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Total nitrogen in soil, biowaste and sewage sludge

Einführendes Element — Haupt-Element — Ergänzendes Element

Élément introductif — Élément central — Élément complémentaire

ICS:

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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	Horizontal Report Desk Study 16
Soil	Different soil types	ISO 13878 Horizontal Desk Study 16
Soil improvers	Fertilized peat	EN 13654-2
Sediment	Not validated yet	Not validated yet
Waste	Bark humus Composted biowaste	EN 13654-2 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 descibes the determination of total nitrogen (organic and inorganic) according to the procedure of Dumas in soil, sewage sludge, biowaste and related waste. Dry samples are used normally, in special situations moist samples can be used.

2 Normative references

This European Standard incorporates by dated or undated reference, 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).

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

ISO 11465 Soil quality – Determaination of dry matter and water content on a mass basis –

gravimetric method

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

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

ISO 13878 Soil quality - Determination of total nitrogen content by dry combustion („elemental analysis“)

EN 13654-2 Soil improvers and growing media - Determination of nitrogen – part 2: Dumas method

3 Terms and definitions

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

3.1

Total Nitrogen

Amount of nitrogen that is released after Dumas combustion of the sample

3.2

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 for use in the Dumas process protective gloves should be used.

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

5 Principle

The total nitrogen content of the analysed material is determined by heating it to a temperature of at least

900°C in the presence of oxygen gas. Mineral and organic nitrogen compounds are oxidized and/or volatilized. The combustion products are oxides of nitrogen (NO_x) and molecular nitrogen. After transforming all nitrogen into molecular nitrogen, the content of the nitrogen gas is measured using thermal conductivity.

6 Interferences and sources of errors

Pores in the material to be analysed are filled with air and, therefore, with nitrogen. Nitrogen also enters the combustion cell when it is opened to exchange the sample. Take care purging of the cell and the material to be analysed by oxygen gas is sufficient leaving no nitrogen gas back. Furthermore samples with high fiber content should be sieved to a maximum particle size of < 2 mm. Moist samples should be handled with care, as they can leach out of sample vials during the process. Fluctuations of total nitrogen may be caused by differeing contents in carrier gases used, thefore a blank determination should be performed after changing gas bottles and each day before starting the analytical series..

7 Reagents

Use only reagents of recognised analytical grade and water grade 1 in accordance with ISO 3696.

The total nitrogen contribution from water, reagents and gases should be significantly less than the lowest total nitrogen content to be determined. The overall total nitrogen content of water, chemicals, and gases shall be checked by measuring the total blank (see 9.4).

7.1 Combustion gas (oxygen)

7.2 Oxygen free of nitrogen (see instruction manual of the apparatus used)

7.3 Chemicals and/or catalysts (see instruction manual of the apparatus used)

7.4 Inert gas as carrier gas, free of nitrogen, e.g. Helium

7.5 Ethylenediaminetetraacetic acid (EDTA)

7.6 Glucose or saccharose as burning assistance or other suitable material, free of nitrogen

For reduction, oxidation, removal and/or fixing of combustion gases which interfere with the analysis of nitrogen, the different manufacturers use different materials. See instruction manual.

8 Apparatus

8.1 Dumas apparatus

Apparatus to combust the material at 900 °C in the presence of oxygen, to reduce the nitrogen oxides, to eleminate the interfering gases and to detect the content of molecular nitrogen gas formed.

8.2 Analytical balance

Analytical balance, capable of weighing acurately to 0,1 mg, or microbalance, capable of weighing accurately to 0,01 mg.

8.3 Equipment

Crucibles adapted to the Dumas apparatus, of variable sizes, e.g. 10 mlor 20 ml of nominal volume or

special foil (see instruction manual of the special Dumas apparatus type).

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.

9.2 Sample pre-treatment

All samples shall be pretreated according to the special standard in the field of soil, sludge, biowaste and related waste. Normally they are dry, homogenuous and of a defined grain size.

During the drying procedure there is taken care not to loose amounts of ammonium-N and/or nitrate-N. Therefore, excessive drying (105 °C) should be avoided. Rapid microwave drying may be a good choice. In special situations moist samples can be used.

Samples with high fiber content (biowaste) are dried and sieved to a quality of < 2mm.

Dry residue of the sample is determined by the specified drying process according to EN 12880:2000

10 Procedure

Homogeneity of the laboratory sample and the test sample has to be guaranteed

In special cases the use of undried samples is necessary. Take care that the material is homogeneous and avoid spattering during the drying process in the Dumas apparatus.

10.1 Calibration

Calibrate the system by analysing calibration substances with known and unchangeable content of nitrogen to controll the combustion and the apparatus. This may be: acetanilid, l-asparagin acid, sulfanil acid or other amino acids with known nitrogen content. Besides this certified reference materials are used to control the whole procedure.Calibrate the analytical instrument daily using one of the two methods described below. Weigh an adequate amount of EDTA (4. 5) or of any calibrating substance, mix thoroughly with burning assistance (4.6) and measure the amount of nitrogen. If necessary control the linearity of the analysator with different amounts of EDTA or the calibrating substances.

10.2 Blank determination

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

10.3 Quality Assurance of the overall procedure

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.

In special cases the use of undried samples is necessary. Take care that the material is homogeneous and avoid spattering during the drying process in the Dumas apparatus.

10.4 Determination of total nitrogen content

Weigh a portion of the dried or undried material to be analysed into the crucible (5.3) to the nearest of 0,1% accuracy. The amount depends on the exspected total nitrogen content and the size of the crucible. Carry out the analysis in accordance with the manufacturer`s manual for the special Dumas apparatus.

11 Expression of results

11.1 Method of calculation

Calculate the total nitrogen content (w_N) in milligrams per gram, on the basis of dry matter according to the following equation:

For primary results given in milligrams of nitrogen:

$$w_N = X_1 \times 100 / (m \times m_t)$$

For primary results, given as percent mass fraction of nitrogen:

$$w_N = X_2 \times 10 \times 100 / (m \times m_t)$$

where

w_N is the content of nitrogen in milligrams per gram of oven dry material

X_1 is the primary result in milligram nitrogen

X_2 is the primary result in percentage nitrogen (mass fraction)

m is the mass of material weight in the crucible

mt is the dry residue (g/100g) on the basis of oven dried material, determined in accordance to the respective standard.

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

Performance data in terms of repeatability and reproducibility .have been determined during desk study 16 using statistical data from 6 repeated measurements of one sample analysed the same day.Repeatability is expressed by standard deviation in %N and as relative standard deviation s rel

Precision data soil:

Sample No	*Content % N*	*S %N*	*S rel %*
SO1	0,26	0,02	8
SO8	0,25	0,01	4
SO9	0,46	0,01	2

Precision data biowaste and sewage sludge:

CW1	1,66	0,02	1
CW5	1,69	0,03	2
SL4	2,04	0,02	1
SL11	0,73	0,02	3

Precision data: Reference materials

SL SRM 2781 sludge	4,74	0,04	1
SO soil WEPAl enquete	0,031	0,002	7
SO soil WEPAl enquete	0,32	0,01	3

Precision data: soil / biowaste: Milling quality:

SO13 ; < 2mm	0,32	0,03	9
SO13 ; < 250 µm	0,33	0,01	3
CW KAS3 ; < 2mm	1,86	0,07	4
CW KAS3 ; < 250 µm	1,78	0,01	1

Linearity of standards and standard addition:

EDTA r: 0,99934 up to 7,2 mg N

Addition soil: r = 0,99931 up to 2,3 mg N

Addition biowaste: r = 0,99496 up to 3 mg N

Addition sewage sludge: r = 0,99994 up to 4,5 mg N

LOQ = 0,02 %N ; LOD = 0,008 %N

Recovery = 100 – 109 %

Annex A (informative)

Validation of methods

The interlaboratory trial organized in the year 1992 with 12 laboratories and in 1993 with 11 laboratories in Germany with three soils resulted in the following data:

Sample No./	Nitrogen content, Average, mg/g	s_r mg/g	s_r %	s_R mg/g	s_R %
1	1,457	0,067	4,6	0,205	14,1
2	2,054	0,073	3,6	0,333	16,2
3	11,16	0,334	3,0	0,982	8,8

Within the work of CEN /TC 223 an interlaboratory trial was organized in 1997 with the following results :

Sample No.	Number of Participants	Nitrogen content, Average, mg/g	s_r mg/g	s_r %	s_R mg/g	s_R %
Bark humus	10	19,5	0,45	2,30	1,32	6,77
Biowaste	12	13,21	0,36	2,73	1,10	8,33
Clay contenting peat	11	9,2	0,25	2,72	0,63	6,85
coarse peat	11	10,7	0,25	2,34	1,69	15,8
Composted sludge	15	29,90	0,96	3,21	2,97	9,93
Composted wood fibre	12	12,07	0,37	3,07	1,72	14,25

s_r mg/kg is standard deviation (repeatability)

s_r % is percentage standard deviation (repeatability)

s_R mg/kg is standard deviation (reproducibility)

s_R % is percentage standard deviation (reproducibility)

In the future the validation has to be done with three samples of different sludges, three different samples of to biowaste related wastes with different contents of nitrogen each. These samples have to be dry samples.

A new ring test with more soils and a wider range of nitrogen content is proposed.

The repeatability and the reproducibility are calculated from the results of the round robin studies with the factor 2,8 .

Annex B
(informative)

The modular horizontal system

Annex C
(informative)

Information on WP xx and the project Horizontal

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