Annex D.9

Revision of CEN/TS 17762:2022, Inorganic fertilizers — Determination of the copper content in ammonium nitrate fertilizers of high nitrogen content

Draft method

1 Scope

This document specifies a method for the determination of the copper 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

The sample is dissolved in dilute hydrochloric acid and the copper is determined by atomic absorption spectrophotometry (AAS) or by inductive coupled plasma - optical emission spectroscopy (ICP-OES).

5 Reagents

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

5.1 Hydrochloric acid, density ρ = 1,18 g/ml, at 20 °C.

5.2 Hydrochloric acid, substance concentration c = 6 mol/l.

5.3 Hydrochloric acid, c = 0,5 mol/l.

5.4 Ammonium nitrate.

5.5 Hydrogen peroxide, 30 % m/V.

5.6 Copper stock solution.

Weigh, to the nearest 0,001 g, 1 g of pure copper (Cu), dissolve in 25 ml of hydrochloric acid (5.2), add 5 ml of hydrogen peroxide (5.5) in portions and dilute to 1 l with water. One ml of this solution contains 1 000 µg of copper.

A commercially available stock copper solution may be used.

5.7 Copper standard solution.

Dilute 10 ml of copper stock solution (5.6) to 100 ml with water and then dilute 10 ml of the resulting solution, to 100 ml with water, 1 ml of the final dilution contains 10 µg of copper.

Prepare this solution at the time of use.

6 Apparatus and equipment

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

6.1 Atomic absorption spectrophotometer with a copper lamp (324,8 nm), or **inductive coupled plasma - optical emission spectrometer.**

The choice of the apparatus is depending on availability of equipment.

6.2 Balance, capable of weighing to the nearest 0,001 g.

6.3 Beaker, capacity 400 ml.

6.4 Graduated flask, capacity 250 ml and 1 000 ml.

6.5 Copper-free filter paper.

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 Preparation of the solution for analysis

Weigh, to the nearest 0,001 g, 25 g of the sample, place it in a 400-ml beaker (6.3), add carefully 20 ml of hydrochloric acid (5.1) (there may be a vigorous reaction due to carbon dioxide formation). Add more hydrochloric acid, if necessary. When gas formation has stopped, evaporate to dryness on a steam bath, stirring occasionally with a glass rod. Add 15 ml hydrochloric acid (5.2) and 120 ml of water. Stir with the glass rod, which should be left in the beaker, and cover the beaker with a watch glass. Boil the solution gently until dissolution is complete and then cool.

Transfer the solution quantitatively into a 250-ml graduated flask (in case of ICP-OES: transfer into 1 000-ml graduated flask), by washing the beaker with 5 ml hydrochloric acid (5.2), and twice with 5 ml of boiling water, fill up to the mark with hydrochloric acid (5.3) and mix carefully.

Filter through a copper-free filter paper (6.5), discarding the first 50 ml.

8.2 Blank solution

Prepare a blank solution from which only the sample has been omitted and allow for this in the calculation of the final results.

8.3 Determination

8.3.1 Preparation of sample and blank solutions

Dilute the sample solution (see 8.1) and the blank solution (see 8.2) with hydrochloric acid (5.3) to a concentration of copper within the optimal measuring range of the spectrophotometer. Normally no dilution is needed.

8.3.2 Preparation of the calibration solutions

By diluting the copper standard solution (5.7) with hydrochloric acid (5.3), prepare at least five standard solutions corresponding to the optimal measuring range of the spectrophotometer (0 mg/l Cu to 5,0 mg/l Cu). Before filling up to the mark, add to every solution ammonium nitrate (5.4) to give mass concentration of 100 mg/ml.

8.4 Measurement

Set up the spectrophotometer (6.1) at a wavelength of 324,8 nm. Use an oxidising air-acetylene flame. In case of ICP-OES determine the optimal wavelength for measuring copper. Spray successively, in triplicate, the calibration solution (8.3.2), the sample solution and the blank solution (8.3.1), washing the instrument through with distilled water between each spraying. Plot the calibration curve using the mean absorbances of every standard used as the ordinates and the corresponding mass concentrations of copper in µg/ml as the abscissae.

Determine the concentration of copper in the final sample and blank solutions by reference to the calibration curve.

9 Expression of the results

Calculate the copper content of the sample taking into account the mass of the test portion, the dilutions carried out in the course of the analysis and the value of the blank. Express the result in mg/kg.

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 (AAS or ICP-OES) with reference to this document, prEN 17762:2024;

c) test result obtained expressed in mg/kg;

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.

Bibliography

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

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