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Total phosphorus in soil, biowaste and sewage sludge

Einführendes Element — Haupt-Element — Ergänzendes Element

Élément introductif — Élément central — Élément complémentaire

ICS:

Descriptors: Horizontal-Inorg Dr Janssen and R.Koopmann

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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.

Material	**Validated for** **(type of sample, e.g. municipal sludge, compost)**	**Document**
Sludge	Domestic sludge Industrial sludge	EN 13346 EN 13650 PrEN14672 Horizontal Report Desk Study 16
Soil	Different soil types	Horizontal Desk Study 16
Soil improvers	Fertilized peat	EN 13650
Sediment	Not validated yet	Not validated yet
Waste	Bark humus Composted biowaste	EN 13650 Horizontal Desk Study 16

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Introduction

This document is developed in the project 'Horizontal'. It is the result of a desk study "DS 16: Determination of total phosphorus, total nitrogen and nitrogen fractions" and aims at evaluation of the latest developments in assessing total nitrogen 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 other horizontal modules that will be available in due time are to be found in the informative annex [*xxx*] which contains a brief overview of the modules that will be worked out in the project 'Horizontal.'

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 standard describes the extraction method for the determination of total phosphorus in soil, sludge, biowaste and related waste. The extraction includes the phosphorus in inorganic and organic chemical bonds.

2 Normative references

ISO 11464 Soil quality – Pretreatment of samples for physico-chemical analysis

ISO 11465 Soil quality – Determination of dry matter and water content on a mass basis – gravimetric method

EN 13346 Characterisation of sludge - Determination of trace elements and phosphorus – aqua regia extraction methods

EN 13650 Soil improvers and growing media – Extraction of aqua regia soluble elements

EN 13657 Characterisation of waste – Digestion for subsequent determination of aqua regia soluble portion of elements

EN 12880 Characterisation of sludge – Determination of dry residue and water content

EN ISO 11885 Water quality – Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy

CEN/TC 292 WI 29292030 Characterisation of waste – Preparation of test portions from the laboratory

3 Terms and Definitions

3.1 Dry residue

Dry mass portion of the sample obtained after the specified drying process. It is expressed as percent (EN 12880:2000)

4 Safety remarks

Waste and sludge samples may contain hazardous and inflammable substances. They may contain pathogens and be liable to biological action. Consequently it is recommended that these samples should be handled with special care.During preparation of sample aliquots protective gloves should be used.

National regulations should be followed with respect to microbiological hazards with this method.

5 Principle

The test material is extracted by boiling under reflux with aqua regia and the phosphorus is solved. The content of phosphorus in the extraction solution is measured by ICP-OES (reference method) or other validated measuring method..

6 Interferences and sources of errors

Inductively coupled plasma optical emission spectrometry technique shows some different interferences, which the laboratory has to overcome.

6.1 Physical interferences

This means especially problems in the introduction and spraying system. Different matrix loaded solutions and different surface tension may be the reason for different spraying efficiency. This affects the behaviour in the plasma and the exitation of the elements. Therefore dilute the extraction solution as maximal possible and adjust the calibration solutions to the matrix und acid concentration.

6.2 Chemical and ionisation interferences

They are not known for the element phosphorus

6.3 Spectral interferences

They are shown in the table. Dilute the solution or choose another spectral line.

Emission lines for the element phosphorus, given concentration by 1 g/l of the interferring element

(VDLUFA, 2001)

Element	line, nm	interferring element	Given content, mg/l
P	178,287	none	
P	213,618	Cu Zn	20 1,9
P	214,914	Cu Fe	14 1,2

7 Reagents

All reagents shall be of recognized analytical grade. Deionised or distilled water used shall conform to purity grade 2 of EN ISO 3696.

7.1 Hydrochloric acid, c (HCl) = 12 mol/l, $\rho \approx 1{,}18$ g/ml, about 37 %

7.2 Nitric acid, c (HNO_3) = 15,8 mol/l , $\rho \approx 1{,}42$ g/ml, about 65 %

7.3 Nitric acid, about 1% (V/V)

Take 10 ml of nitric acid (4.2) and dilute to 1 l in a flask with water.

8 Apparatus

All glassware and plasticsware shall be cleaned by nitric acid and stored in order to avoid contamination.

8.1 Reaction vessel: Glass flask, fitted with round neck, 250 ml

(A glas flask of 500 ml may be necessary for material which have a tendency to froth)

8.2 Reflux condenser

Condenser adaptable to reaktion vessel (5.2)

8.3 Heating devices

Gas burner, heating mantle or aluminium block heater

8.4 Filter paper

Filter paper, hardened and resistant to aqua regia solution

8.5 Analytical balance

Analytical balance with an accuracy of 1mg or better

8.6 Boiling aids

Anti bumping granules or glass beads, acid washed

8.7 Volumetric flasks of different volumes.

9 Sampling and sample pre-treatment

9.1 Sampling

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 stored in suitable containers with an appropriate closure material such as PTFE.

9.1 Sample pre-treatment

All samples shall be pretreated according to the special standard of the section sludge, waste, biowaste and soil (e.g. ISO 11464, EN 12880). Normally they are dry and of a defined grain size (2mm, 500µm or better).

10 Procedure

10.1 Digestion

Weigh approximatly 3,0 g (multielement analysis) or 1,5 – 3,0 g (P analysis), to the nearest of 0,001 g, and transfer them to the 250 ml reaction vessel (5.2). Moisten with about 0,5 ml to 1 ml water and add with swirling 21 ml of hydro chloric acid (4.2) followed by 7 ml of nitric acid (4.3) slowly if necessary to reduce foaming. Connect the reflux condenser (5.3) to the reaction vessel. Stand at room temperature until foaming almost ceases to allow for slow oxidation of the organic mass of the test sample. Add some boiling aids (5.7) into the reaction vessel.

Transfer the reaction vessel with the reflux condenser to the heating device (5.4). Raise the temperature of the reaction mixture slowly to reflux conditions and maintain for 2 h. Ensure that the condensation zone is lower than 1/3 of the height of the reflux condenser. Allow the mixture to cool , rinse the reflux condenser into the reaction vessel with 10 ml of water.

Filter the mixture through the filter paper (5.5) into a volumetric flask (5.8), rinse the filter with water and fill up the volume flask to volume with water.

Microwave assisted digestions can be used as well and are performed using 400 – 500 mg (+/- 1mg) of dried sample. Aqua regia is added in a ratio of 1 : 16 (w/V)

(see table in Annex B and temperature programme given in Andersen, et.al. 2004)

10.2 Calibration

Calibration of the ICP analysis is performed with multi element standards in matrix solution,

containing diluted aqua regia.

10.3 Blank determination

Carry out at least two blank determinations in each series and use the average blank value for subsequent calculations.

10.4 Measurement

Take the extracts and the blank test solution, dilute to a specific volume and perform the analysis according to EN ISO 11885 (Annex A).

Adjust the acid concentration of the calibration solutions (blank and standards) and the matrix of this solutions according to the extraction solutions of the test samples.

Information about the spectral lines for phosphorus, matrix effects and interfering elements see 5.3

10.5 Duplicate determination

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

11 Expression of results

11.1 Method of calculation

The phosphorus content of the analysed material in g/kg dry matter is calculated according to following formular:

$$w_P = \frac{C \times V}{m \times m_t}$$

w_P = content of phosphorus in g/kg (dry matter)

C = concentration of phosphorus measured in the extraction solution, mg/l

V = Volume of the volumetric flask, ml

m = mass of the test sample

m_t = dry mass of the test sample , g/100g

11.2 Expression of results

The result shall be expressed in mg/kg dry matter and reported to two significant figures.

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) expression of results, according to 11.2 ;

d) 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 - Desk study 16

Results on the evaluation study (Desk study 16, Project Horizontal) on determination of total phosphorus using reflux digestion and microwave assisted digestion (2005)

Soil

Sample	Content (% P) Reflux method	Content (% P) Microwave method Closed system	Content (% P) Microwave method Open system
SO4	0.06 +/- 0,01	0,09 +/- 0,01	0,09 +/- 0,01
SO13	0,78 +/- 0,08	0,69 +/- 0,08	n.d.
SO16R	0,11 +/- 0,01	0,14 +/- 0,02	0,15 +/- 0,01
CRM 005-050	1,06 +/- 0,02	1,13 +/- 0,05	n.d.

Biowaste

Sample	Content (% P) Reflux method	Content (% P) Microwave method	Content (% P) Microwave method Open system
CW1	0,41 +/- 0,01	0,44 +/- 0,03	0,45 +/- 0,02
CW5	0,52 +/- 0,03	0,53 +/- 0,01	n.d.

Sewage Sludge

Sample	Content (% P) Reflux method	Content (% P) Microwave method
SL4	2,55 +/- 0,25	2,40 +/- 0,25
SL11	0,68 +/- 0,05	0,56 +/- 0,05
NIST 2781	2,31 +/- 0,03	2,40 +/- 0,05

Samples were provided by the Joint Research Centre, Ispra

Samples were dried at 105°C and milled to < 125 µm

(Gawlik, 2004). Reference samples: NIST 2781 and CRM 005-050

were provided by commercial suppliers. n.d. = not determined

Annex A (informative)

Validation of methods

Within the technical commitee CEN/TC 308 „Characterisation of sludges“ one interlaboratory trial with 55 laboratories out of 12 countries in 1997 has given the following results, according to ISO 5725. (sludge 1 was a mixture of drinking water sludge and sewage sludge, sludge 2 was a mixture of drinking water sludge and industrial sludge)

Analyt	No. of participants	content, average, g/kg	s_r g/kg	s_r %	s_R g/kg	S_R %
Sludge 1						
P	23	10,49	0,33	3,2	0,78	7,5
Sludge 2						
P	23	17,27	0,36	2,1	1,35	7,8

s_r mg/kg repeatability

s_r % percentage repeatability

s_R mg/kg reproducibility

s_R % percentage reproducibility

The dimension in the heading of the table (g/kg) is given in mg/kg in the original standard (EN 13346), one has to doubt the correctness of this dimension, in sludge you can expect g/kg for phosphorus.

Within the technical commitee CEN/TC 223 an interlaboratory trial was organized in 1997 with the following data, according to ISO 5725

bark humus

Analyt	No. of participants	Content, average, mg/kg	S_r mg/kg	s_r %	s_R mg/kg	S_R %
P	16	10469,4	414,33	3,96	1117,25	10,67

biowaste

Analyt	No. of participants	Content, average, mg/kg	S_r mg/kg	s_r %	s_R mg/kg	S_R %
P	15	2603,8	71,02	2,73	92,15	3,54

Clay contenting peat (fertilized)

Analyt	No. of participants	Content, average, mg/kg	S_r mg/kg	s_r %	s_R mg/kg	S_R %
P	15	975,7	45,60	4,67	100,99	10,35

Coarse peat (fertilized)

Analyt	No. of participants	Content, average, mg/kg	S_r mg/kg	s_r %	s_R mg/kg	S_R %
P	17	1065,7	35,16	3,30	190,80	17,9

composted sludge

Analyt	Nb. of participants	Content, average, mg/kg	S_r mg/kg	s_r %	s_R mg/kg	S_R %
P	16	9580,5	207,10	2,16	496,17	5,18

composted wood fibre

Analyt	No. of participants	Content, average, mg/kg	S_r mg/kg	s_r %	s_R mg/kg	S_R %
P	16	1150,7	40,53	3,52	125,36	10,89

s_r mg/kg repeatability

s_r % percentage repeatability

s_R mg/kg reproducibility

s_R % percentage reproducibility

Annex B
(informative)

The modular horizontal system

Annex C
(informative)

Information on WP xx and the project Horizontal

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