

SCHEDULE 2

METHODS OF ANALYSIS

16.

METHODS OF ANALYSIS AND TEST PROCEDURES FOR AMMONIUM NITRATE FERTILISERS CONTAINING MORE THAN 28% NITROGEN BY WEIGHT

C. Determination of the Combustible Ingredients

1 SCOPE AND FIELD OF APPLICATION

1. This method defines the procedure for the determination of the combustible content of straight ammonium nitrate fertilisers containing more than 28% nitrogen by weight.

2 PRINCIPLE

2. The carbon dioxide produced by inorganic fillers is removed in advance with an acid. The organic compounds are oxidised by means of a chromic acid/sulphuric acid mixture. Carbon dioxide formed is absorbed in a barium hydroxide solution. The precipitate is dissolved in a solution of hydrochloric acid and measured by back-titration with sodium hydroxide solution.

3 REAGENTS

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3.1 Analytical-grade chromium VI oxide; Cr-(VI)-O₃.

3.2 Sulphuric acid diluted to 60% by volume:

pour 360 ml of water into a one-litre beaker and carefully add 640 ml of sulphuric acid, density at 20°C = 1.83 g/ml.

3.3 Silver nitrate: 0.1 M solution.

3.4 Barium hydroxide:

weigh out 15 grams of barium hydroxide (Ba(OH)₂.8H₂O), and dissolve completely in hot water. Allow to cool and transfer to a one-litre flask. Fill up to the mark and mix. Filter through a pleated filter paper.

3.5 Hydrochloric acid: 0.1 M standard solution.

3.6 Sodium hydroxide: 0.1 M standard solution.

3.7 Bromophenol blue: solution of 0.4 grams per litre in water.

3.8 Phenolphthalein: solution of 2 grams per litre in 60% by volume ethanol.

3.9 Soda lime: particle dimensions, about 1.0 to 1.5 mm.

3.10 Demineralised water, freshly boiled to remove carbon dioxide.

4 APPARATUS

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4.1 Standard laboratory equipment, in particular:

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- filter crucible with a plate of sintered glass and a capacity of 15 ml; plate diameter: 20 mm; total height: 50 mm; porosity 4 (pore diameter from 5 to 15 μm);
- 600 ml beaker.

4.2 Compressed nitrogen supply.

4.3 Apparatus made up of the following parts and assembled, if possible, by means of spherical ground joints (see Figure 1).

(4.3.1) Absorption tube (A) about 200 mm long and 30 mm in diameter filled with soda lime (3.9) kept in place by fibreglass plugs.

(4.3.2) 500 ml reaction flask (B) with side arm and a round bottom.

(4.3.3) Vigreux fractionating column about 150 mm long (C').

(4.3.4) Double-surface condenser (C), 200 mm long.

(4.3.5) Drechsel bottle (D) acting as a trap for any excess acid which may distil over.

(4.3.6) Ice bath (E) to cool the Drechsel bottle.

(4.3.7) Two absorption vessels (F)₁ and (F)₂, 32 to 35 mm in diameter, the gas distributor of which comprises a 10 mm disc of low-porosity sintered glass.

(4.3.8) Suction pump and suction regulating device (G) comprising a T-shaped glass piece inserted into the circuit, the free arm of which is connected to a fine capillary tube by a short rubber tube fitted with a screw clamp.

Caution:

The use of boiling chromic acid solution in an apparatus under reduced pressure is a hazardous operation and requires appropriate precautions.

5 PROCEDURE

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Sample for analysis

5.1 Weigh approximately 10 grams of ammonium nitrate to the nearest 0.001 grams.

Removal of carbonates

5.2 Place the sample for analysis in the reaction flask B. Add 100 ml of H₂SO₄ (3.2). The prills dissolve in about 10 minutes at ambient temperature. Assemble the apparatus as indicated in the diagram: connect one end of the absorption tube (A) to the nitrogen source (4.2) via a non-return flow device containing 5 to 6 mm of mercury and the other end to the feed tube which enters the reaction flask. Place the Vigreux fractionating column (C') and the condenser (C) with cooling water supply in position. Adjust the nitrogen to provide a moderate flow through the solution, bring the solution to boiling point and heat for two minutes. At the end of this time there should be no more effervescence, if effervescence is seen, continue heating for 30 minutes. Allow solution to cool for at least 20 minutes with the nitrogen flowing through it.

Complete assembly of the apparatus as indicated in the diagram by connecting the condenser tube to the Drechsel bottle (D) and the bottle to the absorption vessels F₁ and F₂. The nitrogen must continue to pass through the solution during the assembly operation. Rapidly introduce 50 ml of barium hydroxide solution (3.4) into each of the absorption vessels (F₁ and F₂).

Bubble a stream of nitrogen through for about 10 minutes. The solution must remain clear in the absorbers. If this does not happen, the carbonate removal process must be *adjusted*.

Oxidation and absorption

5.3 After withdrawing the nitrogen feed tube, rapidly introduce 20 grams of chromium trioxide (3.1) and 6 ml of silver nitrate solution (3.3) via the side arm of the reaction flask (B). Connect the apparatus to the suction pump and adjust the nitrogen flow so that a steady stream of gas bubbles passes through the sintered-glass absorbers F₁ and F₂.

Heat the reaction flask (B) until the liquid boils and keep it boiling for one-and-a-half hours(1). It may be necessary to adjust the suction-regulating valve (G) to control the nitrogen flow since it is possible that the barium carbonate precipitated during the test may block the sintered-glass discs. The operation is satisfactory when the barium hydroxide solution in the absorber F₂ remains clear. Otherwise repeat the test. Stop heating and dismantle the apparatus. Wash each of the distributors both inside and outside to remove barium hydroxide and collect the washings in the corresponding absorber. Place the distributors one after the other in a 600 ml beaker which will subsequently be used for the determination.

Rapidly filter under vacuum firstly the contents of absorber F₂ and then of absorber F₁ using the sintered-glass crucible. Collect the precipitate by rinsing the absorbers with water (3.10) and wash the crucible with 50 ml of the same water. Place the crucible in the 600 ml beaker and add about 100 ml of boiled water (3.10). Introduce 50 ml of boiled water into each of the absorbers and pass nitrogen through the distributors for five minutes. Combine the water with that from the beaker. Repeat the operation once to ensure that the distributors are rinsed thoroughly.

Measurement of the carbonates originating from organic material

5.4 Add five drops of phenolphthalein (3.8) to the contents of the beaker. The solution becomes red in colour. Add hydrochloric acid (3.5) drop by drop until the pink colour just disappears. Stir the solution well in the crucible to check that the pink colour does not reappear. Add five drops of bromophenol blue and titrate with hydrochloric acid until the solution turns yellow, Add a further 10 ml of hydrochloric acid.

Heat the solution to boiling point and continue boiling for a maximum of one minute. Check carefully that no precipitate remains in the liquid.

Allow to cool and back titrate with the sodium hydroxide solution (3.6)

6 BLANK TEST

6. Carry out a blank test following the same procedure and using the same quantities of all reagents.

7 EXPRESSION OF RESULTS

7. The content of combustible ingredients (CC), expressed as carbon, as a percentage by mass of the sample, is given by the formula:

$$C\% = 0.06 \times \frac{V_1 - V_2}{E}$$

where:

E = the mass in grams of the test portion;

(1) A reaction time of one-and-a-half-hours, is sufficient in the case of most of the organic substance in the presence of silver nitrate catalyst.

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V_1 = the total volume in ml of 0.1 M hydrochloric acid added after the change in colour of the phenolphthalein;

V_2 = the volume in ml of the 0.1 M sodium hydroxide solution used for back titration.