Annex D.10

Revision of CEN/TS 17758:2022, Fertilizers and liming materials — Determination of the chloride content by potentiometric titration

Draft method

1 Scope

This document specifies a method for the determination of the chloride content in organic fertilizers, organo-mineral fertilizers, inorganic fertilizers and liming materials by potentiometric titration.

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*

EN 12944-3, *Fertilizers and liming materials — Vocabulary — Part 3: Terms relating to liming materials*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 12944-1, EN 12944-2 and EN 12944-3 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

The chlorides, dissolved in water, are precipitated in an acidified medium by an excess of standard solution of silver nitrate. The chloride concentration in the samples is quantified by potentiometric determination. To detect the end point, the voltage between a reference electrode on the one hand and the silver electrode or an ion selective electrode on the other hand, is tracked. This voltage depends on the logarithm of the chloride ion activity. If it is plotted, in mV, on the ordinate and the silver nitrate solution, in ml, on the abscissa, the point of inflection of the curve obtained in this manner is the equivalence point. Equivalent methods of evaluation are permitted [4, 6].

5 Reagents

Use only reagents of recognized analytical grade and distilled or demineralized water (grade 3 according to EN ISO 3696:1995).

5.1 Nitric acid, substance concentration c = 16 mol/l.

5.2 Nitric acid solution, c = 10 mol/l.

Mix 630 ml of nitric acid (5.1) with 370 ml of water.

5.3 Silver nitrate standard solution, c = 0,1 mol/l.

Stock solution or preparation from $AgNO_3$ salt; since this salt is hygroscopic and cannot be dried without risk of decomposition, it is advisable to weigh out approximately 17 g, dissolve in water and fill up the volume to 1 l.

A commercially available silver nitrate standard solution may be used.

5.4 Polyvinyl alcohol (PVA) solution, acidified with nitric acid.

Mix 2 g of polyvinyl alcohol with 400 ml of hot water (approx. 90 °C) in a 1 000 ml graduated flask and let it cool to room temperature. Add 10 ml of nitric acid solution (5.2) and fill up with water to 1 000 ml.

It is recommended to use an acidified protector colloid medium for the potentiometric titration (8.2 and 8.3).

5.5 Sodium chloride standard solution, c = 0,100 mol/l.

A commercially available sodium chloride standard solution may be used.

5.6 Sodium chloride control test sample.

Prepare a control test sample by dissolving 0,989 1 g ± 0,000 1 g of sodium chloride in 1 000 ml demineralized water and homogenize the solution. This control test sample contains 0,6 g chloride.

6 Apparatus and equipment

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

6.1 Heat plate with magnetic stirrer.

6.2 Pipettes.

6.3 Graduated flask, capacity 500 ml.

6.4 Beaker, capacity 250 ml.

6.5 Potentiometric titration system, incl. millivolt meter and burette or other liquid handling/dosing unit; optional incl. motoric stirrer.

6.6 Silver electrode or ion selective electrode for chloride.

6.7 Reference electrode with chloride-free salt bridge.

6.8 Balance, capable of weighing to the nearest 0,000 1 g.

6.9 Filter paper, pore size 0,45 µm.

6.10 pH testing device, e.g. pH meter, pH indicator paper, or pH rapid test.

7 Sampling

7.1 Sampling

Sampling is not part of the method specified in this document. A recommended sampling method for quality control purposes is given in EN 1482-1 [1]. A recommended sampling method for sampling of static heaps is given in EN 1482-3 [2].

7.2 Sample preparation

The sample preparation for quality control purposes, including sample division shall be performed according to EN 1482-2. Grinding of the sample is recommended for homogeneity reasons.

8 Procedure

8.1 Preparation of the test portion and the sample solution

Place 5 g to 10 g of the sample, weighed to the nearest 0,001 g, in a graduated flask (6.3) and add 250 ml of water. Bring to boil and mix for at least 0,5 h (6.1); after cooling to room temperature fill up to 500 ml with water; mix and filter (6.9) into a beaker (6.4) or into a flask (6.3).

For samples containing easily water soluble chloride compounds, the boiling step may be skipped.

The filtration step may be skipped, provided that the sample solution shows little to no precipitates.

Alternatively, sample preparation can be performed according to EN 15958.

8.2 Calibration of the system (titre factor)

The titre factor of the silver nitrate standard solution (5.3) is determined by titrating 5 ml of sodium chloride standard solution (5.5), diluted with 60 ml of water in a beaker. Then add 5 ml of PVA solution (5.4). The titration is repeated three times. By the mean value of the used volume of the silver nitrate standard solution (5.3) calculate the titre factor.

The titre factor shall be calculated according to the manual of the potentiometric titration system (6.5).

NOTE The volumes of the sodium chloride standard solution and the water can be varied, provided that the volume ratio stays constant.

8.3 Determination

Take an aliquot part of the sample solution (see 8.1) containing not more than 0,150 g of chloride, e.g. 100 ml. Then add 5 ml of PVA solution (5.4). Test for the pH (6.10) and if the pH of the sample solution is > 2, adjust the pH to < 2 by adding dropwise nitric acid solution (5.2) to the sample solution (see 8.1).

Then add silver nitrate standard solution (5.3) with a burette or comparable liquid dosing unit (6.5). The silver nitrate consumptions depends on the chloride content in the sample solution (see 8.1) and shall be between 2 ml and 20 ml, ideally between 5 ml and 10 ml.

The pH shall be adjusted just under pH 2. Adding too much acid can bias the measurement.

If the sample solution (see 8.1) is not filtrated before determination, it is recommended to use a motoric stirrer within the potentiometric titration system (6.5) to prevent a clogging of the electrodes (6.6, 6.7).

8.4 Control test

Before carrying out the estimations check the accuracy of the method by using an aliquot part of 150 ml of a freshly prepared solution of sodium chloride (5.6). This should result in a mass fraction of chlorides equal to 30 g/kg.

9 Calculation and expression of the results

Express the result of the analysis as a percentage of chloride contained in the sample as it has been received for analysis.

Calculate the mass fraction of chlorides (Cl), w_{Cl}, in g/kg according to Formula (1).

$$w_{Cl} = \frac{M_{Cl} \times c_z \times V_z \times F \times V_a}{m \times V_b} \quad (1)$$

where

V_z is the amount of the silver nitrate standard solution (5.3), in ml;

F is the titer factor (8.2) of the silver nitrate standard solution (5.3);

V_a is the volume of the graduated flask used for the sample preparation (6.3), in ml;

m is the mass of the test portion taken (8.1), in g;

V_b is the volume of the sample aliquot taken for determination (8.3), in ml;

M_{Cl} is the molar mass of chlorine, 35,453 2 g/mol;

c_z is the substance concentration of the silver nitrate standard solution (5.3), in mol/l.

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) the test method used with reference to this document, prEN 17758:2024;

c) the test results obtained;

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 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*

[2] EN 1482-3, *Fertilizers, liming materials and inhibitors — Sampling and sample preparation — Part 3: Sampling of static heaps*

[3] EN 15958, *Fertilizers — Extraction of water soluble phosphorus*

[4] EN 16195, *Fertilizers — Determination of chlorides in the absence of organic material*

[5] EN ISO 3696:1995, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*

[6] DIN 38405-1, *Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung; Anionen (Gruppe D); Bestimmung der Chlorid-Ionen (D 1)*