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Determination of pH in soil, sewage sludge and biowaste

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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, 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	X	A horizontal standard for pH measurements – The influence on pH measurements of sample pretreatment,ionic composition / ionic strength of the extractant and centrifugation / filtration S. Ingvar Nilsson, Lars Johnsson & Per Jennische
Soil	X	- “ -
Soil improvers		
Sediment		
Waste	X	- “ -

Contents

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, Larsson & Jennische 2005) and aims at an evaluation of the latest developments in assessing pH in sludge, soil, treated biowaste and neighbouring fields. 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 an 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 soil, sludge or biowaste in either distilled water (pH-H_2O), or a 0.01 mol/l calcium chloride solution (pH-$CaCl_2$). 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 biowaste (EN 13037 as a basis).

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 with one important exception: pH in soils that contain sulphidic material should be measured on fresh samples to avoid sulphide oxidation resulting in the formation of sulphuric acid. Whenever sulphidic soils are to be compared with other soils the comparison should be made on fresh samples.

Distilled water or 0.01 mol/l $CaCl_2$ are recommended as extractants. The use of a 0.01 mol/l $CaCl_2$ solution will in general yield a lower pH value than will distilled 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 (soil, sludge or biowaste) 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 distilled H_2O and 0.01 mol/l $CaCl_2$ have to be used on one and the same sample for comparisons between extractants.

Whenever 0.01 mol/l $CaCl_2$ is used for extraction of cations or anions it is recommended that this extractant is also used for pH measurement.

Extraction with 1 mol/l KCl is sometimes used for pH measurement. This extractant has not been included in the current standard. Although it is normally used for quantitative determinations 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 mol/l) which is unrealistic for pH measurements in soil. The $CaCl_2$ solution on the other hand, has an ionic strength of 0.03 mol/l which is closer to the expected value in soil solutions. Therefore, 0.01 mol/l $CaCl_2$ is a more reasonable choice of a neutral salt extractant.

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

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 Soil quality – Pretreatment of samples for physico-chemical analyses. ....

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 Safety remarks None

5 Principle

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

- water
- a 0.01 mol/l 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, soil and biowaste samples, a 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.

6 Interferences and sources of errors

In samples with a high content of organic matter, the suspension effect can play a role. 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.

Another source of error is associated with materials containing sulphidic minerals. Air-drying of such materials may speed up the oxidation rate resulting in the production of a strong acid (H2SO4). For such materials fresh samples should be preferred.

7 Reagents

Use only reagents of recognised analytical grade.

7.1. 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).

7.2 Calcium chloride solution with the molarity of 0.01 mol/l : Dissolve 1.47 g of calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) 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.

8 Apparatus

8.1 Equipment for sample preparation

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

8.2 pH-meter, with slope adjustment and temperature control

8.3 Glass electrode and a reference electrode of equivalent performance.

9 Sampling and sample pre-treatment

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

Samples should be pretreated according to ISO 11464 (soil; fresh or air-dry), EN 12176 (sewage sludge; fresh) and EN 13037 (biowaste; fresh). The particle size should be < 2mm. Air-dried samples should not be exposed to a temperature higher than 40°C. The pretreated samples should be stored in well aerated but closed polyethylene containers. Samples should be kept cold (< 8°C) and in the dark. The sample pre-treatment should take place within 24 hours of sampling.

NOTE: Sample preparation for liquid sludge is unnecessary. pH should be determined directly according to EN 12176.

10 Procedure

10.1 Preparation of a suspension

10.1.1 Take a representative test portion of at least 5 ml from the laboratory sample (soil, sludge or biowaste) using a spoon of known capacity (at least 5.0 ml). Place the test portion in a polyethylene bottle (capacity at least 50 ml) with a tightly fitting cap or stopper. Add water (7.1) or calcium chloride solution (7.2) at an amount which is 5 times the volume of the test portion.

10.1.2 Shake or mix the suspension for 60 min ± 10 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.

10.2 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°C ± 2°C: Potassium hydrogen phtalate ($C_8H_5O_4K$) at 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 ($Na_2B_4O_7 \cdot 10H_2O$) at pH 9.22 may also be required.

10.3 Measurement of the pH.

Measure the pH in the suspension at 20°C ± 2°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.

10.4 Blank determination

The water (or $CaCl_2$ solution) should be checked before the suspensions are prepared (.7.1 and 7.2). Blank determination in the strict sense is not relevant for pH measurements.

10.3 Quality Assurance of the overall procedure

10.3.1 Duplicate determination

Analyse two individual test samples of each (dried or fresh), homogenised sample submitted for analysis. Establish a control limit for the difference between results for the two sub-samples based on for example laboratory precision data.

10.3.2 Analysis of spiked natural samples

Not relevant for routine pH measurements

11 Expression of results

The results of the determinations should be reported to the nearest 0.1 pH-unit

12 Test report

The test report shall contain the following information:

a) a reference to this European Standard including its date of publication;

b) precise identification of the sample;

c) type of sample preparation: fresh, air-dry or (concerning liquid sludge) no preparation

d) the aqueous medium used to make the suspension: pH-H_2O, pH-$CaCl_2$ or no aqueous medium added (liquid sludge).

e) expression of results, according to 11.

f) 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.

13 Performance characteristics

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

pH range	Acceptable variation (pH units)
pH $\leq$ 7.00	0.15
7.00 < pH < 7.50	0.20
7.50 $\leq$ pH $\leq$ 8.00	0.30
pH > 8.00	0.40

Annex A

(informative)

Validation of methods

Annex B
(informative)

The modular horizontal system

Annex C

(informative)

Information on WP xx and the project Horizontal

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