Annex D.8

Revision of CEN/TS 17761:2022, Inorganic fertilizers — Determination of the chloride content in ammonium nitrate fertilizers of high nitrogen content

Draft method

1 Scope

This document specifies a method for the determination of the chloride content in ammonium nitrate fertilizers of high nitrogen content.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 1482-2, *Fertilizers, liming materials and inhibitors — Sampling and sample preparation — Part 2: General sample preparation provisions*

EN 12944-1, *Fertilizers and liming materials — Vocabulary — Part 1: General terms*

EN 12944-2, *Fertilizers and liming materials — Vocabulary — Part 2: Terms relating to fertilizers*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-1 and EN 12944-2 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at https://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp

4 Principle

Chloride ions dissolved in water are determined by potentiometric titration with silver nitrate in an acidic medium.

5 Reagents

Use only reagents of recognized analytical grade, unless otherwise specified.

5.1 Distilled or demineralized water, free from chloride ions.

5.2 Acetone, analytical grade.

5.3 Concentrated nitric acid, density ρ = 1,40 g/ml, at 20 °C.

5.4 Silver nitrate stock solution, substance concentration c = 0,100 mol/l.

Store this solution in a brown glass bottle. A commercially available standard solution of at least 0,100 mol/l may be used.

5.5 Silver nitrate solution, c = 0,004 mol/l.

Prepare this solution at the time of use.

5.6 Potassium chloride (KCl), analytical grade.

5.7 Potassium chloride (KCl) stock solution, c = 0,100 mol/l.

Weigh, to the nearest 0,1 mg, 3,727 6 g of potassium chloride (5.6), previously dried for one hour in an oven (6.2) at 130 °C and cooled in a desiccator (6.3) to ambient temperature. Add sufficient water (5.1) in order to dissolve the potassium chloride. Transfer the solution without loss into a 500-ml volumetric flask, dilute to the mark with water (5.1) and mix.

A commercially available standard solution of at least 0,100 mol/l may be used.

5.8 Potassium chloride solution, c = 0,004 mol/l.

Prepare this solution at the time of use.

6 Apparatus and equipment

Usual laboratory glassware and equipment and, in particular, the following.

6.1 Analytical balance, capable of weighing to the nearest 0,1 mg.

6.2 Oven.

6.3 Desiccator.

6.4 Potentiometer with silver indicating electrode and calomel reference electrode, sensitivity 2 mV, covering the range -500 mV to +500 mV.

6.5 Bridge, containing a saturated potassium nitrate solution, connected to the calomel electrode (6.4), fitted at the ends with porous plugs.

6.6 Magnetic stirrer, with a polytetrafluoroethylene (PTFE) coated rod.

6.7 Microburette, with fine-pointed tip, graduated in 0,01 ml divisions.

7 Sampling and sample preparation

Sampling is not part of the method specified in this document. A recommended sampling method is given in EN 1482-1.

Sample preparation shall be carried out in accordance with EN 1482-2.

8 Procedure

8.1 Standardization of the silver nitrate solution

Take 5,00 ml and 10,00 ml of the potassium chloride solution (5.8) and place in two low-form beakers of convenient capacity (for example 250 ml). Carry out the following titration of the contents of each beaker.

Add 5 ml of the concentrated nitric acid (5.3), 120 ml of the acetone (5.2) and sufficient water (5.1) to bring the total volume to about 150 ml. Place the rod of the magnetic stirrer (6.6) in the beaker and set the stirrer in motion. Immerse the silver electrode (6.4) and the free end of the bridge (6.5) in the solution. Connect the electrodes to the potentiometer (6.4) and, after verifying the zero of the apparatus, note the value of the starting potential.

Titrate, using the microburette (6.7), adding initially 4 ml or 9 ml respectively of the silver nitrate solution (5.5) corresponding to the potassium chloride solution used. Continue the addition in 0,1 ml portions for the 0,004 mol/l solution (5.5). After each addition, await the stabilization of the potential.

Record the volumes added and the corresponding values of the potential in the first two columns of a table.

In a third column of the table, record the successive increments ($\Delta_1 E$) of the potential E. In a fourth column, record the differences ($\Delta_2 E$) positive or negative, between the potential increments ($\Delta_1 E$). The end of the titration corresponds to the addition of the 0,1 ml or 0,05 ml portion (V_1) of the silver nitrate solution which gives the maximum value of $\Delta_1 E$.

NOTE An example of a table is given in Table 1.

Table 1 — Example of a table

Volume of the silver nitrate solution, *V* ml	**Potential, *E*** mV	**$\Delta_1 E$**	**$\Delta_2 E$**
4,80	176		
4,90	211	35	+37
5,00	283	72	−49
5,10	306	23	−10
5,20	319	13	
NOTE Using Formula (1): $V_{eq} = 4{,}9 + (0{,}1 \times \frac{37}{37+49}) = 4{,}943$ ml.			

Calculate the exact volume (V_{eq}) of the silver nitrate solution corresponding to the end of the reaction, using Formula (1):

$$V_{eq} = V_0 + \left(V_1 \times \frac{b}{B} \right) \tag{1}$$

where

V_0 is the total volume of the silver nitrate solution immediately lower than the volume which gives the maximum increment of $\Delta_1 E$, in ml;

V_1 is the volume of the last portion of the silver nitrate solution added (0,1 ml or 0,05 ml), in ml;

b is the last positive value of $\Delta_2 E$;

B is the sum of the absolute values of the last positive values of $\Delta_2 E$ and the first negative value of $\Delta_2 E$ (see example in Table 1).

8.2 Blank test

Carry out a blank test and take account thereof when calculating the final result.

The result V_4 of the blank test on the reagents is given, in ml, by the Formula (2):

$$V_4 = 2V_3 - V_2 \tag{2}$$

where

V_2 is the value of the exact volume (V_{eq}) of the silver nitrate solution corresponding to the titration of 10 ml of the potassium chloride solution used, in ml (see 8.1);

V_3 is the value of the exact volume (V_{eq}) of the silver nitrate solution corresponding to the titration of 5 ml of the potassium chloride solution used, in ml (see 8.1).

8.3 Check test

The blank test can at the same time serve as a check that the apparatus is functioning satisfactorily and that the test procedure is being implemented correctly.

8.4 Determination

Take a test portion of sample in the range 10 g to 20 g and weigh to the nearest 0,01 g. Transfer quantitatively to a 250-ml beaker. Add 20 ml of water (5.1), 5 ml of nitric acid solution (5.3), 120 ml of acetone (5.2) and sufficient water (5.1) to bring the total volume to about 150 ml.

Place the rod of the magnetic stirrer (6.6) in the beaker, place the beaker on the stirrer and set the stirrer in motion. Immerse the silver electrode (6.4) and the free end of the bridge (6.5) in the solution, connect the electrodes to the potentiometer (6.4) and, after having verified the zero of the apparatus, note the value of the starting potential.

Titrate with the silver nitrate solution (5.5), by additions from the microburette (6.7) in increments of 0,1 ml. After each addition, await the stabilization of the potential.

Continue the titration as specified in 8.1, starting from the fourth paragraph: “Record the volumes added and the corresponding values of the potential in the first two columns of a table ...”.

9 Calculation and expression of the result

Express the result of the analysis as the percentage of chlorine (Cl) contained in the fertilizer as received for analysis. Calculate the percentage of chlorine content, w_{Cl}, from the Formula (3):

$$w_{Cl} = \frac{0,03545 \times T \times (V_5 - V_4) \times 100}{m} \tag{3}$$

where

T is the substance concentration of silver nitrate solution used, in mol/l (i.e. 0,004 mol/l);

V_4 is the result of the blank test (8.2), in ml;

V_5 is the value of V_{eq} corresponding to the determination (8.4), in ml;

m is the mass of the test portion, in g.

10 Test report

The test report shall contain at least the following information:

a) all information necessary for the complete identification of the sample;

b) test method used with reference to this document, prEN 17761:2024;

c) test results obtained expressed as the percentage of chlorine contained in the fertilizer as received for analysis;

d) date of sampling and sampling procedure (if known);

e) date when the analysis was finished;

f) all operating details not specified in this document, or regarded as optional, together with details of any incidents that occurred when performing the method which might have influenced the test result(s).

Bibliography

[1] EN 1482-1, *Fertilizers, liming materials and inhibitors — Sampling and sample preparation — Part 1: General sampling provisions*