BRITISH STANDARD

BS EN 12176:1998

Characterization of sludge — Determination of pH value

The European Standard EN 12176:1998 has the status of a British Standard

ICS 13.030.20

National foreword

This British Standard is the English language version of EN 12176:1998.

The UK participation in its preparation was entrusted to Technical Committee EH/5, Sludge characterization, which has the responsibility to:

- — aid enquirers to understand the text;
- — present to the responsible European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- — monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the BSI Standards Catalogue under the section entitled “International Standards Correspondence Index”, or by using the “Find” facility of the BSI Standards Electronic Catalogue.

Summary of pages

This document comprises a front cover, an inside front cover, the EN title page, pages 2 to 6, an inside back cover and a back cover.

Amendments issued since publication

Amd. No.	Date	Text affected

This British Standard, having been prepared under the direction of the Health and Environment Sector Board, was published under the authority of the Standards Board and comes into effect on 15 June 1998

ISBN 0 580 29142 1

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 12176

February 1998

ICS 13.030.20

Descriptors: Sludges, sewage treatment sludges, tests, measurements, ph, samples, preparation, potentiometric methods

English version

Characterization of sludge — Determination of pH-value

Caractérisation des boues — Détermination de la valeur du pH

Charakterisierung von Schlamm — Bestimmung des pH-Wertes

This European Standard was approved by CEN on 16 January 1998.

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CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

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Ref. No. EN 12176:1998 E

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 308, Characterization of sludges, the secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by August 1998, and conflicting national standards shall be withdrawn at the latest by August 1998.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

Contents

0 Introduction

The pH value is a necessary parameter for monitoring the treatment of urban and comparable industrial sludges as well as of sludges from water supply treatment plants and to assess the suitability of the use of sludge in agriculture or for its disposal to land fill. The pH value of liquid sewage sludge may be used to monitor digester performance.

1 Scope

The scope of this standard is the sludges, i.e. and sludges products from:

- — storm water handling;
- — night soil;
- — urban wastewater collecting systems;
- — urban wastewater treatment plants;
- — treating industrial wastewater similar to urban wastewater (as defined in Directive 91/271 EEC);
- — water supply treatment plants;
- — water distribution systems;
- — but excluding hazardous sludges from industry.

This method is applicable to the determination of pH values of sludges which include liquid, paste-like or solid matter. If the sludge sample is sufficiently liquid, direct measurement should be made. If the sludge sample contains relatively high percentages of solids the measurement should be carried out after dilution with water.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendment 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.

prEN 12880, *Characterization of sludges — Determinaton of dry residue and water content.*

ISO 3696, *Water for analytical laboratory use — Specification and test methods.*

ISO 10523:1994, *Water quality — Determination of pH.*

3 Definitions

For the purpose of this standard the following definitions apply:

3.1

pH-value

the pH value of an aqueous solution is theoretically a function of the electromotive force of a measuring cell (e.g. a glass electrode and a calomel electrode) which is defined by the equation given in annex A of ISO 10523:1994. The practical pH scale refers to exactly specified buffer solutions

3.2

standard buffer solutions

solutions of certain concentrations of pure substances or mixtures thereof with defined pH values

4 Principle

A suitable aqueous suspension of the solid or paste-like sludge is prepared and the pH value of the suspension is determined potentiometrically. In liquid samples the measurement is made directly.

5 Interferences

Substances present at their normal concentration in these types of samples do not cause significant interference. The pH value of suspensions is dependent, to a considerable extent, on the carbon dioxide equilibrium. Therefore manipulation after the sampling of liquid sludge and after the preparation of suspensions should be kept to a minimum. If oil or grease is visible in the sample, it should be removed by filtration through a pad of cotton wool (**8.9**) prior to carrying out the measurement. The presence of sulfides or arsenic may poison the glass interface of the electrode.

Electrodes with a low “alkali error” should be used for the measurement of sludges expected to be of a high pH.

NOTE 1 Glass electrodes normally respond to sodium ions at pH values above 9. This may cause errors in the measurement of the pH values of samples such as lime conditioned sludges.

NOTE 2 A film may form on the surface of the pH-electrodes due to oil and grease. This may lead to errors in the measuring results. Inorganic film-forming substances may also interfere if not removed from the pH-electrodes between determinations.

NOTE 3 If sludge samples are taken from a digester, digester gas may escape causing changes in the carbon dioxide content, which may lead to errors in the measured results.

6 Hazards

Samples of sewage sludge are liable to ferment. Do not store them in the open laboratory. If samples must be stored, then store them at (0 to 4) ˚C. When handling a stored sample wear gloves, face and eye protection and sufficient body protection to guard against bottles bursting. Use bottle carriers. The gas evolved is usually flammable so all equipment in the vicinity should be flame-proof and sources of ignition absent. Bursting glass bottles can produce micro-organism contaminated shrapnel. Plastic bottles can also burst and produce a hazardous spray and aerosol. Ensure that all spillages are cleared up. Do not handle broken glass directly.

There is also a danger of hydrogen sulfide formation during storage. Cap loosely to avoid pressure build-up.

Sludge usually contains harmful organisms. Cleanliness is essential. Keep sludge away from food and eating. Protect all cuts.

7 Reagents

Analytical grade reagents shall be used.

7.1 *Water*

For the preparation of standard buffer solutions (see **3.2**) freshly distilled or deionised water freshly taken from a column according to ISO 3696, Grade 3 shall be used. It shall be free from carbon dioxide and have a conductivity of ≤ 2 µS/cm.

7.2 *Standard buffer solutions*

These shall be in accordance with ISO 10523 and annex A (normative). Such solutions are available commercially.

7.3 *Ethanol*, (CH_3CH_2OH), 70 % *V/V*.

7.4 *Acetone*, (CH_3COCH_3).

8 Apparatus

8.1 *pH-meter*

Temperature compensated input resistance $\geq 10^{12}\ \Omega$ readable to at least pH = ±0,05, slope correction in mV/pH.

8.2 *Glass electrode and reference electrode*

The glass electrode measuring system shall have a zero voltage at pH = 7. This may consist of a glass electrode and a reference electrode, or a combination electrode system, see [2] and [3].

NOTE Some problems are associated with the reference electrodes and it is recommended that these should be tested before use. The use of a symmetrical pH-measuring system is suggested, i.e. glass and reference electrode of the same type, e.g. Ag/AgCl electrode system. Reference electrodes with gelled filling solutions should not be used.

8.3 *Thermometer*, capable of measuring to the nearest 0,5 °C.

8.4 *Mechanical shaking apparatus*

8.5 *Sample bottles*, plastics or borosilicate glass, wide mouthed.

8.6 *Stoppered conical flask*, Erlenmeyer type, 150 ml.

8.7 *Balance*, accuracy ±0,01 g.

8.8 *Drying oven*, (105 ± 5) °C.

8.9 *Cotton pads*

8.10 *Soft tissue*, and other usual laboratory devices.

9 Preparation of samples

9.1 Sample preservation

Sludge samples can change composition through biological or chemical activity. Therefore, they should be analysed as soon as possible after sampling. Liquid sludge samples will lose carbon dioxide on exposure to air. They shall therefore be kept in a closed partially filled container until the pH value is determined. Handling should be minimized to avoid loss of carbon dioxide. If prolonged storage of sludge samples is unavoidable they should be stored at (0 to 4) °C in a refrigerator.

9.2 Preparation of liquid sludge samples

These samples usually contain less than 50 g dry matter per kg sludge and do not require any preparation before pH-measurement.

NOTE If visible oil or grease is present it should be removed by filtration through a cotton wool pad prior to step **10.1**. Use the filtrate at step **10.2**.

9.3 Preparation of paste-like and solid sludges

Weigh an amount of sample equivalent to approximately 5,0 g dry matter into a conical flask (**8.6**). Add water (**7.1**) to make the total weight (100 ± 1) g. Stopper the flask and shake mechanically (**8.4**) for at least 15 min, until the sample is thoroughly dispersed. In some cases it may be necessary to break down the solids prior to shaking. Proceed as in clause **10**.

NOTE 1 Whilst it is preferable that precise quantities of sludge (expressed as dry matter) are used, this may not always be possible. Estimates of the dry matter content may be made in the interests of speed.

NOTE 2 Determine the dry solids content of the sludge in accordance with prEN 12880 by drying the sample at (105 ± 5) °C.

NOTE 3 If visible oil or grease is present after shaking, follow the note given in **9.2**.

10 Measurement of pH value

10.1 pH-meter set up and standardization

Measure the temperature of the sample and set the temperature control on the pH-meter (**8.1**) following the manufacturer's instructions. Standardize the pH-meter using standard pH-buffer solutions (**7.2**).

NOTE The range of pH values of the standard buffer solutions preferably includes that of the sample.

10.2 Measurement

Rinse the electrodes (**8.2**) thoroughly with water (**7.1**). Ensure that the sludge sample is well dispersed by swirling. Immediately, place the electrodes in the sample. Read the steady pH value from the pH-meter (**8.1**) after approximately 30 s to 60 s. Remove the electrodes and rinse with water (**7.1**).

At the end of the batch of samples clean the electrodes with a soft wet tissue (**8.10**) and rinse the electrodes thoroughly with water. If the samples contained organic impurities use ethanol (70 %) (**7.3**), acetone (**7.4**) or warm detergent solution for cleaning.

NOTE 1 Only use organic solvents for a short time as they decrease the sensitivity of glass electrodes by dewatering the leached layer of the glass membrane.

NOTE 2 If the suspended phase separates from the liquid phase, it is preferable that the electrodes are placed in the liquid phase.

11 Expression of results

The pH value shall be rounded to one decimal place. In addition, the temperature to which the pH-meter is compensated shall be specified.

EXAMPLES

pH value at 25 °C:	6,3
pH value in the sludge suspension at 20 °C:	8,8
pH value in the filtrate at 20 °C:	8,4

12 Test report

The test report shall contain the following information:

- — reference to this European Standard;
- — all information necessary for complete identification of the sludge sample;
- — details of sample pretreatment and preparation;
- — results of the determination according to clause **11**;
- — any details not specified in this European Standard or which are optional and any other factors which may have affected the results.

Annex A (normative)

Primary pH-standard reference solutions (according to ISO 10523)

Table A.1 — pH values of standard buffer solutions

Temperature	Primary pH-standard buffer solutions				
	B	**C**	**D**	**F**	**I**
°C	**Potassium hydrogen tartrate**	**Potassium hydrogen phthalate**[1]	**Phosphate**	**Borax**	**Sodium carbonate/sodium hydrogen carbonate**
0	—	4,000	6,984	9,464	10,317
5	—	3,998	6,951	9,395	10,245
10	—	3,997	6,923	9,332	10,179
15	—	3,998	6,900	9,276	10,118
20	—	4,001	6,881	9,225	10,062
25	3,557	4,005	6,865	9,180	10,012
30	3,552	4,011	6,835	9,139	9,966
35	3,549	4,018	6,844	9,102	9,926
40	3,547	4,027	6,838	9,068	9,889
45	3,547	4,038	6,834	9,038	9,856
50	3,549	4,050	6,833	9,011	9,828
Buffer value	0,027	0,016	0,029	0,020	0,029
$\Delta pH_{1/2}$	+ 0,049	+ 0,052	+ 0,080	+ 0,01	+ 0,079

[1] This solution is called “reference value pH-standard”.

Preparation of the standard solutions. Always use water free from carbon dioxide and:

B: Potassium hydrogen tartrate, saturated at (25 ± 2) °C;

C: Potassium hydrogen phthalate, b = 0,05 mol/l;

Dissolve 10,21 g of C_6H_4 (COOH) (COOK), that has been dried for 2 h at (120 ± 5) °C, in water at (25 ± 2) °C and bring to volume with water in a 1 l volumetric flask.

D: Disodium hydrogen phosphate, b = 0,025 mol/l and potassium dihydrogen phosphate, b = 0,025 mol/l. Dissolve 4,45 g of $Na_2HPO_4 \cdot 2\ H_2O$ (or 3,55 g of Na_2HPO_4) and 3,40 g of KH_2PO_4 in water at (25 ± 2) °C and bring to volume with water. The anhydrous salts are dried for 2 h at (120 ± 5) °C;

F: Sodium tetraborate (borax), b = 0,01 mol/l.

Dissolve 3,81 g of $Na_2B_4O_7 \cdot 10\ H_2O$ in water at (25 ± 2) °C and bring to 1 l with water;

I: Sodium carbonate, b = 0,025 mol/l, and sodium hydrogen carbonate, b = 0,025 mol/l.

Dissolve 2,640 g of Na_2CO_3, that has been dried for 90 min at (250 ± 5) °C and 2,092 g of $NaHCO_3$, that has been dried for 2 days ± 2 h over a molecular sieve, in water and bring to 1 l with water.

Annex B (informative)

Bibliographical references

[1] NF X 31-117:1994, *Qualité du sol — Détermination du pH*
[2] DIN 19263, *pH-measurement — Glass electrodes*
[3] DIN 19264, *pH-measurement — Reference electrodes*
[4] DIN 19266, *pH-measurement — Standard buffer solutions*
[5] BS 1647-2, *Specification for reference value standard solutions and operational reference standard solutions*
[6] ISO 10390:1994, *Soil quality — Determination of pH*

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