

**SLOVENSKI STANDARD**  
**oSIST prEN 15933:2009**  
**01-julij-2009**

---

H'UŽV'Urc`j]b`V]ccXdUX\_]!`8c`c Yj Ub`Y'd<

Soil, sludge, and treated biowaste - Determination of pH

Boden, Schlamm und behandelter Bioabfall - Bestimmung des pH-Wertes

Sol, boue et biodéchet traité - Détermination du pH

**Ta slovenski standard je istoveten z: prEN 15933**

<https://standards.iteh.ai/catalog/standards/sist/b2658307-2caf-4e79-8cdf-edc4f68339a1/sist-en-15933-2012>

---

**ICS:**

13.030.01	Odpadki na splošno	Wastes in general
-----------	--------------------	-------------------

**oSIST prEN 15933:2009**

**en,fr,de**



EUROPEAN STANDARD  
NORME EUROPÉENNE  
EUROPÄISCHE NORM

**DRAFT**  
**prEN 15933**

April 2009

---

ICS

English Version

## Soil, sludge, and treated biowaste - Determination of pH

Boden, Schlamm und behandelter Bioabfall - Bestimmung  
des pH-Wertes

This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/SS S99.

If this draft becomes a European Standard, CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

This draft European Standard was established by CEN in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

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.

**Warning** : This document is not a European Standard. It is distributed for review and comments. It is subject to change without notice and shall not be referred to as a European Standard.



EUROPEAN COMMITTEE FOR STANDARDIZATION  
COMITÉ EUROPÉEN DE NORMALISATION  
EUROPÄISCHES KOMITEE FÜR NORMUNG

**Management Centre: Avenue Marnix 17, B-1000 Brussels**

## Contents

Foreword.....	3
Introduction .....	5
1 Scope .....	5
2 Comments to the method .....	5
3 Normative references .....	6
4 Terms and definitions .....	7
5 Principle .....	7
6 Interferences and sources of errors .....	7
7 Reagents .....	8
8 Apparatus .....	8
9 Sampling and sample pre-treatment.....	8
10 Procedure .....	8
10.1 Preparation of a suspension .....	8
10.2 Calibration of the pH meter.....	9
10.3 Measurement of the pH .....	9
10.4 Blank determination .....	9
10.5 Quality Assurance of the overall procedure .....	9
11 Expression of results .....	9
12 Precision data .....	9
13 Test report .....	9
Annex A (informative).....	10
A.1 Materials used in the interlaboratory comparison study .....	10
A.2 Interlaboratory comparison results.....	11
A.3 Repeatability and reproducibility .....	11
Annex B (informative).....	13
Bibliography .....	16

## Foreword

This document (prEN 15933:2009) has been prepared by Technical Committee CEN/SS S99 "Health, environment and medical equipment - Undetermined", the secretariat of which is held by CMC.

The document is currently submitted to the CEN Enquiry.

This draft standard has been prepared by the European project «Horizontal» and presented to CEN/TC BTTF 151 "Horizontal Standards in the Fields of Sludge, Biowaste, and Soil", the secretariat of which is held by DS. Standardisation is carried out under mandate M330 given to CEN by the European Commission, and supports essential requirements of EU Directive(s).

The standard is part of a modular horizontal approach in which this standard belongs to the analytical step.

The results of the desk study as well as the evaluation and validation studies have been subject to discussions with all parties concerned in the CEN structure during the development by project Horizontal. The results of these consultations with interested parties in the CEN structure have been presented to and discussed in CEN BT/TF 151.

Based on data from interlaboratory studies and consultations with interested parties within CEN member bodies, it has been concluded that the draft standard is acceptable for its intended use and is ready for the CEN enquiry.

It is recognized that standardization in the environmental field in most national standardization bodies is organized in national standardization committees that mirror the vertical structure of technical committees in the environmental field in CEN. The present CEN enquiry therefore asks for a special attention by the NSBs to assure that the relevant and interested parties are consulted during the CEN enquiry, i.e. to assure that one single consolidated enquiry reply on the draft standard can be presented by the NSB that covers the entire scope of the draft standard.

## prEN 15933:2009 (E)

The standard is applicable and validated for several types of matrices as indicated below:

Material	Validated for (type of sample, e.g. municipal sludge, compost)	Document
Sludge	Municipal sludge	<p>Andersson, S., Nilsson, S.I. &amp; Jennische, P. (2003). Desk study to assess the feasibility of a draft horizontal standard for pH.</p> <p>Nilsson S.I., Johnsson L. &amp; 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</p>
Soil	Arable soil and forest soil	<p>Andersson, S., Nilsson, S.I. &amp; Jennische, P. (2003). Desk study to assess the feasibility of a draft horizontal standard for pH.</p> <p>Nilsson S.I., Johnsson L. &amp; 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</p>
Treated biowaste	Compost	<p>Andersson, S., Nilsson, S.I. &amp; Jennische, P. (2003). Desk study to assess the feasibility of a draft horizontal standard for pH.</p> <p>Nilsson S.I., Johnsson L. &amp; 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</p>

## Introduction

This draft standard is one of a number of draft standards developed and validated in the European project 'Horizontal' financed by the EU commission and EU member states. The project "Horizontal" was conducted by a European Consortium under the management by ECN, The Netherlands. This draft standard was presented by the project Horizontal to CEN/BT TF 151 in June 2008 with a view to be formally adopted as European Standard under CEN rules.

The standardisation by CEN is carried out on a mandate by the European Commission (Mandate M/330). The mandate considers standards on sampling and analytical methods for hygienic and biological parameters as well as inorganic and organic determinants. It was the aim of the initiative to develop standards that are suitable for a wide range of environmental materials and lead to equivalent results as far as this is technically feasible.

Until now test methods determining properties of materials within the environmental area were prepared in Technical Committees (TCs) working on specific products/matrices (soil, waste, sludge etc). However, it is recognized that many steps in test procedures can be used in test procedures for other products/matrices. By careful determination of these steps and selection of specific questions within these steps, elements of the test procedure can be described in a way that can be used for more matrices and materials with certain specifications. This optimization is in line with the development among end-users of standards. A majority of routine environmental analyses are carried out by institutions and laboratories working under a scope which is not limited to one single environmental matrix but covers a wide variety of matrices. Availability of standards covering more matrices contributes to the optimization of laboratory procedures and standard maintenance costs, e.g. cost related to accreditation and recognition.

A horizontal modular approach was developed in the project 'Horizontal'. 'Modular' means that a test standard developed in this approach concerns a specific step in assessing a property and not the whole "chain of measurement" (from sampling to analyses). A beneficial feature of this approach is that "modules" can be replaced by better ones without jeopardizing the standard "chain".

The modules that relates to this standard are specified in section 3 - Normative references.

## 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-H<sub>2</sub>O), or a 0,01 M calcium chloride solution (pH-CaCl<sub>2</sub>). The standard is applicable to both fresh and air-dry soil samples (ISO 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.

## 2 Comments to the method

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.

## prEN 15933:2009 (E)

Water or 0,01 M  $\text{CaCl}_2$  are recommended as extractants. The use of a 0,01 M  $\text{CaCl}_2$  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 (sludge<sup>1</sup>, 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  $\text{H}_2\text{O}$  and 0,01 M  $\text{CaCl}_2$  have to be used on one and the same sample for comparisons between extractants. Whenever 0,01 M  $\text{CaCl}_2$  is used for extraction of cations or anions other than  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ , 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  $\text{CaCl}_2$  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  $\text{CaCl}_2$  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:

Table 1 — XXX

Sample category	Fresh	Dry
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.		

### 3 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, *Water for analytical laboratory use – Specification and test methods*

ISO 11464, *Soil quality – Pretreatment of samples for physico-chemical analyses*

---

1) Concerning liquid sludge, see Clause 5 and Clause 9.



ISO 10390, *Soil quality – Determination of pH*

EN 12176, *Characterization of sludge – Determination of pH-value*

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

CSS99031 *Sludge, treated biowaste, and soils in the landscape – Sampling – Framework for the preparation and application of a sampling plan*

CSS99058 *Sludge, treated biowaste, and soils in the landscape – Sampling – Part 1: Guidance on selection and application of criteria for sampling under various conditions*

CSS99057 *Sludge, treated biowaste, and soils in the landscape – Sampling – Part 2: Guidance on sampling techniques*

CSS99032 *Sludge, treated biowaste, and soils in the landscape – Sampling - Part 3: Guidance on sub-sampling in the field*

CSS99059 *Sludge, treated biowaste, and soils in the landscape – Sampling – Part 4: Guidance on procedures for sample packaging, storage, preservation, transport and delivery*

CSS99060 *Sludge, treated biowaste, and soils in the landscape – Sampling – Part 5: Guidance on the process of defining the sampling plan*

CSS99034 *Soil, sludge and treated biowaste – Guidance for sample pre-treatment*

## 4 Terms and definitions

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

### 4.1 pH

hydrogen ion activity  $\{H^+\}$  at equilibrium in a water or salt solution suspension, expressed as  $-^{10}\log \{H^+\}$ .

## 5 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.

## 6 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

**prEN 15933:2009 (E)**

an equilibrium value. Other sources of error are associated with materials containing sulphidic minerals or volatile acids (see Clause 2).

**7 Reagents**

- a) Use only reagents of recognised analytical grade.
- b) 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).
- c) 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.b) 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**

- a) Equipment for sample preparation according to EN 12176 (sludge), EN 13037 (treated biowaste) and ISO 11464 (soil samples).
- b) pH-meter, with slope adjustment and temperature control
- c) A glass electrode and a reference electrode

**9 Sampling and sample pre-treatment**

Sampling shall be carried out in accordance with sampling standards CSS99031-32 and 99057-60.

Samples should be pretreated according to CSS99034. The particle size of samples should be  $\leq 2$  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.

**NOTE 3** For treated biowaste the particle size can be between 20 and 40 mm

**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 (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 (see 7.b) or calcium chloride solution (see 7.c)) 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.

**10.1.2** 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.