

## **Determination of Nutrients**

### **Determination of total nitrogen**

#### **Determination of total nitrogen – Dumas method**

### **Introduction**

This document is developed in the project 'Horizontal'. It is the result of desk study “Determination of total phosphorus and nitrogen and fractions” in the project and aims at the description of the determination of total nitrogen (organic and inorganic) according to the procedure of Dumas in soil, sludge, biowaste and related waste. After discussion with all parties concerned in CEN and selection of a number of test methods described in this study will be developed further as an modular horizontal method and validated in the project 'Horizontal' .

Until now test methods determining properties of materials were often prepared in Technical Committees (TC's) 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 each other product.. Consequently this resulted in a lot of duplicate work. To avoid such duplication of work for parts of a testing procedure often was referred to parts of test methods from other TC's. However 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 they 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 a test procedure and not the whole test procedure (from sampling to analyses) but only.

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.

This standard is a module, for determining nutrients in solid materials and liquids. This module concerns with the combustion method according to Dumas and the determination of total nitrogen in soil, sludge, biowaste and related waste .

The other horizontal modules that will be available in due time are to be found in the informative annex B which contains a brief overview of the modules that are or will be worked out in the project 'Horizontal.'

The texts of the chapters 1-11 are normative; annexes are normative or informative, as stated in the top lines of the annexes.

## **1 Normative references**

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  
ISO 13878 Soil quality - Determination of total nitrogen content by dry combustion („elemental analysis“)  
EN 13654-2 Soil improvers and growing media - Determination of nitrogen – part 2: Dumas method

## **2 Scope and working area**

This standard describes the determination of total nitrogen (organic and inorganic) according to the procedure of Dumas in soil, sludge, biowaste and related waste. Dry samples are used normally, in special situations moist samples can be used.

## **3 Principle**

The total nitrogen content of the analysed material is determined by heating it to a temperature of at least 900 °C in the presence of oxygen gas. Mineral and organic nitrogen compounds are oxidized and/or volatilized. The combustion products are oxides of nitrogen (NO<sub>x</sub>) and molecular nitrogen. After transforming all nitrogen into molecular nitrogen, the content of the nitrogen gas is measured using thermal conductivity.

## **4 Reagents**

- 4.1 General  
All reagents shall be of recognized analytical grade
- 4.2 Combustion gas (oxygen)  
Oxygen free of nitrogen (see instruction manual of the apparatus used)
- 4.3 Chemicals and/or catalysts (see instruction manual of the apparatus used)
- 4.4 Inert gas as carrier gas, free of nitrogen, e.g. Helium
- 4.5 Ethylenediaminetetraacetic acid (EDTA)

- 4.6 Glucose or saccharose as burning assistance or other suitable material, free of nitrogen

Note 1: For reduction, oxidation, removal and/or fixing of combustion gases which interfere with the analysis of nitrogen, the different manufacturers use different materials. See instruction manual.

## 5 Apparatus

- 5.1 Analytical balance  
Analytical balance, capable of weighing accurately to 0,1 mg, or microbalance, capable of weighing accurately to 0,01 mg.
- 5.2 Dumas apparatus  
Apparatus to combust the material at 900 °C in the presence of oxygen, to reduce the nitrogen oxides, to eliminate the interfering gases and to detect the content of molecular nitrogen gas formed.
- 5.3 Crucibles adapted to the Dumas apparatus, of variable sizes, e.g. 10 ml or 20 ml of nominal volume or special foil ( see instruction manual of the special Dumas apparatus type).

## 6 Calibration samples

Calibration substances with known and unchangeable content of nitrogen are used to control the combustion and the apparatus. This may be: acetanilid, l-asparagin acid, sulfanil acid or other amino acids with known nitrogen content. Besides this certified reference materials are used to control the whole procedure.

## 7 Pretreatment of test samples

All samples shall be pretreated according to the special standard in the field of soil, sludge, biowaste and related waste. Normally they are dry, homogenous and of a defined grain size.

Note 2: During the drying procedure there is taken care not to lose amounts of ammonium-N and/or nitrate-N. Therefore, excessive drying (105 °C) should be avoided. Rapid microwave drying may be a good choice. In special situations moist samples can be used.

## 8 Working instructions

Note 3 : Homogeneity of the laboratory sample and the test sample has to be guaranteed

### 8.1 Calibrating of the Dumas apparatus

Calibrate the apparatus using the different calibration materials or reference materials mentioned in chapter 6. The substance should have nitrogen content similar to the materials to be analysed. Consider the special instructions given in the instruction manual of the special Dumas apparatus.

Note 4: In special cases the use of undried samples is necessary. Take care that the material is homogeneous and avoid spattering during the drying process in the Dumas apparatus.

## 8.2 Determination of total nitrogen content

Weigh a portion of the dried or undried material to be analysed into the crucible (5.3) to the nearest of 0,1% accuracy. The amount depends on the expected total nitrogen content and the size of the crucible. Carry out the analysis in accordance with the manufacturer`s manual for the special Dumas apparatus.

## 8.3 Quality check

Weigh an adequate amount of EDTA (4. 5) or of any calibrating substance, mix thoroughly with burning assistance (4.6) and measure the amount of nitrogen. If necessary control the linearity of the analyser with different amounts of EDTA or the calibrating substances.

Note 5: Pores in the material to be analysed are filled with air and, therefore, with nitrogen. Nitrogen also enters the combustion cell when it is opened to exchange the sample. Take care purging of the cell and the material to be analysed by oxygen gas is sufficient leaving no nitrogen gas back.

## 9 Calculations and expression of results

Calculate the total nitrogen content ( $w_N$ ) in milligrams per gram, on the basis of dry matter according to the following equation:

- a. For primary results given in milligrams of nitrogen

$$w_N = X_1 / m_1 \cdot (100 + w) / 100$$

- b. For primary results, given as percent mass fraction of nitrogen:

$$w_N = X_2 \cdot 10 \cdot (100 + w) / 100$$

where

$w_N$  is the content of nitrogen in milligrams per gram of oven dry material

$X_1$  is the primary result in milligram nitrogen

$X_2$  is the primary result in percentage nitrogen (mass fraction)

$m_1$  is the mass of material weight in the crucible

$w$  is the percentage water content (mass fraction) on the basis of oven dried material, determined in accordance to the respective standard.

## 10 Validation and Precision

For information see Annex A. Further work to produce the validation/precision data has to be done in the future.

## 11 Test report

The test report is formulated according to the special conditions of accreditation (EN 41001 or EN 17025)

### Annex A

(informative)

Validation and precision data

The interlaboratory trial organized in the year 1992 with 12 laboratories and in 1993 with 11 laboratories in Germany with three soils resulted in the following data:

Sample No./	Nitrogen content, Average, mg/g	$s_r$ mg/g	$s_r$ %	$s_R$ mg/g	$s_R$ %
1	1,457	0,067	4,6	0,205	14,1
2	2,054	0,073	3,6	0,333	16,2
3	11,16	0,334	3,0	0,982	8,8

Within the work of CEN /TC 223 an interlaboratory trial was organized in 1997 with the following results :

Sample No.	Number of Participants	Nitrogen content, Average, mg/g	$s_r$ mg/g	$s_r$ %	$s_R$ mg/g	$s_R$ %
Bark humus	10	19,5	0,45	2,30	1,32	6,77
Biowaste	12	13,21	0,36	2,73	1,10	8,33
Clay contenting peat	11	9,2	0,25	2,72	0,63	6,85
coarse peat	11	10,7	0,25	2,34	1,69	15,8
Composted sludge	15	29,90	0,96	3,21	2,97	9,93
Composted wood fibre	12	12,07	0,37	3,07	1,72	14,25

$s_r$  mg/kg is standard deviation (repeatability)

$s_r$  % is percentage standard deviation (repeatability)

$s_R$  mg/kg is standard deviation (reproducibility)

$s_R$  % is percentage standard deviation (reproducibility)

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

A new ring test with more soils and a wider range of nitrogen content is proposed.

The repeatability and the reproducibility are calculated from the results of the round robin studies with the factor 2,8 .

## **Annex B**

(informative)

### **Bibliography**

Dumas, J.B.A. (1831) Procédes de l'analyse organique , Ann. Chim.Phys., 247, 198-213

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., Przemeczek, 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

ISO 13878 Soil quality - Determination of total nitrogen content by dry combustion („elemental analysis“)

EN 13654-2 Soil improvers and growing media - Determination of nitrogen – part 2: Dumas method