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Sludge, treated biowaste and soil – determination of total nitrogen – dry combustion method

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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.

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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 Dumas nitrogen in sludge, treated biowaste and soil. 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 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

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 – Determination 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 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 (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 and chemical hazards with this method.

5 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. After transforming all nitrogen into molecular nitrogen, the content of the nitrogen gas is measured using thermal conductivity or other device specific detectors.

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. Purging of the cell and the material to be analysed by inert gas is sufficient in leaving no nitrogen gas back. Moist samples should 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 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 free of nitrogen (see instruction manual of the apparatus used)

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

7.3 Inert gas as carrier gas, free of nitrogen, e.g. helium

7.4 Ethylenediaminetetraacetic acid (EDTA) or other calibration substances with known content of nitrogen, e.g. amino acids or reference standards (e.g. NIST) which contain the matrix materials of investigations

7.5 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 a minimum of 850 °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. 1 ml to 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 PE.

9.2 Sample pre-treatment

All samples shall be pretreated according to the special standard in the field of soil, treated biowaste and sludge. 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, excessive drying (105 °C) and prolonged drying at temperatures > 40°C should be avoided. 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 have to be preferred.

In special situations moist samples can be used. If moist samples are used, the dry weight has to be determined on a special sample, so that the result can be referred to dry residue.

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 air dried 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 combustion process in the Dumas apparatus.

10.1 Calibration

Calibrate the system by analysing calibration substances with known and unchangeable content of nitrogen to control the combustion and the apparatus. This may be: acetanilid, l-asparagin acid, sulfanil acid or other amino acids with known nitrogen content. 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 (7. 5) or of any calibrating substance 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 Determination of total nitrogen content

Weigh a portion of the dried or undried material to be analysed into the crucible (8.3) to the nearest of 0,1% accuracy. 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 for the special Dumas apparatus.

11 Expression of results

11.1 Method of calculation

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

$$w_N = X_1 \times 100 / (m \times w_{dm})$$

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

m is the mass of material weight in the crucible (in kg)

w_{dm} is the dry mass portion (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 or % 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

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 (ISO 13878):

Table 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

Within the work of CEN /TC 223 (EN 13654-2) an interlaboratory trial was organized in 1997 with the following results :

Table 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)

s_R % is percentage standard deviation (reproducibility)

Annex B (informativ)

Performance data of air dried test samples were determined during desk study 16 using statistical data from six repeated measurements of one sample.

Table 3: Performance data (Janssen, 2005)

Precision data soil:

Sample No	*Content % N*	*S %N*	S_r %
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 % N

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

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

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

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

Recovery = 100 – 109 %

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