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Sludge, treated biowaste and soil - determination of Kjeldahl nitrogen

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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.

Contents

Page

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 Kjeldahl 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 is applicable to determine Kjeldahl nitrogen according to the Kjeldahl procedure in sludge, treated biowaste and soil. Nitrate and nitrite are not included. Compounds with nitrogen bound in N-N, N-O linkages and some heterocycles (pyridines) are only partially determined.

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 definitions apply:

3.1 Kjeldahl nitrogen

The amount of nitrogen that is determined after Kjeldahl digestion and titration.

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. 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, moist or liquid material is digested in a suitable Kjeldahltube with sulfuric acid.

To rise the temperature potassium sulfate is added and titanium dioxide/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 the cooling system and rinses into a conical flask with boric acid solution. This solution is titrated with sulfuric acid until the endpoint, which is detected potentiometrically or using an indicator.

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. Another source of error include impurities in the apparatus. Therefore the apparatus has to be rinsed after each analytical series and blank determinations have to be carried out. The amount of sulfuric acid used in digestion depends on the composition of the sample. A ratio of sample to acid of at least 1:10 (w/V) should be used for samples with high content of organic matter. Digestion temperature must not rise above 380-400 °C to avoid analyte losses.

Table 1

Amounts of sulfuric acid consumption by various materials during Kjeldahl digestion

(Bremner 1960)

Material	Consumption of $H_2SO_{4\ (36\ mol/l)}$ during digestion in ml/g 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

7 Reagents

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 Catalyst mixture

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.

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

7.4 Boric acid solution , ρ = 20 g /l

7.5 Mixed indicator

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

7.6 Sulfuric acid or Hydrochloric acid, c(H^+) = 0.01 mol/l – 0,50 mol/l according to the expected amount, that is consumed in titration of different sample matrices. For sludges and biowaste the use of 0,50 mol/l c(H+) is recommended, due to nitrogen contents > 0,5%. For soil samples the use of other acid concentrations decreases analytical error but care has to be taken on the contamination of titration acids by carbon dioxide, which changes the acid concentration and therefore reduces its stability.

7.7 Ammonium sulfate NH_4SO_4

Note: Other catalyst mixtures are not allowed, that contain mercury or selenium, due to their toxicity towards human health and the environment. The effectiveness of other catalyst mixtures has to be proven by an expert group, before using them in the Kjeldahl procedure.

8 Apparatus

Usual laboratory equipment is needed

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

To use the semimicro- or the macromethod respective flasks or tubes have to be used with other volumes.

8.2 Digestion stand, suitable for digestion of samples with sulfuric acid at a temperature near to 400 °C.

8.3 Distillation apparatus, e.g. of the Parnas-Wagner type or other suitable distillation 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, for example PE.

9.2 Sample pre-treatment

All samples shall be pretreated according to the special standard in the field of sludge, treated biowaste and soil. Normally, they are dry, homogeneous and of a defined grain size, liquid or moist. Results are referred to dry residue, so that in case of liquid or moist samples a special sample has to be used for the determination of dry residue.

During the digestion procedure care has to be taken not to lose amounts of nitrogen. Therefore, digestion temperatures exceeding 400°C should be avoided.

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

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. 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.

10.1 Digestion

Place a test portion of the dried sample, of about 0.2 g to 1g or undried sample with the corresponding dry matter to the nearest of 0,1% accuracy in the digestion flask or tube (8.2). Add 10 ml sulfuric acid (7.1) 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 (7.2) and heat until the digestion mixture becomes clear. Boil the mixture gently 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. During the digestion procedure care has to be taken not to lose amounts of nitrogen. Therefore, temperatures exceeding 400°C should be avoided. The use of a temperature programme, that ensures gentle heating before reaching the boiling point is recommended, especially for liquid samples or samples with high content of organic matter. To avoid spattering of samples the digest can be left at room temperature for 24 hours or a longer time before digestion.

Note: The amount of sulfuric acid may be adapted to the size of the flask or tube.

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 and catalysts 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 (8.3). Rinse three times with water to complete the transfer. Add 50 ml of boric acid (7.4) 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 (7.3) to the funnel of the apparatus and run the alkali slowly into the distillation chamber. Distill 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 (7.5) to the distillate and titrate with sulfuric or hydrochloric acid (7.6) to a violet endpoint.

Note: The final determination method can be done by other validated methods, than titration (spectrophotometric determination of ammonium, manually or by automated methods).

10.3 Calibration

Calibration substances with known and unchangeable content of nitrogen are used to control the digestion and the apparatus. This may be: ammoniumsulfate, 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.

11 Expression of results

11.1 Method of calculation

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

$$(V_1 - V_0) \times c(H^+) \times M_N \times 100$$

$$w_N = \frac{}{m \times w_{dm}}$$

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 gram per mole (=14)

m is the mass of test sample (in kg)

w_{md} is the dry mass portion, expressed as g / 100g on the basis

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

11.2 Expression of results

The result shall be expressed in mg/kg or % 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) a precise identification of the sample;

c) the method used for the determination of ammonium

d) expression of results, according to 11.2 ;

e) 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 will be available after validation by a round robin test.

Annex A (informative)

Validation of methods

The Kjeldahl procedure is validated in ISO 11261 for soils

Table 2: Validation data for soil (ISO 11261)

Sample No	Content N mg/kg	S_r %	S_R %
1	0,98	6,1	27,0
2	3,11	3,9	18,6
3	6,70	2,8	15,9
4	10,88	2,4	8,2

Annex B
(informative)

Performance data using air dried samples in terms of repeatability and reproducibility have been determined during desk study 16 (Janssen, 2005) using statistical data from 6 repeated measurements of one sample analysed on two days.

Repeatability is expressed by standard deviation in %N and as relative standard deviation : s_r

Table 3 Precision data

Soil:

Sample No	*Content % N*	*S %N*	*S_r %*
SO1	0,24	0,01	4
SO13	0,28	0,01	4
SO9	0,40	0,01	3

Biowaste and 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 %

Bibliography

Bremner, J.M., Mulvaney, C.S. (1982): Methods of soil analysis, part 2 chemical and microbiological properties, 595-624

Hofmann,G. (1997): Methodenbuch des VDLUFA, Band I , Die Untersuchung von Böden, A 2.2.1, VDLUFA Verlag, Bonn

Janssen,E:; Koopmann,R. (2005) Determination of total phosphorus, total nitrogen and nitrogen fractions; Desk study 16 in Project Horizontal; www.ecn.nl/horizontal

Kjeldahl, J. (1883): Neue Methode zur Bestimmung des Stickstoffs in organischen Körpern, Z. Anal. Chem. 22, 366-382

Page, A.L. et al. (1982): Methods of soil analysis, Part 2, American Society of Agronomy and Soil Science of America, Madison, WI.

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 watercontent

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