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Determination of ammonium and nitrate 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 PrEN 14671
Soil	Different soil types	ISO 14255 ; ISO 14256 Horizontal Desk Study 16
Soil improvers	Fertilized peat	Not validated yet
Sediment	Not validated yet	Not validated yet
Waste	Bark humus Composted biowaste	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 describes pretreatment and extraction methods for the nitrogen fractions ammonia and nitrate in soil, sludge, biowaste and related waste. The extraction method is suitable for moist and air dried samples. The determination of the nitrogen fractions can be done manuelly or by automated methods.

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 sample

prEN 14671 Characterisation of sludges – Pretreatment for the determination of extractable ammonia using

2 mol/l potassíum chloride

ISO 14256-1 Soil quality – Determination of nitrate, nitrite and ammonium in field-moist soils by extraction with potassium chloride solution – part 1: manual method

ISO 14256-2 Soil quality – Determination of nitrate, nitrite and ammonium in field-moist soils by extraction with potassium chloride solution – part 2: automated method

E DIN 19746 Soil quality – Determination of mineral nitrogen (nitrate and ammonium) in soil profiles (Nmin laboratory method)

EN 11732 Water quality – Determination of ammonium nitrogen by flow analysis (CFA and FIA) and spectrometric detection

ISO 5664 Water quality - Determination of ammonium: distillation and titration method

EN ISO 13395 Water quality – Determination of nitrite nitrogen, nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection

3 Terms and definitions

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

3.1

Nitrogen fractions

Amount of ammonium-nitrogen and nitrate-nitrogen that is released after single or repeated 1 M KCl extraction 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. National regulations should be followed with respect to microbiological hazards with this method.

5 Principle

An aliquot of the homogenised moist material is shaken for one hour with 1 mol/l potassium chloride solution at room temperature. The ratio of extractant to material is ten to one. Repeated extractions are recommended for some materials (9.1) The extraction solution is filtered and the nitrogen fractions are analysed by flow injection analysis (FIA, EN 11732, ISO 7150-2) or continous flow analysis (CFA, EN 14256-2, EN 11732, ISO 7150-2) or by manual methods as distillation and titration (ammonia, ISO 5664) or spectrophotometric method (ammonia, nitrate, nitrite, EN 14256-1,).

6 Interferences and sources of errors

The deep frozen homogenised test sample is directly transferred to the extraction bottel and the potassium chloride solution if change in the content of the nitrogen fractions is to be suggested. Drying of the material , even rapid microwave drying will result in change of content especially of ammonia. Drying is not subject within this standard. Data for dried samples have been integrated for the process of validation and exchange of samples.

7 Reagents

All reagents have to be of recognized analytical grade

7.1 Potassium chloride c(KCl) = 1 mol/l. Dissolve 373 g of potassium chloride, dried at 105 ° C, in approximately 3 litres of water and dilute to 5 litres with water.

8 Apparatus

Usual laboratory equipment is needed

8.1 Analytical balance with an accuracy of 0,05 **g**

8.2 Wide necked glass or plastic bottles with secure stopper or caps, nominal volume 250 or 500 ml or other. The material must not adsorb ammonia, nitrate or nitrite or contaminated with this species.

8.3 Shaking apparatus; End-over-end shaker, frequency 30 min^{-1} to 40 min^{-1}

8.4 Filter paper, free of nitrogen fractions

9 Sampling and sample pre-treatment

9.3 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.

9.4 Sample pre-treatment

All samples shall be pretreated according to the special standard in the fields of soil, sludge, biowaste and related waste. The samples shall be analysed as soon as possible. The samples can change composition through biological and/or chemical activity. The samples shall be protected from being warmed up during the sampling procedure. The transportation to the laboratory shall be organised in such a way that no warming up occurs. Transportation in a cool box is recommended. If the samples are analysed within three days it is enough to store them at 4 °C, otherwise they should be stored at -20 °C (deep-frozen), which enables storing for several weeks, without any significant change in the content of mineral nitrogen. It is advantageous to homogenise the moist sample, to divide it into the test sample before storing them at -20 °C .

When the content of mineral nitrogen is determined in deep-frozen samples, the temperature and the duration of the thawing process have to be controlled. The samples can be thawed at room temperature, if they are homogenised and extracted within 4 h after beginning of thawing. Thawing at 4 °C is also possible, but the thawing period should not exceed 48 h.

10 Procedure

10.1 Extraction

Transfer a known weight of the homogenised test sample (equal to 1,0 to 5,0 g dry mass) to an extraction bottel (5.3), add potassium chloride solution (4.2) in the ratio test sample (dry mass) to extraction solution of one to ten (m/V). Replace the bottel cap and place the extraction bottle to the shaking apparatus (5.4). Shake the extraction bottel for 1 hour at room temperature. A minimum of one repetition of extraction after filtration is necessary for dry soil samples < 250 µm and fresh or dry biowaste and sewage sludge samples.The amount of test sample is related to the homogenising procedure. Take care, that the test sample is a homogeneous part of the collected sample and the laboratory sample.

10.2 Filtration

Filter the extraction solution through the filter . Collect the filtrate for determination of the nitrogen fractions in a volumetric flask and fill up to volume with potassium chloride solution. Centrifugation is recommended for samples , which are subjected to repeated extractions. The analysis of the nitrogen fractions shall be done as soon as possible. For the high concentration of potassium chloride avoids biological activity, the extracts can be stored at 4 °C for 30 days.

10.3 Measuring

Analysis is done according to EN ISO 11732, ISO 14256-2, ISO 14256-1, ISO 5664, EN ISO 14911. State of the art is to use the flow injection analysis (FIA, reference method) or the continuous flow analysis (CFA, reference method) , their desciption is presented in the standard EN ISO 11732 and ISO 14256-2

10.4 Calibration

Calibration of the analytical part is done according to the descriptions given in standards in 10.3. using ammonium and nitrate in inorganic salts, e.g. ammoniumchloride and potassiumnitrate.

10.5 Blank determination

Carry out at least two blank determinations in each series and use the average blank value for subsequent calculations. Blank determinations are carried out by using 1M KCl without sample addition throughout the whole procedure.

10.6 Duplicate determination

Analyse two individual test samples of each 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

11.3 Method of calculation

The calculation is described in the mentioned standards.

11.2 Expression of results

The results of extractable ammonium, nitrate or nitrite are expressed in g/kg dry mass. The dry mass is determined according to the related standard.

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

Sample	**NH_4-N (mg/kg)**	**S rel %**	**NO_3-N (mg/kg)**	**S rel %**
Soil K1	0,23	17	< LOQ	< LOQ
Soil K3	0,11	18	0,11	18
Biowaste KG	154	1,4	31	2
Biowaste KF	85	13	< LOQ	< LOQ
Sludge K19	685	2	< LOQ	< LOQ
Sludge K20	697	2	< LOQ	< LOQ

Variation of Extraction conditions – Repetition of extraction

Fresh Sample: Biowaste CW KG + addition of KNO_3 and NH_4Cl

KCl	**Ratio: sample / extractant**	**Shaking time** (hours)	**NH_4-N** % Recovery
2 M	1 : 5	1 x 1 h	71 +/- 6
2 M	1 : 10	1 x 1 h	85 +/- 7
2 M	1 . 5	2 x 1 h	87 +/- 7
2 M	1 . 10	2 x 1 h	92 +/- 7
1 M	1 : 5	1 x 1h	66 +/- 6
1 M	1 : 10	1 x 1h	80 +/- 7
1 M	1 : 10	2 x 1h	81 +/- 7
1 M	1 . 10	1 x 2h	76 +/- 6
1 M	1 : 10	1 x 1h + 16h ** stand at 20°C	60 +/- 6

Recovery for nitrate was > 87 % in all samples investigated

Recovery was estimated by addition of 50 mg/l NH_4-N and NO_3-N to the extraction solution

** The filtrate was left at room temperature over night to test the stability of filtrates

Each data point represents the mean of 2-6 extractions

Analysis of dry samples

Dry sample: soil SO K3

KCl	Ratio: sample / extractant	Shaking time (hours)	NH_4-N (mg/kg)	NO_3-N (mg/kg)
1 M	1 : 10	1 x 1 h	0,20	0,32
1 M	1 : 10	2 x 1 h	0,27	0,32
1 M	1 : 10	3 x 1 h	0,27	0,32

Dry sample: soil WEPAL standard (< 2 mm)

KCl	Ratio: sample / extractant	Shaking time (hours)	NH_4-N (mg/kg)	NO_3-N (mg/kg)
1 M	1 : 10	1 x 1 h	2,25	2,37
1 M	1 : 10	2 x 1 h	2,50	2,49
1 M	1 : 10	3 x 1 h	2,57	2,52

Dry sample: soil SO 9, < 125 µm

KCl	Ratio: sample / extractant	Shaking time (hours)	NH_4-N (mg/kg)	NO_3-N (mg/kg)
1 M	1 : 10	1 x 1 h	5,64	3,82
1 M	1 : 10	2 x 1 h	6,58	4,15
1 M	1 : 10	3 x 1 h	6,85	4,30

Each data point represents the mean of 2-4 extractions; S rel: < 2%

Stability of filtrates in 1M KCl

Test portion 2 of CW KF (1 : 10) in 1M KCl

T = 4 °C

Time **(days)**	**NH_4-N** **mg/kg**	**NO_3-N** **mg/kg**
0	46,2 +/- 3,7	< LOQ
22	46,3 +/- 3,7	
30	45,4 +/- 3,6	
42	46,4 +/- 3,7	
56	45,6 +/- 3,6	

T = - 18°C

Time **(days)**	**NH_4-N** **mg/kg**	**NO_3-N** **mg/kg**
0	46,2 +/- 3,7	< LOQ
22	46,4 +/- 3,7	
30	46,0 +/- 3,7	
42	45,3 +/- 3,6	
56	43,4 +/- 3,5	

LOQ = 0,5 mg/l test solution (CFA)

Test mixture of KNO_3 and NH_4Cl in 1M KCl

T = 4 °C

Time (days)	NH_4-N mg/kg	NO_3-N mg/kg
0	46,6 +/- 0,5	44,8 +/- 0,5
22	46,1 +/- 0,5	44,7 +/- 0,5
30	46,7 +/- 0,5	46,9 +/- 0,5
42	44,4 +/- 0,4	44,4 +/- 0,4
56	41,2 +/- 0,4	47,4 +/- 0,5

T = - 18 °C

Time (days)	NH_4-N mg/kg	NO_3-N mg/kg
0	46,6 +/- 0,5	44,8 +/- 0,5
22	46,2 +/- 0,5	46,1 +/- 0,5
30	46,9 +/- 0,5	45,4 +/- 0,5
42	44,9 +/- 0,4	44,7 +/- 0,5
56	40,5 +/- 0,4	46,5 +/- 0,5

Remark: mg/kg refers to a hypothetical amount of 5g sample in 50 ml, though the test mixture was extracted without any sample matrix. Extraction, analysis in CFA and storage was performed as described for sample extraction and analysis.

Standard deviation was < 1 % for the analysis of both ions in artificial solution, as calculated by two repeated measurements in CFA

Annex A (informative)

Validation of methods

The extraction procedure is not validated. This has to be done for all materials in future. The determination of nitrogen species is validated in EN ISO 11732**.**

Annex B
(informative)

The modular horizontal system

Annex C
(informative)

Information on WP xx and the project Horizontal

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