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Determination of Kjeldahl 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 (EN 13342)
Soil	Different soil types	ISO 11261 Horizontal Desk Study 16
Soil improvers	Fertilized peat	EN 13654-1
Sediment	Not validated yet	Not validated yet
Waste	Bark humus Composted biowaste	EN 13654-1 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 is to determine Kjeldahl nitrogen according to the Kjeldahl procedure in soil, sludge, biowaste and related waste. Nitrate and nitrite are not included. Compounds with special chemical N-bonding (N-N, N-O and heterocycles) are not digested entirely.

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

ISO 11261: Soil quality – Determination of total nitrogen – modified Kjeldahl 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

EN 13342 Characterization of sludges - Determination of Kjeldahl nitrogen

EN 13654-1: Soil improvers and growing media – Determination of nitrogen – modified Kjeldahl method

3 Terms and definitions

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

3.1

Kjeldahl nitrogen

Amount of nitrogen that is determined after Kjeldahl digestion and titration

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. National regulations should be followed with respect to microbiological hazards with this method.Concentrated sulfuric acid is used in Kjeldahl digestion. Sulfuric acid causes severe damages to skin and eyes, therefore protective gloves and glasses have to be worn. Special instructions of the manufacturer of the digestion apparatus have to be followed. National regulations should be followed with respect to microbiological and chemical hazards with this method.

5 Principle

The dried and homogenised material is digested in a suitable Kjeldahltube with sulfuric acid. To rise the temperature potassium sulfate is added and titanium dioxid/copper sulfate is used as a catalyst. After adding sodium hydroxide to the digestion solution the produced ammonium from all nitrogen species is evaporated by distillation as ammonia. This is condensed in a conical flask with boric acid solution. The amount is titrated against indicator with sulfuric acid.

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6 Interferences and sources of errors

The Kjeldahl method in principle does not capture all nitrogen compounds.The nitrogen, that occurs in N-N and N-O linkages (e,g. azo-, nitro- and nitroso compounds, hydrazines, hydrazones, oximes, pyrazolones, isooxazoles, dia- and triazines) is not completely recorded. Furthermore the inorganic fraction: nitrate and nitrite is not determined. Other sources of error include fluctuations in residual water content of samples, impurities in the apparatus and fluctuations during titration. Therefore the apparatus has to be rinsed after each analytical series and blank determinations have to be carried out. The amount of sulfuric acid has to be investigated with different materials to yield the highest digestion efficiency Reagents

Material	Acid consumption ml of 36 mol/l H_2SO_4/ g of material
Soil organic C	10,0
Soil organic matter	5.8
Al_2O_3	1,63
Fe_2O_3	1,04
Clay	0,60
$CaCO_3$	0,55
Silt	0,33
Sand	0
Salicylic acid	6,76
$Na_2S_2O_3$	0,58
Reduced Fe	1,50

Amounts of sulfuric acid consumption by various materials during Kjeldahl digestion (Bremner 1960)

All reagents shall be of analytical grade. Use water of grade 2 complying with ISO 3696

7.1 Sulfuric acid, ρ = 1.84 kg /l

7.2 Potassium sulfate catalyst mixture

7.3 Grind and thoroughly mix 200 g of potassium sulfate, 20 g of copper sulfate pentahydrate and

20 g of titanium dioxide, with the crystal structure of anatase.

7.4 Sodium hydroxide, c (NaOH) = 10 mol/l

7.5 Boric acid solution , ρ = 20g /l

7.6 Mixed indicator

Dissolve 0.1 g of bromocresol green and 0.02 g of methyl red in 100 ml ethanol.

7.7 Sulfuric acid, $c(H^+)$ = 0.01 mol/l

7.8 Ammonium sulfate NH_4SO_4

7 Apparatus

Usual laboratory equipment is needed

7.1 Kjeldahl digestion flasks or tubes, of nominal volume 50 ml, suitable for digestion stand (6.2).

To use the semimikro- or the makromethod respective flasks or tubes are to be used.

8.2 **Digestion stand**, suitable for digestion of samples with sulfuric acid at temperature near to 400 °C and fit to evaporate the fume

8.3 **Distillation apparatus**, e.g. of the Parnas-Wagner type or other suitable distillattion apparatus with steam generator

8.4 **Burette**, graduated in intervals of 0.01 ml or smaller.

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 digestion procedure there is taken care not to loose amounts of nitrogen. Therefore, temperatures exceeding 400°C should be avoided.

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

10.1 Digestion

Place a test portion of the dried and grinded sample, of about 0.2 g (exspected nitrogen content ≈ 0.5 %) to 1g (exspected nitrogen content ≈ 0.1 %) or undried sample with the corresponding dry matter to the nearest of 0,1% accuracy in the digestion flask or tube (5.2). Add 10 ml sulfuric acid (4.2) and swirl until the acid is thoroughly mixed with the sample. Allow the mixture to stand for cooling. Add 2,5 g of the catalyst mixture (4.3) and heat until the digestion mixture becomes clear. Boil the mixture gently for up to 5 h so that the sulfuric acid condenses about 1/3 of the way up to the neck of the flask or the end of the tube. Ensure that the temperature of the solution does not exceed 400 °C .

The amount of sulfuric acid may be adopted

The time of boiling period may be different and depends on the sample material. The solution has to be clear at the end of boiling.

The amount of test material and added chemicals can be changed in the ratio described in the working instructions. The semimicro and the macro version of the Kjeldahl procedure are suitable for some materials.

10.2 Titration

After completion of the digestion step, allow the flask or tube to cool and add 20 ml of water slowly while shaking. Then swirl the flask or tube to bring any insoluble material into suspension and transfer the contents to the distillation apparatus (5.4). Rinse three times with water to complete the transfer. Add 5 ml of boric acid (4.5) to a 200 ml conical flask and and place the flask under the condenser of the distillation apparatus in such a way that the end of the condenser dips into the solution. Add 20 ml of sodium hydroxide (4.4) to the funnel of the apparatus and run the alkali slowly into the distillation chamber. Distil about 100 ml of condensate (the amount for quantitative results depends on the dimensions of the apparatus), rinse the end of the condenser, add a few drops of mixed indicator (4.6) to the distillate and titrate with sulfuric acid (4.7) to a violet endpoint.

The best way of distillation is steam distillation. A rate of up to 25 ml/min is applicable. Stop the distillation when 100 ml of distillate have been collected.

Modern Kjeldahl apparatus use the digestion tubes for distillation and the addition of chemicals is programmed. The distillation is done automatically. A potentiometric titration with an endpoint of pH = 5.0 is possible.

10.3 Calibration

Calibration substances with known and unchangeable content of nitrogen are used to control the digestion and the apparatus. This may be: acetanilid, l-asparaginacid, sulfanilacid or other aminoacids with known nitrogen content. Besides these substances certified reference materials are used to control the whole procedure

10.4 Blank determination

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

10.5 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.

11 Expression of results

11.1 Method of calculation

The content of nitrogen, (w_N), in milligrams per gram, is calculated using the formula:

$$w_N = \frac{(V_1 - V_0) \times c(H^+) \times M_N \times 100}{m \times m_t}$$

where

V_1 is the volume, in ml, of the sulfuric acid (4.7) used in the titration of the sample

V_0 is the volume, in millilitres, of the sulfuric acid (4.7) used in the titration of the blank test

$c(H^+)$ is the concentration of H^+ in the sulfuric acid (4.7) in moles per litre

(e.g. if 0.01 mol/l sulfuric acid is used, $c(H^+)$ = 0.02 mol/l)

M_N is the molar mass of nitrogen, in grams per mole (=14)

m is the mass of test sample

m_t is the dry residue, expressed as g / 100g on the basis

of oven dried material according to the standard of the spezial material

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	0,24	0,01	4
SO13	0,28	0,01	4
SO9	0,40	0,01	3

Precision data biowaste and sewage sludge:

CW1	1,48	0,03	2
CW5	1,52	0,03	2
SL4	1,92	0,02	1
SL11	0,66	0,03	5

Linearity of standards and standard addition:

Glycine r: 0,9997 up to 3,7% N

Addition soil: r = 0,9997 up to 1,5 % N

Addition biowaste: r = 0,9977 up to 4,7% N

Addition sewage sludge: r = 0,99996 up to 4,7 % N

LOQ = 0,1 %N ; LOD = 0,03 %N (for use of 0,25 N sulfuric acid in titration)

Recovery = 94 – 103 %

Annex A (informative)

Validation of methods

Within the work of CEN TC 308 a ring test was organized with four samples of different sludges. The following results were obtained:

Sample No.	Number of participants	Nitrogen content, Average, g/kg m_T	s_r mg/kg	s_r %	s_R mg/kg	s_R %
1	4	28,48	2,13	12,65	2,15	16,84
2	4	21,87	3,5	21,47	3,22	16,3
3	4	27,52	0,7	7,13	1,07	9,81
4	4	16,28	0,65	4,79	0,718	13,58

These results were obtained on the basis of only four laboratories and this does not agree with EN 5725.

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

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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