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Dry matter (DM), loss on ignition (LOI) and total organic carbon (TOC)

Report on an evaluation study

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INTRODUCTION

The report in hand deals with an evaluation study (Phase II) under WP 6: Inorganic Parameters: Evaluation of the draft horizontal standards for:

- dry matter (DM), loss on ignition (LOI) and total organic carbon (TOC)

in sludge, soil, biowaste and neighbouring fields

The evaluation study is based on the recommendations as given in the desk study reports /1,2/ and suggestions from interested parties following the consultation period of Phase I of the Horizontal Project. The desk study reports as well as the draft standards are published at www.ecn.nl/library/horizontal. Comments and suggestions from the 1st consultation round are given in Annex 2

The evaluation study includes:

- Evaluation of temperatures for the determination of loss on ignition. The possibility of including more temperatures for ignition in the standard is discussed.
- Evaluation of the draft standard on TOC, the use of oxidizing materials and oxidation time
- Ruggedness studies and
- Precision experiments

The present report describes the results of the evaluation study.

1. EVALUATION OF DRAFT STANDARDS

1.1 Determination of dry matter

The desk study on the comparison of standards for the determination of dry matter and water content by the gravimetric method /1/ demonstrated the possibility of preparing a harmonized and horizontal standard covering sediment, sludge, soil, biowaste and waste. A horizontal standard could technically replace the following standards: sludge (EN 12880:2000), soil (ISO 11465:1993) and biowaste (EN 13040:1999), the later only in respect to the determination of dry matter. Technically, the proposed standard can replace the gravimetric method in prEN14346:2004 (waste), however, this standard contains two distinctively different methods (a gravimetric method (A) and a distillation method (B)). The proposed method includes waste and sediment in the scope of the standard; however, excludes samples with a high content of volatile substances.

A description of the principles of the above-mentioned methods is included in Annex 1.

The comparison of the standards /1/ showed that the standards differ mainly in terminology, which needs harmonisation, and in relation to the applied drying temperature interval. The use of the drying temperature interval of 105 ± 5ºC and the term "dry matter" was proposed. The draft standard on the determination of dry matter was largely endorsed during the 1st consultation period.

Chapter 3 contains results from precision experiments. Chapter 4 gives an overview of changes to the draft standard compared to the latest draft standard (1st consultation).

1.2 Determination of loss on ignition (LOI)

The desk study on the comparison of standards for the determination of loss on ignition /1/ demonstrated the possibility of preparing a harmonized and horizontal standard for sediment, sludge, soil, biowaste and waste. The major difference observed and discussed in the desk study included the use of different ignition temperatures and ignition periods in the standards. Furthermore, it was observed that the standard on the determination of waste included demands that were not mentioned in the standards on the other matrices included in the study, i.e. the determination of LOI on waste with high contents on volatile substances and treatment of samples with black particles left after ignition.

A draft standard was prepared that proposed the use of an ignition temperature interval of (550 ± 25)ºC /4/. The present chapter describes experiments carried out with a view to evaluating the draft standard.

1.2.1 Comparison of loss on ignition at 450ºC and 550ºC

In EN 13039 (soil improvers and growing media) a temperature of 450ºC is applied, whereas in EN 12879 (sludge) and in a draft standard proposed by TC 292/WG5 (prEN 15169) a temperature of 550ºC is applied. (TC 292 submitted the draft standard prEN 15169 in February 2005: Characterization of waste – Determination of loss on ignition in waste, sludge and sediments). The proposed draft horizontal standard (as discussed during the 1st consultation period) proposed the use of a temperature of (550 + 25) ºC. The use of different ignition temperatures and time intervals is evaluated on a number of samples with different content of carbonates. The ignition principles of the methods tested are outlined in Table 1.

Table 1 Ignition conditions in the proposed draft standard and in EN 12879

Methods	**Principle**
A. Proposed draft standard /4 /	Dry a known amount of the sample in pre-ignited basin. Place a crucible (8.1) in the furnace (8.2) and heat at (550 ± 25)°C for at least 30 min. After cooling in the desiccator (8.3) to ambient temperature, weigh to the nearest 1 mg, (m_a). Weigh into the crucible 0.5 - 5 g of the dried sample to the nearest 1 mg, (m_b) and heat in the furnace (8.2) at (550 ± 25)°C for at least 60 min. Place the hot crucible containing the residue on ignition in the desiccator and leave to cool. After cooling in the desiccator to ambient temperature, weigh the crucible containing the dry residue to the nearest 1 mg (m_c). The crucible is weighed immediately after removal from the desiccator and the weighing operation is completed as quickly as possible. The mass of the residue on ignition and thus the loss on ignition shall be regarded as constant if the mass obtained after a further half-hour period of ignition at 550°C in the preheated furnace, (m_c - m_a) differs max. 0.5% of the previous value or 2 mg, whichever is the greater.
B. EN 13039 (soil improvers and growing media) /7/.	Dry a known amount of the sample in pre-ignited basin. Place the basin and contents in the cool muffle furnace and raise the temperature over approximately 1 h to 450°C ± 10°C. Maintain this temperature for 6 h. Allow the basin and contents to cool to room temperature in the desiccator and weigh to the nearest 0,001 g. Place the basin and contents in the muffle furnace maintained at 450°C ± 10°C for a further 1 h. Allow the basin and contents to cool to room temperature in the desiccator and weigh to the nearest 0,001 g. Repeat the operations of heating, cooling and weighing until the difference between two successive weighings is less than 0,01 g.

There is a major difference in the energy input prescribed in the two standards: At least 1 hour at 550ºC for the proposed method /4/ and at least 6 hours at 450ºC in EN 13039 /7/. Apart from the difference in energy input, EN 13039 gives attention to the time for reaching the ignition temperature. EN 13039 specifies that the temperature should be raised over approximately one hour to the given temperature of 450ºC and the 6 hours heating is explicitly counted from there, whereas for the proposed standard /4/ it is stated that the samples shall be heated in the furnace (8.2) at (550 ± 25)°C for at least 60 min – not mentioning specifically the time elapse for heating the oven to the specified 550°C.
Both standards prescribe heating until constant weight, however determined differently.

The differences of the ignition principles are outlined in Table 2.

The materials as used for the ignition experiments are described in Chapter 2 and the results of the study are given in Chapter 3.

Table 2 Ignition principles - differences

	Proposed draft standard /4/	EN 13039 (soil improvers and growing media) /7/
Ignition temperature and interval	(550 ± 25)^{o}C	(450 ± 10)^{o}C
Ignition period	at least 60 min. + 30 min. (+30 min.)	Six hours + 1 hour (+ heating until constant weight)
Description of heating of the furnace	No description	…raise the temperature over approximately 1 h
Definition of constant weight	…..differ max. 0.5% of the previous value or 2 mg, whichever is the greater	…difference between two successive weighing is less than 0,01 g.

1.2.2 Ruggedness and precision - Loss on ignition

Ruggedness to variations in temperature during the ignition period is studied for the loss on ignition method. The choice of (550 ± 25)^{o}C for the ignition of solid samples dictates that the oven temperature shall be maintained between 525^{o}C and 575^{o}C during the ignition periods. Therefore, samples were digested with temperature settings at 525^{o}C and 575^{o}C, which are the maximum variation in temperature expected upon proper use of the described method. A number of different sample types were tested.

Initial tests showed non-constant weights of more samples of compost and polluted soil samples after repeated ignition and a tendency towards identification of black particles present in the ignited samples. Note 4 of Chapter 9.2 in prEN 15169 includes a possibility to add a few drops of ammonium nitrate prior to ignition. Thus ruggedness upon addition of ammonium nitrate solution during the ignition was included in an investigation, where the same samples were tested with and without addition of ammonium nitrate.

The materials as used for the ignition experiments are described in Chapter 2 and the results of the study are given in Chapter 3.

1.3 Determination of total organic carbon

The desk study on comparison of standards for the determination of total organic carbon /5/ demonstrated that preparation of a harmonized and horizontal standard would be possible. It was proposed that EN 13137, which was developed to cover waste, sludge and sediment, should be used as the basis for a harmonized standard and that some proposed updates should be included in the text. Apart from the matrices already covered, soil was included in the scope of the draft horizontal standard. To a large extent, EN 13137 includes the principles covered in ISO 14235 (soil).

Comments received during the 1st consultation period are presented in the Annex 2. Some comments suggested that an evaluation on the use of different non-oxidising mineral acids and determination of requirements on oxidation time should be carried out. The suggestion is related to the removal of inorganic carbon in Method B (indirect methods) on addition of a non-oxidizing acid - the choices on non-oxidizing acid being phosphoric acid and hydrochloric acid.

Experience from the application of method B on solid samples is discussed in Chapter 3, as are results from a limited number of precision experiments.

2. MATERIALS

Samples (so-called playground samples) for the evaluation study were samples made available through Work package 1 and samples made available through the Eurofins proficiency test scheme. The general characteristics of the samples provided and used in the evaluation study are described in /6/ and the respective reports of interlaboratory comparisons. A list of samples is given in Table 3.

Table 3 Characterisation of playground samples

Sample id.	**Sample description**		**C_{org} wgt. %**
SO-1	Brown soil, Ispra, Italy	Ball-milled and sieved <125 µm	2,652
SO-4	Clay soil, Speyer, Germany	Ball-milled and sieved <125 µm	1,652
SO-9	Soil from Hagen, Germany	Ball-milled and sieved <125 µm	4,576
Solid-5 (2001-4), sample A	Sandy soil, Denmark	Ball-milled and sieved <2mm	
Solid-5 (2001-4), Sample B	Loamy soil, contaminated site, Denmark	Ball-milled and sieved <2mm	
Solid-9 (2003-5), sample A	Soil from soil recycling plant, Denmark	Sieved <1 mm	
Solid-9 (2003-5), sample B	Soil from soil recycling plant, Denmark	Sieved <1 mm	
CW-1	Composted garbage, Munich, Germany	Ball-milled	12,122
CW-5	Compost, Fulda, Germany	Dried	11,45
Compost – KH	Compost	Dried and sieved, 2 mm	
SL-4	Sewage sludge, domestic, Essen, Germany (= BCR 144)	Ball-milled and sieved <125 µm	29,035
SL-11	Sewage sludge, electronic industry, Turin, Italy	Ball-milled and sieved <125 µm	3,177
Solid-5 (2002-5), sample A	Municipal sludge	Crushed and sieved to <4 mm	
Solid-5 (2002-5), sample B	Municipal sludge	Crushed and sieved to <4 mm	
Solid-5 (2004-7), sample A	Municipal sludge pH 7,5 Alkalinity 1 mmol/kg	Air dried, crushed and sieved to <1 mm	
Solid-5 (2004-7), sample B	Calcium carbonate stabilized sludge pH 12 Alkalinity 10 mmol/kg	Air dried, crushed and sieved to <1 mm	

PP1995-3Marine sediment	Harbour sediment	Freeze dried, sieved <250, homogenised	
Lake Arresoe	Fresh water sediment	Air dried, sieved <250 µm	

3. EXPERIMENTS AND RESULTS

3.1 Dry matter

Dry matter was determined in a number of samples covering a broad range of matrices (as part of the evaluation of the method on loss on ignition). The samples were dried samples, some of which were well-homogenised samples from proficiency test or used as reference material. An average coefficient of variation of <1% was obtained /Annex 3 /. It must be borne in mind that the precision experiment also reflects the particle size and thus also the homogeneity of a sample. Larger variances are expected when determining dry matter on natural laboratory samples.

3.2 Loss on ignition

3.2.1 Comparison of loss on ignition at 450ºC and 550ºC

The differences in test results when using the two different test methods for the determination of LOI has been tested in a number of experiments using different available samples of soil, sediment, sludge and biowaste.

Seven samples of soil, two samples of compost, six samples of sludge and two samples of sediment have been tested by using both the method described in EN 13039:2000 (450ºC) and the method proposed in the desk study as draft horizontal standard for LOI (550ºC).

The results of the tests are given in Table 4. The difference in results obtained from using the two principles are expressed in percent based on the lowest result. For all samples, loss on ignition is, as expected, higher when using a temperature of 550ºC, than when using 450ºC. For the soil samples and sediment samples with a content of LOI lower than 100 g/kg DM, a difference between 15 and 61% is seen; for compost, sludge and sediment samples with LOI higher than 100 g/kg DM, smaller relative differences of from 2 to 13% are observed. The relatively high and varying difference seen when comparing the results for the two principles related to the samples of relatively low contents of LOI indicates that an establishment of a correlation of the two different methods may not be simple. For the samples of a higher content of LOI, the difference is smaller; however, for all the samples, the LOI is systematically higher when using the proposed method than when using EN 13039.

Sample "Solid-5 (2004-7) sample B" is a calcium carbonate stabilized sludge from a municipal wastewater treatment plant (pH of 12 and alkalinity of 10 mol/kg). Compared to the other sludge sample with a lower Ca content used in the study (and therefore with expected lower carbonate concentrations, e.g. Sample "Solid-5 (2004-7) sample C – pH 7,5 and alkalinity 1 mol/kg) these results do not support the anticipation that particularly carbonates are lost to a higher degree when using a temperature of 550ºC than when using a temperature of 450ºC.

Table 4 Results from ignition using proposed method A - 550ºC and B - 450ºC

	EN 13039:2000 450ºC	Draft horizontal standard 550ºC	Difference	Calcium content
	g/kg DM	g/kg DM	%	g/kg DM
Soil samples				
SO-1	68,9	79,1	15	12
SO-4	40,3	52,2	30	4,7
SO-9	80,7	92,4	15	13
Solid-5 (2001-4) sample A	7,13	11,3	59	1
Solid-5 (2001-4) sample B	19,8	24,1	21	0,7
Solid-9 (2003-5) sample A	9,0	14,2	58	
Solid-9 (2003-5) sample B	12,1	19,4	61	40
Compost samples				
CW-1	299	316	6	86
CW-5	271	280	3	41
Compost KH				16
Sludge samples				
Solid-5 (2002-5) sample A	607	618	2	29
Solid-5 (2002-5) sample B	497	507	2	34
Solid-5 (2004-7) sample A	588	603	3	37
Solid-5 (2004-7) sample B	313	327	4	210
SL-4	581	591	2	41
SL-11	222	248	12	59
Sediment samples				
PP1995-3Marine sediment	40,8	52,1	28	10
Lake sediment Arresoe	166	187	13	

Given the differences observed for the two temperatures, loss on ignition must be taken as a method dependent parameter. Given the absence of a simple relation between the observed results for the two method principles, it is not recommended that a choice between two temperatures be included in the standard. In other words, it is proposed that only the temperature of 550ºC be included in the horizontal standard.

3.2.2 Ruggedness and precision experiments

From the principle of the proposed method for loss on ignition, see Table 5, two issues have been selected for further investigations: temperature interval for ignition of the sample and the option of addition of ammonium nitrate. Further, it has been shown through experiments with different ovens that there is a need for specification of the heating of the oven.

Heating time

The time for heating the oven to (550 ± 25)^{o}C depends upon the dimension, isolation, heating principles and loading of the oven and needs to be evaluated and known for each oven. A temperature reduction will occur in a pre-heated oven (e.g. a temperature of (550 ± 25)^{o}C) during and after the loading of oven. Thus it is important to assure that the correct temperature is reached before starting the ignition period. It was observed in one oven that it took up to 40 minutes to reach the temperature interval of (450 ± 10)^{o}C after the crucibles had been placed in the oven pre-heated to 458^{o}C, and 65 minutes to reach a stable temperature in the interval of (550 ± 25)^{o}C after having loaded the oven pre-heated to 528^{o}C. The example illustrates the importance of controlling the temperature measurements for the oven and of controlling the actual temperature prior to starting the ignition period. This leads to a revision of the text of the draft standard, so that it is reflected clearly that the ignition period starts after heating the oven to the adequate temperature. Table 5 describes the proposed text amendment, with the proposed change indicated in bold.

Table 5 Principle – proposed method

…………..

Place a crucible (8.1) in the furnace (8.2) and heat at (550 ± 25)°C for at least 30 min. After cooling in the desiccator (8.3) to ambient temperature, weigh to the nearest 1 mg, (m_a).

Weigh into the crucible 0.5 g to 5 g of the dried sample to the nearest 1 mg, (m_b), and **raise the furnace temperature to (550 ± 25)°C and hold this temperature for at least 1 hour.** Place the hot crucible containing the residue on ignition in the desiccator and leave to cool.

After cooling in the desiccator to ambient temperature, weigh the crucible containing the dry residue to the nearest 1 mg (m_c).

The crucible is weighed immediately after removal from the desiccator and the weighing operation is completed as quickly as possible. The mass of the residue on ignition, and thus the loss on ignition, shall be regarded as constant if the mass obtained after a further half-hour period of ignition at 55°C in the pre-heated furnace ($m_c - m_a$), differs max. 0.5% of the previous value or 2 mg, whichever is the greater.

……..

Heating interval

The proposed method for the determination of loss on ignition prescribes the use of a muffle furnace or equivalent equipment, capable of maintaining a temperature of (550 ± 25)°C. Thus, samples ignited according to the standard have been maintained at minimum 525°C and maximum 575°C for the given period of time. The samples were kept at the given temperature until constant masses were achieved. The temperature difference between 525°C and 575°C is expected to account for the maximum difference to be observed, thus the observed mass differences should indicate the ruggedness of the method. The influence of the ignition temperature in the interval of (550 ± 25)°C was studied in a number of ignition tests. All experiments were carried out in triplicate.

The results of the analyses are given in Annex 4. It is calculated from the results that a coefficient of variation of 4% can be attributed to the maximum fluctuation in temperature in the range of 525°C to 575°C specified in the proposed standard. The average difference in results, when comparing the two temperatures, is 3%. Provided that the temperature setting is the major difference, when more laboratories analyse the same sample, a coefficient of variance (attributable to laboratory variations) of less than 4% is expected in validation studies of similar samples. Repeatability is calculated to an average of 2% for the samples analysed (Annex 4).

Addition of ammonium nitrate

The ruggedness shown in results after the addition of an ammonium nitrate solution during the ignition has been studied in a number of tests, where results after the addition of ammonium nitrate have been compared with results of LOI without any addition of ammonium nitrate. Results of LOI on duplicate samples without any addition of ammonium nitrate were compared to results of LOI on the same sample after addition of ammonium nitrate. The results are given in Table 6. The experiments were carried out both using the ignition principle at 450°C and 550°C and on samples where black particles were not left over after ignition.

For two soil samples (soil from recycling plant – oil contamination), for one compost sample (garden compost) and possibly for one sludge sample, higher loss on ignition results were observed when adding ammonium nitrate to the test sample. For the other samples, no significant difference was observed.

Table 6 Difference in LOI (%) after addition of ammonium nitrate compared to no addition of ammonium nitrate.

	EN 13039:2000 450°C	Draft horizontal standard 550°C
	%	%
Soil samples		
SO-1	+ 3	+ 2
SO-4	- 0,5	- 0,5
SO-9	- 1,3	+ 1,4
Solid-9 (2003-5) sample A	+ 40	+ 15
Solid-9 (2003-5) sample B	+ 21	+ 17
Compost samples		
CW-1	- 1,3	- 1,4
CW-5	+ 0,0	- 0,4
Compost KH	+ 0,6	+ 11
Sludge samples		
SL-4	+ 0,2	+ 1
SL-11	+ 2,4	- 0,6

The results indicate higher ignition efficiency. For the compost sample a difference is only seen for the 550°C ignited samples, and for the sludge sample the difference is only seen for the 450°C ignited samples.

The results of samples (all without the presence of black particles left after ignition) indicate that an addition of ammonium nitrate may enhance ignition efficiency at the given temperature of some samples, even though visible black particles are not present, and that other samples are left with a relatively unchanged loss on ignition. An option of adding ammonium nitrate is amended in the draft standard to be applied only for samples were black participles are left after ignition (as is given in prEN 15169). It is recommended that LOI determined both with and without the addition of ammonium nitrate be quoted in the report for those samples to indicate the relative importance of the slow-burnt material in the sample.

3.3 Total organic carbon

Numerous validation data on the use of method B of the proposed method for different solid samples are presented in an annex to EN 13137. Relative reproducibility standard deviations are quoted as 6 - 26% for Method B and 9 – 24% for Method A. For Method B three out of six samples in the interlaboratory study achieved relative reproducibility standard deviations over 20%. In other words, the results from two participating laboratories for those samples may be expected to deviate between 50 and 60% from each other. The results obtained for Method A are slightly better, where only one sample obtained relative standard deviations between laboratories of more than 20%. The relative repeatability standard deviation is estimated to 2 – 5% for method A and 3 – 6% for method B. The difference of the repeatability and reproducibility standard deviation can possibly be explained by the fact that the description of the procedures opens for variations in the actual procedure and instrument variations. Thus, the results indicate that the individual laboratories can repeat the analyses by using the practical principles and the instrumentation; however, the reproducibility among laboratories indicates a need for improvements.

Practical experiments within this study, by using instrumentation that fulfils the specification in the standard, have shown that the acid used for removal of inorganic carbon must be added very slowly, i.e. dropwise, or the sample will foam. The identification of when enough acid has been added may be individual. The manual addition of acid to samples containing high carbonate concentrations was very difficult with the equipment and crucibles used in this study, due to excess foaming. A note in Clause 5.3 of EN 13137 reads: “The quality of results of Method B is more dependent on experience and practice, especially regarding the steps before combustion”. It is further written, that in case of doubt about the comparability between method A and method B, method A should be preferred.

One laboratory has reported success from using an automatic dispensing unit for the addition of acid. Increments of 50 µl hydrochloric acid diluted 1:10 is added 12 timers per 10 – 25 mg sample. To instruct users in the practical complications, a note on the use of an automatic dispensing unit is amended.

The lack of a specification of the min. sample size may be a major course of deviations. Most commercial instruments allow sample sizes less than 3 g, some describe sample sizes about 0,5 g. In the given case, a loading of 0,2 g of sample were used in crucibles that could hold 0,5 g. Extra space is needed in the crucibles for the addition of drops of acids and for any foaming that may occur. Experiments with the given instrument and given samples showed that only a maximum of 0,05 g and 0,1 g of sample could be handled successfully without excessive foaming.

After addition of phosphorous acid the drying of the sample is extremely slow. A comment was given during the consultation period that the time for removal of carbon dioxide was too long – 4 hours. For samples soaked in acid, the time for removal of the excess acid is longer than 4 hours, even if elevated temperatures of about 40ºC is used. More than 24 hours were used for removal of drop wise addition of phosphorous acid from a number of solid samples.

Results from application of method B on a certified reference material (Eurosoil 2) is given in Annex 6. The results are selected from a number of experiments where the majority was not accepted due to excess foaming of the sample compared to the size of the vessel or due to lack of drying within an acceptable period of time.

4. PROPOSAL FOR CHANGES TO THE DRAFT HORIZONTAL STANDARD

4.1 Dry matter and water content

The present draft standard includes waste in the scope. A horizontal standard that includes all the matrices sludge, sediment, soil, soil improvers and growing media and waste will be a major advantage, especially for the users of standards. It will be an advantage to laboratories – both technically and economically - to have to validate, maintain and accredit only one single method for dry matter covering all possible solid matrices.

References to e.g. standards on sampling and pre-treatment are to be included in accordance with the decisions made on scope and will have to await the draft standard on pre-treatment.

The revised draft standard has been set up according to the guide for writing standards/Horizontal. Table 7 gives an overview of the major changed compared to the 1st draft standard (1st consultation).

Table 7 Overview of major revisions from the 1st draft - Dry mater and water content

2nd draft horizontal standard	**Revision from 1st draft standard**	**Comments**
Front page, foreword and introduction	Changed according to general set-up of Horizontal Standards	Subject to changes due to general set-up of horizontal standards
1. Scope	“All types of soil samples” were changed to “All types of air-dried soil samples and field moist soil samples.” Soil improvers and growing media included.	
2. Normative references		Subject to changes due to provision of reference numbers etc.
9. Procedure Note 1	Amended:… To assure a representative sample a larger test portion may be needed for e.g. composted bark samples. For air-dried soil samples 10 – 15 g are suitable.	
10.1 Quality control	Amended: At least one duplicate analysis should be carried out in each batch of analyses.	
10.3 Precision data	Deleted: The repeatability of separate duplicate determinations shall satisfy the conditions given in Annex A for similar sample types. Amended: Results obtained from duplicate analyses shall be quoted in the test report.	Repeatability for DM depends largely on the homogeneity of the sample, thus comparability to samples used in proficiency test cannot be expected fulfilled always.

4.2 Loss on ignition

The present chapter describes proposals for changes of the draft standard on loss on ignition. The proposed changes are results of the conclusions drawn on the basis of the evaluation study as described in the previous chapter and comments of the draft standard as received from interested parties during the 1st consultation round. Comments received during the 1st consultation round are included in Annex 2.

In February 2005 a draft standard prEN 15169 was submitted from TC 292 prepared on an earlier working draft prepared by TC 292. The latter was discussed in the desk study report /1/. The prEN 15169 as well as the working draft include the matrices waste, sludge and sediments. Seen from a laboratory user point of view, a harmonization of standards covering more fields of analyses is to be preferred to the extent that it is possible. Only few differences exit. One important difference between the 1st draft horizontal standard /4/ and the standard proposed for waste (prEN 15169) is that waste with high content of volatile substances was not included in the 1st draft horizontal standard. As an interest towards including all relevant matrices is identified, waste with high content of volatile is included in the text of the 2nd draft horizontal standard. The scope of the standard is a main issue for discussion and clarification during the second consultation, after which the scope of the standard will be revised/amended accordingly.

Table 8 presents an overview of changes to the draft standard, with a view to underline the technical differences of the existing standards on the determination of LOI in sludge (EN 12879), soil improvers and growing media (EN 13039) and waste (prEN 15169). On LOI the desk study report /1/ concluded that a harmonised and horizontal standard for sediment, sludge, soil, and waste could be produced. The horizontal standard can possibly replace the standard for sludge (EN 12879:2000). Given the temperature proposed (550 ± 25)ºC, it cannot replace the EN 13040:1999, Soil improvers and growing media – Determination of organic matter content and ash, which prescribe a temperature of 450ºC. With the amendment of a special section for waste of high content of volatile substances (apart from water) it is technically identical with the proposed prEN 15169 for waste.

As the evaluation study revealed, larger differences in results depending on the applied temperature and as no clear identification of any relationship is seen, it is not recommend that two arbitrary temperatures be included in one standard. A choice was made for the temperature of 550ºC in the horizontal standard.

Table 8 Overview of major revisions from the 1st draft - Loss on ignition.

2nd draft horizontal standard	Revision from 1st draft standard	Comments
Front page, foreword and introduction	Changed according to general set-up of Horizontal Standards	Subject to changes due to general set-up of horizontal standards
1. Scope	Waste with high content of volatile substances are included	
2. Normative references		Subject to changes due to provision of reference numbers etc.
3.2 Residue of ignition	Rewording/clarification	
3.5 Constant mass	Rewording/clarification Note 2 moved to section 9.1, Note 3	
4. Safety remarks	Rewording	
5. Principles	The following sentence is added: “The determination is performed on a dried sample or directly on the un-dried sample including a drying step or by referring to the dry matter”.	

6. Interferences	The following sentence is added: “It should be noted that elementary carbon in the sample will be included in the loss on ignition value. Furthermore, any volatilisation or chemical reaction of inorganic compounds will also be included in the loss on ignition value”	
7.1 Flat bottom crucible (50 to 70) mm	Changed to: Crucible typically 50 to 70 mm in diameter….	
8. Sampling		Subject to changes depending on standard on pre-sampling and pre-treatment.
9. Procedure 1st chapter	Rewording	
9. Procedure 2nd chapter	Technical change for practical reasons: Initial cooling on metal plate included: ……..Transfer the crucible from the furnace after initial cooling on a metal plate to a desiccator and finish cooling to ambient temperature. Weigh the empty ……………..	
9. Procedure 3rd chapter	Rewording Emphasis on correct temperature during the whole period of ignition: Weigh into the crucible 0.5 g to 5 g of the dried sample to the nearest 1 mg, (m_b), and **raise the furnace temperature to (550 ± 25)^{o}C and hold this temperature for at least 1 hour.**	
9. Procedure 4th chapter	Note 1. A sequential heating procedure is included for certain waste types.	
9. Procedure 5th chapter	Note 2 inserted: Note 2 If the sample contains higher amounts of moisture, insert the crucible in a cold furnace and raise the furnace temperature to (550 ± 25)^{o}C over a period of 1 hour.	
9. Procedure 6th and 7th chapter	Technical change for practical reasons: Initial cooling on metal plate included as above: Place the hot crucible containing the residue on ignition on a metal plate) for a few minutes. While still warm, transfer the crucible to a desiccator and leave to cool to ambient temperature. As soon as ambient temperature is reached, weigh the crucible containing the dry residue to the nearest 1 mg (m_c).	
9. Procedure Note 3	Note 2 Usually, ignition for 2 h is sufficient for most soils, sludge, and waste samples, but certain sample types and large samples require longer drying periods. In cases when even after the third ignition period constant mass is not obtained, record the value determined in the last of the three measurements. The lack of constant mass should be reported together with the result.	
9. Procedure Note 4	Option for addition of ammonium nitrate to samples with black particles still present	

4.3 Total organic carbon

Table 9 presents an overview of proposed changes to the second draft standard compared to the earlier version. Based on experience, it is recommended that the complications by using Method B (Direct method) be described more specifically and underlined.

References to e.g. standards on sampling and pre-treatment are to be included in according with the decisions made on scope and will have to await the draft standard on pre-treatment.

The revised draft standard has been set up according to the guide for writing horizontal standards.

Table 9 Overview of major revisions from the 1st draft - Total organic carbon

2nd draft horizontal standard	Revision from 1st draft standard	Comments
Front page, foreword and introduction	Changed according to “Guidelines for writing Standards”	Subject to further changes due to general set-up of horizontal standards
1. Scope	Interference from natural or non-natural compounds moved to interferences, except elementary carbon, which is mentioned in the scope as well as under interferences.	
2. Normative references		Subject to changes due to provision of reference numbers etc.
3. Terms and def.	“…according to this standard” is amended to the definitions. The note is removed.	
5.1 Method A	Amendment of alternative method for determination of carbonate for soil samples.	According to AFNOR comments on desk study
5.3 Applicability	Comparability of method A and B is not fully proved from results in annexes. Sentence removed. The Note is converted to standard text Use of automatic dispensing equipment amended.	
6 Interferences	Text on interferences removed from “Scope”.	
8.5 Boats and crucibles	Tin deleted. A note is amended: Note: Tin and nickel crucibles are not acid-resistant.	Tin is corroded by addition of HCl
10.1.1 General	Requirement on duplicate measurements removed.	Decision on quality requirement is not part of the standard
10.3 Control measurements	-the use of modifiers is amended	
11.1.1	Requirement on duplicate measurements removed.	

REFERENCES

1. Jensen V & K.J.Andersen. “Desk study on dry matter and loss on ignition” January 2004. www.ecn.nl/horizontal.
2. Jensen V, K.J.Andersen & m. Krysell. Desk study on total organic carbon (TOC) January 2004. www.ecn.nl/horizontal
3. Solid material – Determination of dry matter and water content on a mass basis in sediment, sludge, soil, and waste – Gravimetric method. Draft January 2004. www.ecn.nl/horizontal.
4. Solid material – Determination of loss on ignition in sediment, sludge, soil, and waste – Gravimetric method. Draft January 2004. . www.ecn.nl/horizontal.
5. Solid material - Determination of total organic carbon (TOC) in soil, sludge, sediments, and waste. Draft June 2004. www.ecn.nl/horizontal
6. Gawlik, B.M., F. Bo, F. Sena, L. Roncari, G. Locoro & R. Vivian: Characterisation of “Playground” samples to be used in the context of Project “Horizontal”. Part 1: Inorganic parameters. SWCR-Report No 03/07/2004.
7. EN 13039 (soil improvers and growing media)

ANNEX 1 METHODS AND PRINCIPLES

Dry matter and water content on a mass basis

Number	Title	Sample material	Principle
EN 12880 2000	**Characterization of sludge** – Determination of dry residue and water content	Sludge and sludge products	Sludge samples are dried to constant mass at (105 ± 5)°C. The difference in mass before and after drying is used to calculate the dry matter.
ISO 11465 1993	**Soil quality** – Determination of dry matter and water content on a mass basis – Gravimetric methods	Air-dried soil samples and field-moist soil samples	Soil samples are dried to constant mass at (105 ± 5)°C. The difference in mass before and after drying is used to calculate the dry matter.
PrEN 14346 2004	**Characterization of waste** – Calculation of dry matter by determination of dry residue or water content	Waste	Method A: The waste sample is dried to constant mass at (105 ± 5)°C. The difference in mass before and after drying is used to calculate the dry matter. For samples containing significant amount of volatile components, the dry matter cannot be determined as dry residue. In this case the dry matter is calculated from the water content.
EN 13040 1999	**Soil improvers and growing media** – Sample preparation for chemical and physical tests, determination of dry matter content, moisture content and laboratory compacted bulk density	Soil improvers and growing media	Samples are dried to constant mass at (103 ± 2)°C. The difference in mass before and after drying is used to calculate the dry matter.
DS 204 SFS 3008, NS 4764, and SS 028113	Determination of total residue and total fixed residue in **water, sludge and sediment**	Water, sludge and sediment	Sludge and sediment samples are dried for approx. 20 hours at (105 ± 3)°C. The difference in mass before and after drying is used to calculate the dry matter.

Loss on ignition (LOI)

Number	**Title**	**Scope, sample material**	**Principle**
EN 12879 2000	**Characterization of sludge** – Determination of loss on ignition of dry mass	Sludge and sludge products	Samples of dried sludge are heated in a furnace at (550 ± 25)°C. The difference in mass before and after the ignition process is used to calculate the loss on ignition.
3. draft standard (May 2002) Prepared in co-operation between CEN/TC 292 and CEN/TC 308	**Characterization of waste, sludge and sediments** – Determination of loss on ignition	Waste, sludge, and sediment	A test portion is heated in a furnace up to (550 ± 25)°C. The difference in mass before and after the heating process is used to calculate the loss on ignition.
EN 13039 2000	**Soil improvers and growing media** – Determination of organic matter and ash	Soil improvers and growing media	The test portion - dried at 103°C - is heated in a furnace at (450 ± 10)°C. The ash is determined as the residue on ignition. The organic matter is taken to be the loss of mass on ignition. Both are expressed as a percentage by mass of the dried sample.
DS 204 SFS 3008 NS 4764 SS 028113	Determination of dry matter and loss on ignition in **water, sludge and sediment**	Water, sludge, and sediment	Samples of dried matter are heated in a furnace at (550 ± 25)°C for 2 hours. The difference in mass before and after the ignition is used to calculate the loss on ignition.

Total organic carbon (TOC)

Number	**Title**	**Scope, sample material**	**Principle**
ISO 10694:1995	Soil quality – Determination of organic and total carbon after dry combustion (elementary analysis)	All types of air dried soil samples	The carbon is oxidised to CO_2 by heating the soil to at least 900°C in a flow of oxygen-containing gas. The amount of CO_2 released is then measured by titrimetry, gravimetry, conductometry, gas chromatography or using an infrared detection method, depending on the apparatus used.
ISO 14235:1998	Soil quality – Determination of organic carbon by sulfochromic oxidation	All types of air dried soil samples	The organic carbon is oxidised in a mixture of potassium dichromate solution and sulphuric acid at a temperature of 135 °C. The dichromate ions are reduced to Cr^{3+}. The intensity of the green colour is measured by spectrophotometry. As the oxidation of one carbon atom of the organic matter procedures four electrons, there is a direct relationship between the Cr^{3+} and the organic carbon. The method is calibrated using glucose.
EN 1484:1997	Water analysis – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)	Drinking water Ground water Surface water Sea water Waste water	Oxidation of organic carbon in water to carbon dioxide by combustion, by addition of an appropriate oxidant, by UV-radiation or any other high-energy radiation. Inorganic carbon is removed by acidification and purging, or is determined separately. The carbon dioxide formed by oxidation is determined either directly or after reduction. The final determination of carbon dioxide is carried out by a number of different procedures, for example: infrared spectrophotometry, titration, thermal conductivity, conductometry, coulometry, carbon dioxide-sensitive sensors and flame ionisation detection.
ISO 8245:1999	Water quality – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)	Drinking water Ground water Surface water Sea water Waste water	Oxidation of organic carbon in water to carbon dioxide by combustion, by addition of an appropriate oxidant, by UV-radiation or any other high-energy radiation. The carbon dioxide formed is determined either directly or after reduction. The final determination of carbon dioxide is carried out by a number of different procedures, for example: infrared spectrophotometry, titration, thermal conductivity, conductometry, coulometry, carbon dioxide-sensitive sensors and flame ionisation detection. Inorganic carbon is removed by acidification and purging, or is determined separately.
EN 13137: 2001	Characterization of waste - Determination of total organic carbon (TOC) in waste, sludge and sediments	Waste, sludge, sediments and comparable materials.	Method A (indirect procedure): The total organic carbon (TOC) is obtained by the difference between the results of the measurements of total carbon (TC) and total inorganic carbon (TIC). TC is converted to carbon dioxide by combustion in an oxygen-containing gas flow free of carbon dioxide. The released amount of carbon dioxide is measured by infrared spectrometry, gravimetry, coulometry, conductometry, thermal conductivity

Number	Title	Scope, sample material	Principle
			detection, flame ionisation detection after reduction to methane, or other suitable techniques. The TIC is determined separately from another sub-sample by means of acidification and purging of the released carbon dioxide. Method B (direct procedure): In this procedure the carbonates present in the un-dried sample are previously removed by treating the sample with acid. The carbon dioxide released by the following step is measured by one of the techniques mentioned under Method A and indicates the TOC directly.

ANNEX 2 1ST CONSULTATION ROUND, COMMENTS AND SUGGESTIONS

Horizontal project no 17-1 - Dry matter (DM)

Comments from NSB	General comment/proposal	Technical comment/ proposal	Proposal from the project
ON-Austria		Only water vapour is mentioned as an important volatile element. Others are missing.	Mentioned in section 5
	This study is only based on standards published in the field of sludge. Some considerations on waste have been added. Nevertheless, the pre-treatment of the sample is still missing.		The desk study as well as the draft proposal has taken existing standards on sludge, soil, waste soil improvers and growing media into consideration. Reference to standard on sample preparation is included in the draft standard.
	It seems that an approach by decision table by matrix is not suitable because there are too much significant differences.		The final standard will be worked out according to the instructions regarding writing of standards.
AFNOR		The draft standards are not relevant for pre-treated samples. We propose to include the determination of dry matter and loss on ignition on pre-treated and partially dried samples in agreement with the ISO standard 11464 (air dried soil samples) or with ISO/DIS 16720 (freeze drying of sludge, soil and sediment samples). For LOI the correct value is then calculated taking into account the residual humidity.	Option of using the standard for partially dried samples - be considered.
	The choice for a single temperature (105 °C) seems pertinent. This for sludge, growing media, soil improvers, soils and wastes. We need to keep mass for DM essays (50 g). We need to keep the names "growing media" and "soil improvers". In France these two names are used for two		General remark – GM and SI included

	different uses. The choice for a possible discard of 5 °C is pertinent. These parameters are the same than the French method on dry matters (NF U44-171) for growing media and soil improvers. Conclusion: we agree on the desk study except for the use of the name « biowaste ». We request the use of the actual names: growing media and soil improvers		
DIN mirror committee	The title and the scope of the DM/draft standard need to be clearly defined. SI and GM are not included. If sludge, soil, and biowaste are to be considered as SI and GM constituents, then SI and GM themselves should be tested in the same way acc sto the same standard.	If the study is the basis for a harmonized standard which is supposed to include SI and GM, then the title should be changed accordingly	
	Once harmonization is sought and found on defining the terms dry matter and loss on ignition, and on the temperatures used (one temp for) DM and one temperature for LOI in the 3 methods compared, it should be possible to come up with a standard valid for all product groups, including SI and GM.		
Comments representing/collated by			
CEN/TC292 WG5	Supports the approach to have one harmonised standard for dry matter.		-
	Suggests taking prEN 14346 as the basis of the paper.		To a large extend fulfilled
	Understood that the materials covered do not need method B (water content, liquid waste), nevertheless this method should be part of the harmonized doc to result in a real horizontal doc. It should be possible to make clear that the method B only refers to waste		If samples for validation are secured, the authors are willing to include section B in next draft.
		The temp range should vary by max 3°C to exclude a temperature of 100°C	Point taken – plus/minus 3°C implies higher technical demands for drying oven. Plus/minus 5°C is in accordance to ISO 11465 and EN 12880 and prEN 14346.
		Storage at room temperature must be	EN 12880 (sludge) require 0 – 4 °C

		possible	
		Agreement about equipment	-
	General hazards shall be added as informative part (introduction)		According to standard writers instructions
	A table of requirements and recommendations as having been presented by WG5 at a 2nd brainstorming meeting of TC 292 shall be prepared		The comment is not specific for standard on DM
CEN/TC 223		Table 2 dry matter: It is better to have the lower temperature just above 100ºC to ensure loss of moisture A range of 10ºC appears to be excessive, a 2 or 3ºC is readily achievable with modern ovens and is recommended.	
		3.1. equipment The weight taken for dry matter must reflect the sample type, e.g. composted bark may require 500 g to be representative.	
		Table 3 There is no precision data for EN13040:1999 The data in EN 13040 is moisture so dry matter can readily be obtained	
		There appears to be information missing under EN 13039:2000 procedure	
		4.1 Do not see the need for such a wide temperature range as 105±5ºC	
		4.1 the equipment needs to reflect the sample type	
		Drying time – 4.1 It may be better to prepare a suggested table of drying time for the various samples under test.	
		4.2	

		Whilst the loss of carbonates is noted the writer continuous to use the higher temperature.	
		Draft methods Note that SI/GM not included in the title If SI/GM not included the existing TCF 223 methods remain. If SI/GM to be included then the comments above need to be taken into account.	
Susanne Westborg, dk-TEKNIK, Denmark, representing S-284		Proposal of alteration of text cl 1: This standard specifies a method for determination of the dry matter and the water content of samples for which the results of performed analysis are to be calculated to a dry matter basis	Not accepted
		Text cl 1. For samples of heterogeneous and coarse waste materials also a test portion resulting in a mass of dry matter less than 0,5 g is completely insufficient	Point to be considered. Text is equivalent to prEN14346 (waste)
		Text cl 1. A statement that sample preparation is not included in the standard should be included	Reference to standard on sample preparation is included in the draft standard.
		Text cl 1. A statement that DM determination is to be determined on identical portions of the sample as used for determination of parameters that relates to DM	Accepted as a note.
		Text cl. 4 and 5. Mention the possibility of drying in an inert atmosphere (materials susceptible to oxidation or alkaline materials)	Not accepted.
		Text cl. 5. Delete note 2 as it is not relevant.	?
		Text cl. 6. Consider storage time for samples (biological activity)	Is already included
		Text cl. 9. Reword the text, inclusive the	Related to pre-treatment of samples

		problem concerning the size of the test portion in relation to the particle size of the material	
		Reconsider particle size and amount of test sample	Relates to pre-treatment of samples
		Specify loading of crucible in min. bottom area or as g/cm2	Requirement not fulfilled, so far. If mentioned a method for control of loading must be included as well

Horizontal project no 17-1 - Loss o n ignition (LOI)

Comments from NSB	**General comment/proposal**	**Technical comment/ proposal**	**Proposal from the project leader**
AFNOR		The described way to determine loss on ignition on samples containing high levels of volatile compounds is inadequate and dangerous. We cannot accept it without a relevant pre-treatment of the sample.	Included according to procedure of TC 292
AFNOR, mirror com of 223	The choice for a single temperature (105°C) seem pertinent This for sludge, growing media, soil improvers, soils and waste We need to keep mass for DM essays (50 g). We need to keep the names "growing media" and "soil improvers". In France these two names are used for two different uses. The choice for a possible discard for 5 °C is pertinent. These parameters are the same than the French method on dry matter (NF U44-171) for growing media and soil improvers. Conclusion: We agree on the desk study except for the use of the name "biowaste". We request the use of the actual names: growing media and soil improvers		General question
Comments representing/collated by technical committees			
AFNOR, mirror com of 223	We agree on the document on loss of ignition But we propose to do some researches for the same temperature, 550 °C, for soil improvers, growing media, soils, and sludge. This because we can find the principal interferents (carbonates, oxides) in all the product of the study. Conclusion: we can try to have two different temperatures 450 °C for soil improvers and growing media and 550		It is proposed to investigate the differences between the two temperatures before a harmonisation of temperature takes place

	°C for other products. But we can try 550 °C for all products.		
CSNI, Czech republic (via TC345)	Documents concerning determination of loss on ignition are of a good quality and this horizontal project should be successful		-
CEN/TC292 WG5	The method on waste is unfortunately not mentioned even through it is prepared with CEN/TC 308		Is mentioned, Table 2 – Desk study
		It should be defined whether the dried or original sample should be analysed	Included
		An ignition temperature of 550 °C is preferred	550 °C is proposed
		Nickel crucibles should be added	Accepted
		General hazards shall be added as informative part (introduction)	To be in accordance to standard writers instructions
CEN/TC 223		Table 2 Loss on ignition: EN 13039 refers to “organic matter” and not “loss on ignition”. The lower temperature was chosen to reduce losses of other materials than organic matter. ISO 10694:1995 “Determination of organic matter and total carbon after dry combustion” use a temperature of 900ºC. consideration must be given as to what information the method is intended to provide.	
Susanne Westborg, Denmark		Text cl ?. Include sample preparation or specification of the max. particle size of the test portion	Reference to standard on sample preparation given
		Text cl 4. Include both alternatives to carry out LOI on dried and non-dried samples	To be considered
		Text cl. 6. Text cl. 6. Consider storage time for samples (biological activity)	Is considered already
		Text cl. 9.1. Reword the text, including the problem concerning particle size of the test	The proposal is a result of harmonisation of existing standards
		Text cl. 9.1 and 9.2. Prefer at least 2 hours of heating	Same
		Text cl. 10.1. Formula 1 is only valid if LOI is	To be considered

		carried out in same crucible as DM. Include formula for other alternatives.	
		Text cl. 11. Consider other sample materials than sludge	Editorial error
		Reconsider particle size and amount of test sample	To be considered along with the discussion to included waste in the standard

Horizontal project no 17-2 - Total organic carbon (TOC)

Comments from NSB	General comment/proposal	Technical comments/ proposals	Proposal from the project leader
ON (Austria)	Endorsement (largely) of the recommendations for the next phase of this part of the work		-
NEN (NL)	Endorsement (largely) of the recommendations for the next phase of this part of the work	Principles and procedures. Phosphoric acid is preferred, possible diluted 1:1 because of the handling of conc. acid is more difficult (phosphoric acid is pref due to corrosion by HCL)	Accepted as an improvement of the existing standard –given as recommendation.
		Sample prep. Stirring of the sample could be mentioned to shorten the time necessary for removal of inorganic carbon	Accepted as an improvement of the existing standards –given as a recommendation
		Calibration Add oxalic acid and EDTA (acid form). The latter eventually also for measurement of total nitrogen in combination with carbon	Not accepted. EDTA is used as control substance (10.4). The standard already opens for other substances (10.4)
AFNOR		a. Even if a horizontal standard already exists for sludge and waste on which this study is based, it seems that information on test sample are missing. b.In addition, the sulfochromic method has been eliminated without justification. c.The pre-treatment of the sample is not sufficiently described.	a. The text was not ijntended taken out of the present draft horizontal standard b Sulfochromic acid method has only been identified for soil and thus may be less relevant (as compared to the other principle) as a horizontal standard and sulfochromic acid is hazardous compared to chemical used in selected method/principle. c. No, reference to pre-treatment standard is given – awaits the horizontal standard for pre-treatment
AFNOR	We agree that dry combustion could be used as a harmonized method for the determination of TOC. However this method have serious limits in soils: - In often gives an overestimation of organic carbon as "elementary		The choice was made for continuing development of the already existing harmonized standard. Remark on interferences from e.g. elemental carbon was removed from the scope to section on interferences.

	carbon” is measured as organic carbon. This interference cannot be avoided. As “elementary carbon”, we consider, for instance, charcoal, which is very common in cultivated and forest soils, and also coal which is very common in garden, urban or industrial soils. - It often gives an overestimation of organic carbon in carbonated soils and particularly in dolomitic soils, as the technique used to destroy carbonates is not always efficient. - It needs an expensive apparatus, which not all good laboratories can buy. Therefore, we consider unacceptable that the used of sulfochromic oxidation was not to taken into account by the desk study. This method is cheap and very robust. It gives very reproducible results, which suffer less interference than the dry combustion. The potassium dichromate can be handled securely as the method can be automated and miniaturized. The desk study does not consider the possible measurement of total carbonates as an alternative to carbonate destruction.		
AFNOR	The sulfochromic method (ISO 14235) is not retained in this draft standard, for safety reasons. It is really a pity because this method is very robust, cheap and gives very reproducible results, which suffer less interference than dry		Agree – calculation of TOC from TC and subtracting inorganic carbon measured with ISO 10693 is included as a recommendationf for dolomite and dolomitic limestone soil.s.

	combustion. The safety reasons may get a solution in miniaturization and in the automation of the different steps of the manipulation. Therefore we do not agree to that removal. The described method, dry combustion, is applicable to each material, (soil, sludge, sediment, etc.), but in the case of dolomitic soils, TIC determination by means of method A is highly expected to fail because of the slow kinetic of MgCO$_3$ destruction. Especially for soils, we recommend to keep the possibility of using the calculation method described in standard ISO 10694, where total inorganic carbon is measured separately by volumetric method (ISO 10693). ver, the dry combustion method cannot distinguish organic carbon and fossil carbon. This must be in the scope of the method, because in the case of aterials as composts or soils containing charcoal, al carbon may be at significant levels. size characteristics of the test sample for carbon ogen determinations by means of dry combustion the same.		
Comments from technical com.			
CEN/TC292 WG5	The experts of WG5 support the use of EN 13137 as the basis of a harmonized document		-
	Normative references shall be added		Accepted (as also stated in Table 3 of desk study)
	A table of requirements and recommendations as having been presented by WG5 at a 2nd brainstorming meeting of TC 292 shall be prepared		The comment is not specific for the TOC standard.
		General hazards shall be added as informative part (introduction)	Action dependent on general decision
		Air drying only applies to soil	Accepted, air-drying to be included in 10.1

		Hydrochloric acid should be substituted by phosphoric acid	Accepted - added as recommendation
		A reaction time of 4 h for method B is considered as too long	Subject to consideration during next phase
		There is agreement regarding additional control charts and calibration substances	-
		If the harmonized method will not deviate too much from EN 13137 re-validation for waste and sludge is not required. The validation of additional materials covered by the scope of Horizontal should be funded by Horizontal	No change. Sample types for which no validation data exist (or is not representative for modern equipment) should be included in validation, as stated in the desk study report

ANNEX 3 REPEATABILITY - DRY MATTER

	DM	DM	Average n =6	Standarddeviation n =6	CV %	
SO-1 - soil	977,21	977,44	976,91	0,47	0,05	
	976,56	976,77				
	977,26	976,24				
SO-9 - soil	974,55	975,58	975,51	0,72	0,07	
	975,18	975,12				
	976,54	976,07				
CW-1 - sludge	953,89	952,05	954,15	1,62	0,17	
	953,96	954,16				
	957,06	953,78				
CW-5 - sludge	942,82	940,77	941,39	0,89	0,09	
	942,06	941,17				
	940,41	941,13				
SL-11 - sediment	883,51	879,85	880,62	2,18	0,25	
	880,54	876,95				
	881,28	881,62				
Lake sediment Arresø	978,38	974,66	976,12	1,27	0,13	
	976,47	975,32				
	975,94	975,96				
Compost KH	980,65	978,78	979,08	1,22	0,12	
	980,09	979,16				
	977,17	978,59				
Lab control sample	992,48	991,09	991,70	0,58	0,06	
	991,61	991,60				
				Average CV	**0,12**	**%**

ANNEX 4 LOSS ON IGNITION - ROBUSTNESS TO TEMPERATURE RANGE SPECIFIED IN PROPOSED STANDARD

		575				525			Maximum uncertainty temperature 525 to 575		
% Loss on ignition	DM	% Loss on ignition			DM	% Loss on ignition			Range/LOI 2 H	Range %	Average/LOI
		1 hour	1,5 hours	2 hours		1 hour	1,5 hours	2 hours			
SO-1 - soil	977,01	7,89	8,00	8,07	976,82	7,44	7,81	7,83	0,245	3,08	7,95
SO-9 - soil	975,42	9,08	9,32	9,37	975,59	8,55	8,96	9,08	0,292	3,17	9,23
CW-1 - sludge	954,97	28,56	32,92	33,35	953,33	29,91	31,72	32,00	1,346	4,12	32,68
CW-5 - sludge	941,76	25,23	27,34	28,75	941,03	24,22	28,19	28,35	0,404	1,41	28,55
SL-11 - sediment	881,77	25,78	25,96	26,11	879,47	24,27	24,54	24,65	1,458	5,75	25,38
Lake sediment Arresø 150703	976,93	15,73	17,23	17,48	975,31	15,85	17,45	17,58	0,094	3,21	17,53
Compost KH	979,31	10,10	11,24	11,29	978,84	8,84	10,81	10,86	0,426	3,85	11,07
Lab control sample	992,05	4,22	4,26	4,27	991,35	3,96	4,12	4,15	0,125	2,97	4,21
									Average range	**3,4 %**	
									CV	**3,9 %**	

ANNEX 5 PRECISION - REPEATABILITY - LOSS ON IGNITION

	Dry matter	575 % Loss on ignition			Standarddeviation (%) on LOI 575			Average (%) on LOI 575			Cofficient of variation (%)		
		1 hour	1,5 hours	2 hours	1 hour	1,5 hours	2 hours	1 hour	1,5 hours	2 hours	1 hour	1,5 hours	2 hours
SO-1 - soil	977,21	7,898	7,984	8,099	0,074	0,045	0,048	7,887	7,996	8,073	0,939	0,560	0,599
	976,56	7,956	8,046	8,102									
	977,26	7,809	7,959	8,017									
SO-9 - soil	974,55	9,204	9,387	9,406	0,105	0,088	0,124	9,083	9,324	9,374	1,158	0,941	1,318
	975,18	9,024	9,224	9,237									
	976,54	9,021	9,362	9,478									
CW-1 - sludge	953,89	26,03	32,55	33,16	3,982	0,695	0,667	28,564	32,916	33,350	13,941	2,110	2,001
	953,96	26,51	32,49	32,80									
	957,06	33,15	33,72	34,09									
CW-5 - sludge	942,82	27,92	28,94	29,11	4,228	2,617	0,403	25,230	27,342	28,749	16,756	9,572	1,402
	942,06	27,41	28,77	28,82									
	940,41	20,36	24,32	28,31									
SL-11 - sediment	883,51	25,81	26,14	26,32	0,867	0,921	0,910	25,782	25,965	26,106	3,364	3,546	3,485
	880,54	26,63	26,79	26,89									
	881,28	24,90	24,97	25,11									
Lake sediment Arresø 150703	978,38	16,00	17,49	17,61	0,312	0,252	0,182	15,729	17,229	17,484	1,986	1,465	1,041
	976,47	15,39	17,21	17,56									
	975,94	15,80	16,99	17,28									
Compost KH	980,65	10,53	11,01	11,04	0,602	0,970	0,989	10,097	11,235	11,287	5,965	8,633	8,762
	980,09	9,41	10,40	10,44									
	977,17	10,35	12,30	12,37									
Lab control sample	992,48	4,187	4,229	4,247	0,041	0,046	0,033	4,216	4,262	4,271	0,967	1,079	0,781
	991,61	4,244	4,294	4,294									
											Average CV		**2,4 %**

ANNEX 6 PRECISION - REPEATABILITY – TOTAL ORGANIC CARBON

Sample	Sample size	Total carbon TC mg/kg DM	Sample	Sample size	Total organic carbon TOC (HCl) mg/kg DM
Eurosoil2	0,1477	105,7	Eurosoil2	0,1159	37,0
Eurosoil2	0,1227	108,4	Eurosoil2	0,1057	35,84
Eurosoil2	0,1438	99,3	Eurosoil2	0,0896	34,46
Eurosoil2	0,166	103,8	Eurosoil2	0,088	36,07
Eurosoil2	0,1475	103,5	Eurosoil2	0,1139	34,33
Eurosoil2	0,1418	105,2	Eurosoil2	0,1466	35,39
Eurosoil2	0,1864	103,7	Eurosoil2	0,1087	32,97
Eurosoil2	0,13190	104,7	Eurosoil2	0,0919	33,42
Eurosoil2	0,1195	102,3			
Eurosoil2	0,1671	105,4			
Average		104,2 mg/kg DM	Average		34,9 mg/kg DM
Certified value		108 mg/kg DM	Certified value		37,2 mg/kg DM
Recovery		96,5%	Recovery		93,4%

Sample	Sample size	Total organic carbon TOC (H_3PO_4) mg/kg DM
Eurosoil2	0,0258	36,8
	0,0178	30,4
Average		33,6 mg/kg DM
Certified value		37,2 mg/kg DM
Recovery		90,3%