Deskstudy on dry matter and loss on ignition

Vibeke Jensen and Kirsten Jebjerg Andersen

Eurofins A/S

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SUMMARY

The present report concerns an evaluation of the possibility of harmonizing standards for dry matter and loss on ignition and prepare horizontal standards in regard to sludge, soil and biowaste.

Dry matter
The detailed comparison of standards for the determination of dry matter demonstrates the possibility of preparing a harmonized and horizontal standard for sediment, sludge, soil, and waste. The horizontal standard may 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. It is proposed to include waste and sediment in the scope of the standard, however excluding samples with a high content of volatile substances.

The comparison shows that the present standards differ mainly in regard to terminology, which needs harmonisation, and in regard to the applied drying temperature intervals. A draft standard has been prepared, which proposes the use of the term "dry matter". Many European Standards require analytical results to be based on "dry matter", which is the main reason for the choice made.

A temperature interval for the drying process is set to $(105 \pm 5)\ ^{o}C$. This interval includes other intervals applied. As the accuracy of the determination is primarily determined by the weighings performed and drying to constant mass, it is considered feasible to allow the enlarged temperature interval.

Loss on ignition
The detailed comparison of standards for the determination of loss on ignition demonstrates the possibility of preparing a harmonized and horizontal standard for sediment, sludge, soil, and waste. The horizontal standard may replace the standard for sludge (EN 2879:2000). However, given the temperature proposed $(550 \pm 25)^{o}C$) it cannot replace the EN 13040:1999, Soil improvers and growing media – Determination of organic matter content and ash.

A draft standard has been prepared, which proposes the use of the term "loss on ignition", and furthermore, it proposes the use of the ignition temperature interval of $(550 \pm 25)^{o}C$.

1. INTRODUCTION

The objective of the project "Horizontal" is to develop horizontal and harmonised European standards in the fields of sludge, soil and treated biowaste to facilitate regulation of these major streams in the multiple decisions related to different uses and disposal governed by EU Directives.

The revision of the Sewage Sludge Directive 86/278/EEC, the upcoming Directive on the biological treatment of biodegradable waste and the Soil Monitoring Directive call for standards on sampling, on hygienic and biological parameters, on methods for inorganic and organic contaminants and for mechanical properties of these materials. This project considers development and implementation of horizontal standards to be used for sludge, soil and bio-waste.

The work for developing horizontal and harmonised European standards is split up in coherent Work Packages (WPs), each of which addresses a main aspect of all relevant standards required or likely to be required in EU regulations regarding sludge, biowaste and soil. The report in hand deals with a desk study under WP 6: Inorganic Parameters: Assessment of the feasibility of draft horizontal standards for:

- Dry matter (DM) and
- Loss on ignition (LOI)

in sludge, soil, treated biowaste and neighbouring fields

Existing standards and/or draft standards are assessed and key points where possible differences exist are identified and the differences evaluated in order to prepare draft horizontal and harmonized standards.

In addition, assessments of ongoing activities in the CEN/TC workgroups are included in the reports:

CEN/TC 292/WG 5 Waste (a member of the group, Vagn S. Christensen, has been consulted).

CEN/TC 308/WG 1, Sludge (a member of the group, Preben Østfeldt, has been consulted).

CEN/TC 345, Soil (the TC is newly established and therefore no contact has been established to members of the TC).

2. EXISTING STANDARDS OR DRAFT STANDARDS

The available standards and draft standards for dry matter (DM) and loss on ignition (LOI) are listed in the tables below together with an outline of the principles and sample material.

Table 1 Dry matter (DM)

Number	Title	Sample material	Principle
EN 12880 2000	**Characterization of sludges** – Determination of dry residue and water content	Sludges 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 2001	**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.

Table 2 Loss on ignition (LOI)

Number	**Title**	**Scope, sample material**	**Principle**
EN 12879 2000	**Characterization of sludges** – Determination of loss on ignition of dry mass	Sludges 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** (translation corrected from the original)	Water, sludge, and sediment	Samples of dried matter 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. EVALUATION OF THE POTENTIAL FOR HARMONIZED AND HORIZONTAL STANDARDIZATION

3.1 Dry Matter (DM)

The content of water (and of dry matter) in a solid environmental sample, indirectly calculated from the content of dry matter, may be used to physically characterise the sample. Furthermore, many European Standards require analytical results to be based on dry matter. Thus, it is essential to have methodologies that can determine the dry residue or water content of solid samples.

A comparison of the existing international standards for the determination of dry matter is given in Table 3. The Danish Standard DS 204 (which is in compliance with SFS 3008 (Finish Standard), NS 4764 (Norwegian Standard), and SS 028113 (Swedish Standard)) is included in the table to demonstrate a standard which include sediment samples in the scope and do contain alternative directions on drying time.

Freeze-drying is generally considered as an alternative pre-treatment method prior to analysis. The sample obtained after freeze-drying has to be considered as a partially dried sample. Thus, standards for freeze-drying are not included in the present study as such. However, freeze-drying may be used as a first step in the determination of dry matter in case of samples with a high water content.

Terms and definitions
Terminology differs between the matrices. In the title of ISO 11465:1993 (soil), prEN 14346:2001 (waste) and in EN 13040:1999 (soil improvers and growing media) the term "dry matter and water content" is used, whereas in EN 12880:2000 (sludge) the parameter is mentioned as “dry residue”. The mass being weighed may technically be characterised as the empty container, the subsample taken for analyses and the residue of the subsample after the specified drying. The dry matter (in EN 12880 mentioned as dry residue) is calculated from the obtained masses.

Most European standards, for which the results are related to the dry residue/dry matter content of the samples, require results to be based on "dry matter".

Principles and procedures
The major difference encountered by comparison of the standards listed in Table 1 concerns the temperature at which the sample is heated and the demand of accuracy by weighing.

Samples analysed according to the EN and ISO standards regarding sludge, soil and waste (and the cited Nordic standards on water, sludge and sediment) are heated to 105^{o}C, whereas the samples analysed according to EN 13040:1999 on soil improvers and growing media are heated to 103^{o}C. The tolerances given (105 ± 5)^{o}C, (103 ± 2)^{o}C and (105 ± 3)^{o}C point out that the temperature interval in EN 13040:1999 on soil improvers and growing media is contained in the intervals given in the ISO 11465:1993 (soil), prEN 14346:2001 (waste) and in EN 12880 (sludge).

A demand on the temperature interval, such as ± 2^{o}C of the oven temperature tolerance seems not to be justified for the samples in question, as the demand of constant mass is determining the drying time. However, it could be argued that compounds exist in sludge (and other samples) that are volatile at temperatures of 105 – 110^{o}C, which are likely to be determined as

water by using the temperature interval (105 ± 5)^{o}C, but which will not be determined as water by using the interval (103 ± 2)^{o}C. In any case, if volatile substances are present, the method will not give a reliable determination of the water content.

Equipment
An analytical balance with an accuracy of 1 mg or better is prescribed in EN 12880 (sludge) and in PrEN 14346 (waste). With a demand of a minimum residue content of 500 mg in EN 12880 an accuracy of 1 mg is needed. An error of 1 mg is equivalent to an error of maximum 0,4% in a sample containing 500 mg dry residue.

ISO 11465 (soil) prescribes accuracy of 10 mg or better. EN 13040 (soil improvers and growing media) prescribes an analytical balance with a scale interval of 0,01 mg. These standards specify the quantity of subsample to be taken to: 10 – 15 g of air-dried soil sample, 30 – 40 g of field-moist soil sample and 50 g of soil improver or growing media.

The drying and weighing processes are slightly different in the standards consulted. ISO 11465 demands a re-weighing after further drying for 4 hours, where prEN14346 and EN 12880 prescribes further drying for 1 hour.

General hazards, sample storage and pre-treatment, interferences and precision
Other differences are encountered, most of which concern the material in question. ISO 11465 (soil) refers to ISO 11464 in regard to the pre-treatment of the laboratory sample prior to analysis. For EN 13040 pre-treatment is an integrated part of the standard. For prEN 14346 reference is made to prEN WI 292030, Characterisation of waste – preparation of test portions from the laboratory sample. EN 12880 (sludge) does not cover sample preparation and does not contain references.

DS 204:1980
DS 204:1980 (in compliance with SFS 3008, NS 4764, and SS 028113) are in principle technically equivalent to the proposed standard, however, drying for at least 20 hours are prescribed without control of constant mass.

DS 204:1980 includes the determination of dry matter in sediment samples. It is recommended that the sediments be included in the European standard on dry matter determination. Practically identical principles for the determination of sediments and e.g. soil and waste are being used throughout Europe. Furthermore, the possible reclamation of marine areas or of freshwater lake areas for agriculture use or land disposal of dredge material calls for comparability of analytical methods used.

Table 3 Comparison of standards for the determination of dry matter. Only information deemed most relevant for the comparison is listed below. Further details are found in the standards.

Standard	**ISO 11465:1993**	**EN 13040:1999**	**EN 12880:2000**	**prEN 14346:2001**
Scope/sample materials	Determination of dry matter content and water content in **soil samples** on a mass basis.	Determination of dry matter content in **soil improvers and growing media**.(Other parameters are included in the standard)	Determination of dry residue and water content of **sludges and sludge products.**	Determination of dry residue or water content in **waste**.
Terms and definitions	**Dry matter:** Dry residue of soil, expressed as a percentage by mass after specified drying process.	**Dry matter:** Dry residue, expressed as a percentage by mass after specified drying process. (Definition not directly quoted as such in the standard).	**Dry residue:** The dry mass portion of the sludge obtained after specified drying process. It is expressed in percentages or in grams per kilogram. **Dry mass (dry matter):** The mass of solids obtained after the specified drying process. It is expressed as grams or kilograms.	**Dry residue:** The remaining mass fraction of a sample after specified drying. **Dry matter:** The fraction of a sample excluding water.
Principle	Soil samples are dried to constant mass at **105°C ± 5°C**. The difference in mass before and after drying is used to calculate the dry matter.	Samples are dried to constant mass at **103°C ± 2°C**. The difference in mass before and after drying is used to calculate the dry matter.	Sludge samples are dried to constant mass at **105°C ± 5°C**. The difference in mass before and after drying is used to calculate the dry matter.	Method A: The waste sample is dried to constant mass at **105°C ± 5°C**. The difference in mass before and after drying is used to calculate the dry matter.
Sample storage and preparation	For sample preparation reference is made to ISO 11464.	Sample preparation is an integrated part of the standard.	If samples are to be stored, store them at 0°C to 4°C. Sample preparation is not covered.	Biologically active samples should be analysed immediately or stored at at least –18°C. For sample preparation reference is made to pr EN WI 292030.
General Hazards	With soil samples from contaminated soils, special measures must be taken. It is important to avoid any contact with the skin and special measures must be taken during the drying process		Samples are liable to ferment and usually contain harmful micro-organisms. It is essential to keep them away from any food or drink, and to protect any cuts of the skin. Bursting glass bottles containing	Samples may consist of hazardous and flammable material, may be liable to biological action and may be infectious.

Standard	ISO 11465:1993	EN 13040:1999	EN 12880:2000	prEN 14346:2001
	to prevent contamination of the laboratory atmosphere and other samples.		sludge can produce micro-organism contaminated shrapnel. Plastic bottles can burst and produce a hazardous spray and aerosol. When handling sludge samples, it is necessary to wear gloves, a face and eye protection, and sufficient body protection. Gas evolved is usually flammable.	
Interferences	The drying must be performed as quickly as possible to minimise evaporation.		During storage, sludge samples can be subject to changes (e.g. uptake or liberation of water, carbon dioxide and other substances). The samples can also change chemically during the drying process.	The samples can change during the process, e.g. by absorption of carbon dioxide in the case of alkaline samples, or of oxygen by reducing substances. Volatiles are measured as water.
Equipment	Drying oven, thermostatically controlled with forced air ventilation and capable of maintaining a temperature of 105°C ± 5°C. Desiccator with active drying agent. Analytical balance with an accuracy of 10 mg. Container (moisture box) with lid, of capacity 25 ml to 100 ml for air-dried soil samples, and made of waterproof material that does not absorb moisture.	Drying oven, ventilated, fan assisted, capable of maintaining a temperature of 103°C ± 2°C. Analytical balance with a scale interval of 0,01 g and capacity of weighing 500 g. Sample tray, capable of holding not less than 50 g sample and be constructed of material thermally stable.	Drying oven thermostatically controlled and capable of maintaining a temperature of 105°C ± 5°C. Desiccator with active drying agent. Analytical balance with an accuracy of 1 mg or better. Temperature tolerant evaporating dish or crucible.	Drying system thermostatically controlled and capable of maintaining a temperature of 105°C ± 5°C. Desiccator with active drying agent. Analytical balance with an accuracy of 1 mg or better. Temperature tolerant evaporating dish or crucible.
Procedure	The standard contains procedures for both air-dried soil samples and for field-moist soil samples. 10 to 15 g air-dried soil or 30 to 40 g field-moist soil samples are used. Drying at 105°C until constant mass is reached.	Approximately 50 g sample is used. Drying until the difference between two successive weighings does not exceed 0,1 g.	Suitable amount of sample material (the residue obtained should have a weight of at least 0,5 g) is used. Drying until the residue appears dry, typically overnight.	Suitable amount of sample material (the residue obtained should have a weight of at least 0,5 g) is used. Drying until the residue appears dry, typically overnight.

Standard	**ISO 11465:1993**	**EN 13040:1999**	**EN 12880:2000**	**prEN 14346:2001**
Calculation		The dry residue is expressed as percentage by mass.	The dry residue is expressed as percentage by mass or grams per kilogram.	The dry matter is expressed in percentages by mass or grams per kilogram.
Quality control				Where uncertainty exists about the homogeneity or behaviour of the sample it is recommended that the analysis be carried out in duplicate. For quality control, an accurate control mixture of macerated filter paper in deionised water can be used.
Precision	Repeatability is found to be 0,2% absolute and 0,5% of the mean value for air-dried soil samples, and 1,5% absolute and 5% of the mean value for filed-moist soil samples.		The coefficient of variation of reproducibility is found to be 2-17% The coefficient of variation of repeatability is found to be 1 to 7%	

Loss on ignition (LOI)

Determination of organic matter
Organic matter influences many of the physical, chemical and biological properties of solid environmental samples. Some of the properties influenced by organic matter include e.g. for soil the properties such as structure, water holding capacity, nutrient contributions, biological activity, water content and air infiltration rate.

For soil, more principles have been used: ISO 14235 – soil quality - determination of organic carbon by sulfochromic oxidation – is a method where the organic matter is oxidised by sulfochromic acid and the content measured by spectrometry. Concern for the disposal of the chromium and the hazard of using this acid by laboratory technicians has prompted the use towards estimation of organic carbon by measurement of loss of ignition, the measurement of total organic carbon (TOC) or the determination of organic and total carbon after dry combustion (elementary analyses). However, presently there is no ISO method developed for the determination of LOI and TOC in soil. A method exists for the determination of organic and total carbon after dry combustion (elementary analyses) in soil samples - ISO 10694:1995.

The present report is limited to the analyses of LOI. Due to potential hazards, the method using sulfochromic acid is not recommended. So far, a method for the determination of organic matter by elementary analyses has not been developed for sludge and waste. A limited investigation on the use of elementary analyses for the estimation of organic matter content suggests that the use of the method for sludge and waste is limited.

Loss on ignition
A comparison of the existing international standard for the determination of loss on ignition is given in Table 3. The Danish Standard DS 204 is included in the table to demonstrate a standard which in the scope includes sediment samples and contains alternative directions on drying time.

Scope
EN 13039 concerns the determination of the organic matter and the ash content of soil improvers and growing media. The organic matter is taken as equal to the loss on dry incineration. Organic matter is not covered by the determination of LOI according to EN 12879 on sludge or in document N295 in TC 292/WG5 for waste, sludge and sediment, although it is mentioned that LOI is often used as an estimate for the content of non-volatile organic matter. Due to the different temperatures applied (see below), it is questionable to directly compare results derived by using the two different approaches applied.

Principle - harmonisation of temperature
A temperature of $(550 \pm 25)^{o}C$ is being used for sludge (EN 12879) and also proposed for waste, sludge and sediment in document N295 in TC 292/WG5 on method for determination of loss on ignition.

A temperature of $(450 \pm 10)^{o}C$ is used for soil improvers and growing media in EN 13039:2000. Results from quantification of loss on ignition depend on the temperature applied as different amounts of carbonate and volatile organic matter or chemical reactions influence the results obtained. Thus, results from using different ignition temperatures may likely not provide comparable results.

Terminology
Residue on ignition and loss on ignition are used in EN 12879 (sludge) and in N295 in TC 292/WG5 (waste, sludge and sediment) as complementary, thus the residue on ignition + the loss on ignition is 100%. EN 13039 operates with the term "organic matter", which is defined as equal to the loss on dry incineration. The residue after ignition is defined as "ash".

For the purpose of a harmonized standard use, the definitions as described in EN 12879 are recommended.

Table 4 Comparison of standards for the determination of loss on ignition matter. Only information deemed most relevant for the comparison is listed below. Further details are found in the standards.

Standard	**EN 13039:2000**	**EN 12879:2000**	**Preliminary 3. Draft standard dated May 2002** **Prepared in co-operation between CEN/TC 292 and CEN/TC 308**
Scope/sample materials	Determination of the organic matter and the ash content of **soil improvers and growing media**.	Determination of loss on ignition of dry mass of **sludges and sludge products at 550°C** after the dry residues have been determined in accordance with the method of EN 12880.	Determination of loss on ignition in waste.
Terms and definitions	**Organic matter:** Carbon fraction of a sample that is free from water and inorganic substances. The organic matter for the purpose of this standard is taken as equal to loss on dry incineration. **Ash:** Residual mineral matter remaining after the destruction of organic matter/material by controlled burning.	**Loss on ignition:** The portion of mass escaping as gas as a result of the ignition of the dry mass of a sludge under specified condition. The loss on ignition is related to the dry mass and expressed in percentages. **Residue on ignition:** The portion of mass remaining after the ignition of the dry mass of sludge under specified conditions. The residue on ignition is related to the dry mass and expressed in percent **Dry mass (dry matter):** The mass of solids obtained after the specified drying process. It is expressed as grams or kilograms. **Dry mass (dry matter):** The mass of solids obtained after the specified drying process. It is expressed as grams or kilograms. **Constant mass**: Constant mass is reached when, during the ignition process, the difference between two successive weighings of the sample, first heated, then cooled to room temperature and with an interval of 1 hour between them, is within 0,5% (m/m) of the last determined mass or 2 mg, whichever is the greater.	**Loss on ignition:** The change in mass as a result of heating a sample under specified conditions. The loss on ignition is expressed in weight percentage of the dry matter. **Residue on ignition:** The mass remaining after heating a sample under specified conditions. The residue on ignition is expressed in weight percentage of the dry matter. **Dry matter:** Reference to prEN14346 (The fraction of a sample excluding water). **Constant mass:** Constant mass is reached when, during the ignition process, the difference between two successive weighings of the sample, first heated, then cooled to ambient temperature and with an interval of 1 hour between them, is within 0,5% (m/m) or 2 mg, whatever is the greater.

Standard	**EN 13039:2000**	**EN 12879:2000**	**Preliminary 3. Draft standard dated May 2002** **Prepared in co-operation between CEN/TC 292 and CEN/TC 308**
Principle	Samples are dried at 103°C, and then ashed at **450°C** The ash is determined as the residue on ignition. The organic matter is taken to be the loss of mass on ignition.	Samples of dried sludge are heated in a furnace and are dried to constant mass at (550 ± 25)°C. The difference in mass before and after the ignition process is used for calculating the loss of ignition.	A test portion is heated in a furnace up (550 ± 25)°C. The difference in mass before and after the heating process is used for calculating the loss on ignition.
Sample storage and preparation		If samples are to be stored, store them at 0°C to 4°C.	If samples are to be stored, store them in a well ventilated place. Biologically active samples should be frozen.
General Hazards		Samples are liable to ferment and usually contain harmful micro-organisms. It is essential to keep them away from any food or drink, and to protect any skin cuts.	Samples may consist of hazardous and flammable material, may be liable to biological action and may be infectious. The gases that may be produced are potentially flammable. It is recommended that the sample be handled with special care.
Interferences		There are normally no interferences with the loss on ignition determination. However, for many purposes this determination is used as an assessment of the organic part of the sludge dry mass. In case the loss of volatile inorganic substances can occur giving high results ???.	In principle, there are no interferences connected to the determination, as loss on ignition is an empirical parameter. However, for many purposes the determination is used for an assessment of the content of organic matter in waste, sludge or sediment samples. It should be noted that any elementary carbon in the sample would be included in the loss on ignition value. Furthermore, any volatilisation or chemical reactions of inorganic compounds will also be included in the loss of ignition value.
Equipment	Drying oven, capable of maintaining a temperature of (103± 2)°C. Electrical muffle furnace, capable of maintaining a temperature of (450 ± 10)°C. Desiccator with active drying agent.	Muffle furnace or equivalent equipment, capable of maintaining a temperature of (550 ± 25)°C. Desiccator with active drying agent. Analytical balance with an accuracy of 1 mg or better.	Muffle furnace or equivalent equipment, capable of maintaining a temperature of (550 ± 25)°C. Desiccator with active drying agent. Analytical balance with an accuracy of 1 mg or better.

Standard	**EN 13039:2000**	**EN 12879:2000**	**Preliminary 3. Draft standard dated May 2002** **Prepared in co-operation between CEN/TC 292 and CEN/TC 308**
	Analytical balance with a scale interval of 0,001 g and capacity of weighing 500 g. Basin, made from fused silica or quartz, of shallow form with a flat bottom, capable of holding a sample of 5 g.	Crucible, 50 to 70mm in diameter, suitable for ignition at 550°C e.g. porcelain, silica or platinum.	Flat bottom crucible suitable for heating at 550°C e.g. porcelain, silica or platinum.
Procedure	Approximately 5 g sample is used and dried in an oven at a temperature of 103°C ± 2°C. Place the basin containing the dried sample in the cool muffle furnace and raise the temperature over approximately one hour to (**450** ± **10)°C**. Maintain the temperature for **6 hours**, cool to room temperature in the desiccator and weigh to the nearest 0,001 g. Place the basin into the muffle furnace maintained at 450°C ± 10°C for **a further 1 hour**. Repeat the operations of heating, cooling and weighing until the difference between two successive	0,5 g to 5 g of dried sludges is heated in the furnace at **(550** ± **25)°C** for at least **one hour** in a pre-ignited crucible. Place the hot crucible containing the residue on ignition in the desiccator and leave to cool. Weighing is carried out immediately after removal of the crucible from the dessiccator and the weighing operation is completed as quickly as possible. The mass of the residue on ignition and therefore 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 does not differ by more than 0,5% from the previous value or 2 mg, whichever is the greater.	Procedure for samples not containing volatiles: 0,5 g to 5 g of dried sludges is heated in the furnace at **(550** ± **25)°C** for at least **one hour**. Remove the hot crucible from the furnace and allow cooling on a clean metal plate for a few minutes. While still warm, transfer the crucible to a desiccator and allow cooling to ambient temperature. Weigh the crucible containing the ignition residue to the nearest 1 mg. Ignition can be regarded as complete when constant mass is obtained. Procedures for samples containing volatiles: For samples containing a 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 (see prEN 14346) and the loss on ignition may be performed directly on the un-dried sample.
Calculation	The organic matter content is expressed as a percentage by mass of the dried sample. The ash content is expressed as a percentage by mass of the dried sample.	The loss on ignition of the dry mass of sludge is expressed in percentages.	The loss on ignition is expressed in weight percentage of the dry matter.

Standard	**EN 13039:2000**	**EN 12879:2000**	**Preliminary 3. Draft standard dated May 2002 Prepared in co-operation between CEN/TC 292 and CEN/TC 308**
Quality control			
Precision	Repeatability relative standard deviation is found to be from 3 - 8%. The reproducibility relative standard deviation is found to be from 5 – 14%	The coefficient of variation of reproducibility is found to be 1 to 5%. The coefficient of variation of repeatability is found to be 1 to 3%.	

4. CRITICAL POINT AND RECOMMENDATIONS

4.1 Dry matter

The detailed comparison of standards for the determination of dry matter demonstrates the possibility of preparing a harmonized and horizontal standard for sludge, soil, sediment, and biowaste. However, some decisions have to be taken, of which the major ones are:

- Harmonization of terminology
- Harmonization of the temperature to proposed (105 ± 5)°C.

Terminology
Thus, the term "dry matter" is recommended in a horizontal standard, however, defined from the dry residue.

Sample preparation/sample pre-treatment
In general, sample pre-treatment is considered differently in the different TCs. Some TCs include the pre-treatment of samples as an integral part of the analytical standard, whereas other TCs have prepared or are preparing separate standards covering pre-treatment, including sub-sampling, homogenisation, fractionation etc. In line with the modular approach it is recommended to consider the elaboration of one (or more) pre-treatment, preferably horizontal, standards, on pre-treatment and consequently make the necessary references to those in the analytical standards.

Temperature during the drying process
The interval tolerance for drying given in EN 13040 (soil improvers and growing media), (103 ± 2)°C, is included in the interval given in the other ISO and EN standards considered, (105 ± 5)°C. There are no clear arguments for choosing one temperature interval instead of the other, apart from equipment requirements. However, as the accuracy of the measurement is mainly determined by the requirement of drying to constant temperature, an interval tolerance of ± 5°C is considered satisfactory.

A temperature of (105 ± 5)°C is proposed for the draft harmonized standard.

Equipment requirement
The accuracy requirement for the analytical balance should be related to the mass of the residue weighed. For samples with a residue of 5 g or more, an accuracy of 10 mg is sufficient. For samples with a dried residue of 0,5 – 5 g, an accuracy of 1 mg is required.

For practical reason, if the residue is to be used for further determination of loss on ignition, an analytical balance with an accuracy of 1 mg or better is required.

The requirement of analytical balances of accuracy of 1 mg or better is recommend in the horizontal standard, however, to open for the use of analytical balances with an accuracy of max. 10 mg for samples with dry residue of 5 g or higher.

Drying time
For practical reasons, it is recommend to include an option in the standard that will allow 20 hours drying and anticipation of constant mass, for samples for which the laboratory have documented experience that the necessary drying time for specific sample types are less than 20 hours.

Sample types
It is proposed to include sediment samples in the scope of the standard.

Table 5 Outline of the content of the proposed horizontal standard in regard to issues, where differences are identified among matrices

Scope/sample materials	Determination of dry matter/dry residue and water content in biowaste, sediment, soil, and sludge.
Terms and definitions	The following definitions are proposed: **Dry residue:** The remaining mass fraction of a sample after the specified drying process. It is expressed in percentage or in grams per kilogram **Dry mass:** The mass of solids obtained after the specified drying process. It is expressed in grams or kilograms. **Water content:** The mass fraction determined as the loss of mass after the specified drying process. It is expressed in percentage or in grams per kilogram **Dry matter:** Dry residue after drying according to the specified drying process. It is expressed in percentages or in grams per kilogram **Constant mass:** Mass reached when, during the drying process, the differences between two successive weighings of the sample, first heated, then cooled to room temperature and with an interval of minimum 1 h between them, do not exceed 0,5% (m/m) of the last determined mass or 2 mg, whichever is the greater.
Principle	Samples are dried to constant mass at **105°C ± 5°C**. The difference in mass before and after drying is used to calculate the dry matter and water contents.
Sample storage and preparation	If samples are to be stored, store them at 0°C to 4°C. Biologically active samples may be stored at 0°C to 4°C and analysed within 3 hours, alternatively these samples must be stored at maximum –18°C.
General Hazards	When samples are contaminated, special measures must be taken. It is important to avoid any contact with the skin and special measures must be taken during the drying process to prevent contamination of the laboratory atmosphere and other samples. Samples may consist of hazardous and flammable material, may be liable to biological action and may be infectious. Sludge samples are liable to ferment and usually contain harmful micro-organisms. When handling contaminated samples or sludge samples, it is necessary to wear gloves, and sufficient face, eye and body protection.
Interferences	During storage, samples can be subject to changes (e.g. uptake or liberation of water, carbon dioxide and other substances). The samples can also change chemically during the drying process. The samples can change during the process, e.g. by absorption of carbon dioxide in the case of alkaline samples, or of oxygen by reducing substances. Volatile substances are measured as water.
Equipment	Drying oven thermostatically controlled and capable of maintaining a temperature of 105°C ± 5°C. Desiccator with active drying agent. Analytical balance with an accuracy of 1 mg or better. For samples with dry residue of 10 g or higher, an analytical balance with an accuracy of 10 mg may be used. Temperature tolerant evaporating dish or crucible.
Procedure	Suitable amount of sample material (the residue obtained should have a weight of at least 0,5 g) is used. Drying until constant weight, typically overnight.
Calculation	The dry matter is expressed in percentage by mass or grams per kilogram.
Quality control	Where uncertainty exists about the homogeneity or behaviour of the sample it is recommended that the analysis be carried out in duplicate.
Precision	Data from the validation study to be included for biowaste, sediment, soil, and sludge.

4.2 Loss on ignition

The detailed comparison of standards for the determination of loss on ignition demonstrates the possibility of preparing a harmonized and horizontal standard for sludge, soil, sediment and biowaste. Especially one critical decision needs consideration:

Harmonization of the temperature and time
For preparation of a horizontal standard, harmonization of temperatures for ignitions is needed. Elementary carbon in the sample will to some extent be included in the loss on ignition value, depending on the temperature. Furthermore, any volatilisation or chemical reactions of inorganic compounds will also be included in the loss of ignition value. Thus, LOI is an empirical parameter, determined by the temperature interval chosen for ignition. The temperature should be harmonized. For soil improvers and growing media, a temperature of $(450 \pm 10)^{o}C$ for about 6 hours + at least one hour is used for the determination of organic matter. For sediment, sludge and waste, a higher temperature of $(550 \pm 25)^{o}C$ for a shorter time (for one hour + at least half an hour) is suggested for determination of loss on ignition.

A change of temperature from $(450 \pm 10)^{o}C$ to temperatures of $(550 \pm 25)^{o}C$ will likely cause higher results due to evaporation of inorganic carbon, such as carbonates. The significance of the change is dependent on the amount of organic material and e.g. carbonates in the sample. Lower results of LOI are expected for changing from higher to lower results.

For the purpose of preparing a draft horizontal standard, a temperature of $(550 \pm 25)^{o}C$ is chosen. Table 5 contains an outline of the technical content of the proposed draft horizontal standard.

Sample types
It is proposed to include sediment samples in the scope of the standard

Table 6 Outline of the content of the proposed horizontal standard on loss on ignition in regard to issues, where differences are found among matrices

Scope/sample materials	Determination of loss on ignition waste, sediment, soil, and sludge.
Terms and definitions	**Loss on ignition:** The change in mass as a result of heating a sample under specified conditions. The loss on ignition is expressed in weight percentage of the dry residue/dry matter/dry mass.
Principle	Dried samples are heated in a furnace and are dried to constant mass at **$(550 \pm 25)^{o}C$**. The difference in mass before and after the ignition process is used for calculating the loss of ignition.
Sample storage and preparation	If samples are to be stored, store them at $0^{o}C$ to $4^{o}C$. Biologically active samples should be analysed immediately or stores at least $-18\ ^{o}C$.
General hazards	When samples are contaminated, special measures must be taken. It is important to avoid any contact with the skin and special measures must be taken during the drying process to prevent contamination of the laboratory atmosphere and other samples. Samples may consist of hazardous and flammable material, may be liable to biological action and may be infectious. Sludge samples are liable to ferment and usually contain harmful micro-organisms. When handling sludge samples, it is necessary to wear gloves, a face and eye protection, and sufficient body protection.
Interferences	In principle, there are no interference connected to the determination, as loss on ignition is an empirical parameter. However, for many purposes the determination is used for an assessment of the content of organic matter in waste, sludge or sediment samples. It

	should be noted that any elementary carbon in the sample would be included in the loss on ignition value. Furthermore, any volatilisation or chemical reactions of inorganic compounds will also be included in the loss of ignition value.
Equipment	Muffle furnace or equivalent equipment, capable of maintaining a temperature of (550 ± 25)^{o}C. Desiccator with active drying agent. Analytical balance with an accuracy of 1 mg or better. Crucible, 50 to 70 mm in diameter, suitable for ignition at 550^{o}C, e.g. porcelain, silica or platinum.
Procedure	0,5 g to 5 g of dried sample is heated in the furnace at (550 ± 25)^{o}C for at least 60 min. Place the hot crucible containing the residue on ignition in the desiccator and leave to cool. Weighing is carried out immediately after removal of the crucible from the dessiccator and the weighing operation is completed as quickly as possible. The mass of the residue on ignition and therefore the loss on ignition shall be regarded as constant if the mass obtained after a further half-hour period of ignition at 550^{o}C in the pre-heated furnace does not differ by more than 0,5% from the previous value or 2 mg, whichever is the greater. For samples containing a 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 (see prEN 14346) In this case, the loss on ignition is performed directly on the un-dried sample.
Calculation	The loss on ignition is expressed in weight percentage of the dry mass.
Quality control	Where uncertainty exists about the homogeneity or behaviour of the sample, it is recommended that the analysis be carried out in duplicate.
Precision	

5. DRAFT STANDARD

Separate format

REFERENCES

DS/ISO 11074-1:1997. Soil quality – Vocabulary – Part 1: Terms and definitions relating to the protection and pollution of the soil

DS/EN 12832:1999. Characterisation of sludges – Utilisation and disposal of sludges - Vocabulary

DS/EN 12944-1:1999. Fertilizers and liming materials and soil improvers – Vocabulary – Part 1: General terms

DS/EN 12944-2:1999. Fertilizers and liming materials and soil improvers – Vocabulary – Part 2 Terms relating to fertilizers

DS/EN 12944-3:2001. Fertilizers and liming materials and soil improvers – Vocabulary – Part 3 Terms relating to liming materials

prEN 13965-1:2003. Characterization of waste – Terminology – Part 1: Material related terms and definitions