

Desk study on total organic carbon (TOC)

Vibeke Jensen, Kirsten J. Andersen and Mikael Krysell

Eurofins A/S



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SUMMARY

The present report concerns an evaluation of the possibility of harmonising existing standards for the determination of total organic carbon (TOC) and identification of relevant environmental fields, for which a harmonised standard may be applicable.

The detailed comparison of standards for the determination of TOC demonstrates the possibility of preparing a harmonised and horizontal standard for sediment, sludge, soil, and waste. The horizontal standard may potentially replace the following standards: Soil (ISO 10694) and waste, sludge and sediment (EN 13137). It is proposed to include soil, sludge, sediment and waste in the scope of the harmonised standard.

The comparison shows that two of the present standards, both using high temperature combustion to oxidise the present carbon, differ mainly in small details and scope, whereas one standard (ISO 14235) uses a chemical oxidation technique involving the use of potassium dichromate and concentrated sulphuric acid. It is proposed not to include this technique in the harmonised standard. EN 13137 is a well-developed standard, and in order for preparing a harmonised standard, it is recommended to use EN 13137 with a few updates, among others in the scope section.

A robustness study is proposed for the harmonised standard prior to the organisation of an interlaboratory comparison. Data from interlaboratory comparisons are needed in regard to sample types not included in the present standards. Further, newer data in regard to soil should be included due to instrumental development and better implementation of quality control procedures during the last 10 years.

1. INTRODUCTION

The objective of the project 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:

- Total organic carbon (TOC)

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 harmonised standards.

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

The work groups are:

CEN/TC 292/WG 5, Waste

CEN/TC 308/WG 1, Sludge

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

CEN/TC 223, soil improvers and growing media

2. EXISTING STANDARDS OR DRAFT STANDARDS

The available standards and draft standards for TOC in solid materials and in water are listed in the tables below together with an outline of the principles and sample material.

Table 1 International standards on the determination of total organic carbon

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 spectrophotometrically. 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.

Number	Title	Scope, sample material	Principle
EN 13137: 2001	Characterization of waste - Determination of total organic carbon (TOC) in waste, sludges and sediments	Waste, sludges, sediments and comparable materials.	<p>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 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.</p> <p>Method B (direct procedure): In this procedure the carbonates present in the undried 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.</p>

CEN/TC 292/WG 5 "Analysis of waste – Selected group parameters" was responsible for the recent preparation of EN 13137. The standard was prepared in co-operation with CEN/TC 308/WG 1 and covers waste, sludges, sediments and comparable materials.

3. EVALUATION OF THE POTENTIAL FOR HARMONISED AND HORIZONTAL STANDARDIZATION

Five international standards were identified for the determination of total organic carbon (TOC). Two of the standards – both developed for water (EN 1484 and ISO 8245) - have the status as guidelines. Of the two standards developed for soil, ISO 14235 is a spectrometric method after oxidation by use of potassium dichromate solution and sulphuric acid. The other standard - ISO 10694 – is in principle comparable to the standard EN 13137 developed for waste, sludges and sediments.

EN 13137: 2001 is an updated and relatively new standard that includes the use of advanced instruments. Further, it has useful definition of the quality control procedures needed. EN 13137: 2001 is in line with both EN 1484:1997 and ISO 8245:1999, the two standards describing the procedure for the determination of TOC in water. All these three standards describe well the sample pre-treatment, the principles for calculation and the general working principles, but leave the actual determination and detection step open, given that several principles, leading to comparable results, may be used. A further advantage is that the same basic equipment (to a large extent) can be used for the determination of TOC in water and in solid matrices.

A comparison of ISO 10694 (soil), ISO 235 (soil) and EN 13137 (waste, sludges and sediments) is given below:

Scope

Though using almost identical techniques, the standards ISO 10694 and EN 13137 have been developed for different purposes and thus have different scopes. In the first case, soil is the only matrix mentioned, whereas in the latter case the scope is defined as “waste, sludge, sediments and similar matrices”. In ISO 14235, the scope is soil.

Terms and definitions

EN 13137:2001 has a section of definitions, defining TC, TIC and TOC. These definitions are general and should be applicable also to laboratories that are used to work according to the other two standards. These standards lack similar definitions of the properties being measured.

Principles and procedures

The principles and procedures described in EN 10964:1995 and EN 13137:2001 are similar. In both standards, the carbon in the sample is released as carbon dioxide after combustion at elevated temperature. For determination of organic carbon, inorganic carbon is removed by the addition of a mineral acid (in ISO 10694 defined as 4 M hydrochloric acid, in EN 13137 phosphoric acid is mentioned as an example). The combustion temperature is given as “at least 900°C” in ISO 10694, whereas EN 13137 mentions that the commercially available instruments provide a combustion temperature of 900°C to 1500°C. Parts of the procedure are, thus, less precisely defined in the latest of the two standards. However, as a “close to 100% stripping of the inorganic carbon” is expected using either method, and a “close to 100% conversion of organic carbon to carbon dioxide” in the combustion step is also expected, the temperature (as long as it is above 900°C) and the exact choice of acidifying procedure could not be expected to affect the final result.

Similar procedures for calibration and calculation are applied in both standards. Similar substances are recommended for calibration. In both cases, the water content is taken into account when calculating the TOC on a dry weight basis.

EN 14235 applies a different analytical principle, using chemical oxidation of the carbon followed by a photometric procedure to determine the carbon. According to the standard, a comparison with results from ISO 10694 shows that 95% of the organic carbon is oxidised. For calibration purposes, the use of glucose is specified. This substance is not mentioned as an alternative in the other two standards. This standard thus applies a separate procedure for both the release of carbon from the sample, for the determination of the released carbon and for the calibration of the measurement.

Equipment

Neither ISO 10694 nor EN 13137 specifies the type of apparatus to be used, other than that it should be an apparatus capable of heating the sample, passing a stream of carrier gas through it, and passing the carrier gas on to some kind of detection system. In both cases, the laboratories will almost inevitably purchase a commercially available instrument dedicated to elementary analysis.

The equipment specified in ISO 14235 is less advanced and consists, in principle, of items available in most environmental laboratories (for example, the heating block specified is of the same kind as used for determination of the standard parameter COD_{Cr} in wastewater).

Regarding balances, ISO 10694 specifies that the analytical balance used should be capable of accurately weighing 0.1 mg (or, optionally, a microbalance capable of weighing 0.01 mg), the same as specified in ISO 14235. In EN 13137, the demand on the balance is that it should be capable of weighing accurately at 0.5% of the test portion weight. With test portion weights of 20-500 mg, this means accuracy at 0.1-2.5 mg. A balance accurate at 0.1 mg will thus satisfy all three standards.

General hazards, sample storage and pre-treatment, interferences and precision

It is quite obvious that ISO 14235 has several disadvantages from a working environment and from a general environment point of view, as it involves the use of potassium dichromate and concentrated sulphuric acid. Chromate from the potassium dichromate solution is toxic to the laboratory staff and provides a potential hazard to the environment, if not handled appropriately. The general hazards in the other two standards are limited to the use of mineral acids (e.g. hydrochloric acid or phosphoric acid) and to the use of compressed gases.

ISO 10694 and EN 13137 differs in the sample pre-treatment section. Whereas ISO 10694 prescribes that the samples should be air-dried and made to less than 2 mm prior to the analysis, EN 13137 prescribes a sample particle size of less than 200 μm , but no drying of the samples. However, in both cases the water content is determined separately, and the results calculated on a dry weight basis. Furthermore, EN 13137 recommends a separate drying step as part of the analytical procedure, to remove excess moisture prior to combustion when determining TOC.

The interferences are naturally different when using the two different principles. Whereas ISO 14235 mentions reducing compounds such as chloride and ferrous ion giving false positive signals, the high temperature combustion methods will be sensitive to non-organic compounds that contain carbon but that may be transformed into carbon dioxide in the combustion, whereas volatile organic compounds may be lost in the drying step or in the step where inorganic carbon is liberated by acidification. The interference/loss problem is well treated in EN 13137, but not mentioned at all in ISO 10694.

From the data given in the standards, it is hard to evaluate and compare the precision of the three methods. It appears that the precision (as repeatability and reproducibility) given in EN 13137 is better than that stated in the other two standards. This is possibly an effect of the latter standard being more recent, i.e. the laboratories referred to having used more modern equipment, but could also be an effect of the quality control procedures being much better described in EN 13137.

Quality control

Internal quality control is given sound attention in EN 13137, mentioning e.g. the preparation of internal control solutions (the nomenclature used in the standard is “control mixture”) and requirements on the “recovery” (90-110%) and coefficient of variation (<10% or <5%) on the analyses of the control mixtures. It is, however, unclear if the coefficient of variation refers to within-day or between-day repeatability. The determination of a blank value for equipment and reagents is mentioned. Furthermore, a list of suggested actions, should the analyses of the control mixtures fail, is given. Nothing of this kind is mentioned in the other two standards.

In ISO 10694 and ISO 14235, on the other hand, requirements are given on the repeatability of two determinations of a natural sample. In ISO 10694 a variation of 10% is mentioned for the concentration range 2.5-75 g/kg carbon, which is very similar to the 10% required for TIC in 13137, but not as strict as the 5% for TOC control mixtures required in EN 13137. For concentrations below 2.5 g/kg the repeatability requirement in ISO 10694 is given as an absolute value (0.25 g/kg), which is a very sound approach. ISO 14235 requires a better repeatability, 6.5%, for concentrations above 10 g/kg, and 1 g/kg absolute below 10 g/kg.

Table 2 Comparison of standards for the determination of TOC in solid matrices

Standard	ISO 10694:1995	ISO 14235:1998	EN 13137:2001
Scope/sample materials	This international standard specifies a method for the determination of the total carbon content in soil after dry combustion. The standard is applicable to all types of air-dried soil samples.	This international standard specifies a method for the spectrometric determination of organic carbon content in soil by oxidation in a sulfochromic medium. The standard is applicable to all types of air-dry soil samples. The standard is not applicable to soils containing mineral-reducing compounds , e.g. Cl^- or Fe^{2+} . By convention, the chloride content should not exceed 2 mg in the test portion.	This European standard specifies two methods for the determination of TOC in undried waste samples containing more than 1 g of carbon per kg of dry matter. The standard can be applied as well to sludges, sediments and comparable materials . When present, elemental carbon, carbides, cyanides, cyanates, isocyanates, isothiocyanates and thiocyanates are determined as organic carbon using the described methods.
Terms and definitions			<p>TC, total carbon: the quantity of carbon present in waste in the form of organic, inorganic and elemental carbon.</p> <p>TIC, total inorganic carbon: the quantity of carbon that is liberated as carbon dioxide by acid treatment.</p> <p>TOC, total organic carbon: the quantity carbon that is converted into carbon dioxide by combustion and which is not liberated as carbon dioxide by acid treatment.</p>
Principle	The carbon present in the soil is oxidised to carbon dioxide by heating the soil to at least 900°C in a flow of oxygen-containing gas that is free from carbon dioxide. The amount of carbon dioxide released is then measured by titrimetry, gravimetry, conductometry, gaschromatography or using an infrared detection method, depending on the apparatus used.	The organic carbon present in the soil is oxidised in a mixture of potassium dichromate solution (in excess) and sulphuric acid at a temperature of 135°C . The dichromate ions, which colour the solution orange-red, are reduced to Cr^{3+} ions that colour the solution green. The intensity of the green colour is measured spectrophotometrically. As it is assumed that the oxidation of one carbon atom of the organic matter procedures four electrons, there is a direct relationship between the Cr^{3+} formed and the amount of organic	Method A (indirect procedure): The total organic carbon (TOC) is obtained by the difference between total carbon (TC) and total inorganic carbon (TIC). TC present in the undried sample is converted to CO_2 by combustion in an oxygen-containing gas flow. To ensure complete combustion, catalysts and/or modifiers can be used. The released amount of CO_2 is measured by infrared spectrometry, gravimetry, coulometry, conductometry, thermal conductivity detection, flame ionisation detection after reduction to methane, or other suitable techniques.

Standard	ISO 10694:1995	ISO 14235:1998	EN 13137:2001
		carbon. The method is calibrated using glucose as a source of readily oxidizable carbon	<p>The TIC is determined separately from another sub-sample by means of acidification and purging of the released CO₂. The carbon is measured by one of the techniques mentioned above.</p> <p>Method B (direct procedure): In this procedure the carbonates present in the undried sample are previously removed by treating the sample with acid. The CO₂ released by the following step is measured by one of the techniques mentioned under Method A and gives the TOC directly.</p>
Sample storage and preparation	Use the fraction <2 mm of air-dried soil samples pre-treated according to ISO 11464. Use part of the sample to determine the water content according to ISO 11465 and, if necessary, the carbonate content according to ISO 10693.	Use the fraction of particles <2 mm of air-dry soils samples pre-treated in accordance with ISO 11464. Use part of the sample to determine the water content in accordance with ISO 11465. For the determination of carbon , a representative sub-sample shall be milled until it passes a 250 µm sieve (ISO 11464).	<p>The samples are collected in glass or other suitable containers. Biologically active samples should be analysed immediately or preserved by freezing. Different sample preparation procedures can be used, depending on the type of sample. Solid samples may be comminuted and reduced to a particle size less than 200 µm. Moist samples may be mixed with aluminium oxide and then comminuted to less than 200 µm. For liquid sludges, freeze-drying may be used.</p> <p>The determination of the water content should be carried out on a separate subsample according to ISO 11465 or EN 12880. For samples containing volatile organic compounds, the water content should be determined by, e.g., ISO 3733 (distillation) or ISO 6296 (Karl Fischer).</p>
General hazards	The crucibles used should be large enough to avoid problems when transporting crucibles containing samples to which hydrochloric acid has been added.	<p>The chromate ion is potentially toxic and may damage the environment. Appropriate precautions should be taken to protect the staff and the environment.</p> <p>The addition of water to sulphuric acid is potentially hazardous. Suitable protection is essential.</p>	Not mentioned, but acids are used to liberate inorganic carbon.

Standard	ISO 10694:1995	ISO 14235:1998	EN 13137:2001
Interferences	Not mentioned, but should be very similar to those mentioned in EN 13137.	Mineral reducing compounds , e.g. Cl⁻ and Fe²⁺ , will give false signals. By convention, the chloride content in the test portion should not exceed 2 mg, corresponding to an apparent carbon content of about 0.7 mg.	Method B may lead to incorrect results if the sample contains volatile substances that evaporate during the acidification or if side reactions between the acid and the sample take place. The procedure may lead to unreliable results if the TIC to TOC ratio is higher than approx. 10. Depending on detection method, different interferences may occur. The presence of cyanide can interfere with the coulometric detection of TIC by modifying the pH value. High content of halogenated compounds may lead to an overestimation of TOC when coulometric detection is used. When present, elemental carbon, carbides, cyanides, cyanates, isocyanates, isothio-cyanates and thiocyanates are determined as organic carbon using the described methods.
Equipment	Analytical balance capable of weighing 0.1 mg or microbalance capable of weighing 0.01 mg. Apparatus for determination of the TC content by combustion at a temperature of at least 900°C, including a detector for measuring the CO ₂ formed (titrimetry, gravimetry, conductometry, gas chromatography and IR measurement). Crucibles , made of porcelain, quartz, silver, tin or nickel of various sizes	Analytical balance capable of weighing 0.1 mg. Heating block , capable of maintaining 135°C ± 2°C, including 75 mL volumetric glass tubes. Centrifuge Glass fibre filters Automatic pipette Spectrophotometer (10 mm cuvette, 585 nm) Water bath	Analytical balance , accurate at 0.5% of test portion weight Homogenisation device Crucibles , made of e.g. ceramics, silica glass, platinum or tin Equipment for determination of carbon (not specified) Purging unit for TIC (for method A)
Procedure	The procedure can either determine the TC content including carbonates or the TC content after removal of carbonate. Calibrate the apparatus according to the relevant manual. Use acetanilide, atropine, calcium carbonate, spectrographic graphite powder or potassium hydrogen phthalate.	Transfer a test portion (20-500 mg, depending on expected carbon content) to a volumetric tube. Add 5.0 mL dichromate solution and then 7.5 mL of sulphuric acid. Homogenise. Place the tubes in the preheated heating block and leave for 30 minutes. Remove the	The standard gives no recommendation concerning the construction of the apparatus or the method of operation. Operational characteristics should be selected in accordance with the manufacturer's instructions. The temperature range of available instruments is 900°C to 1500°C. If a relative detection method is used, calibration is carried out

Standard	ISO 10694:1995	ISO 14235:1998	EN 13137:2001
	<p>Weigh out a test portion of the sample in a crucible (amount depending on expected TC content and the apparatus used). Carry out the analysis according to the manufacturer's manual. For determination of the organic carbon content, add an excess of hydrochloric acid to the sample and mix. Wait 4 hours and dry the sample for 16 h at 60-70°C. Then carry out the analysis according to the manual.</p>	<p>tubes and cool rapidly in a water bath. Slowly add 50 mL of water and again cool in the water bath. Transfer the contents to a 100 mL volumetric flask, make up to volume with water and mix. Prepare a standard series by the use of glucose in dichromate solution, digest as above. Measure the absorbance at 585 nm.</p>	<p>using e.g. calcium carbonate or potassium hydrogen phthalate.</p> <p>Method A: TC: The sample is weighed in a crucible, then burned or decomposed in a flow of carrier gas containing oxygen. The CO₂ is measured using a detection method mentioned under "Principles". TIC: The sample is weighed in a crucible. The system is closed and flushed free of CO₂. Acid is added, and the CO₂ is stripped by purging or stirring and/or heating and detected.</p> <p>Method B: The sample is weighed into a crucible. To remove inorganic carbon the sample is treated with a small volume of mineral acid, added slowly. Add as little acid as possible, but enough to soak the whole sample. The sample is transferred to the combustion unit and heated to remove moisture. Then the sample is burnt in the carrier gas containing oxygen. The CO₂ is measured using a detection method mentioned under "Principles".</p>
Calculation	<p>The calculation of TOC can either be carried out as a direct calculation on a sample pre-treated with acid, or by subtracting 0.12 times the CaCO₃ content of the soil (according to ISO 10693) from the TC content determined on a non-acidified sample. The water content according to ISO 11465 is included in the calculations. A formula for the calculation of organic matter is also given, where the TOC content is multiplied by a soil depending factor, which for</p>	<p>Prepare a graph and calculate the amount of carbon present in each sample. Recalculate to the organic carbon content in oven-dry soil using the water content according to ISO 11465 and the mass of the test portion. A formula for the calculation of organic matter is also given, where the TOC content is multiplied by a soil depending factor, which for agricultural soils may vary between 1.7 and 2.5. Comparison between results by this</p>	<p>The TOC mass content is calculated from the calibration function (or if absolute detection methods are used) and the sample mass. The results are reported as the mean of at least two measurements. The TOC is then calculated on a dry matter basis using the calculated water content.</p>

Standard	ISO 10694:1995	ISO 14235:1998	EN 13137:2001
	agricultural soils may vary between 1.7 and 2.0.	standard and ISO 10694 shows that 95% of the TOC present was oxidised.	
Quality control	The repeatability of two separate measurements should satisfy the following: At 0-2.5 g/kg: 0.25 g/kg absolut At 2.5-75 g/kg: 10% Above 75 g/kg: 7.5 g/kg absolut	The repeatability of two separate measurements should satisfy the following: At 0-10 g/kg: 1 g/kg absolute Above 10 g/kg: 6.5%	Control measurements shall be performed each working day to check that the equipment is working correctly. A control mixture made from sodium carbonate, EDTA and aluminium oxide shall be used for Method A and a mixture of sodium salicylate, calcium carbonate, EDTA and aluminium oxide is suitable for Method B. Triplicate analysis of a mixture in the middle of the working range is enough. The mean recovery should be 90-110% with a coefficient of variation of 10% for samples and TOC control mixtures and 5% for TC/TIC control mixtures. A blank value shall be determined for all equipment and reagents used, and shall be taken into account if necessary.
Precision	In an interlaboratory trial, the repeatability standard deviation was between 1-11% and the between laboratory reproducibility 11-65%.		In a European intercomparison study, the repeatability standard deviation was 2-5% for method A and 2-6% for Method B, whereas the between laboratory reproducibility varied between 8-24% for Method A and 5-26% for Method B.

4. CRITICAL POINT AND RECOMMENDATIONS

4.1 Selection of method

The detailed comparison of standards for the determination of TOC demonstrates the possibility of preparing a harmonised and horizontal standard for sludge, soil, sediment, and waste. However, some decisions have to be taken of which the by far most vital concerns the abolition of the chemical oxidation technique prescribed by ISO 14235. Harmonisation of the two standards using thermal oxidation, ISO10694 and 13137, is fairly straightforward.

The suggestion is to use the existing EN 13137 as a basis for a harmonised standard, widening the scope and updating a few sections with elements from ISO 10694. The chemical oxidation technique from ISO 14235 will thus not be part of the harmonised standard. Table 3 presents an outline of the content of the proposed horizontal standard on TOC in regard to issues, where EN 13137 should be updated.

Scope

The scope of the harmonised standard will be sediment, sludge, soil, and waste. Provided the sample handling and pre-treatment techniques are harmonised, it will be possible to widen the scope to incorporate all these matrices in the harmonised standard.

Terminology

The definition of TC, TIC and TOC in EN 13137, which is lacking in ISO 10694, covers the need, and will thus be kept unchanged. There are no obvious contradictions in the terminology used in the current standards.

Principle

ISO 10694 specifies that an air-dried sample should be used, whereas EN 13137 refers to undried samples. On the other hand, EN 13137 mentions drying of the sample as part of the sample preparation process, for example by drying at 105°C or by the addition of aluminium oxide, so in both cases the actual analysis is carried out on a dried sample. This can be solved in the harmonised standard by quite simple rephrasing.

Sample preparation/sample pre-treatment

This is one of the points where there are apparently vital differences between the standards. Whereas ISO 10694 prescribes the use of the fraction <2mm, both ISO 14235 and EN 13137 mentions that the sample should be fractionated to <250 or <200 µm, respectively. It is suggested to use the sample preparation definition from EN 13137, as it is more rigorous and also mentions the possibility of drying the sample chemically (with aluminium oxide) prior to the analysis. All standards prescribe separate determination of the water content by ISO 11464 using a separate sub-sample. EN 13137 gives a few optional techniques suitable if volatile organic compounds are present.

ISO 10694 prescribes the use of “an excess of 4 M HCl” for driving off inorganic carbon as carbon dioxide prior to measurement of organic carbon. EN 13137 does not specify the acid other than “mineral acid”, but mentions 85% phosphoric acid as a possibility. Furthermore, ISO 10694 mentions that the acid treatment should last for 4 hours, whereas no time is specified in EN 13137. It is suggested to use the more specified procedure prescribed in ISO 10694, but to mention phosphoric acid as an alternative acid. Provided a minimum time period is specified, there is no reason to believe that the choice of acid should affect the final result of the analysis.

Calibration

Whereas EN 13137 only mentions calcium carbonate and potassium hydrogen phthalate as examples of suitable calibration substances for TC, ISO 10694 also mentions acetanilide, atropine and spectrographic graphite powder as possibilities. These should all be incorporated in the harmonised standard.

Equipment requirement

Neither of the two combustion principle standards specifies the type of equipment that should be used for the combustion or the detection of the released carbon dioxide, other than it shall be capable of heating the sample to at least 900°C. The specifications in the current EN 13137 will satisfy the needs of the harmonised standard.

Quality control

Only EN 13137 gives quality control proper attention, and it is suggested to use the chapter in this standard in the harmonised standard. However, the use of control charts (X-charts and r-charts) should be recommended more strongly. The repeatability requirement of 5% for TC/TIC control mixtures and 10% for samples and TOC control mixtures (as coefficient of variation) is in line with what is mentioned in ISO 10694 and should thus be kept unchanged.

Table 3 presents an outline of the content of the proposed horizontal standard on TOC in regard to issues, where EN 13137 should be updated.

4.2 Performance characteristics

The standard EN 13137 on TOC in waste, sludge and sediment was validated in an interlaboratory comparison on the following materials: A synthetic mixture, filter cake, bottom ash, electro-plating sludge, dredged sludge and rubble (10 – 20 participants). The standard ISO 10694 was validated in an interlaboratory study on the following soil types: Muck soil, andosol, garden soil, forest soil and sandy soil (9 participants).

The reproducibility, as calculated from the data from the interlaboratory comparisons, shows for TOC for the first mentioned standard an estimate of the relative reproducibility standard deviation of between 12 and 24% (for synthetic sample 9 %). The same figures are seen for four of the soil samples (11 to 23%), however, a relative standard deviation of 62% was obtained for the sandy soil with low carbon content (2,6 g/kg dry soil). For soil samples the total carbon determination exhibited a standard deviation of 5 to 10%, indicating that the uncertainty is related to the determination of the inorganic carbon in samples of high organic matter content, except for the sandy soil sample with low total carbon content. There is no information on the particle size for the samples used in the studies.

There is a lack of validation data on municipal sludge and biowaste. It is therefore proposed to include these sample types in a coming validation study. Other sample types seem well represented, however, laboratory data for soil samples may have developed due to equipment development since the study in 1993.

It is proposed to perform a robustness study prior to the organisation of an interlaboratory study. The study should, among other factors, determine the effects (if any) on using different non-oxidising mineral acids.

Table 3 Outline of the content of the proposed horizontal standard on TOC in regard to issues, where EN 13137 should be updated.

Scope/sample materials	Determination of TOC in sediment, sludge, soil and waste.
Normative references	To be added to the currently referenced standards: ISO 3696:1987 , Water for analytical laboratory use – specification and test methods References to appropriate horizontal standard on sample pre-treatment References to horizontal standard on determination of dry matter and water content
Terms and definitions	--
Principle	The TOC can be measured either by Method A (indirect procedure) or by Method B (direct procedure). Method A: In this procedure the TOC is obtained by the difference between the results of the measurements of TC and TIC. The total carbon present in the un-dried or previously air-dried sample is converted to carbon dioxide by combustion in an oxygen-containing gas flow free of carbon dioxide. To ensure complete combustion, catalysts and/or modifiers can be used. The released amount of carbon dioxide is measured by infrared spectrometry, gravimetry, coulometry, conductometry, thermal conductivity detection, flame ionisation detection after reduction to methane, or other suitable techniques. Method B: In this procedure the carbonates present in the un-dried or previously air-dried sample are previously removed by treating the sample with acid. The carbon dioxide released by the following combustion step is measured by one of the techniques mentioned above and indicates the TOC directly.
Sample storage and preparation	--
General hazards	--
Interferences	--
Reagents	The current reagents list in EN 13137 should be updated with: Calibration substances , e.g. acetanilide (C ₈ H ₉ NO), atropine (C ₁₇ H ₂₃ NO ₃), calcium carbonate (CaCO ₃), spectrographic graphite powder (C), and potassium hydrogen phthalate (C ₈ H ₅ KO ₄). Sodium carbonate and EDTA compounds should not be used for calibration, as they are used in the control mixtures. Non-oxidising mineral acid for carbon dioxide expulsion, e.g. hydrochloric acid (4 M) or phosphoric acid (85%).
Equipment	Standard laboratory glassware Homogenisation device , for example mixers, stirrers, grinders, mills Analytical balance , accurate to at least 0.5% of the test portion weight Boats or crucibles , made of e.g. ceramics, silica glass, silver or platinum Equipment for determination of carbon in solids; with accessories Purging unit for TIC determination (Method A only)
Procedure	Under 10.4 Calibration , reference should be given to the calibration substances for TC mentioned under 7 Reagents . Under 11.3.2 Removal of the inorganic carbon and determination of TOC , the second paragraph should read: To remove the inorganic carbon prior to the determination of the TOC the sample is carefully treated with a small volume of non-oxidising mineral acid (7.10). Add the acid very slowly to avoid foaming and splashing of the sample. Add as little acid as possible but enough to soak the entire sample and to remove the inorganic carbon completely. Allow at least 4 hours for the complete removal of the carbon dioxide.
Calculation	--
Quality control	Under 10.5 and 11.5 Control measurements the sentence “When control charts are used one measurement per batch is sufficient” should be updated to “The use of control charts for documentation of the analytical quality is strongly recommended. When X-charts and r-charts are used, duplicate measurement of one control mixture sample per batch is sufficient”.
Precision	--

5. DRAFT STANDARD

The draft harmonised standard is proposed to be text equivalent to EN 13137:2001 with the amendments as given in Table 3.

REFERENCES

CEN/TC 308/WG 1 Minutes of the 18th meeting, 29th March 2002, London

EN 1484:1997 Water analysis – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)

EN 13137:2001 Characterization of waste - Determination of total organic carbon (TOC) in waste, sludges and sediments

ISO 3696:1987, Water for analytical laboratory use – specification and test methods

ISO 8245:1999 Water quality – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)

ISO 10694:1995 Soil quality – Determination of organic and total carbon after dry combustion (elementary analysis)

ISO 11464:1994 Soil quality – pre-treatment of samples for physico-chemical analysis

ISO 14235:1998 Soil quality – Determination of organic carbon by sulfochromic oxidation