Determination of Nutrients

Determination of total phosphorus

Extraktion with aqua regia, reflux method

Introduction

This document is developed in the project 'Horizontal'. It is the result of desk studies “Determination of total phosphorus and nitrogen and fractions” in the project and aims the description of the extraction for the determination of total phosphorus 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 the content of nutrients in solid materials and liquids.

This module concerns the extraction of soil, sludge, biowaste and related waste for determination of the content of phosphorus.

The other horizontal modules that will be available in due time are to be found in the informative annex C 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 – Determaination of dry matter and water content on a mass basis – gravimetric method
EN 13346 Characterisation of sludge - Determination of trace elements and phosphorus – aqua regia extraction methods
EN 13650 Soil improvers and growing media – Extraction of aqua regia soluble elements
EN 13657 Characterisation of waste – Digestion for subsequent determination of aqua regia soluble portion of elements
EN 12880 Characterisation of sludge – Determinjation of dry residue and water content
EN ISO 11885 Water quality – Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy
CEN/TC 292 WI 29292030 Characterisation of waste – Preparation of test portions from the laboratory

2 Scope and working area

This standard describes the extraction method for the determination of total phosphorus in soil, sludge, biowaste and related waste. The extraction includes the phosphorus in inorganic and organic chemical bonds.

3 Principle

The test material is extracted by boiling under reflux with aqua regia and the phosphorus is solved. The content of phosphorus in the extraction solution is measured by ICP-OES (reference method) or other validated measuring method.

4 Reagents

4.1 General
All reagents shall be of recognized analytical grade. Deionised or distilled water used shall conform to purity grade 2 of EN ISO 3696.

4.2 Hydro chloric acid, c (HCl) = 12 mol/l, $\rho \approx 1{,}18$ g/ml, about 37 %

4.3 Nitric acid, c (HNO_3) = 15,8 mol/l , $\rho \approx 1{,}42$ g/ml, about 65 %

4.4 Nitric acid, about 1% (V/V)
Take 10 ml of nitric acid (4.2) and dilute to 1 l in a flask with water.

5 Apparatus

5.1 General
Usual laboratory equipment is needed.
All glassware and plasticsware shall be cleaned by nitric acid (4.3) and stored in order to avoid contamination.

5.2 Reaktion vessel
Glass flask, fitted with round neck, 250 ml

Note 1: A glas flask of 500 ml may be necessary for material which have a tendency to froth

5.3 Reflux condenser
Condenser adaptable to reaktion vessel (5.2)
5.4 Heating devices
Gas burner, heating mantle or aluminium block heater
5.5 Filter paper
Filter paper, hardened and resistant to aqua regia solution
5.6 Analytical balance
Analytical balance with an accuracy of 1mg or better
5.7 Boiling aids
Anti bumping granules or glass beads, acid washed
5.8 Volumetric flasks of different volumes

6 Calibration samples

Certified reference materials from the different matrix types with guaranteed phosphorus content shall be taken through the entire procedure with each batch of analysis.

7 Pretreatment of test samples

All samples shall be pretreated according to the special standard of the section sludge, waste, biowaste and soil (e.g. ISO 11464, EN 12880). Normally they are dry and of a defined grain size (2mm, 500µm or better).

8 Working instructions

Note 1: Homogeneity of the laboratory sample and the test sample has to be guaranteed

8.1 Extraction

Weigh approximatly 3 g, to the nearest of 0,001 g, and transfer them to the 250 ml reaction vessel (5.2). Moisten with about 0,5 ml to 1 ml water and add with swirling 21 ml of hydro chloric acid (4.2) followed by 7 ml of nitric acid (4.3) slowly if necessary to reduce frothing. Connect the reflux condenser (5.3) to the reaction vessel . Stand at room temperature until frothing almost ceases to allow for slow

oxidation of the organic mass of the test sample. Add some boiling aids (5.7) into the reaction vessel.
Transfer the reaction vessel with the reflux condenser to the heating device (5.4). Raise the temperature of the reaction mixture slowly to reflux conditions and maintain for 2 h. Ensure that the condensation zone is lower than 1/3 of the height of the reflux condenser. Allow the mixture to cool , rinse the reflux condenser into the reaction vessel with 10 ml of water.
Filter the mixture through the filter paper (5.5) into a volumetric flask (5.8), rinse the filter with water and fill up the volume flask to volume with water.

8.2 Blank test

A blank test shall be carried out in parallel by the same extraction procedure, using the same quantities of all reagents but omitting the test sample. Fill up to the same volume as the test sample.

8.3 Measurements

Take the extracts and the blank test solution, dilute to a specific volume and perform the analysis according to EN ISO 11885 (Annex A).
Adjust the acid concentration of the calibration solutions (blank and standards) and the matrix of this solutions according to the extraction solutions of the test samples.

Note 2: Information about the spectral lines for phosphorus, matrix effects and interfering elements see Annex A.

9 Calculations and expression auf results

The phosphorus content of the analysed material in g/kg dry matter is calculated according to following formular:

$$w_P = \frac{C \times V}{m \times m_t}$$

w_P = content of phosphorus in g/kg (dry matter)
C = concentration of phosphorus measured in the extraction solution, mg/l
V = Volume of the volumetric flask, ml
m = mass of the test sample
m_t = dry mass of the test sample , g/100g

10 Validation and Precision

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

11 Test report

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

Annex A
(informative)

Inductively coupled plasma optical emission spectrometry technique shows some different interferences, which the laboratory has to overcome.

1. Physical interferences
   This means especially problems in the introduction and spraying system. Different matrix loaded solutions and different surface tension may be the reason for different spraying efficiency. This affects the behaviour in the plasma and the exitation of the elements. Therefore dilute the extraction solution as maximal possible and adjust the calibration solutions to the matrix und acid concentration.

2. Chemical and ionisation interferences
   They are not known for the element phosphorus

3. Spectral interferences
   They are shown in the table 1. Dilute the solution or choose another spectral line.

Table 1 Emission lines for the element phosphorus, given concentration by 1 g/l of the interferring element (VDLUFA, 2001)

Element	line, nm	interferring element	Given content, mg/l
P	178,287	none	
P	213,618	Cu Zn	20 1,9
P	214,914	Cu Fe	14 1,2

Annex B
(Informative)
Validation and precision data

Within the technical commitee CEN/TC 308 „Characterisation of sludges“ one interlaboratory trial with 55 laboratories out of 12 countries in 1997 has given the following results, according to ISO 5725. (sludge 1 was a mixture of drinking water sludge and sewage sludge, sludge 2 was a mixture of drinking water sludge and industrial sludge)

Analyt	No. of participants	content, average, g/kg	s_r g/kg	s_r %	s_R g/kg	S_R %
Sludge 1						
P	23	10,49	0,33	3,2	0,78	7,5

Sludge 2						
P	23	17,27	0,36	2,1	1,35	7,8

s_r mg/kg repeatability

s_r % percentage repeatability

s_R mg/kg reproducibility

s_R % percentage reproducibility

The dimension in the heading of the table (g/kg) is given in mg/kg in the original standard (EN 13346), one has to doubt the correctness of this dimension, in sludge you can expect g/kg for phosphorus.

Within the technical commitee CEN/TC 223 an interlaboratory trial was organized in 1997 with the following data, according to ISO 5725

bark humus

Analyt	No. of participants	Content, average, mg/kg	S_r mg/kg	s_r %	s_R mg/kg	S_R %
P	16	10469,4	414,33	3,96	1117,25	10,67

biowaste

Analyt	No. of participants	Content, average, mg/kg	S_r mg/kg	s_r %	s_R mg/kg	S_R %
P	15	2603,8	71,02	2,73	92,15	3,54

Clay contenting peat (fertilized)

Analyt	No. of participants	Content, average, mg/kg	S_r mg/kg	s_r %	s_R mg/kg	S_R %
P	15	975,7	45,60	4,67	100,99	10,35

Coarse peat (fertilized)

Analyt	No. of participants	Content, average, mg/kg	S_r mg/kg	s_r %	s_R mg/kg	S_R %
P	17	1065,7	35,16	3,30	190,80	17,9

composted sludge

Analyt	Nb. of participants	Content, average, mg/kg	S_r mg/kg	s_r %	s_R mg/kg	S_R %
P	16	9580,5	207,10	2,16	496,17	5,18

composted wood fibre

Analyt	No. of participants	Content, average, mg/kg	S_r mg/kg	s_r %	s_R mg/kg	S_R %
P	16	1150,7	40,53	3,52	125,36	10,89

s_r mg/kg repeatability

s_r % percentage repeatability

s_R mg/kg reproducibility

s_R % percentage reproducibility

To validate the extraction procedure only the following proposal is made:
The test material is extracted by aqua regia in an amount to get sufficient extraction solution to distribute this solution to the participants of the round robin study. Additionally the organizer of the round robin study supplies the participants with calibration solutions for ICP-OES, adopted in acid and matrix content. The participants do their own extraction and measure this solution together with the delivered solution against the delivered calibration solution and their own calibration solution. The statistical operation of these data can explain the contribution of the extraction and the measuring to the standard deviation or the uncertainty of the result.

In the future the validation has to be done with three samples of different soils, three samples of different to biowaste related wastes, with different contents of phosphorus each. These samples must be dry samples. One has to discuss, if more different sludges should be involved in the validation.

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

Annex C
(informative)

Bibliography

VDLUFA (2001) : Methodenbuch des VDLUFA , Band III, Die chemische Untersuchung von Futtermitteln, Methode 2.2.6, VDLUFA Verlag, Bonn

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 13346 Determination of trace elements and phosphorus – aqua regia extraction methods

EN 13657 Characterisation of waste – Digestion for subsequent determination of aqua regia soluble portion of elements

EN 12880 Characterisation of sludge – Determination of dry residue and water content

EN ISO 11885 Water quality – Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy

CEN/TC 292 WI 29292030 Characterisation of waste – Preparation of test portions from the laboratory