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Sludge, treated biowaste and soil — Determination of total Nitrogen — Dry combustion method

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Foreword

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This document BT/TF151 WI99020 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).

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		(reference)
Soil		
Treated biowaste		
Sediment		
Waste		

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 Dumas nitrogen in sludge, treated biowaste and soil. After an evaluation study, in which e.g. the ruggedness of the method was studies, a European wide validation of the draft standard has taken place. The results of the desk studies as well as the evaluation and validation studies have been subject to discussions with all parties concerned in CEN. The standard is part of a modular horizontal approach in which the standard belongs to the analytical step.

Until now test methods determining properties of materials were often prepared in Technical Committees (TCs) working on specific products or specific sectors. In those test methods often steps as sampling, extraction, release or other processing, analyses, etc were included. In this approach it was necessary to develop, edit and validate similar procedural steps over and over again for every material or product. Consequently this has resulted in duplication of work. To avoid such duplication of work for parts of a testing procedure references to parts of test methods from other TCs were introduced. However the following problems are often encountered while using references in this way: 1) The referenced parts are often not edited in a way that they could easily be referred to, 2) the referenced parts are often not validated for the other type of material and 3) the updates of such test standards on products might lead to inadequate references.

In the growing amount of product and sector oriented test methods it was recognised that many steps in test procedures are or could be used in test procedures for many products, materials and sectors. It was supposed that, by careful determination of these steps and selection of specific questions within these steps, elements

of the test procedure could be described in a way that can be used for all materials and products or for all materials and products with certain specifications.

Based on this hypothesis 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 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 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 modules that relates to this standard are specified in section XX Normative references.

An overview of modules and the manner, in which modules are selected will be worked out later, at which time proper reference in this standard will be provided.

Sludge, treated biowaste and soil — Determination of total nitrogen — Dry combustion method

WARNING — 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 and chemical hazards with this method.

1 Scope

This European Standard describes the determination of total nitrogen (organic and inorganic) according to the procedure of Dumas in sludge, treated biowaste and soil. Dry samples are used normally, in special situations moist samples can be used.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 12880, *Characterisation of sludge — Determination of dry residue and water content*.

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

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

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
total nitrogen
amount of nitrogen that is released after Dumas combustion of the sample

3.2
dry residue
dry mass fraction of the sample obtained after the specified drying process. It is expressed as percent or in grams per kilogram

4 Principle

The total nitrogen content of the material is determined by heating it to a temperature of at least 850 °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 (N_2). After transforming all nitrogen into molecular nitrogen, the content of the nitrogen gas is measured using thermal conductivity or other device specific detectors.

5 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. Purging of the cell and the material to be analysed by inert gas is sufficient in leaving no nitrogen gas back. Moist samples shall be used only in special cases and handled with care, as they can leach out of sample vials during the process or contaminate the device by spattering. Fluctuations of total nitrogen may be caused by different contents of nitrogen in carrier gases used. Therefore a blank determination shall be performed after changing gas bottles and each day before starting the analytical series.

6 Reagents

Use only reagents of recognized analytical grade, unless otherwise specified.

6.1 Water, complying with grade 2 as defined in EN ISO 3696.

6.2 Combustion gas (oxygen), free of nitrogen.

6.3 Inert gas, carrier gas, free of nitrogen, e.g. helium.

6.4 Ethylenediaminetetraacetic acid (EDTA), or other calibration substances with known content of nitrogen, e.g. acetanilide (C_8H_9NO), L-aspartic acid ($C_4H_7NO_4$), sulfanil acid or other amino acids or reference standards (e.g. NIST) which contain the matrix materials of investigations.

7 Apparatus

Usual laboratory apparatus, and in particular the following:

7.1 Dumas apparatus.

7.2 Crucibles, adapted to the Dumas apparatus (7.1) of variable sizes, e.g. 1 ml to 20 ml of nominal volume or special foil.

8 Sampling and sample pre-treatment

8.1 Sampling

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

Samples shall be stored in suitable containers with an appropriate closure material such as PE.

8.2 Sample pre-treatment

All samples shall be pretreated according to the special standard (CSS99034) in the field of sludge, treated biowaste and soil. In principle, they are air dried or dried at a maximum of 40 °C in a ventilated oven, homogeneous and of a defined grain size (< 2 mm).

During the drying procedure or a milling process there is taken care not to lose amounts of ammonium-N and/or nitrate-N. Therefore, avoid excessive drying (105 °C) and prolonged drying at temperatures > 40 °C. Prolonged drying at 40 °C or at room temperature may cause losses of nitrogen due to microbial activity within the sample. Therefore rapid drying methods are preferred.

In special situations moist samples can be used. If moist samples are used, determined the dry weight on a special sample, so that the result can be referred to dry residue. Determine the dry residue of the sample by the specified drying process according to EN 12880.

9 Procedure

9.1 General

The total nitrogen contribution from water (6.1), reagents and gases (6.2, 6.3) shall be significantly less than the lowest total nitrogen content to be determined. The overall total nitrogen content of water (6.1), reagents and gases (6.2, 6.3) shall be checked by measuring the total blank (see 9.4).

Homogeneity of the laboratory sample and the air dried test sample has to be guaranteed.

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

The Dumas apparatus (7.1) is used to combust the material at a minimum of 850 °C in the presence of oxygen (6.2), to reduce the nitrogen oxides, to eliminate the interfering gases and to detect the content of molecular nitrogen gas formed.

9.2 Calibration

Calibrate the apparatus by analyzing calibration substances (6.4) to control the combustion and the apparatus. Use certified reference materials to control the whole procedure. Calibrate the analytical instrument on the day of use using one of the two methods described below.

Weigh an adequate amount of EDTA or of any calibrating substance (6.4) and measure the amount of nitrogen. If necessary control the linearity of the analysator with different amounts of EDTA or the calibrating substances (6.4).

9.3 Blank determination

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

9.4 Determination of total nitrogen content

Weigh a portion of the dried or undried sample to be analyzed to the nearest of 0,1 % accuracy into the crucible (7.2). The amount depends on the expected total nitrogen content and the size of the crucible.

Carry out the analysis in accordance with the manufacturer's manual. Use oxygen (6.2) as combustion gas. For reduction, oxidation, removal and/or fixing of combustion gases that interfere with the analysis, refer to the manufacturer's instructions.

10 Calculation

Calculate the content of nitrogen w_N, in milligram per kilogram, on the basis of dry matter using the equation

$$w_N = \frac{X \times 100}{m \times w_{dm}} \quad (1)$$

where

w_N is the content of nitrogen on the basis of dry matter, in milligrams per kilogram;

X is the primary result in milligram nitrogen;

m is the numerical value of the mass of the test sample in the crucible, in kilogram;

w_{dm} is the dry mass portion, expressed as g/100 g on the basis of oven dried material, determined in accordance with EN 12880.

11 Expression of results

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

12 Precision data

The performance characteristics of the method (Annex C) data have been evaluated. Table 1 gives the resulting typical values for repeatability and reproducibility limits as their observed ranges. The typical value is derived from the data in Table C.2 in Annex C by taking the median value and rounding the numbers.

Table C.1 — Typical values and observed ranges of the repeatability and reproducibility limits

The reproducibility limit provides a determination of the differences (positive and negative) that can be found (with a 95 % statistical confidence) between a single test result obtained by a laboratory using its own facilities and another test result obtained by another laboratory using its own facilities, both test results being obtained under the following conditions : The tests are performed in accordance with all the requirements of the present standard and the two laboratory samples are obtained from the same primary field sample and prepared under identical procedures. Conversely, the repeatability limit refers to measurements obtained from the same laboratory, all other conditions being identical. The reproducibility limit and the repeatability limit do not cover sampling but cover all activities carried out on the laboratory sample including its preparation from the primary field sample.

Results of the validation of the determination of total nitrogen – Dry combustion method in soil, sludge and treated biowaste	Typical value %	Observed range %
Repeatability limit, r	8	*2 – 18*
Reproducibility limit, R	21	5 – 63

NOTE 1. The above results refer to the difference that may be found between two test results performed on two laboratory samples obtained under the same conditions. In the case when reference is made to the dispersion of the values that could reasonably be attributed to the parameter being measured, the above typical reproducibility values and observed reproducibility ranges should be divided by √2 to obtain the corresponding typical dispersion limit and its observed range. In the example of Total N in Compost 1 the result and its dispersion limit is 18.1 ± 2.03 (2 * sR = 11.2 % of 18.1). This means that with a 95 % statistical confidence, the values reasonably attributable to the measured parameter are larger than 16 g/kg and lower than 20 g/kg.

NOTE 2. The repeatability limit (r) and the reproducibility limit (R) as given in Table C.2 (Annex C) and in this table are indicative values of the attainable precision if the determination of total nitrogen – dry combustion method is performed in accordance with this standard [CSS99020].

NOTE 3 A limited number of materials and parameters were tested. Consequently, for other materials and parameters, performance characteristics may fall outside the limits as derived from the validation of the the determination of total nitrogen – dry combustion method in soil, sludge and treated biowaste.

NOTE 4 In particular for relatively heterogeneous materials, the repeatability and the reproducibility limits may be larger than the values given in Table C.2 (Annex C) and this table.

13 Test report

The test report shall contain the following information:

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

b) all information necessary for identification of the sample tested;

c) the results, calculated as specified in 10 and expressed according to 11;

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:200x in the report in case all deviations from the procedures prescribed in this standard are indicated in the report stating the reason for deviation.

Annex A
(informativ)

Performance data ISO 13878 and EN 13654-2

Performance data have been determined during an interlaboratory trial organized in the year 1992 with 12 laboratories and in 1993 with 11 laboratories in Germany with three soils (ISO 13878). The results are given in table A.1.

Table A.1 — Performance data for soil samples

Sample No.	**Nitrogen content, average** % N	s_r %	s_R %
1	0,15	4,6	14,1
2	0,21	3,6	16,2
3	1,12	3,0	8,8
s_r is percentage standard deviation (repeatability), expressed as percentage; s_R is percentage standard deviation (reproducibility), expressed as percentage.			

Within the work of CEN/TC 223 an interlaboratory trial was organized in 1997 (EN 13654-2). The results are given in table A.2.

Table B.2 — Performance data for biowaste and sludge

Sample No.	**Number of Participants**	**Nitrogen content, average** % N	s_r %	s_R %
Composted bark	10	1,95	2,30	6,77
Biowaste	12	1,3	2,73	8,33
Clay contenting peat	11	0,92	2,72	6,85
Coarse peat	11	1,07	2,34	15,8
Composted sludge	15	2,99	3,21	9,93
Composted wood fibre	12	1,21	3,07	14,25
s_r is percentage standard deviation (repeatability), expressed as percentage; s_R is percentage standard deviation (reproducibility), expressed as percentage.				

Annex B
(informativ)

Repeatability data of this European Standard

Performance data of air dried test samples were determined during desk study 16 [x] using statistical data from six repeated measurements of one sample. The results obtained are given in table B.1 to table B.4.

Table C.1 — Performance data for soil

Sample No.	**Nitrogen content, w_N %**	***S*** % N	**S_r** %
SO1	0,26	0,02	8
SO8	0,25	0,01	4
SO9	0,46	0,01	2
S is the XXXXXXXXXXXXX, in % N; S_r is the XXXXXXXXXXXXX, in %.			

Table C.2 — Precision data biowaste and sewage sludge:

Sample No.	**Nitrogen content, w_N %**	***S*** % N	**S_r** %
CW1	1,66	0,02	1
CW5	1,69	0,03	2
SL4	2,04	0,02	1
SL11	0,73	0,02	3
S is the XXXXXXXXXXXXX, in % N; S_r is the XXXXXXXXXXXXX, in %.			

Table C.3 — Precision data: Reference materials

Sample No.	**Nitrogen content, w_N %**	***S*** % N	**S_r** %
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
S is the XXXXXXXXXXXXX, in % N; S_r is the XXXXXXXXXXXXX, in %.			

Table C.4 — Precision data: soil / biowaste: milling quality

Sample No.	**Nitrogen content, w_N %**	***S*** % N	**S_r** %
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
S is the XXXXXXXXXXXXX, in % N; S_r is the XXXXXXXXXXXXX, in %.			

Linearity of standards and standard addition:

EDTA *r*: 0,99934 % N up to 7,2 % N

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

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

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

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

Recovery = 100 % – 109 %

Annex C (informative)

Repeatability and reproducibility data

C.1 Performance characteristics

C.1.1 Objective of the interlaboratory comparison

In a European wide interlaboratory comparison study according to ISO 5725-2, the performance characteristics of the standard “Determination of total nitrogen – dry combustion method in soil, sludge and treated biowaste” were established.

C.1.2 Materials used in the interlaboratory comparison study

The interlaboratory comparison of determination of total nitrogen – dry combustion method in soil, sludge and treated biowaste was carried out with 12 - 13 European laboratories on 6 materials. The materials selected for the interlaboratory comparison were chosen to represent soil, sludge and biowaste as broad as possible, because the standard will find general application across different types of soil and soil related materials. (detailed information can be found in the final report on the Interlaboratory comparison study mentioned in the Bibliography).

In the interlaboratory comparison study the following starting points were used:

- The laboratory samples were all taken from one large batch of the different materials according to the normal practice. The normal size reduction and the normal repeated mixing were carried out as needed to obtain representative laboratory samples from the large batch sample (ref JRC).
    - Note : the samples provided for the validation should not be confused with reference samples provided for certification purposes, as the performance results obtained have to be directly applicable to daily practice (less rigorous sample preparation than for a reference material).
- The experimental plan was designed by project HORIZONTAL on the basis of each laboratory being given two laboratory samples of each material to be tested. This is in accordance with ISO 5725-2.
- The materials examined cover all the grain size classes to which the the determination of total nitrogen – dry combustion method in soil, sludge and treated biowaste applies: very fine grained materials (like sludge: 0 µm to about 125 µm) and fine-grained materials (soil and compost: 0 mm to 4 mm).
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Table A.1 provides a list of the types of materials chosen for testing and the selected components.

Table A.CD.1 — Material types tested and components analysed in the interlaboratory comparison of the determination of total nitrogen – dry combustion method in soil, sludge and treated biowaste.

Grain size class	Sample code	Material type tested	Parameters/congeners
Sludge (<0.5 mm)	Sludge 1	Mix 1 of municipal WWTP sludges from North Rhine Westphalia, Germany	Total N
	Sludge 2	Mix 2 of municipal WWTP sludges from North Rhine Westphalia, Germany	Total N
Fine grained (< 2 mm)	Compost 1	Fresh compost from Vienna, Austria	Total N
	Compost 2	Compost from Germany	Total N
	Soil 4	A sludge amended soil from Hohenheim, Germany	Total N
	Soil 5	An agricultural soil from Reading, UK	Total N

C.1.3 Interlaboratory comparison results

The statistical evaluation was conducted according to ISO 5725-2. The average values, the repeatability standard deviation (s_r) and the reproducibility standard deviation (s_R) were obtained (Table C.2).

The repeatability is determined as an interval around a measurement result (i.e. "repeatability limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another, both test results being obtained under the following conditions: The tests are performed in accordance with all the requirements of the present standard by the same laboratory using its own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures.

The repeatability limit was calculated using the relationship : $r_{test} = f \cdot \sqrt{2} \cdot s_{r,test}$ with the critical range factor f = 2.

For instance, the repeatability limit around a measurement result of 20 g N total/kg is ± 1.65 g N total/kg (i.e ± 8 % of 20).

NOTE The above relationship refers to the difference that may be found between two measurement results performed each on two laboratory samples obtained under the same conditions. The value f = 2 used in the factor f · √2 corresponds to the theoretical factor of 1,96 for a pure normal distribution at 95 % statistical confidence. Also, this value f = 2 corresponds to the usual value k = 2 of the coverage factor recommended in the Guide to the expression of Uncertainty in Measurement (GUM). However it may be necessary to use a larger value for f in situation as described in clause 12.

The reproducibility, like repeatability is also determined as an interval around a measurement result (i.e. "reproducibility limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another test result obtained by another laboratory, both test results being obtained under the following conditions : The tests are performed in accordance with all the requirements of the present standard by two different laboratories using their own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures.

The reproducibility limit was calculated using the relationship: $R = f \cdot \sqrt{2} \cdot s_R$ with the critical range factor f = 2.

For instance, the reproducibility limit around a measurement result 20 g N total /kg is ± 4.26 g N total /kg (i.e ± 21 % of 20).

NOTE The above relationship refers to the difference that may be found between two measurement results performed each on two laboratory samples obtained under the same conditions. The value f = 2 used in the factor f · √2 corresponds to the theoretical factor of 1,96 for a pure normal distribution at 95 % statistical confidence. Also, this value f = 2 corresponds to the usual value k = 2 of the coverage factor recommended in the Guide to the expression of Uncertainty in Measurement (GUM). In the case when reference is made to the dispersion of the values that could reasonably be attributed to the parameter being measured, the dispersion limit is equal to $k \cdot s_R$ with the usual value k = 2, resulting in a dispersion limit lower than the reproducibility limit (i.e. a ratio of √2). However it may be necessary to use a larger value f · √2 (or k) in situation as described in clause 12 .

In case of relatively heterogeneous materials, the repeatability and the reproducibility limits may be larger than the values given in Tables C.2 (this means that the value chosen for the critical range factor f is larger than 2 as well as for the coverage factor k for dispersion). This is because the extreme results may have been obtained in accordance with the present standard and/or be caused by the variability within, or in between, the laboratory samples.

Table C.CD.2 — Results of the interlaboratory comparison studies of the determination of total nitrogen – dry combustion method in soil, sludge and treated biowaste. All concentrations in g/kg.

Matrix	Parameter	Mean	sr	sR	r	R	p	Outliers	Used number of data	Number of data reported below detection	Total no of data reported
Sludge 1	N tot	39.15	0.84%	1.80%	0.917	1.970	9	2	51	0	60
Sludge 2	N tot	35.88	1.54%	5.03%	1.547	5.054	11	1	57	0	63
Compost 1	N tot	18.07	2.02%	5.61%	1.024	2.840	11	1	57	0	61
Compost 2	N tot	13.79	3.86%	9.59%	1.489	3.701	12	2	64	0	64
Soil 4	N tot	1.79	5.89%	22.5%	0.295	1.127	11	1	58	0	61
Soil 5	N tot	1.92	6.52%	15.3%	0.350	0.821	9	2	52	0	58

Abbreviations: sr Repeatability standard deviation; SR Reproducibility standard deviation; r Repeatability limit (comparing two measurements); R Reproducibility limit (comparing two measurements); p Number of labs.

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