stated, 1/2 of the amount stated.
39. Any article mentioned in this Part of this Schedule containing copper.	(a) Where the amount of copper stated is between 70 parts per million and 200 parts per million, 1/2 of the amount stated, (b) Where the amount stated exceeds 200 parts per million, 3/10 of the amount stated.
40. Any article mentioned in this Part of this Schedule containing magnesium.	In the case of a deficiency of magnesium, 3/10 of the amount stated; in the case of an excess, no limit.
41. Any article mentioned in this Part of this Schedule containing coccidiostats or anti-blackhead drugs.	One half of the amount of coccidiostats or anti-blackhead drugs stated.

SCHEDULE 5

(ARTICLES 4(1), 12(4), (5), (6) AND 19(1) OF THE LAW)

FORMS OF CERTIFICATE OF ANALYSIS

PART 1

CERTIFICATE OF ANALYSIS OF FERTILISER[1]

I, the undersigned, Official Analyst for the Island of Jersey, in pursuance of the provisions of the Fertilisers and Feeding Stuffs (Jersey) Law 1950, certify that I received on the day of , 20 , from [2] 2 parts of a sample of [3] for analysis; which parts were duly sealed and fastened up and marked [4] and were accompanied by a [5] , as follows –[6]

and also by a signed statement that the sample was taken in the prescribed manner; and that one of the said parts has been analyzed by me, or under my direction, and I declare the results of analysis to be as follows: -[7]

	%		%	ppm.
Nitrogen (N)		Boron		
Phosphoric acid (P_2O_5)		Cobalt		
Total		Copper		
Soluble in water ...		Iron		
Insoluble in water ...		Magnesium		
Soluble in citric acid		Manganese		
Potash (K_2O)		Molybdenum		

Neutralising value expressed in terms of calcium oxide %

Amount that will pass through a British Standard Sieve[8] %

Names of herbicides and pesticides found[9] ... ...

and I am of opinion that[10]

The analysis was made in accordance with the Fertilisers and Feeding Stuffs (Jersey) Order 1972.

As witness my hand this day of , 20 .

(*Signature of Official Analyst*).

(1) Statements made in certificates are to be confined to matters which either are necessarily to be stated for the purposes of the Law or are voluntarily stated by the seller. They may extend to relevant matters of analysis, such as moisture content, but not to unrelated matters such as price.

(2) Here insert the name of the inspector who submitted the sample for analysis.

(3) Here insert the name of the article as stated in the statutory statement, warranty or particulars marked on or indicated by a mark applied to the article, or as the case may be.

(4) Here insert the distinguishing mark on the sample.

(5) Here insert either "statutory statement", "copy of statutory statement", "warranty", "copy of warranty", "copy of particulars marked on the article" or "copy of particulars indicated by a mark applied to the article", or as the case may be.

(6) Here insert the particulars contained in the statutory statement, or warranty, or particulars marked on or indicated by a mark applied to the article, or as the case may be.

(7) Insert relevant results under the appropriate headings, i.e. percentage or parts per million.

(8) Insert the number or size of the B.S. sieve used.

(9) Here insert the names and percentages of other ingredients found in the sample, or particulars of the fineness of grinding, when any statement as to the amount of such ingredients or as to the fineness of grinding is made in any written document (other than the statutory statement).

(10) Here enter information as follows: -

(a) If the article was sold under a name mentioned in the first column of Schedule 4 to the Law state whether it accords with the definition contained in the second column; and if not, in what respect.

(b) If the composition of the article agrees with or does not differ by more than the limits of variation from the statement of particulars contained in the statutory statement or warranty, or the particulars marked on or indicated by a mark applied to the article, or as the case may be, state that the particulars are correct within the limits of variation.

(c) If the composition of the article differs by more than the limits of variation from the particulars contained in the statutory statement, or warranty, or the particulars marked on or indicated by a mark applied to the article, or as the case may be, state the difference between the amount found and the amount stated, and that the difference is in excess of 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).

PART 2

CERTIFICATE OF ANALYSIS OF FEEDING STUFF[1]

I, the undersigned, Official Analyst for the Island of Jersey, in pursuance of the provisions of the Fertilisers and Feeding Stuffs (Jersey) Law 1950, certify that I received on the day of , 20 , from [2] 2 parts of a sample of [3] for analysis; which parts were duly sealed and fastened up and marked[4] and were accompanied by a[5] as follows –[6]

and also by a signed statement that the sample was taken in the prescribed manner; and that one of the said parts has been analyzed by me, or under my direction, and I declare the results of analysis to be as follows: -[7]

	%		%	ppm.
Oil		Copper		
Protein: Total, including protein equivalent of urea		Magnesium		
Protein equivalent of urea		Coccidiostats:[8]		
Fibre		:		
Sugar		:		
Salt (NaCl)		:		
Sand and other silicious matter... ...				
Phosphoric acid (P_2O_1)		Antiblackhead drugs[8]		
		:		
		:		

Natural or synthetic hormones present[9] ... ...

and I am of opinion that[10]

The analysis was made in accordance with the Fertilisers and Feeding Stuffs (Jersey) Order 1972.

As witness my hand this day of , 20 .

(*Signature of Official Analyst*).

[1] Statements made in certificates are to be confined to matters which either are necessarily to be stated for the purposes of the Act or are voluntarily stated by the seller. They may extend to relevant matters of analysis, such as moisture content, but not to unrelated matters such as price.

[2] Here insert the name of the inspector who submitted the sample for analysis.

[3] Here insert the name of the article as stated in the statutory statement, warranty or particulars marked on or indicated by a mark applied to the article, or as the case may be.

[4] Here insert the distinguishing mark on the sample.

[5] Here insert either "statutory statement", "copy of statutory statement", "warranty", "copy of warranty", "copy of particulars marked on the article" or "copy of particulars indicated by a mark applied to the article", or as the case may be.

[6] Here insert the particulars contained in the statutory statement, or warranty, or particulars marked on or indicated by a mark applied to the article, or as the case may be.

[7] Insert relevant results under the appropriate headings, i.e. percentage or parts per million.

[8] Insert name.

[9] Here insert: -

(a) the names and percentages of other ingredients found in the sample, when any statement as to the amount of such ingredients is made in any written document (other than the statutory statement).

(b) the name and estimated percentage of any ingredient included in Schedule 3 to the Law which is found in the sample and not expressly stated in the statutory statement.

(c) the name and estimated percentage of any ingredient found in the sample, being an ingredient deleterious to cattle (as defined by the Law) or to poultry, having regard to Article 8(2) and Schedule 5 to the Law.

(10) Here enter information as follows: -

(a) If the article was sold under a name mentioned in the first column of Schedule 4 of the Law state whether it accords with the definition contained in the second column; and if not, in what respect.

(b) If the composition of the article agrees with or does not differ by more than the limits of variation from the statement of particulars contained in the statutory statement, or warranty, or the particulars marked on or indicated by a mark applied to the article, or as the case may be, state that the particulars are correct within the limits of variation.

(c) If the composition of the article differs by more than the limits

of variation from the statement of particulars contained in the statutory statement, or warranty, or the particulars marked on or indicated by a mark applied to the article, or as the case may be, state the difference between the amount found and the amount stated, and that the difference is in excess of the limits of variation; and that the difference is to the prejudice of the purchaser, if such is believed to be the case.

(d) If the article is not suitable for feeding purposes for cattle (as defined by the Law) or for poultry, state in what respect.

(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).

ENDNOTES

Table of Legislation History

Legislation	Year and No	Commencement
Fertilisers and Feeding Stuffs (Jersey) Order 1972	R&O.5668	1 August 1972

Table of Renumbered Provisions

Original	Current
1	14
2	spent, omitted from this revised edition
3(1)	1
(2)	spent, omitted from this revised edition
4	spent, omitted from this revised edition
5	2
6	3
7	4
8	5
9	6
10	7
11	8
12	9
13	10
14	11
15	12
16	13
First Schedule	spent, omitted from this revised edition
Second Schedule	spent, omitted from this revised edition
Third Schedule	spent, omitted from this revised edition
Fourth Schedule	spent, omitted from this revised edition
Fifth Schedule	spent, omitted from this revised edition
Sixth Schedule	SCHEDULE 1
Part I	PART 1
Part II	PART 2
Part III	PART 3
Seventh Schedule	SCHEDULE 2
Eight Schedule	SCHEDULE 3
Ninth Schedule	SCHEDULE 4

Original	Current
Part I	PART 1
Part II	PART 2
Tenth Schedule	SCHEDULE 5
Part I	PART 1
Part II	PART 2

Table of Endnote References

[1] *chapter 01.800*
[2] *chapter 01.800*