SCHEDULE 2

METHODS OF ANALYSIS

PART I

3c.

DETERMINATION OF NITRIC AND AMMONIACAL NITROGEN — DEVARDA METHOD

SCOPE

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

FIELD OF APPLICATION

2. See Method 3a.

PRINCIPLE

3. Reduction of nitrates and nitrites to ammonia in a strongly alkaline solution by means of a metallic alloy composed of 45% A1, 5% Zn and 50% Cu (Devarda's alloy). Distillation of the ammonia and absorption in a known volume of standard sulfuric acid; titration of the excess sulfuric acid with a standard solution of sodium or potassium hydroxide.

4 REAGENTS

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4.1	Hydrochloric acid solution, 50% (V/V): dilute an appropriate volume of hydrochloric acid (p=1.18 g/ml) with an equal volume of water.	
4.2	Sulfuric acid, 0.05 M solution	for variant (a) (see page 16)
4.3	Sodium or potassium hydroxide, 0.1 M solution, carbonate free	
4.4	Sulfuric acid, 0.1 M solution	for variant (b) (see page 16)
4.5	Sodium or potassium hydroxide, 0.2 M solution, carbonate free	
4.6	Sulfuric acid, 0.25 M solution	for variant (c) (see page 16)
4.7	Sodium or potassium hydroxide, 0.5 M solution, carbonate free	

4.8	Devarda's alloy — powdered so that 90 to 100% will pass through a sieve with apertures less than 0.25 mm square, 50 to 75% will pass through a sieve with apertures of less than 0.075 mm square. (Pre-packed bottles containing a maximum of 100 g are recommended.)
4.9	Sodium hydroxide solution, 30 g per 100 ml, ammonia free.
4.10	Indicator solutions:
	4.10.1 Mixed indicator:
	Solution A: dissolve 1 g methyl red in 37 ml 0.1 M sodium hydroxide solution and make up to 1 litre with water.
	Solution B: dissolve 1 g methylene blue in water and make up to 1 litre. Mix 1 volume of A with 2 volumes of B.
	This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0.5 ml (10 drops).
	4.10.2 Methyl red indicator:
	Dissolve 0.1 g methyl red in 50 ml 95% ethanol, make up to 100 ml with water and filter if necessary. This indicator (4 to 5 drops) may be used instead of the preceding one.
4.11	Ethanol, 95%.
4.12	Sodium nitrate.

5 APPARATUS

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

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

PREPARATION OF THE SAMPLE

6. See Method 1.

7 PROCEDURE

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Preparation of the solution for analysis

7.1 See Method 2.

Determination

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

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

(Note) In the presence of calcium salts such as calcium nitrate and calcium ammonium nitrate, it is necessary to add 0.7 g disodium hydrogen phosphate (Na2HPO4.2H2O) before distillation for each gram of sample present in the aliquot part, to prevent the formation of calcium hydroxide.

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

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

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

Blank test

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

Control test

7.4 Before carrying out the analysis, check that the apparatus is working properly and that the correct application of the method is used, by taking an aliquot portion of a freshly prepared solution of sodium nitrate (4.12) containing, according to the variant chosen, 0.050 g to 0.150 g.

EXPRESSION OF RESULTS

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