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Organsko-mineralna gnojila - Identifikacija kompleksirajočih agensov - 1. del: Metoda z ultravijolično in vidno (UV/VIS) spektrofotometrijo in gravimetrijo

Organo-mineral fertilizers - Identification of complexing agents - Part 1: Method using UV-Vis spectrophotometry and gravimetry

Organisch-mineralische Düngemittel - Identifizierung von Komplexbildnern - Teil 1: Verfahren mittels UV/VIS-Spektralphotometer und Gravimetrie

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Organo-mineral fertilizers - Identification of complexing agents - Part 1: Method using UV-Vis spectrophotometry and gravimetry

Organisch-mineralische Düngemittel - Identifizierung von Komplexbildnern - Teil 1: Verfahren mittels UV/VIS-Spektralphotometer und Gravimetrie

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Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
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European foreword

This document (FprCEN/TS 17784-1:2021) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN.

This document is currently submitted to the Vote on TS.

This document has been prepared under a Standardization Request given to CEN by the European Commission and the European Free Trade Association.

Introduction

Micronutrients are considered to be, in plant nutrition, a number of elements known to be needed in small amounts for proper plant growth and development. The most common are Iron (Fe), Manganese (Mn), Molybdenum (Mo), Copper (Cu), Zinc (Zn) and Boron (B).

If an organo-mineral fertilizer contains a substance, or one of the substances in the mixture, which is intended to enhance the long term availability to plants of micronutrients in the EU fertilizing product, that substance can be either a chelating agent or a complexing agent.

The incorporation of lignosulfonates as complexing agents in organo-mineral fertilizers is intended to enhance the long term availability to plants of micronutrients in such EU fertilizing products.

WARNING — Users of this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety issues, if any, associated with its use. It is the responsibility of the user to establish appropriate health and safety practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this document are carried out by suitably trained staff.

1 Scope

This document specifies two methods required for the identification of lignosulfonate by UV-Vis spectrophotometry (method A) and gravimetry (method B) in organo-mineral fertilizers.

NOTE Lignosulfonate, as a complexing agent, is a natural polymer produced as a by-product of the sulfite method for manufacturing paper from wood pulp in the paper industry. As a natural polymer, it presents a poorly defined and variable chemical structure. It is an intricate mixture of small- to moderate-sized polymeric compounds with sulfonate groups attached to the molecule, and diverse complexing capacity.

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 12944-1, *Fertilizers and liming materials and soil improvers - Vocabulary - Part 1: General terms*

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

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696)*

3 Terms and definitions

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

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

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

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

3.1
complexing agent
organic substance forming a flat or steric structure with one di- or tri-valent transition metal cation (zinc (Zn), copper (Cu), iron (Fe), manganese (Mn) or cobalt (Co))

4 Sampling and sample preparation

Sampling and sample preparation are not part of the method specified in this document.

Recommended sampling methods are given in EN 1482-1 and, for sample preparation, in EN 1482-2.

5 Method A: Determination of phenolic hydroxyl content and 232,5 nm absorption for the identification of lignosulfonates

5.1 Principle

The method for the determination of the phenolic hydroxyl content is based on the ultraviolet absorption of phenols in alkaline solution (phenolate). The absorbance of an alkaline solution of the sample is measured directly against an acid solution of the same sample. The phenolic hydroxyl content of the sample is calculated from the molar extinction coefficient maximum of the resulting curve and the molar extinction coefficient of reference compounds determined in the same way.

The determination of the absorption at 232,5 nm is normally considered the method for the quantification of lignosulfonates, providing that no other ultraviolet absorbing organic compounds are present.

NOTE For additional information, see [5] and [6].

5.2 Reagents

All reagents shall be of recognized analytical grade.

5.2.1 Water.

All water used should conform to EN ISO 3696, be degassed and be free of organic contaminants.

5.2.2 Hydrochloric acid solution, substance concentration $c(\mathrm{HCl}) = 6$ mol/l.

5.2.3 Sodium hydroxide solution, $c(\mathrm{NaOH}) = 0,1$ mol/l.

5.2.4 Analytical grade fine mesh strong cation exchange resin.

Styrene/DVB type, 8 % crosslinked[1]. Hydrogen form. Functional group: sulphonic acid. Nominal exchange capacity: 1,7 mmol/ml. Mesh: 50 to 100.

5.3 Apparatus

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

5.3.1 Magnetic stirrer.

5.3.2 Balance, capable of weighing to the nearest 1 mg.

5.3.3 Filter paper, pore size 15 µm to 20 µm[2].

5.3.4 pH-meter, equipped with a glass electrode.

5.3.5 UV-Vis spectrophotometer, equipped with 10 mm quartz cells.

5.4 Procedure

5.4.1 Preparation of stock solution

Weigh, to the nearest 1 mg, 0,15 g to 0,20 g of the sample in a 100 ml beaker. Add 4 g of cation exchange resin (5.2.4) and about 20 ml to 25 ml of water. Allow the ion-exchange process to take place for 20 min, ensuring proper mixing by means of a magnetic stirrer.

Filter (5.3.3) into a 250 ml volumetric flask to remove the resin and thoroughly wash the filter. Dilute to the mark with water (stock solution).

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[1] Biorad AG® 50 W-X8 (50-100) Cat. No. 142-1431 is an example of a suitable product commercially available. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of this product.

[2] Albet 412 filter paper or equivalent is an example of a suitable product commercially available. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of this product.

5.4.2 Solution A (acid)

Take an aliquot (40 ml ± 5 ml) of the stock solution into a 100 ml beaker and adjust pH between 2,0 and 2,2 with few drops of hydrochloric acid solution (5.2.2). Pipette 5 ml of the pH-adjusted solution into a 50 ml volumetric flask and dilute to the mark. Final concentration 0,06 g/l to 0,08 g/l.

5.4.3 Solution B (basic)

Pipette 5 ml of the stock solution into a 50 ml volumetric flask. Add 10 ml of sodium hydroxide solution (5.2.3) to adjust pH over 11,0. Dilute to the mark. Final concentration 0,06 g/l to 0,08 g/l. Check that the pH of the solution is over 11,0, if not prepare solution B adding more sodium hydroxide.

5.4.4 Solution C

Pipette 10 ml of the stock solution into a 100 ml beaker and fill with water to 60 ml ± 5 ml. Adjust the pH of the solution between 4,0 and 5,0 with the sodium hydroxide solution (5.2.3). Transfer quantitatively into a 100 ml volumetric flask, dilute to the mark with water and homogenize. See 5.4.6.

5.4.5 Measurement of phenolic hydroxyl content

Fill both cells in the UV spectrophotometer with water. Enter background correction. Scan from 340 nm to 220 nm to check baseline. Fill the sample cell with solution B (5.4.3), and the reference cell with solution A (5.4.2). Scan from 340 nm to 220 nm. Rinse cells with water.

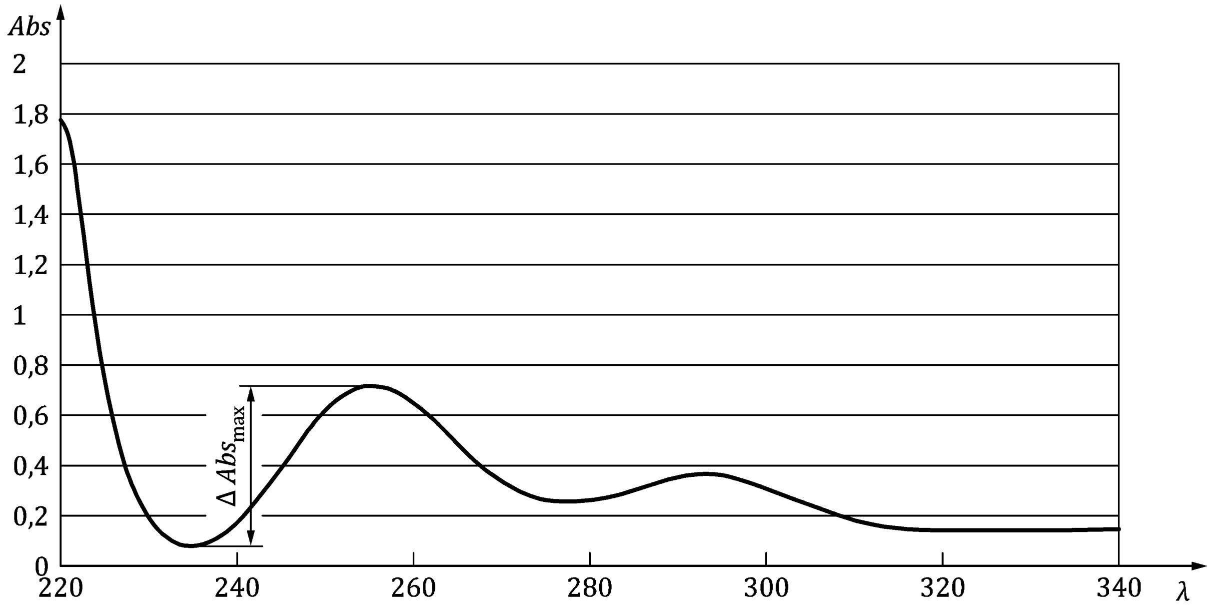
5.4.6 Measurement of 232,5 nm absorption

Fill the sample cell with solution C (5.4.4), and the reference cell with water and record absorbance at 232,5 nm. The absorbance of the final solution should be between 0,2 and 0,8 to minimize deviations from Beer's Law instrumental error. If necessary, the volume to be taken from stock solution (5.4.1) to prepare solution C (5.4.4) should be adapted.

5.5 Calculation

5.5.1 Phenolic hydroxyl content

Plot the spectrum in terms of absorbance. Record wavelength and absorbance for the maximum peak at 240 nm to 260 nm and for the minimum on either the right or the left side of the maximum. Subtract minimum absorbance from the maximum height (ΔA_{max}) (see Figure 1).



Key

A	absorbance units
$\Delta A_{\max}$	is the value obtained subtracting the minimum from the maximum absorbance
λ	wavelength

Figure 1 — Example of the spectrum of solution B against A for the determination of phenolic hydroxyl content of a lignosulfonate showing the maximum and the minimum (in this case at the left side) absorbances

Calculate the phenolic hydroxyl content, w_{ph}, of the sample, expressed as mass fraction in percent using the $\Delta A_{\max}$ value of the sample and an average $\Delta\varepsilon_{\max}$ value for reference compounds (8 867,5 l mol^{-1} cm^{-1}) by the following Formula (1):

$$w_{ph} = \frac{\Delta A_{max}}{m} \times \mathrm{d}_1 \times 17 \times \frac{1}{\Delta\varepsilon_{max}} \times \frac{100}{1\,000} \tag{1}$$

$$d_1 = \frac{50 \times 250}{5} \tag{2}$$

where

m	is the mass of the test portion in g;
d_1	is the dilution factor included in 5.4.1, 5.4.2. and 5.4.3, in ml;
$\Delta A_{\max}$	is the value obtained subtracting the minimum from the maximum absorbance;
17	is the number of OH mol $\frac{17\ \mathrm{g\ OH}}{\mathrm{mol\ OH}}$;
$\Delta\varepsilon_{\max}$	is the average molar extraction coefficient for reference compounds (8 867,5 l mol^{-1} cm^{-1}).