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Foreword

This document CEN/BT TF 151 WI CSS 99022 has been prepared by CEN/BT TF 151 "Horizontal standards in the fields of sludge, bio-waste and soil", the secretariat of which is held by DS.

This document is currently submitted to the CEN Enquiry.

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 Z.

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)**	**Reference:**
Sludge	Eight sludge samples Municipal sludge, North Rhine Westphalia	EN 12880:2000, Annex A Horizontal Project Interlab comp.
Soil	Soil samples Sludge amended soil, Barcelona	ISO 11465:1993 Horizontal Project Interlab comp.
Soil improvers and growing media	Unfertilised peat perlite, coarse bark, composted straw and domestic sewage	EN 13040:1999, Annex B
Biowaste	Fresh compost, Vienna	Horizontal Project Interlab comp.
Waste	Contaminated soil, dredged sludge, nickel sludge	EN 14346:2006

Introduction

It is the result of a desk study "Desk study on dry matter and loss on ignition". After discussion with all parties concerned in CEN the standard has been developed further as a modular horizontal method and has been validated within in the project ‘Horizontal’.

After an evaluation study, in which e.g. the ruggedness of the method was studies, 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.

1 Scope

This European Standard specifies a method for the determination of the dry matter on a mass basis of samples of:

— sludges, including liquid, paste-like or solid sludges,

— all types of air-dried soil samples and field moist soil samples,

— sediment, and

— treated biowaste.

NOTE Determination of water content of a sample using this method is possible provided that other compounds other than water do not contribute significantly to the weight loss by heating to 105 ºC.

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).

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

CSS99035 Soil, sludge and treated biowaste – Pre-treatment for inorganic characterization

CSS99023 Soil, sludge and treated biowaste – Determination of loss on ignition

3 Terms and definitions

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

3.1
dry matter w_{dm}
dry residue after drying according to the specified drying process. It is expressed as a percentage or in grams per kilogram

3.2
water content w_{wc}
mass fraction determined as the loss on mass after the specified drying process. It is expressed as a percentage or in grams per kilogram

3.3
constant mass
mass reached when, during the drying process, the difference between two successive weighings of the sample at an interval of minimum 1 h, first heated, then cooled to room temperature, does not exceed 0,5 % (m/m) of the last determined mass or 2 mg, whichever is the greater

NOTE 1 These definitions do not - for technical reasons - apply to samples containing volatile substances.

NOTE 2 Usually 16 h to 24 h are sufficient for most soil, sludge, sediment and waste samples, but certain sample types and large samples may require longer drying periods.

4 Safety remarks

Samples of sludge, bio-waste or contaminated soils are liable to ferment and usually contain harmful microorganisms. It is essential to keep them away from any food or drink, and to protect any cuts. Bursting bottles containing e.g. sludge can produce microorganisms-contaminated shrapnel and/or infectious aerosols.

When handling sludge and bio-waste samples, it is necessary to wear gloves, face and eye protection, and sufficient body protection to guard against bottles bursting. Gasses evolved may be flammable.

Special measures must be taken during the drying process to prevent contamination of the laboratory atmosphere by flammable, explosive or toxic gasses.

5 Principle

Samples are dried to constant mass in an oven at (105 $\pm$ 5) ^{o}C. The difference in mass before and after the drying process is used to determine the dry matter and the water content.

6 Interferences and sources of errors

The samples may change chemically during the drying process (e.g. by absorption of carbon dioxide in the case of basic samples or of oxygen caused by reducing substances).

NOTE 1 When determining the water content, volatile substances (such as organic solvents or substances deriving from the decomposition of organic or inorganic substances) are also included either completely or partially.

NOTE 2 In case of samples with a high content of solids (e.g. dry matter $w_{dr} \geq 30\%$) there is the risk of water still remaining trapped in the sample after drying.

NOTE 3 Decomposition of organic matter can, in general, be neglected at this temperature. However, for soil samples with a high content of organic matter (> 10% (m/m)), for example peaty soils, the method of drying should be adapted. In this case, the sample should be dried to constant mass at 50^{o}C. Use of a vacuum will speed up the operation.

NOTE 4 Some minerals similar to gypsum lose water of crystallisation at a temperature of 105 ^{o}C.

7 Apparatus

7.1 Drying oven

Thermostatically controlled with forced air ventilation, maintaining a temperature of (105 ± 5) ^{o}C.

7.2 Desciccator

With active drying agent such as silica gel.

7.3 Temperature tolerant evaporating dish or crucible

Withstanding at least 105^{o}C for dry matter analyses or 550^{o}C for further analyses of loss on ignition is required (WI CSS 99023). Suitable materials are nickel, porcelain, silica, and platinum.

7.4 Analytical balance

With an accuracy of 1 mg or better. For samples with dry residue of 10 g or higher, an analytical balance with an accuracy of 10 mg may be used.

8 Sampling and sample pre-treatment

Sampling and sample pre-treatment shall be carried out in accordance with the methods specified in WI CSS 99031+32+33+57+58+59+60.

9 Procedure

Place an evaporating dish or crucible (see 7.3) in the drying oven (see 7.1) set at (105 ± 5) ^{o}C for a minimum of 30 minutes and then cool to ambient temperature in a desiccator (see 7.2), with the lid closed. After cooling, weigh the dish or crucible to the nearest 1 mg, m_a.

If the same crucible is to be used for the subsequent loss on ignition measurement (WI CSS 99023), it shall be pre-ignited at 550^{o}C for a minimum of 30 min.

Depending on the expected water content, weigh into the evaporating dish or crucible (see 7.3) a suitable amount of sample, m_b, so that the dry matter obtained has a mass of not less than 0,5 g.

NOTE 1 Sample amounts of 30 g to 50 g are suitable for field-moist soil samples, paste-like and solid sludge and solid waste. A larger test portion may be needed to assure a representative sample for e.g. composted bark samples. For air-dried soil samples 10 g to 15 g are suitable.

NOTE 2 Determination of dry matter shall be determined on samples identical to those used for determination of parameters that relates to dry matter.

Place the evaporating dish or crucible (see 7.3) containing the sample in the drying oven (see 7.1) set at 105 ^{o}C until the residue appears dry, typically overnight.

NOTE 3 There is a risk of a cake surface forming. The formation of such cake surface impedes even drying. To avoid this, a glass rod can be weighed along with the crucible. If cake formation occurs during drying, the glass rod is used to stir the sludge to break up the cake and bring the liquid surface into contact with hot air. This is repeated as necessary.

NOTE 4 In the case of samples containing considerable amounts of water careful evaporation of the major part of the water is preferred (e.g. in a water bath) in order to avoid loss of substances by splashing. Alternatively freeze-drying may be used as a first step for the determination of dry matter.

After cooling in the desiccator (see 7.2), weigh the evaporating dish or crucible and contents for the first time, m_c.

The mass ($m_c - m_a$) shall be regarded as constant if the mass obtained after another hour of drying does not differ by more than 0.5% of the previous value or 2 mg, whichever is the greater (see 0).

Otherwise, repeat drying until constant mass is reached.

NOTE 5 In cases when even after the third drying process it is not possible to obtain a constant value, record the value determined after at further 2 h together with a remark on the unfinished process.

NOTE 6 20 hours of drying and omission of re-drying/re-weighing can be applied for sample types with documented evidence that the necessary drying time is less than 20 hours.

10 Quality assurance of the overall procedure

10.1 Quality control

At least one duplicate analysis should be carried out in each batch of analyses. Where uncertainty exists about the homogeneity or behaviour of the sample it is recommended that the analysis be carried out in duplicate.

11 Calculation and expression of results

Calculate the dry matter (w_{dm}) or the water content (w_{wc}) expressed as a percentage of mass or grams per kilogram using the following equations:

$$w_{dm} = \frac{m_c - m_a}{m_b - m_a} \times f$$

$$w_{wc} = \frac{m_b - m_c}{m_b - m_a} \times f$$

where:

w_{dm} = is the dry matter of the sample, in percentages or grams per kilogram;

w_{wc} = is the water content of the sample, in percentages or grams per kilogram;

m_a = is the mass of the empty dish or crucible in grams;

m_b = is the mass of the dish or crucible containing the sample in grams;

m_c = is the mass of the dish or crucible containing the dry matter in gram

f is a conversion factor, f = 100 for expression of results as a percentage and factor f = 1 000 for expression in grams per kilogram.

Values should be rounded to the nearest 0,1% (w/w) or alternatively to the nearest 1 g/kg.

12 Precision data

The performance characteristics of the method (Annex A) 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 A.2 in Annex A 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 dry matter – Gravimetric method in soil, sludge and treated biowaste	Typical value %	Observed range %
Repeatability limit, r	0.5	*0.2 – 1.1*
Reproducibility limit, R	1.4	0.4 – 1.7

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 dry matter in Sludge 2 the result and its dispersion limit is 95.5 ± 0.97 % (2 * S_R = 1.02 % of 95.5). This means that with a 95 % statistical confidence, the values reasonably attributable to the measured parameter are larger than 94.49 % and lower than 96.44%.

NOTE 2. The repeatability limit (r) and the reproducibility limit (R) as given in Table A.2 (Annex A) and in this table are indicative values of the attainable precision if the determination of dry matter method is performed in accordance with this standard [CSS99022].

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 as presented.

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

13 Test report

The test report shall contain the following information:

a) Reference to this European Standard;

b) All information necessary for the complete identification of the sample;

c) Details of sample pre-treatment, if carried out;

d) Particular characteristics of the sample;

e) Results of the determination according to Clause 11;

f) Any detail not specified in this European Standard and any other factor that may have affected the results.

Annex A (informative)

Repeatability and reproducibility data

A.1 Performance characteristics

A.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 “Sludge, treated biowaste and soil — Determination of dry matter — Gravimetric method“.

A.1.2 Materials used in the interlaboratory comparison study

The interlaboratory comparison of “Sludge, treated biowaste and soil — Determination of dry matter — Gravimetric method“ was carried out with 25 - 29 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).

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 determination of dry matter in soil, sludge and treated biowaste applies: very fine grained materials (like sludge: 0 µm to about 125 µm) and fine-grained materials (soil and compost: 0 mm to 4 mm).

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

Table A.1 — Material types tested and components analysed in the interlaboratory comparison of the method for the determination of dry matter 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	Dry matter
	Sludge 2	Mix 2 of municipal WWTP sludges from North Rhine Westphalia, Germany	Dry matter
Fine grained (< 2 mm)	Compost 1	Fresh compost from Vienna, Austria	Dry matter
	Compost 2	Compost from Germany	Dry matter
	Soil 4	A sludge amended soil from Hohenheim, Germany	Dry matter
	Soil 5	An agricultural soil from Reading, UK	Dry matter

A.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 A.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: $r_{test} = f \cdot \sqrt{2} \cdot s_{r,test}$ with the critical range factor f = 2. For instance, the repeatability limit around a measurement result of 90 % Dry Matter is ± 0.50 % Dry Matter (i.e ± 0.6 % of 90).

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 90 % Dry Matter is ± 1.28 % Dry Matter (i.e ± 1.4 % of 90).

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

Table A.2 — Results of the interlaboratory comparison studies of the determination of dry matter – gravimetric method in soil, sludge and treated biowaste. All contents in %.

Matrix	Parameter	Mean	sr	sR	r	R	p	Outliers	Total number of data	No of LOD
Sludge 1	Dry Matter	96.57	0.34%	0.63%	0.93	1.70	22	3	105	0
Sludge 2	Dry Matter	95.47	0.24%	0.51%	0.65	1.36	27	2	130	0
Compost 1	Dry Matter	93.72	0.15%	0.51%	0.40	1.33	24	4	125	0
Compost 2	Dry Matter	91.73	0.42%	0.59%	1.07	1.50	24	5	123	0
Soil 4	Dry Matter	95.28	0.14%	0.41%	0.36	1.10	24	4	112	0
Soil 5	Dry Matter	98.39	0.08%	0.14%	0.22	0.37	22	6	106	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.

Note: In the framework of characterisation of waste the method described in this document is equal to the protocol describing the quantification of dry matter in waste (prEN 14346) and of dry matter in soil improvers (13040). Based on the results, which complement the present standard very well, a broader horizontal standard could be developed covering the matrices covered in this standard, soil improvers and waste.