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## **Sludge, treated biowaste and soil — Determination of ammonium nitrogen and nitrate nitrogen after extraction with 1 mol/l potassium chloride**

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## Foreword

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).

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		(reference)
Soil		
Treated biowaste		
Sediment		
Waste		

## 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 an evaluation study, in which e.g. the ruggedness of the method was studied, a European wide validation of the draft standard has taken place. The results of the desk studies as well as the evaluation and validation studies have been subject to discussions with all parties concerned in CEN. The standard is part of a modular horizontal approach in which the standard belongs to the analytical step.

Until now test methods determining properties of materials were often prepared in Technical Committees (TCs) working on specific products or specific sectors. In those test methods often steps as sampling, extraction, release or other processing, analyses, etc were included. In this approach it was necessary to develop, edit and validate similar procedural steps over and over again for every material or product. Consequently this has resulted in duplication of work. To avoid such duplication of work for parts of a testing procedure references to parts of test methods from other TCs were introduced. However the following problems are often encountered while using references in this way: 1) The referenced parts are often not edited in a way that they could easily be referred to, 2) the referenced parts are often not validated for the other type of material and 3) the updates of such test standards on products might lead to inadequate references.

In the growing amount of product and sector oriented test methods it was recognised that many steps in test procedures are or could be used in test procedures for many products, materials and sectors. It was supposed that, by careful determination of these steps and selection of specific questions within these steps, elements

of the test procedure could be described in a way that can be used for all materials and products or for all materials and products with certain specifications.

Based on this hypothesis 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 assessing a property and not the whole "chain of measurement" (from sampling to analyses). A beneficial feature of this approach is that "modules" can be replaced by better ones without jeopardizing the standard "chain".

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 modules that relates to this standard are specified in section XX Normative references.

An overview of modules and the manner, in which modules are selected will be worked out later, at which time proper reference in this standard will be provided.

**WARNING — 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.**

## 1 Scope

This European standard specifies a procedure for the determination of ammonium nitrogen and nitrate nitrogen in sludge, treated biowaste and soil after extraction with a 1 mol/l potassium chloride solution. The extraction method is suitable for fresh samples.

The determination of nitrogen fractions can be done manually or by automated methods.

## 2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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 with segmented flow analysis.*

EN ISO 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.*

ISO 7150-2, *Water quality — Determination of ammonium — Part 2: Automated spectrometric method.*

EN ISO 3696, *Water for analytical laboratory use — Specification and test methods.*

EN ISO 14911, *Water quality — Determination of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  using ion chromatography — Method for water and waste water.*

CSS99031 *Sludge, treated biowaste, and soils in the landscape – Sampling – Framework for the preparation and application of a sampling plan*

CSS99058 *Sludge, treated biowaste, and soils in the landscape – Sampling – Part 1: Guidance on selection and application of criteria for sampling under various conditions*

CSS99057 *Sludge, treated biowaste, and soils in the landscape – Sampling – Part 2: Guidance on sampling techniques*

CSS99032 *Sludge, treated biowaste, and soils in the landscape – Sampling - Part 3: Guidance on sub-sampling in the field*

CSS99059 *Sludge, treated biowaste, and soils in the landscape – Sampling – Part 4: Guidance on procedures for sample packaging, storage, preservation, transport and delivery*

CSS99060 *Sludge, treated biowaste, and soils in the landscape – Sampling – Part 5: Guidance on the process of defining the sampling plan*

CSS99034 *Soil, sludge and treated biowaste – Guidance for sample pre-treatment*

### 3 Terms and definitions

For the purpose of this document , the following terms and definitions apply.

#### 3.1 nitrogen fractions

mass of ammonium nitrogen and nitrate nitrogen (mineral nitrogen), that is released after single or repeated 1 mol/l potassium chloride extraction of the sample

#### 3.2 dry matter

dry mass fraction of the sample obtained after the specified drying process. It is expressed as percent or in grams per kilogram.

(EN 12880:2000)

### 4 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).

### 5 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 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. Use separate equipment 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

Use only reagents of recognized analytical grade, unless otherwise specified.

**6.1 Water**, complying with grade 2 as defined in EN ISO 3696.

**6.2 Potassium chloride**,  $c(\text{KCl}) = 1 \text{ mol/l}$ .

Dissolve 373 g of potassium chloride, dried at 105 °C, in approximately 3 l water (6.1) and dilute to 5 l with water (6.1).

## 7 Apparatus

Usual laboratory apparatus, and in particular the following:

- 7.1 Analytical balance** with an accuracy of 0,01 g, at least.
- 7.2 Wide necked glass or plastic bottles with secure stopper or caps**, nominal volume 250 ml or 500 ml or other. The material shall not adsorb ammonium, nitrate or nitrite and shall not be contaminated with this species.
- 7.3 Shaking apparatus**; End-over-end shaker, frequency 30 min<sup>-1</sup> to 40 min<sup>-1</sup> or other appropriate shakers.
- 7.4 Filter paper**, free of nitrogen fractions, pore size: 8 µm to 12 µm.

## 8 Sampling and sample pre-treatment

### 8.1 Sampling

Sampling shall be carried out in accordance with sampling standards CSS99031-32 and 99057-60.

Samples shall be stored in suitable containers with an appropriate closure material, for example PE.

### 8.2 Sample pre-treatment

All samples shall be pretreated according to CSS99034 . 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 shall 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.

NOTE The use of gloves is recommended when homogenising test samples.

## 9 Procedure

### 9.1 Extraction

Transfer a known amount of the homogenised test sample (equal to 1,0 g to 10,0 g dry mass) into an extraction bottle (7.2), add potassium chloride solution (6.2) 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 (7.3). Shake it for 1 h 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 shall be avoided. 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.

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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.

### 9.2 Filtration

Filter the extraction solution through the filter (7.4). Discard the first 10 ml and collect an aliquot from the subsequent filtrate for determination of the nitrogen fractions.

NOTE 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 filtrate can be stored at 4 °C for at least 7 days.

### 9.3 Determination

Determine the ammonium nitrogen and ammonium concentration according to EN ISO 11732, ISO 14256-2, ISO/TS 14256-1, ISO 5664, EN ISO 14911.

NOTE 1 State of the art is to use the flow injection analysis (FIA, reference method) or the continuous flow analysis (CFA, reference method) according to EN ISO 11732 and ISO 14256-2.

NOTE 2 Methods of determination have to prove similarity of results obtained by the cited reference methods.

### 9.4 Calibration

Calibrate the analytical part according to the standard used for the determination, using ammonium and nitrate organic salts, e.g. ammonium chloride and potassium nitrate.

### 9.5 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 1 mol/l potassium chloride (6.2) without sample addition throughout the whole procedure.

## 10 Calculation and expression of results

### 10.1 Method of calculation

Calculate the ammonium nitrogen and nitrate nitrogen according to the standard used for the determination.

### 10.2 Expression of results

The results of extractable ammonium nitrogen and nitrate nitrogen are expressed in mg/kg dry mass. The dry mass is determined according to the standard used for the determination.

## 11 Precision data

The performance characteristics of the method (Annex B) data have been evaluated. Table 1 gives the resulting typical values for repeatability and reproducibility limits as their observed ranges. The typical value is derived from the data in Table B.2 in Annex B by taking the median value and rounding the numbers.



**Table 1 — Typical values and observed ranges of the repeatability and reproducibility limits**

The reproducibility limit provides a determination of the differences (positive and negative) that can be found (with a 95 % statistical confidence) between a single test result obtained by a laboratory using its own facilities and another test result obtained by another laboratory using its own facilities, both test results being obtained under the following conditions : The tests are performed in accordance with all the requirements of the present standard and the two laboratory samples are obtained from the same primary field sample and prepared under identical procedures. Conversely, the repeatability limit refers to measurements obtained from the same laboratory, all other conditions being identical. The reproducibility limit and the repeatability limit do not cover sampling but cover all activities carried out on the laboratory sample including its preparation from the primary field sample.		
Results of the validation of the determination of ammonium nitrogen and nitrate nitrogen after extraction with 1 M potassium chloride in soil, sludge and treated biowaste	Typical value %	Observed range %
Repeatability limit, r NH <sub>4</sub>	15	9 – 146
Reproducibility limit, R NH <sub>4</sub>	190	120 – 300
Repeatability limit, r NO <sub>3</sub>	39	17 – 100
Reproducibility limit, R NO <sub>3</sub>	160	105 - 300

NOTE 1. The above results refer to the difference that may be found between two test results performed on two laboratory samples obtained under the same conditions. In the case when reference is made to the dispersion of the values that could reasonably be attributed to the parameter being measured, the above typical reproducibility values and observed reproducibility ranges should be divided by  $\sqrt{2}$  to obtain the corresponding typical dispersion limit and its observed range. In the example of NH<sub>4</sub> in Sludge 2 the result and its dispersion limit is  $4.4 \pm 6.7$  ( $2 \cdot sR = 154$  % of 4.4). This means that with a 95 % statistical confidence, the values reasonably attributable to the measured parameter are larger than 0 g/kg and lower than 11 g/kg.

NOTE 2. The repeatability limit (r) and the reproducibility limit (R) as given in Table C.2 (Annex C) and in this table are indicative values of the attainable precision if the determination of ammonium nitrogen and nitrate nitrogen after extraction with 1 M potassium chloride is performed in accordance with this standard [CSS99019].

NOTE 3 A limited number of materials and parameters were tested. Consequently, for other materials and parameters, performance characteristics may fall outside the limits as derived from the validation of the the Determination of ammonium nitrogen and nitrate nitrogen after extraction with 1 M potassium chloride in soil, sludge and treated biowaste.

NOTE 4 In particular for relatively heterogeneous materials, the repeatability and the reproducibility limits may be larger than the values given in Table B.2 (Annex B) and this table.

## 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 10.2;
- 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.



## Annex A (informative)

### Data from Desk study 16

**Table AB.1 — Performance data for the extraction with 1 mol/l potassium chloride of fresh sludge, treated biowaste and soil**

Sample	Ammonium nitrogen mg/kg dry mass	$S_{rel}$ %	Nitrate nitrogen mg/kg dry mass	$S_{rel}$ %
Soil K1, < 10 mm	0,23	17	< LOQ <sup>a</sup>	< LOQ <sup>a</sup>
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 <sup>a</sup>	< LOQ <sup>a</sup>
<sup>a</sup> LOQ is .				

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 potassium nitrate and ammonium chloride 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 AB.2 — Analysis of fresh soil samples, dry soil samples and dry sludge after extraction with a 1 mol/l potassium chloride solution**

Sample	Ratio: sample / extractant	Shaking time  h	Ammonium nitrogen  mg/kg dry mass	Nitrate nitrogen  mg/kg dry mass
Soil SO K3, sandy soil, > 10 mm, Hessen	1:10	1 × 1 h	0,20	0,32
Soil SO K3, sandy soil, > 10 mm, Hessen	1:10	2 × 1 h	0,27	0,32
Soil SO K3, sandy soil, > 10 mm, Hessen	1:10	3 × 1 h	0,27	0,32
Soil WEPAL standard (< 2 mm)	1:10	1 × 1 h	2,25	2,37

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Soil WEPAL standard (< 2 mm)	1:10	2×1 h	2,50	2,49
Soil WEPAL standard (< 2 mm)	1:10	3×1 h	2,57	2,52
Sludge amended sandy soil SO 9 < 125 µm from Germany, NRW	1:10	1×1 h	5,64	3,82
Sludge amended sandy soil SO 9 < 125 µm from Germany, NRW	1:10	2×1 h	6,58	4,15
Sludge amended sandy soil SO 9 < 125 µm from Germany, NRW	1:10	3×1 h	6,85	4,30
Each data point represents the mean of 2 to 4 extractions; $S_{rel}$ : < 2 %				
Recovery varies between: 90 % – 102 % (ammonium nitrogen) and 98 % – 100 % (nitrate nitrogen) after repeated extractions.				

**Table AB.3 — Stability of ammonium in 1 mol/l potassium chloride filtrates**

Time	Ammonium nitrogen <sup>a</sup>	Ammonium nitrogen <sup>b</sup>
days	mg/kg dry mass	mg/kg dry mass
0	46,2 +/- 3,7	46,2 +/- 3,7
22	46,3 +/- 3,7	46,4 +/- 3,7
30	45,4 +/- 3,6	46,0 +/- 3,7
42	46,4 +/- 3,7	45,3 +/- 3,6
56	45,6 +/- 3,6	43,4 +/- 3,5
NOTE 1 Test portion 2 of CW KF (1:10) in 1 mol/l potassium chloride.		
NOTE 2 LOQ = 0,5 mg/l test solution (CFA).		
<sup>a</sup> T = 4 °C		
<sup>b</sup> T = - 18 °C		

## Annex B (informative)

### Repeatability and reproducibility data

#### B.1 Performance characteristics

##### B.1.1 Objective of the interlaboratory comparison

In a European wide interlaboratory comparison study according to ISO 5725-2, the performance characteristics of the standard "Determination of ammonium nitrogen and nitrate nitrogen after extraction with 1 M potassium chloride in soil, sludge and treated biowaste" were established.

##### B.1.2 Materials used in the interlaboratory comparison study

The interlaboratory comparison of determination of ammonium nitrogen and nitrate nitrogen after extraction with 1 M potassium chloride in soil, sludge and treated biowaste was carried out with 9 - 10 European laboratories on 6 materials. The materials selected for the interlaboratory comparison were chosen to represent soil, sludge and biowaste as broad as possible, because the standard will find general application across different types of soil and soil related materials. (detailed information can be found in the final report on the Interlaboratory comparison study mentioned in the Bibliography).

In the interlaboratory comparison study the following starting points were used:

- The laboratory samples were all taken from one large batch of the different materials according to the normal practice. The normal size reduction and the normal repeated mixing were carried out as needed to obtain representative laboratory samples from the large batch sample (ref JRC).
  - Note : the samples provided for the validation should not be confused with reference samples provided for certification purposes, as the performance results obtained have to be directly applicable to daily practice (less rigorous sample preparation than for a reference material).
- The experimental plan was designed by project HORIZONTAL on the basis of each laboratory being given two laboratory samples of each material to be tested. This is in accordance with ISO 5725-2.
- The materials examined cover all the grain size classes to which the the determination of ammonium nitrogen and nitrate nitrogen after extraction with 1 M potassium chloride in soil, sludge and treated biowaste applies: very fine grained materials (like sludge: 0  $\mu\text{m}$  to about 125  $\mu\text{m}$ ) and fine-grained materials (soil and compost: 0 mm to 4 mm).
  - 
  - 
  -

Table B.1 provides a list of the types of materials chosen for testing and the selected components.

**Table B.AD.2 — Material types tested and components analysed in the interlaboratory comparison of the determination of ammonium nitrogen and nitrate nitrogen after extraction with 1 M potassium chloride in soil, sludge and treated biowaste.**

Grain size class	Sample code	Material type tested	Parameters/congeners
Sludge (<0.5 mm)	Sludge 1	Mix 1 of municipal WWTP sludges from North Rhine Westphalia, Germany	Kjeldahl N
	Sludge 2	Mix 2 of municipal WWTP sludges from North Rhine Westphalia, Germany	Kjeldahl N
Fine grained (< 2 mm)	Compost 1	Fresh compost from Vienna, Austria	Kjeldahl N
	Compost 2	Compost from Germany	Kjeldahl N
	Soil 4	A sludge amended soil from Hohenheim, Germany	Kjeldahl N
	Soil 5	An agricultural soil from Reading, UK	Kjeldahl N

### B.1.3 Interlaboratory comparison results

The statistical evaluation was conducted according to ISO 5725-2. The average values, the repeatability standard deviation ( $s_r$ ) and the reproducibility standard deviation ( $s_R$ ) were obtained (Table B.2).

The repeatability is determined as an interval around a measurement result (i.e. "repeatability limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another, both test results being obtained under the following conditions: The tests are performed in accordance with all the requirements of the present standard by the same laboratory using its own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures.

The repeatability limit was calculated using the relationship :  $r_{\text{test}} = f \cdot \sqrt{2} \cdot s_{r,\text{test}}$  with the critical range factor  $f = 2$ .

For instance, the repeatability limit around a measurement result of 2 g NH<sub>4</sub><sup>+</sup> /kg is  $\pm 0.31$  g NH<sub>4</sub><sup>+</sup> /kg (i.e  $\pm 15$  % of 2).

NOTE The above relationship refers to the difference that may be found between two measurement results performed each on two laboratory samples obtained under the same conditions. The value  $f = 2$  used in the factor  $f \cdot \sqrt{2}$  corresponds to the theoretical factor of 1,96 for a pure normal distribution at 95 % statistical confidence. Also, this value  $f = 2$  corresponds to the usual value  $k = 2$  of the coverage factor recommended in the Guide to the expression of Uncertainty in Measurement (GUM). However it may be necessary to use a larger value for  $f$  in situation as described in clause 12.

The reproducibility, like repeatability is also determined as an interval around a measurement result (i.e. "reproducibility limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another test result obtained by another laboratory, both test results being obtained under the following conditions : The tests are performed in accordance with all the requirements of the present standard by two different laboratories using their own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures.

The reproducibility limit was calculated using the relationship:  $R = f \cdot \sqrt{2} \cdot s_R$  with the critical range factor  $f = 2$ .

For instance, the reproducibility limit around a measurement result 2 g NH<sub>4</sub><sup>+</sup> /kg is  $\pm 3.75$  g NH<sub>4</sub><sup>+</sup> /kg (i.e  $\pm 187$  % of 2).

NOTE The above relationship refers to the difference that may be found between two measurement results performed each on two laboratory samples obtained under the same conditions. The value  $f = 2$  used in the factor  $f \cdot \sqrt{2}$  corresponds to the theoretical factor of 1,96 for a pure normal distribution at 95 % statistical confidence. Also, this value  $f = 2$  corresponds to the usual value  $k = 2$  of the coverage factor recommended in the Guide to the expression of Uncertainty in Measurement (GUM). In the case when reference is made to the dispersion of the values that could reasonably be attributed to the parameter being measured, the dispersion limit is equal to  $k \cdot s_R$  with the usual value  $k = 2$ , resulting in a dispersion limit lower than the reproducibility limit (i.e. a ratio of  $\sqrt{2}$ ). However it may be necessary to use a larger value  $f \cdot \sqrt{2}$  (or  $k$ ) in situation as described in clause 12 .

In case of relatively heterogeneous materials, the repeatability and the reproducibility limits may be larger than the values given in Tables B.2 (this means that the value chosen for the critical range factor  $f$  is larger than 2 as well as for the coverage factor  $k$  for dispersion). This is because the extreme results may have been

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obtained in accordance with the present standard and/or be caused by the variability within, or in between, the laboratory samples.

Table B.AD.3 — Results of the interlaboratory comparison studies of the Determination of ammonium nitrogen and nitrate nitrogen after extraction with 1 M potassium chloride in soil, sludge and treated biowaste. All concentrations in g/kg.

Matrix	Parameter	Mean	sr	sR	r	R	P	Outliers	Used number of data	Number of data reported below detection	Total of data reported
Sludge 1	NH4+	2.259	5.30%	92%	0.3351	5.7954	9	2	44	4	
Sludge 2	NH4+	4.363	3.21%	77%	0.3921	9.4563	9	2	50	0	
Compost 1	NH4+	0.123	5.70%	50%	0.0196	0.1719	10	2	50	0	
Compost 2	NH4+	0.343	4.35%	42%	0.0418	0.4000	11	1	58	0	
Soil 4	NH4+	0.035	40%	56%	0.0392	0.0552	10	2	50	0	
Soil 5	NH4+	0.014	52%	110%	0.0200	0.0421	9	2	53	0	
		g/kg			g/kg	g/kg					

Matrix	Parameter	Mean	sr	sR	r	R	p	Outliers	Used number of data	Number of data reported below detection	Total of data reported
Sludge 1	NO3-	0.019	11.85%	56%	0.0064	0.0303	5	2	26	12	
Sludge 2	NO3-	0.009	13.97%	109%	0.0033	0.0260	7	1	35	9	
Compost 1	NO3-						8	0	44	0	
Compost 2	NO3-	0.125	6.06%	56%	0.0212	0.1947	7	0	38	0	
Soil 4	NO3-	0.032	35.2%	45%	0.0315	0.0404	7	3	35	0	
Soil 5	NO3-	0.025	14.0%	38%	0.0097	0.0261	6	3	34	0	

Abbreviations: sr Repeatability standard deviation; SR Reproducibility standard deviation; r Repeatability limit

(comparing two measurements); R Reproducibility limit (comparing two measurements); p Number of labs.



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