CEN/TC BT TF 151

Date: 2007-02

TC BT TF 151 WI CSS 99037

CEN/TC BT TF 151

Secretariat: DS

Sludge, treated biowaste and soil — Determination of specific electrical conductivity

Einführendes Element — Haupt-Element — Ergänzendes Element

Élément introductif — Élément central — Élément complémentaire

ICS:

Descriptors:

Document type: European Standard
Document subtype:
Document stage: CEN Enquiry
Document language: E

C:\User\Texts\NORMALIS\HORIZONTAL\HORIZONTAL\HORIZONTAL\Phase III\BT TF151 WI CSS 99037 - EC 472007.doc STD Version 2.1c2

Contents

Foreword

This document has been prepared by CEN /TC BT TF 151, "Horizontal standards in the fields of sludge, bio-waste and soil".

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).

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		Johnsson, L., Nilsson, S.I. & Jennische, P. (2005). Desk study to asses the feasibility of a draft horizontal standard for electrical conductivity
Soil		- " – TEXT MISSING?
Soil improvers		
Sediment		
Treated Biowaste		- " - TEXT MISSING?

Introduction

This document is developed in the project 'Horizontal'. It is the result of a desk study prepared by Lars Johnsson, S. Ingvar Nilsson & Per Jennische entitled “Desk study to assess the feasibility of a draft horizontal standard for electrical conductivity” and aims at an evaluation of the latest developments in assessing specific electrical conductivity in sludge, treated biowaste, soil and neighbouring fields. 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 (CSS99037) describes an instrumental method for routine determinations of specific electrical conductivity in aqueous extracts of sludge (fresh), treated biowaste (fresh) or soil (fresh or air-dry). Please note that soil improvers and growing media are not included in this standard. The EC determination is carried out to obtain an indication of the content of water-soluble electrolytes in the materials mentioned. The standard is based on ISO 11265. There is presently no international standard for sludge or treated biowaste. For practical reasons, for instance if there is a need to make strict comparisons with previous measurements, soils should generally be air-dried. Air-drying can be used for all soils, except for those containing sulphidic minerals or volatile acids. In both cases fresh soil should be used to avoid either sulphide oxidation resulting in the formation of sulphuric acid, or volatilisation of low-molecular organic acids. Regarding sludge and treated biowaste, fresh samples are recommended. In these materials air-drying may introduce artefacts due to a stimulation of oxidation processes and should therefore be avoided.

Table 1 — XXX

Fresh samples versus air-dry, depending on sample category:		
Sample category	**Fresh**	**Dry**
Sludge	X	
Treated biowaste	X	
Soils containing sulphide minerals	X	
Soils containing volatile acids	X	
Other Soils	X*	X*
* Optional depending on whether comparisons are to be made with previous measurements on fresh or air-dry samples		

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 11265, *Soil quality – Determination of the specific electrical conductivity*

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*

3 Terms and definitions

For the purpose of this European Standard, the following definition applies:

3.1
Specific Electrical Conductivity (EC)
numerical expression of the ability of an aqueous solution to carry an electrical current

NOTE EC at equilibrium in a water suspension of sludge, treated biowaste or soil is expressed as milli-Siemens per meter (mS/m).

4 Principle

A suspension of either fresh sludge, fresh treated biowaste or air-dried (or fresh) soil is made up in 5 times its weight with water, to dissolve the electrolytes. Concerning liquid sludge the measurements are made without adding any water (cf. the procedure used for determination of pH in sewage sludge, treated biowaste or soil). The specific electrical conductivity of the filtered extract is measured and the result is corrected to a temperature of 25 °C. Temperature corrections of the measured values are made by adding 2 % of the measured value (measurement temperature < 25 °C) or subtracting 2 % of the measured value (measurement temperature > 25 °C) for each degree's difference (Bower & Wilcox 1965).

5 Interferences and sources of errors

The measured values of the specific electrical conductivity can be influenced by contamination of the electrodes. Air bubbles on the electrodes perturb the measurements. Measurements < 1 mS/m are influenced by gaseous carbon dioxide (CO_2) or ammonia (NH_3) coming from the atmosphere. In these cases, measurements are carried out in an adapted measuring cell. Other sources of error are associated with materials containing sulphidic minerals or volatile acids (see Clause 1).

6 Reagents

a) Use only reagents of recognised analytical grade.

b) Water, with a specific electrical conductivity not higher than 0,2 mS/m at 25 °C (grade 2 water according to EN ISO 3696).

c) Potassium chloride solution, c(KCl) = 0,1 M.

Dissolve in water 7,456 g of potassium chloride, previously dried for 24 h at 220 °C ± 10°C (see 6.a)) and dilute to 1000 ml at 25°C. The specific electrical conductivity of this solution is 1290 mS/m at 25°C.

d) Potassium chloride solution, c(KCl) = 0,0200 M.

Pour 200,0 ml of the potassium chloride solution (see 6.b)) into a 1000 ml volumetric flask and dilute to volume with water at 25 °C. The specific electrical conductivity of this solution is 277 mS/m at 25 °C.

e) Potassium chloride solution, c(KCl) = 0,0100 M.

Pour 100,0 ml of the potassium chloride solution (see 6.b)) into a 1000 ml volumetric flask and dilute to volume with water at 25 °C. The specific electrical conductivity of this solution is 141 mS/m at 25 °C.

All the potassium chloride solutions (see 6.b), 6.c), 6.d)). used for calibration shall be stored in tightly sealed bottles which do not release alkali or alkali-earth metals in amounts that would compromise the specific electrical conductivity of the solutions.

NOTE Polyethylene bottles could be used. The use of commercially available conductivity standards is permitted.

7 Apparatus

7.1 Equipment for sample preparation

According to EN 12176, EN 13040 and ISO 11464. The latter standard refers to air-dry soil. Except for the drying procedure, it is applicable to fresh soil samples as well.

7.2 Conductivity meter, fitted with a conductivity cell, equipped with an adjustable measuring range setting and automatic temperature correction and having an accuracy of 1 mS/m at 20°C. Preferably, the conductivity meter should also be equipped with a cell-constant control.

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

7.4 Thermometer, capable of measuring to the nearest 0,1 °C.

7.5 Shaking machine, with a horizontal movement sufficiently vigorous to produce and maintain 1:5 substrate-water suspensions. It should be placed in a constant room, where the temperature is maintained at 25°C ± 1°C.

7.6 Filter paper, with low ash content and high retentive properties.

7.7 Shaking bottles, of sufficient capacity, made of polyethylene.

8 Sampling and sample pre-treatment

8.1 Sampling should be carried out in accordance with CSS99031-32 and 57-60 (Horizontal standard module(s) for sampling of sludge, treated biowaste and soil).

8.2 Samples should be pretreated and preserved according to EN 12176, EN 13040 or ISO 11464. The particle size of soils should be ≤ 2 mm, while that of treated biowaste should be 20 mm to 40 mm.

NOTE 1 Sample preparation for liquid sludge is unnecessary. EC should be determined directly according to EN 12176. Pastelike sludge may need a breakdown of solid particles before the preparation of a suspension.

NOTE 2 ISO 11464 refers to air-dry soil. Except for the drying procedure, it is applicable to fresh soil samples as well.

9 Procedure

9.1 Extraction

Weigh 20,00 g of the laboratory sample (sewage sludge or soil) and transfer to a shaking bottle (see 7.7). Add 100 ml of water (see 6.1) at a temperature of 25°C ± 1°C. Close the bottle and place it in a horizontal position in the shaking machine. Shake for 30 minutes. Filter directly through a filter paper (see 7.6). For treated biowaste the procedure and weight ratio water sample should be similar. For a detailed description, see EN 13038.

NOTE Extraction is not applicable to liquid sludge. Measurements should be made directly.

9.2 Calibration by checking the cell constant.

9.2.1 Measure the specific conductivity (EC_M) of the potassium chloride solutions (see 6.2, 6.3 and 6.4) according to the instruction manual of the instrument.

9.2.2 Calculate for each potassium chloride solution, a cell constant according to

$K = EC_S/EC_M$

where

K is the cell constant in reciprocal metres (1/m)

EC_S is the specific electrical conductivity of one of the potassium chloride solutions in mS/m, according to its concentration

EC_M is the measured specific electrical conductivity of the same potassium chloride solution, in mS/m.

Use the average of the calculated values as the cell constant of the instrument. The calculated cell constant should not differ by more than 5% from the value given by the manufacturer.

9.2.3 Adjust the cell constant on the conductivity meter.

9.3 Measurement of the specific electrical conductivity of the filtrates

Measure the specific electrical conductivity of the filtrates (EC_M) according to the instructions provided by the manufacturer of the conductivity meter (see 9.2). Carry out the measurements with the temperature corrected to 25 ^oC.

9.4 Blank determination

Carry out a blank determination in each batch of samples by treating water (see 6.1) in the same way as the samples. The value of the blank should not exceed 1 mS/m. If the EC of the blank > 1 mS/m, the extraction should be repeated from the beginning. Carry out at least two blank determinations in each series and use the average blank value for subsequent calculations.

9.5 Quality Assurance of the overall procedure

If duplicate measurements are made (optional), the average value should be reported. A reference sample should be included in each batch of samples. The reference could be either “home made” or consist of a certified reference material.

10 Expression of results

Note the results to 1 decimal place, expressed in mS/m.

11 Precision data

The performance characteristics of the method (Annex A) data have been evaluated. Table 2 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 2 — 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 Specific Electrical Conductivity in soil, sludge and treated biowaste	Typical value %	Observed range %
Repeatability limit, r	6	*4 – 17*

Reproducibility limit, R	148 #	45 – 158 #

Still under evaluation 3-7-2007.

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 √2 to obtain the corresponding typical dispersion limit and its observed range. In the example of EC in Sludge 2 the result and its dispersion limit is 358 ± 403 mS/m at 20 deg (2 * sR = 112 % of 358). This means that with a 95 % statistical confidence, the values reasonably attributable to the measured parameter are larger than 0 mS/m at 20 deg and lower than 761 mS/m at 20 deg..

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 Specific Electrical Conductivity is performed in accordance with this standard [CSS99037].

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 Specific Electrical Conductivity 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 A.2 (Annex A) 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) Precise identification of the sample;

c) Type of sample preparation: fresh, air-dry or (concerning liquid sludge) no preparation;

d) Expression of results, according to Clause 10;

e) Any deviation from this standard, and any facts which may have influenced the result stating the reason for deviation.

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 “Determination of Specific Electrical Conductivity in soil, sludge and treated biowaste” were established.

A.1.2 Materials used in the interlaboratory comparison study

The interlaboratory comparison of Determination of Specific Electrical Conductivity in soil, sludge and treated biowaste was carried out with 14-16 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 the determination of Specific Electrical Conductivity 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.2 — Material types tested and components analysed in the interlaboratory comparison of the method for the determination of Specific Electrical Conductivity 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	EC
	Sludge 2	Mix 2 of municipal WWTP sludges from North Rhine Westphalia, Germany	EC
Fine grained (< 2 mm)	Compost 1	Fresh compost from Vienna, Austria	EC
	Compost 2	Compost from Germany	EC
	Soil 4	A sludge amended soil from Hohenheim, Germany	EC
	Soil 5	An agricultural soil from Reading, UK	EC

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 50 mS/m at 20 deg EC is ± 3.07 mS/m at 20 deg EC (i.e ± 6 % of 50).

> 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 11.

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 50 mS/m at 20 deg EC is ± 74.1 mS/m at 20 deg EC (i.e ± 148 % of 50).

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 11 .

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.3 — Results of the interlaboratory comparison studies of the determination of Specific Electrical Conductivity in soil, sludge and treated biowaste. All concentrations in mS/m at 20 deg.

Matrix	**Parameter**	**Mean**	**sr**	**sR**	**r**	**R**	**p**	**Outliers**	**Used numbe r of data**	**Number of data reported below detection**	**Total no of data reported**
Sludge 1	EC	319	1.62%	53.1%	14.4	475	14	2	66	0	78
Sludge 2	EC	358	1.67%	56.3%	16.8	565	14	2	61	0	73
Compost 1	EC	237	1.50%	52.8%	9.95	350	13	2	64	0	74
Compost 2	EC	207	2.71%	56.3%	15.7	325	16	0	78	0	78
Soil 4	EC	10.3	4.30%	17.8%	1.24	5.13	14	2	62	0	74
Soil 5	EC	10.26	6.00%	16.2%	1.72	4.64	13	2	58	0	67

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.

Bibliography

[1] ISO 1770, *Solid-stem general purpose thermometers*

[2] EN ISO 3696, *Water for analytical laboratory use – Specification and test methods*

[3] ISO 7888, *Water quality – Determination of electrical conductivity*

[4] ISO 11464, *Soil quality – Pretreatment of samples for physico-chemical analyses*

[5] EN 13040, *Soil improvers and growing media – Sample preparation for chemical and physical tests, determination of dry matter content, moisture content and laboratory compacted bulk density*

[6] EN 12176, *Characterization of sludge – Determination of pH-value*

[7] EN 13038, *Soil improvers and growing media – Determination of electrical conductivity*

[8] Johnsson, L., Nilsson, S.I. & Jennische, P. 2005. Desk study to assess the feasibility of a draft horizontal standard for electrical conductivity.

[9] Bower, C.A. & Wilcox, L. V. 1965. Soluble salts by electrical conductivity. In Black, C. A. (Editor-in Chief) Methods of Soil Analysis Part 2. Chemical and Microbiological Properties, pp. 936-940. American Society of Agronomy, Inc., Publisher Madison, Wisconsin, USA.