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Sludge, Treated Biowaste and Soil – Determination of pH

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Foreword

This document is a working document.

This document TF WI has been prepared by CEN/BT/Task Force 151 – Horizontal Standards in the Field of Sludge, Treated Biowaste and Soil, the secretariat of which is held by Danish Standards.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

For relationship with EU Directive(s), see informative Annex A, B, C or D, which is an integral part of this document.

This standard is applicable and validated for several types of matrices. The table below indicates which ones.

[table to be filled and amended by the standards writer]

Material	Validated for (type of sample, e.g. municipal sludge, compost)	Document
Sludge	Municipal sludge	Andersson, S., Nilsson, S.I. & Jennische, P. (2003). Desk study to assess the feasibility of a draft horizontal standard for pH. Nilsson S.I., Johnsson L. & Jennische, P. (2005). A horizontal standard for pH measurements – The influence on pH measurements of sample pretreatment, ionic composition / ionic strength of the extractant and centrifugation / filtration
Soil	Arable soil and forest soil	- “ - - “ -
Soil improvers		
Sediment		
Treated biowaste	Compost	- “ - - “ -

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Introduction

This document is developed in the project 'Horizontal'. It is the result of a desk study entitled "Desk study to assess the feasibility of a draft horizontal standard for pH (Andersson, Nilsson & Jennische, 2003) and a ruggedness study entitled "A horizontal standard for pH measurements – The influence on pH measurements of sample pretreatment, ionic composition/ionic strength of the extractant and centrifugation/filtration" (Nilsson, Johnsson & Jennische 2005) and aims at an evaluation of the latest developments in assessing pH in sludge, treated biowaste and soil. Please note that soil improvers and growing media are not included. After discussion with all parties concerned in CEN and selection of a number of test methods described in this study the standard has been developed further as a modular horizontal method and has been validated within in the project 'Horizontal' .

A horizontal modular approach is being investigated and developed in the project 'Horizontal'. 'Horizontal' means that the methods can be used for a wide range of materials and products with certain properties. 'Modular' means that a test standard developed in this approach concerns a specific step in a test procedure and not the whole test procedure (from sampling to analyses).

The use of modular horizontal standards implies the drawing of test schemes as well. Before executing a test on a certain material or product to determine certain characteristics it is necessary to draw up a protocol in which the adequate modules are selected and together form the basis for the test procedure.

The texts of the chapters 1 to 12 are normative; annexes are normative or informative, as stated in the top lines of the annexes.

1 Scope

This European Standard describes an instrumental method for the routine determination of pH using a glass electrode in a 1:5 (V/V) suspension of sludge, treated biowaste or soil in either water (pH-H₂O), or a 0,01 M calcium chloride solution (pH-CaCl₂). The standard is applicable to both fresh and air-dry soil samples (ISO/FDIS 10390 as a basis), sludge (EN 12176 as a basis) or treated biowaste (EN 13037 as a basis). Soil improvers and growing media are not included.

For practical reasons, for instance if there is a need to make strict comparisons with previous measurements, soils should generally be air-dried, even if fresh samples would represent the field conditions in a better way (Andersson, Nilsson & Jennische 2003). Air-drying can be used for all soils, except for those containing sulphidic minerals or volatile acids. In both cases fresh soil should be used to avoid either sulphide oxidation resulting in the formation of sulphuric acid, or volatilisation of low-molecular organic acids. Regarding sludge and treated biowaste, fresh samples are recommended. In these materials air-drying may introduce artefacts due to a stimulation of oxidation processes and should therefore be avoided.

Water or 0,01 M CaCl₂ are recommended as extractants. The use of a 0,01 M CaCl₂ solution will in general yield a lower pH value than will water. The use of the two extractants is largely based on previous empirical experience, and there is no unequivocal scientific support for choosing one or the other. The choice may be made according to the tradition in the specific setting where the determination is carried out. If pH of different materials (sludge¹, treated biowaste or soil) should be compared, it is obvious that the same extractant has to be used for all the materials tested. It is equally obvious that both H₂O and 0,01 M CaCl₂ have to be used on one and the same sample for comparisons between extractants.

Concerning liquid sludge, see sections 4. Principle, and 8. Sampling and sample pre-treatment.

Whenever 0,01 M CaCl₂ is used for extraction of cations or anions other than Ca²⁺ and Cl⁻, it is recommended that this extractant is also used for pH measurement.

Extraction with 1 M KCl is sometimes used for pH measurement. This extractant has not been included in the current standard. Although it is normally used for quantitative determination of exchangeable soil acidity by titration there is no obvious advantage of using it for routine measurements of pH. The KCl solution has a high ionic strength (1,0 M) which is unrealistic for pH measurements in soil. The CaCl₂ solution on the other hand, has an ionic strength of 0,03 M which is closer to the expected value in soil solutions. Therefore, 0,01 mol/l CaCl₂ is a more reasonable choice of a neutral salt extractant.

For sludge and treated biowaste, fresh samples should be preferred. Air-drying may introduce artefacts due to stimulation of oxidation processes and should therefore be avoided. Water should primarily be used as an extractant.

The issue of fresh samples versus air-dried samples is specified according to the following table:

	Fresh	Dry
Sample category		
Sludge	X	
Treated biowaste	X	
Soils containing sulphide minerals	X	
Soils containing volatile acids	X	
Other soils	X*	X*

*Optional depending on whether comparisons are to be made with previous measurements on fresh or air-dry samples.

2 Normative references

This European Standard incorporates by dated or undated references, provisions from other publications. These normative references are cited at appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN ISO 3696: 1997, Water for analytical laboratory use - Specification and test methods.

ISO 1770:1981, Solid-stem general purpose thermometers

ISO 11464:1994, Soil quality – Pretreatment of samples for physico-chemical analyses.

EN 13040: 1999, Soil improvers and growing media – Sample preparation for chemical and physical tests, determination of dry matter content, moisture content and laboratory compacted bulk density.

ISO/FDIS 10390: 2005, Soil quality – Determination of pH.

EN 12176: 1998, Characterization of sludge - Determination of pH-value.

EN 13037: 1999, Soil improvers and growing media – Determination of pH

3 Terms and definitions

For the purpose of this European Standard, the following definition applies:

3.1 pH refers to the hydrogen ion activity $\{H^+\}$ at equilibrium in a substrate – water (alternatively salt solution) suspension, expressed as $-^{10}\log \{H^+\}$.

4 Principle

A suspension of sludge (fresh), treated biowaste (fresh) or soil (fresh or air-dry) is made up in five times its volume of one of the following:

- water
- a 0,01 M solution of $CaCl_2$

The pH of the suspension is measured using a pH-meter.

NOTE To make the procedure generally applicable to all types of sludge, treated biowaste and soil samples, one V/V shaking ratio is chosen because then all types of samples can be treated in the same way. For the purpose of this standard, taking the required volume of test portion with a measuring spoon is sufficiently accurate. Measurements in liquid sludge should only be made directly in the water suspension. No extra water should be added.

5 Interferences and sources of errors

In samples with a high content of charged particles (organic matter, clay) the suspension effect can modify the potential difference between the electrodes, and thereby have an influence on the recorded pH value. This problem is minimized by a gentle stirring of the suspension. For calcareous material, it is possible that carbon dioxide is absorbed by the suspension. Under the circumstances mentioned, it is difficult to reach an equilibrium value. Other sources of error are associated with materials containing sulphidic minerals or volatile acids (see section 1).

6 Reagents

Use only reagents of recognised analytical grade.

6.1. Water, must have a specific electric conductivity not greater than 0,2 mS/m at 25°C, and a pH not greater than 5,6 (grade 2 water in accordance with EN ISO 3696).

6.2 Calcium chloride solution with the molarity of 0,01 M : Dissolve 1,47 g of calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) in water (7.1) in a 1000 ml volumetric flask and make up to volume with water.

This solution may be stored for several months in a refrigerator in a closed volumetric flask or other type of closed glass vessel.

7 Apparatus

7.1 Equipment for sample preparation

According to EN 12176 (sludge), EN 13037 (treated biowaste) and ISO 11464 (soil samples).

7.2 pH-meter, with slope adjustment and temperature control

7.3 A glass electrode and a reference electrode

8 Sampling and sample pre-treatment

Sampling should be carried out in accordance with EN yyyy:2003 (Horizontal standard module(s) for sampling of sludge, treated biowaste and soil).

Samples should be pretreated according to EN 12176 (liquid or pastelike sludge; fresh), EN 13040 (treated biowaste; fresh) and ISO 11464 (soil). The particle size of soils should be ≤ 2 mm, while that of treated biowaste should be 20-40 mm.

NOTE 1: Sample preparation for liquid sludge is unnecessary. pH should be determined directly according to EN 12176. Pastelike sludge may need a breakdown of solid particles before the preparation of a suspension (9).

NOTE 2: ISO 11464 refers to air-dry soil. Except for the drying procedure, it is applicable to fresh soil samples as well.

9 Procedure

9.1 Preparation of a suspension

9.1.1 Take a representative test portion of at least 5 ml from the laboratory sample (solid sludge, soil) using a spoon of known capacity (at least 5,0 ml). Place the test portion in a polyethylene or glass bottle (capacity at least 50 ml) with a tightly fitting cap or stopper. Add water (6.1) or calcium chloride solution (6.2) at an amount which is 5 times the volume of the test portion. For treated biowaste the procedure and volume ratio (1:5) is the same, except that a 60 ml sample is added to 300 ml of water or calcium chloride solution according to EN 13037.

9.1.2 Shake or mix the suspension for $60 \text{ min} \pm 10 \text{ min}$ using a mechanical shaker. Wait for at least 1 h, but not longer than 3 h. Ingress of air during standing after shaking should be avoided.

9.2 Calibration of the pH meter

Adjust the pH-meter as indicated in the manufacturer's manual. Calibrate the pH-meter as specified in the manufacturer's manual, using buffer solutions at $20^\circ\text{C} \pm 2^\circ\text{C}$: Potassium hydrogen phthalate ($\text{C}_8\text{H}_5\text{O}_4\text{K}$) at

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pH 4,00, and potassium dihydrogen phosphate (KH_2PO_4) + disodium hydrogen phosphate (Na_2HPO_4) at pH 6,88. For strongly alkaline materials disodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) at pH 9,22 may also be required. The use of commercially available standards within the same pH range can also be used.

9.3 Measurement of the pH.

Measure the pH in the suspension at $20^\circ\text{C} \pm 2^\circ\text{C}$ immediately after or whilst being stirred. The stirring should be at such a rate to achieve a reasonably homogenous suspension of the soil particles, but entrainment of air should be avoided. Note the recorded values to 2 decimal places.

9.4 Blank determination

The water (or CaCl_2 solution) should be checked before the suspensions are prepared (6.1 and 6.2). Blank determination in the strict sense is not relevant for pH measurements.

9.5 Quality Assurance of the overall procedure

If duplicate measurements are made (optional), the average value should be reported. A reference sample should be included in each batch of samples. The reference could be either "home made" or consist of a certified reference material.

10 Expression of results

The results of the determinations should be reported to the nearest 0,1 pH-unit.

11 Test report

The test report shall contain the following information:

- A reference to this European Standard including its date of publication;
- Precise identification of the sample;
- Type of sample preparation: fresh, air-dry or (concerning liquid sludge) no preparation
- The aqueous medium used to make the suspension: pH- H_2O , pH- CaCl_2 or no aqueous medium added (liquid sludge).
- Expression of results, according to the nearest 0,1 pH-unit.
- Any deviation from this standard, and any facts which may have influenced the result. Where the test is not carried out in accordance with this standard, reference may only be made to EN xxxx:2003 in the report in case all deviations from the procedures prescribed in this standard are indicated in the report stating the reason for deviation.

12 Performance characteristics

Performance data in terms of repeatability and reproducibility in two separately prepared suspensions shall satisfy the following requirements¹⁾:

<u>pH interval</u>	<u>Acceptable difference (pH units)</u>
$\text{pH} \leq 7,00$	0,15
$7,00 < \text{pH} < 7,50$	0,20

$7,50 \leq \text{pH} \leq 8,00$ 0,30

$\text{pH} > 8,00$ 0,40

*) This table is preliminary, and will be adjusted during validation step 1.

Annex A
(informative)

Validation of methods

Annex B
(informative)

The modular horizontal system

Annex C
(informative)

Information on WP xx and the project Horizontal

Bibliography

Andersson, S., Nilsson, S.I. & Jennische (2003). Desk study to assess the feasibility of a draft horizontal standard for pH. Swedish University of Agricultural Sciences, Uppsala.

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