

CEN/TF

Date: 2006 -07

TC WI

CEN/TF

Secretariat: DS

Sludge, treated biowaste and soil - determination of ammonium nitrogen and nitrate nitrogen after extraction with 1 M potassium chloride

Einführendes Element — Haupt-Element — Ergänzendes Element

Élément introductif — Élément central — Élément complémentaire

ICS:

Descriptors: Horizontal-Inorg Dr Janssen

Document type: European Standard
Document subtype:
Document stage: Working Document
Document language: E

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

Foreword	2
Introduction.....	4
1 Scope.....	5
2 Normative references	5
3 Terms and definitions.....	6
4 Safety remarks	6
5 Principle	6
6 Interferences and sources of errors	6
7 Reagents	7
8 Apparatus	
8.1 Analytical Balance.....	7
8.2 Extraction Bottles.....	7
8.3 Shaking apparatus	7
8.4 Filter paper	7
9 Sampling and sample pre-treatment.....	8
9.1 Sampling.....	8
9.2 Sample pre-treatment	8
10 Procedure	8
10.1 Extraction.....	9
10.2 Filtration	9
10.3 Analysis of natural samples	9
10.4 Calibration	9
10.5 Blank determination.....	9
11 Expression of results.....	9
11.1 Method of calculation	9
11.2 Expression of results.....	9
12 Test report	9
13 Performance characteristics	10
Annex A (informative) Validation of methods.....	11
Annex B (informative) Data from Desk study 16.....	12-14
Bibliography.....	15

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 nitrogen fractions (ammonium and nitrate) 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 pretreatment and extraction methods for the nitrogen fractions: ammonium and nitrate in sludge, treated biowaste and soil. The extraction method is suitable for fresh samples. The determination of nitrogen fractions can be done manually 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 2,5 mol/l potassium chloride

ISO 14255 Soil quality – Determination of nitrate nitrogen, ammonium nitrogen and total soluble nitrogen in air dry soils using calcium chloride solution – part 1: manual method

ISO/TS 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

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 definitions apply:

3.1 Nitrogen fractions

Mass of ammonium-nitrogen and nitrate-nitrogen (= mineral nitrogen), that is released after single or repeated 1 M KCl extraction 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. National regulations should be followed with respect to microbiological and chemical hazards with this method.

5 Principle

An aliquot of the homogenised fresh material is shaken for one hour with 1 mol/l potassium chloride solution at room temperature. The ratio of extractant to material varies according to the material tested. The extraction solution is centrifuged or filtered and an aliquot of the filtrate is analysed by flow injection analysis (FIA, EN 11732, ISO 7150-2) or continuous flow analysis (CFA, ISO 14256-2, EN 11732, ISO 7150-2) or by manual methods as distillation and titration (ammonia, ISO 5664) or spectrophotometric method (ammonia, nitrate, nitrite, ISO/TS 14256-1,).

6 Interferences and sources of errors

The fresh or the deep frozen homogenised test sample is directly transferred to the extraction bottle, which is filled with the potassium chloride solution, if a change in the content of the nitrogen fractions can be expected. Drying of the material, even rapid microwave drying will result in a change of the nitrogen content especially of ammonium. Drying is not subject within this standard. Data for dried samples have been integrated for the process of validation and exchange of samples. Take care to use purified glassware and equipment and filter papers free of contaminations with nitrate and ammonium. Purification of glassware with distilled water has to be performed after each use, especially to avoid cross contaminations from samples with high contents of nitrogen fractions, like sludges or biowaste. Separate equipment should be used for the analysis of soil samples, as contents of nitrogen fractions can be near the detection limit. A blank test has to be carried out to assure purity of reagents and equipment.

6 Reagents

All reagents have to be of recognized analytical grade

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

7 Apparatus

Usual laboratory equipment is needed

8.1 Analytical balance with an accuracy of 0,01 g, at least.

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 ammonium, nitrate or nitrite and must not be contaminated with this species.

8.3 Shaking apparatus; End-over-end shaker, frequency 30 min^{-1} to 40 min^{-1} or other appropriate shakers.

8.4 Filter paper, free of nitrogen fractions, pore size: 8-12 μm

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, for example PE.

9.4 Sample pre-treatment

All samples shall be pretreated according to the special standard in the fields of sludge, treated biowaste and soil. The samples shall be analysed as soon as possible. The samples can change composition due to biological and/or chemical activity. The samples shall be protected from being warmed 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 sufficient 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 and to divide it into the test portions 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. The fresh test sample can be homogenised by manual methods which have to be performed in a way, that avoids contamination of the test sample with nitrogen fractions. The use of gloves is recommended when homogenising test samples.

10 Procedure

10.1 Extraction

Transfer a known amount of the homogenised test sample (equal to 1,0 to 10,0 g dry mass) into an extraction bottle (8.2), add potassium chloride solution (7.1) in a mass (dry mass of the sample) to volume (of the extracting solution) ratio of one to five (m/V) for field moist fresh soil (< 10 mm) or one to ten (m/V) for dry soil samples (< 2 mm) and one to twenty up to one to eighty (m/V) for treated biowaste, sludge or sludge amended soils. Close the bottle cap and place the extraction bottle to the shaking apparatus (8.3). Shake it for 1 hour at room temperature, in general 20 °C (+/- 1°C). A minimum of one repetition of extraction after filtration is necessary for dry soil samples < 250 µm and dried biowaste and sludge samples. In general, drying leads to changes in the original composition of nitrogen fractions and should be avoided (9.4). 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.

Note: The amount of test sample can be adapted to macromethods – the ratio of sample to extractant should be the same as stated above. The used extraction temperature should be noted in the test report, as temperature affects the effectiveness of the extraction.

10.2 Filtration

Filter the extraction solution through the filter. Discard the first 10 ml and collect an aliquot from the subsequent filtrate for determination of the nitrogen fractions. Centrifugation is recommended for samples, which are subjected to repeated extractions. The analysis of the nitrogen fractions shall be done as soon as possible. Because the high concentration of potassium chloride avoids biological activity, the filtrates can be stored at 4 °C for at least 7 days.

10.3 Measuring

Analysis is done according to EN ISO 11732, ISO 14256-2, ISO/TS 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 description is presented in the standard EN ISO 11732 and ISO 14256-2

Note: Methods of determination have to prove similarity of results obtained by the cited reference methods.

10.4 Calibration

Calibration of the analytical part is done according to the descriptions given in the standard procedures of paragraph 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.

11 Expression of results

11.1 Method of calculation

The calculation is described in the mentioned standards for analytical determination.

11.2 Expression of results

The results of extractable ammonium-N and nitrate-N are expressed in mg/kg dry mass. The dry mass is determined according to the cited 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) a precise identification of the sample;
- c) the method used for the determination of ammonium and nitrate
- 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 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)

Table 1: Performance data for the extraction of fresh soil, sludge and treated biowaste in 1M KCl

Sample	NH ₄ -N (mg/kg)	S rel %	NO ₃ -N (mg/kg)	S rel %
Soil K1, < 10 mm	0,23	17	< LOQ	< LOQ
Soil K3, < 10 mm	0,11	18	0,11	18
Biowaste KG, < 10 mm	135	5,2	6,8	1,5
Sludge K19, < 10 mm	753	2,3	< LOQ	< LOQ

Samples were used after freezing of fresh and moist samples and they were extracted in a ratio of sample to extractant of 1:10 for soils and 1:20 for biowaste/sludges (w/V); Recovery after addition of potassiumnitrate and ammoniumchloride in a concentration similar to the concentration found in test samples were for ammonium: > 90% (+/- 7%) in dry soils and > 87% (+/- 7%) in biowaste and sludges and for nitrate: > 95% (+/- 5%) in dry soils and > 87% (+/- 7%) in biowaste and sludges.

A detailed sample description and interpretation of results can be found in desk study 16, page 51.

Soil samples were loamy and sandy soils from Hessen, treated biowaste originated from composted leaves and cuttings and sludges originated from pressed sludges produced from domestic sewage sludge.

Data are mean values of 6 sample extractions and analysis.

Table 2: Analysis of soil samples

Fresh sample: soil SO K3, sandy soil, > 10 mm, Hessen

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: sludge amended sandy soil SO 9 < 125 µm from Germany, NRW

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%

Recovery varies between: 90 – 102 % (ammonium) and 98 – 100 % (nitrate) after repeated extractions.

Table 3: Stability of ammonium in 1M KCl filtrates

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

TC WI :2003 (E)**T = 4 °C**

Time (days)	NH₄-N mg/kg
0	46,2 +/- 3,7
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)	NH₄-N mg/kg
0	46,2 +/- 3,7
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)

Bibliography

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

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

Lickfett, T., Merkel, D., von Hörstein, D., Przemec, E., Lücke, W. (1996): Konservierung von Nmin-Proben durch Mikrowellentrocknung? Agrobiol.Res. 49, 169-178

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 watercontent

CEN/TC 22 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 potassium 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