International Standard 5315

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Fertilizers — Determination of total nitrogen content — Titrimetric method after distillation

Engrais — Dosage de l'azote total — Méthode titrimétrique après distillation

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 5315 was developed by Technical Committee ISO/TC 134, *Fertilizers and soil conditioners*, and was circulated to the member bodies in May 1982.

It has been approved by the member bodies of the following countries:

China	Kenya	South Africa, Rep. of
Czechoslovakia	Korea, Rep. of	Spain
Egypt, Arab Rep. of	Mexico	Sri Lanka
France	Netherlands	Thailand
Germany, F.R.	New Zealand	United Kingdom
Hungary	Norway	USA
India	Poland	USSR
Italy	Portugal	

No member body expressed disapproval of the document.

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INTERNATIONAL STANDARD ISO 5315-1984 (E)

Fertilizers — Determination of total nitrogen content — Titrimetric method after distillation

1 Scope and field of application

This International Standard specifies a titrimetric method, after distillation, for the determination of the total nitrogen content of fertilizers in all forms, including those which have to be digested.

The method is not recommended for fertilizers containing more than 7 % of organic matter.

2 Principle

Reduction of nitrate to ammonia by chromium powder in acid medium. Conversion of organic and urea nitrogen into ammonium sulfate by digestion with concentrated sulfuric acid in the presence of a catalyst. Distillation of the ammonia from an alkaline solution, absorption in an excess of standard volumetric sulfuric acid solution and back-titration with standard volumetric sodium hydroxide solution in the presence of methyl red or screened methyl red as indicator.

3 Reagents

During the analysis, use only reagents of recognized analytical grade having, in particular, low nitrogen contents (see 5.3), and only distilled water or water of equivalent purity.

3.1 Chromium metal, powder, of particle size less than or equal to 250 µm.

3.2 Aluminium oxide, fused. Pumice is suitable.

3.3 Anti-foaming agent, for example paraffin wax of melting point not lower than 100 °C, or a silicone.

3.4 Ammonium nitrate, dried at 100 °C to constant mass.

3.5 Digestion catalyst mixture, finely ground, comprising

- potassium sulfate (K_2SO_4) : 1 000 g ;
- copper(II) sulfate pentahydrate ($CuSO_4.5H_2O$) : 50 g.

3.6 Sulfuric acid, concentrated, ϱ approximately 1,84 g/ml.

3.7 Hydrochloric acid, concentrated, ϱ approximately 1,18 g/ml.

3.8 Sodium hydroxide, approximately 400 g/l solution.

3.9 Sodium hydroxide, standard volumetric solution, $c(NaOH) = 0{,}10$ mol/l.[1)]

3.10 Sulfuric acid, standard volumetric solution, $c(H_2SO_4) = 0{,}25$ mol/l.[2)]

3.11 Sulfuric acid, standard volumetric solution, $c(H_2SO_4) = 0{,}10$ mol/l.[3)]

3.12 Sulfuric acid, standard volumetric solution, $c(H_2SO_4) = 0{,}05$ mol/l.[1)]

3.13 Indicator, solution.

Use either the screened methyl red solution (3.13.1) or the methyl red solution (3.13.2).

3.13.1 Screened methyl red, ethanolic indicator solution.

Mix 50 ml of a 2 g/l ethanolic solution of methyl red with 50 ml of a 1 g/l ethanolic solution of methylene blue.

3.13.2 Methyl red, ethanolic indicator solution.

Dissolve 0,1 g of methyl red in 50 ml of 95 % (V/V) ethanol.

3.14 pH indicator paper, wide range.

1) Hitherto expressed as "0,10 N standard volumetric solution".

2) Hitherto expressed as "0,50 N standard volumetric solution".

3) Hitherto expressed as "0,20 N standard volumetric solution".

4 Apparatus

Usual laboratory equipment, and

4.1 Digestion apparatus, comprising an 800 ml Kjeldahl flask and a pear-shaped hollow glass stopper.

4.2 Distillation apparatus.

The components of the distillation apparatus may be connected by means of rubber bungs and tubing or by the use of spherical ground glass joints.

Spherical ground glass joints should be held by spring clamps to ensure that they are leak-tight. Rubber bungs and tubing shall be replaced when they begin to perish or show signs of wear.

A suitable apparatus is illustrated in the figure and comprises the following components.

4.2.1 Flask.

Either the Kjeldahl flask (4.1) or 1 000 ml round-bottomed flask may be used.

4.2.2 Single-bulb splash head and separate open-top **dropping funnel,** of capacity 100 ml, followed by a delivery tube at the outlet.

4.2.3 Allihn condenser, seven bulb (or other suitable condenser), with an expansion bulb, of approximate capacity 100 ml, followed by a delivery tube at the outlet.

4.2.4 Receiver: conical flask or beaker, of capacity 500 ml.

4.3 Anti-bumping granules or an **anti-bumping device** consisting of a 100 mm × 5 mm glass rod connected to a 25 mm length of polyethylene tubing.

4.4 Two burettes, of capacity 50 ml, complying with the requirements of ISO 385/1, class A.

4.5 Glass beads, of diameter 2 to 3 mm.

5 Procedure

5.1 Test portion

Weigh, to the nearest 0,001 g, between 0,5 and 2,0 g of the test sample, containing not more than 60 mg of nitrate nitrogen and 235 mg of total nitrogen.

NOTE — The preparation of test samples of fertilizers will form the subject of a future International Standard.

5.2 Determination

5.2.1 Reduction (this step is not required if nitrate nitrogen is known to be absent)

Transfer the test portion (5.1) to the flask (4.1) and add sufficient water to make up the total volume to 35 ml. Allow the flask to stand for 10 min with occasional gentle swirling to ensure dissolution of all nitrate salts.

Add 1,2 g of the chromium powder (3.1) and 7 ml of the hydrochloric acid solution (3.7). Allow the flask to stand for at least 5 min, but not more than 10 min, at ambient temperature.

Place the flask on a heating device in a fume cupboard with the heat input regulated to pass a 7 to 7,5 min boil test[1)] and heat the flask for 4,5 min. Remove from the heat and allow to cool.

5.2.2 Hydrolysis [this step can be used instead of the digestion (5.2.3) if it is known that the only forms of organic nitrogen present are urea and cyanamide forms]

Stand the flask in a fume cupboard and add 1,5 g of the fused aluminium oxide (3.2). Carefully add 25 ml of the sulfuric acid (3.6) to the flask. Insert the pear-shaped hollow glass stopper into the neck of the flask and place on a heating device and initially heat until gently boiling. Then adjust the heat input to pass a 7 to 7,5 min boil test.[1)]

Continue to heat the flask and contents until dense white fumes of sulfuric acid have been evolving for at least 15 min. Allow the flask to cool to room temperature and carefully add 250 ml of water. Allow the flask to cool.

5.2.3 Digestion [this step is necessary only if organic forms of nitrogen other than urea or cyanamide forms are present (see 5.2.2) or in the case of fertilizers of unknown composition]

Place the flask in a fume cupboard and add 22 g of the digestion catalyst mixture (3.5) and 1,5 g of the fused aluminium oxide (3.2). Carefully add 30 ml of the sulfuric acid (3.6) to the flask and add 0,5 g of the anti-foaming agent (3.3) to reduce foaming. Insert the pear-shaped hollow glass stopper into the neck of the flask and place on a heating device with the heat input adjusted to pass a 7 to 7,5 min boil test.[1)]

If considerable foaming occurs, reduce the heat input until this phase is over. Continue to heat the flask and contents until dense white fumes are cleared from the bulb of the flask. Gently swirl the flask and continue digestion for a further 60 min or until the solution is clear, whichever is the longer. Allow the flask to cool to room temperature and carefully add 250 ml of water. Allow the flask to cool.

5.2.4 Distillation

If distillation from the round-bottomed flask is preferred, transfer the test portion (5.1) or the hydrolysed (5.2.2) or digested (5.2.3) solution to it quantitatively. Otherwise, place the test portion, or retain the solution, in the Kjeldahl flask.

1) The heat input is that required to bring 250 ml of water at 25 °C to a "rolling" boil in 7 to 7,5 min.

Place the anti-bumping granules or anti-bumping device (4.3), in the latter case with the polyethylene in contact with the bottom of the flask, in the flask, and add a few of the glass beads (4.5). Assemble the apparatus as shown in the figure.

Measure into the receiver (4.2.4), according to the expected mass of nitrogen in the test portion, the appropriate volume shown in the table of one of the sulfuric acid solutions (3.10, 3.11 or 3.12).

Table

Expected mass of nitrogen in the test portion	Concentration of sulfuric acid solution	Volume of sulfuric acid solution
mg	mol/l	ml
0 to 30	0,05	25,0
30 to 50		40,0
50 to 65	(solution 3.12)	50,0
65 to 80	0,10	35,0
80 to 100		40,0
100 to 125	(solution 3.11)	50,0
125 to 170	0,25	25,0
170 to 200		30,0
200 to 235	(solution 3.10)	35,0

Add 4 or 5 drops of the indicator solution (3.13) and place the receiver so that the end of the delivery tube is below the surface of the acid, adding water to the receiver if necessary.

Pour at least 120 ml of the sodium hydroxide solution (3.8), or 20 ml if there was neither hydrolysis (5.2.2) nor digestion (5.2.3), into the dropping funnel and carefully run all but about 2 ml of this solution into the distillation flask. Close the stopcock, leaving the remaining 2 ml in the dropping funnel. Bring the contents of the flask to the boil, increasing the rate of heating progressively until, finally, the contents of the flask are boiling briskly. The contents of the flask shall remain alkaline during the distillation period.

When at least 150 ml of distillate have been collected, partially withdraw the receiver so that the delivery tube rests on the rim of the receiver. Test the subsequent distillate with the pH indicator paper (3.14) to ensure that all the ammonia is completely distilled. Remove the source of heat.

Detach the splash head from the condenser and wash the insides of the condenser and expansion bulb with water, collecting the rinsings in the receiver. Also rinse the outside of the delivery tube and collect the rinsings in the receiver.

5.2.5 Titration

Back-titrate the excess of acid with the standard volumetric sodium hydroxide solution (3.9) to the neutral colour of the indicator.

5.3 Blank test

Carry out a blank test, at the same time as the determination, using the same procedure, using the same reagents, but omitting the test portion, and using the 0,05 mol/l standard volumetric sulfuric acid solution (3.12).

The result of the blank test should not exceed 1,0 ml of standard volumetric solution. If the result is greater than 1,0 ml, check the reagents, especially the chromium powder (3.1).

5.4 Check test

Carry out a periodic check on the efficiency of the apparatus and the accuracy of the method using an aliquot portion of a solution of freshly prepared ammonium nitrate (3.4) containing 100 mg of nitrogen. The check shall be made using the same conditions as for the determination and the blank test and using the same indicator.

6 Expression of results

6.1 Calculation

The total nitrogen content, expressed as nitrogen (N) as a percentage by mass, is given by the formula

a) if the 0,05 mol/l sulfuric acid solution (3.12) was used:

$$\frac{[(V_1 - V_2) - (V_3 - V_4)] \times 0{,}140\ 1}{m}$$

b) if the 0,10 mol/l sulfuric acid solution (3.11) was used:

$$\frac{[(2\ V_1 - V_2) - (V_3 - V_4)] \times 0{,}140\ 1}{m}$$

c) if the 0,25 mol/l sulfuric acid solution (3.10) was used:

$$\frac{[(5\ V_1 - V_2) - (V_3 - V_4)] \times 0{,}140\ 1}{m}$$

where

V_1 is the volume, in millilitres, of the sulfuric acid solution (3.10, 3.11 or 3.12, as appropriate) used for the determination;

V_2 is the volume, in millilitres, of the sodium hydroxide solution (3.9) used for the determination;

V_3 is the volume, in millilitres, of the sulfuric acid solution (3.12) used for the blank test;

V_4 is the volume, in millilitres, of the sodium hydroxide solution (3.9) used for the blank test;

m is the mass, in grams, of the test portion (5.1).

NOTE — If the concentrations of the standard volumetric solutions are not exactly as specified in the list of reagents, appropriate corrections should be made.

6.2 Precision

Precision data have been analysed statistically from an inter-laboratory study in which 19 laboratories participated with 3 levels. No statistical relationship between repeatability (r) or reproducibility (R) and the mean value of the total nitrogen content of the samples was found.

6.2.1 Repeatability, r

The difference between two individual test results, obtained simultaneously or in rapid succession by the same analyst, using the same apparatus, on identical test material, under the same operating conditions, should not exceed 0,36 % (m/m), expressed as nitrogen (N) content, at a confidence level of 95 %.

6.2.2 Reproducibility, R

The difference between two individual and independent test results, obtained by different analysts in different laboratories, on identical test material, should not exceed 1,3 % (m/m), expressed as nitrogen (N) content, at a confidence level of 95 %.

7 Test report

The test report should include the following information:

a) the reference of the method used, i.e. ISO 5315;

b) the result and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard or regarded as optional.

Dimensions in millimetres

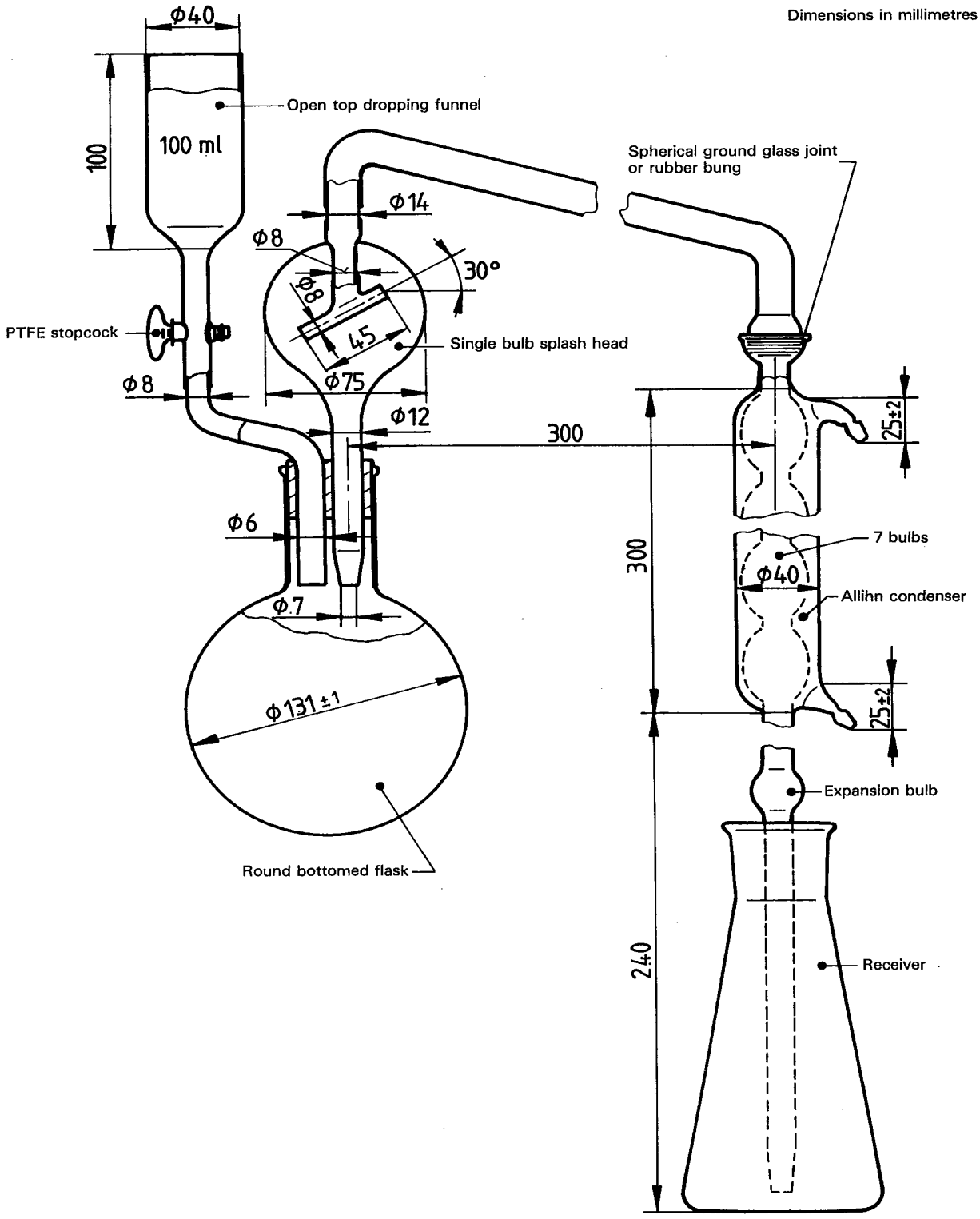

Figure — Typical distillation apparatus (using a round bottomed flask)