SCHEDULE 2

METHODS OF ANALYSIS

PART I

3b.

DETERMINATION OF NITRIC AND AMMONIACAL NITROGEN — ARND METHOD

SCOPE

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

FIELD OF APPLICATION

2. See Method 3a.

PRINCIPLE

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

Distillation of the ammonia and absorption in a known volume of standard sulfuric acid solution. Titration of the excess acid with a standard solution of sodium or potassium hydroxide.

4 REAGENTS

4

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 page16)
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	Sodium hydroxide solution, approximately 2 M.
4.9	Arnd's alloy — powdered to pass through a sieve with square apertures less than 1.00 mm.
4.10	Magnesium chloride solution, 20% (W/V): Dissolve 200 g magnesium chloride (MgCl2.6H2O) in approximately 600 – 700 ml water in a one litre flat bottomed flask. To prevent frothing, add 15 g magnesium sulfate (MgSO4.7H2O). After dissolution add 2 g magnesium oxide and a few anti-bump granules of pumice stone and concentrate the suspension to 200 ml by boiling, thus expelling any trace of ammonia from the reagents. Cool, make up the volume to 1 litre and filter.
4.11	Indicator solutions: 4.11.1 Mixed indicator: Solution A: dissolve 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). 4.11.2 Methyl red indicator solution: Dissolve 0.1 g methyl red in 50 ml 95% ethanol, make up to 100 ml with water and filter if necessary. This indicator may be used (4 to 5 drops) instead of the preceding one. 4.11.3 Congo red indicator solution: Dissolve 3 g Congo red in 1 litre warm water and filter if necessary after cooling. This indicator may be used, instead of the two described above, in the neutralisation of acid extracts before distillation, using 0.5 ml per 100 ml of liquid to be neutralised.
4.12	Anti-bump granules of pumice stone washed in hydrochloric acid and ignited.
4.13	Sodium nitrate.

APPARATUS

5. See Method 2.

PREPARATION OF SAMPLE

6. See Method 1.

7 PROCEDURE

7

Preparation of the solution for analysis

7.1 See Method 2.

Determination

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

Using a pipette, take, according to the Table, an aliquot part of the clear solution and place in the distillation flask. Add sufficient water to obtain a total volume of about 350 ml (see Note), 10 g Arnd's alloy (4.8), 50 ml magnesium chloride solution (4.10) and a few fragments of pumice stone (4.12). Rapidly connect the flask to the distillation apparatus. Heat gently for about 30 minutes. Then increase the heating to distil the ammonia. Continue the distillation for about an hour.

After this time, the residue in the flask ought to have a syrupy consistency. When the distillation has finished, titrate the quantity of excess acid in the receiving flask according to the procedure in Method 2.

(Note) When the sample solution is acidic (addition of 20 ml hydrochloric acid (4.1) to dissolve the sample) the aliquot part taken for analysis is neutralised in the following way: to the distillation flask containing the aliquot part add about 250 ml water, the necessary quantity of one of the indicators (4.11.1, 4.11.2, 4.11.3) and swirl or mix carefully. Neutralise with 2 M sodium hydroxide solution (4.8) and acidify again with a drop of hydrochloric acid (4.1). Then proceed as indicated in 7.2.

Blank test

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

Control test

7.4 Before analysis, check that the apparatus is working properly and that the correct technique is applied using a freshly prepared solution of sodium nitrate (4.13) containing 0.050 g to 0.150 g nitrogen depending on the variant chosen.

EXPRESSION OF RESULTS

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