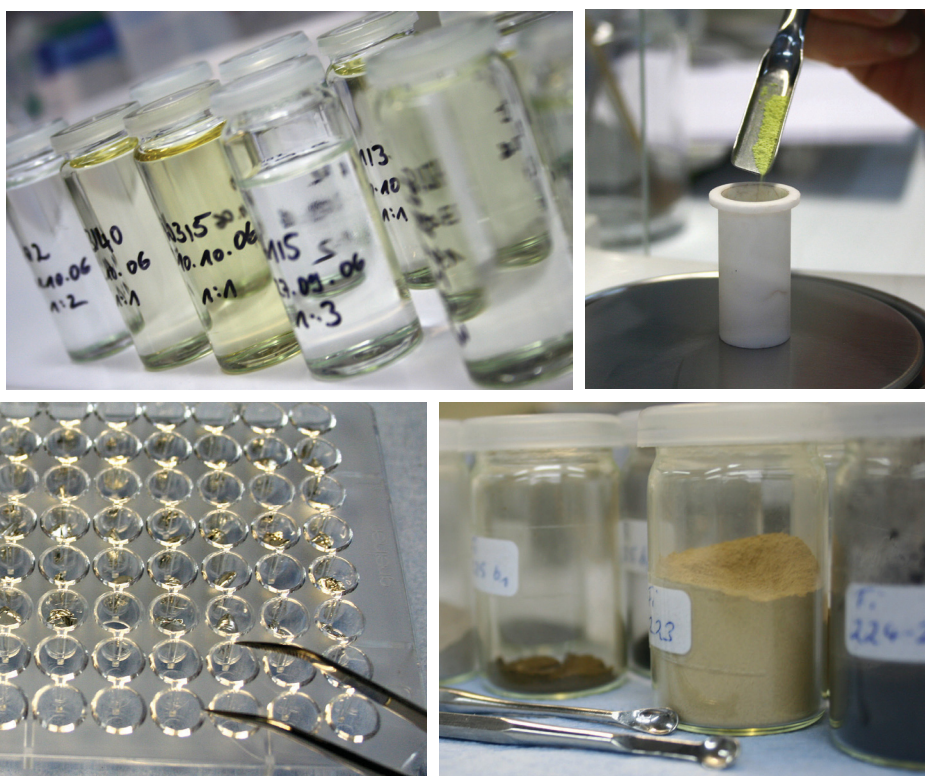


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General principles for the quantification of
Total Organic Carbon (TOC)
in environmental solid and liquid samples

by
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General principles for the quantification of
Total Organic Carbon (TOC)
in environmental solid and liquid samples

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1 TOC analysis in environmental science

The analytical determination of carbon is an essential tool in environmental research for understanding biogeochemical processes. In addition to direct measurements in the atmosphere, scientific investigations in the biosphere, geosphere, and hydrosphere are needed. These require chemical analyses from many different materials and matrices, including soil cores, sediment layers, bedrock, or plants and further biological materials. Aqueous environments are sampled and analysed extensively as well. Ground-, surface- and sea waters, soil solutions, rain- and throughfall are part of this sample spectrum. Measurements of gaseous compounds derived from chemical processes or microbial activities deliver additional data for calculation of element cycles and mass transfer.

For the quantification of carbon, elemental analysers are the suitable instruments to handle a broad range of the aforementioned sample materials [Watson, R.T. 2000, chapter 2.4.2.3.6]. Depending on the configuration of the analyzing systems, solid or liquid samples can be introduced. Some instruments offer the capability to measure both kinds of samples, ideally in an automated fashion. In addition to carbon analysis, elemental analysers can also be used to measure nitrogen, sulphur, and hydrogen simultaneously. Thus, information about the family of chemical compounds present in the sample as well as the biological availability of the elements can be obtained. Further applications of elemental analysis in biogeochemical research are the assessment of the degree of humification in soil organic matter (SOM), the investigation of the storage potential for carbon in soils, and the calculation of carbon fluxes and -budgets in terrestrial systems on regional and global scales [Watson, R.T. 2000, chapter 2.4.2.3.3].

In the environment, the total carbon (TC) can be divided into total organic (TOC) and total inorganic carbon (TIC), depending on origin and chemical characteristics. From an analytical point of view, TOC and TIC are defined measurement categories, also referred to as “sum parameters”, whereas each part can contain several substances in varying proportions.

TOC measurements deliver analytical primary data for scientific investigations and research projects not only of national but also of international importance. The observation, quantification and prediction of carbon sources and sinks within the terrestrial carbon cycle involve among others TOC data originated from elemental analysis. Data are used to develop and check climate models and to assess changes in climate, implemented for example in the IPCC reports [Parry, M. 2007]. On top of organic carbon, the inorganic carbon fraction is of interest as well, e.g. in soil studies, when interactions between TIC amount and the capacity to store TOC need to be quantified [Watson, R.T. 2000, chapter 2.2.5.5].

Separation techniques can be used to determine the sum parameter in question. However, analytical difficulties can arise when the samples contain significant amounts of TIC on top of the TOC fraction. The speciation of the sum parameters can also affect the quantitative results, caused by the thermal behaviour and the chemical resistance of the carbon compounds. This aspect is of particular concern for soils developed from various parent materials like different carbonates, for soils managed under different kinds of land use as well as soil or water samples contaminated by anthropogenic activities.

2 Sample preparation

Qualitative and quantitative performance criteria for modern instrumental analysis are high accuracy and precision combined with a preferably high sample throughput. These criteria are essential to observe and quantify small differences of a parameter within a heterogeneous environment. For instance, several hundred soil samples have been measured for repeated soil inventories of national and European research networks. Analyzing the carbon data, the researchers were able to quantify soil organic carbon stocks of different sites across Europe and to detect small differences in soil carbon stocks between sampling years [Steinbeiss, S. 2008, Schrumpf, M. 2011].

A prerequisite for high accuracy and precision is a well-founded sampling strategy, followed by a careful sample preparation including separation into major components and avoiding contamination at all costs. Today, the technical advances in instrumental analysis allow the use of rather small sample sizes. This not only saves resources such as energy, gases and other consumables; often, after sample separation and isolation of the important components, only a small sample amount remains and must be sufficient for precise quantification. However, the smaller the sample, the more important homogeneity issues become.

Solid samples are coarsely crushed at first. To inhibit microbial alterations, wet materials like field-fresh soils or plants need to be stabilized before further treatment. In general, soil samples are dried at 40 °C [DIN 19747, Schlichting, E. 1995, chapter 5.2], provided that microbial analyses are not planned. This procedure results in “air-dry” samples, a common expression in soil analysis. Note, that the calculation of contents is usually related to “absolute dry” weights (105°C) to overcome differences in water absorption from ambient air. To handle this rarely known and never constant value, the residual water content of the air-dry samples has to be determined at the same time as the weighing process for TOC- or other content analysis [DIN ISO 11465, Schlichting, E. 1995, chapter 5.2.3]. Organic layer and plant materials are de-humidified at temperatures between 60 and 70 °C for storage and prior to analysis. Alternatively, samples can be stored frozen for some month.

For soils, the soil skeleton, fine roots, soil animals and their remains have to be removed and weighed separately. The skeleton comprises stones and mineral parts > 2 mm. Standard stainless steel sieves with defined meshes or sieving machines separate the skeleton from the further used fine soil. In order to avoid the formation of sclerotic aggregates, clay samples should be sieved before complete air-drying [Schlichting, E. 1995, chapter 5.2]. The separation of fine roots from soils is notoriously prone to operator errors and, thus, can influence the TOC measurements considerably [Schneider, K. 2015]. The error can amount up to 10 % [Scheffer, F. 2002, chapter 3.1.7].

Partitioning of sample material into representative subsamples can be carried out with a sample splitter device, thus avoiding possible segregation of constituent parts with different particle densities. The subsamples thus obtained can be finely ground manually, for instance using an abrasion-proof mortar, whereas agate is more suitable than hard porcelain. Better (but also more expensive) alternatives are ball mills or planetary mills. Grinding bowls and balls must be made of low-abrasion and contamination-free material [Schlichting, E. 1995, chapter 5.2]. Zirconium oxide, for example, serves these criteria. The sample material should not grow warm during the fine grinding process as this may result in loss of volatile compounds. Plant material usually requires shorter milling times than the more siliceous soil samples. If the sample is warming-up, it is recommend to work with intervals or to precool the milling equipment. For extreme requirements, cryo-mills are available, which can work

with liquid nitrogen. Plant samples often contain fibers which are almost impossible to pulverize by milling. However, by freezing the sample with liquid nitrogen prior to grinding, an improvement can be achieved [de Groot, P.A. 2004, chapter 9.3.5]. Very sensitive or very small samples should be homogenized using a single ball in small cups, with reduced grinding time and -frequency. Finely pulverized samples usually are stored in dark glass bottles.

Sample preparation tests have shown that soil samples, which have not been ground sufficiently, do not achieve reliable and precise results (see Tab. 1). Elemental analysis of soils (A, B, C) with still visible grain structures results in carbon data with low precision. Higher sample weights, often used to solve homogeneity problems, do not lead to more precise results for these samples. Compared to this, soil reference material (R) ground to powder without visible structures shows precise data with a relative standard deviation < 1%.

Tab. 1: Total carbon content and coefficient of variation (cv) from repeated measurements, ~80 mg* and ~250 mg# sample material, Max-Planck-Institute for Biogeochemistry. Soils (A, B, C) with still visible structures compared to powder-like soil reference material (R)

sample	soil depth [cm]	total carbon [%]						cv [%]
A	0- 5	3.88*	1.88*	5.75*	5.33*	6.12#	4.61#	33.83
B	30-40	6.00*	6.54*	5.35*	4.89*	8.67#	5.89#	21.30
C	20-30	3.11*	1.67*	5.20*	2.90*	3.92#	3.04#	35.56
R	topsoil	3.44*	3.39*	3.42*	3.48#	3.46#	3.47#	0.98

The grinding procedure should result in a powder-like material, without residual and optically recognizable structures [de Groot, P.A. 2004, chapter 9.3.5]. This must be checked regularly. Grinding intensity can vary depending on soil depth and soil type. Especially silicate-rich soil samples often require longer grinding.

Great care must be exerted when collecting and storing water samples and soil solutions. The content of biodegradable material, dissolved oxygen and carbon dioxide may be altered during storage by biological activity and by physico-chemical processes. Organic substances may be oxidized by dissolved oxygen. Some substances may precipitate, e.g. calcium carbonate, or may be subject to outgassing, like CO₂ and other dissolved gases. Water samples and solutions, especially with a non-acidic pH are prone to CO₂ absorption. To avoid possible alterations change, it is best to analyze a sample immediately after collection. For many types of analysis, this is not feasible. Hence, appropriate conservation methods need to be applied. Physical or chemical sample preservation methods are possible, also a combination of both can be useful. Physical methods include preservation by cooling (2-5 °C, for a few days), by freezing (-18 °C, for several month) or by deep-freezing (-80 °C), when the samples need to be stored much longer. Physical preservation mostly is preferred compared to chemical methods because the samples retain their original composition. However, especially for soil extracts, humic substances may precipitate after freezing and thawing. As a consequence, the measurement of dissolved organic carbon (DOC) leads to inaccurate results, and the observed changes are not reproducible [Landgraf, D. 1999]. Chemical methods include acidic preservation with non-oxidizing mineral acids. They can be used for example for measurement of Non-Purgeable Organic Carbon (NPOC), a special category of DOC. Because acidification releases carbonate and bicarbonate carbon, TIC quantification is no longer possible in such preserved samples, rendering carbon balance measurements useless. Volatile organic compounds (VOC) can also be influenced. To avoid

loss of VOC's the samples should neither be acidified, nor homogenized in open vials. Dissolved humic substances may precipitate in acidic solutions as well [Scheffer, F. 2002, chapter 3.1.7., de Groot, P.A. 2004, chapter 15.3]. Alkalinization, which can be used for detecting anionic parameters, will result in carbon dioxide absorption from ambient air and, therefore, is no viable option. Rather, for TIC- and TOC-analysis, a chemical preservation only using substance specific reagents can be made in order to suppress microbial activity. Copper sulfate (CuSO_4) and mercury chloride (HgCl_2) are common examples for this technique, also silver ions (Ag^+) or azides (N_3^-). However, for environmental and health protection hazard reasons, this method should be handled with great care.

Sample pretreatment such as filtration has to be performed before preservation, immediately after sample collection. For high sample volumes, a pressure filtration is preferred over vacuum filtration, because it prevents outgassing of volatile components. Filters typically used for DOC-measurements are made of glass-fiber, cellulose nitrate or polycarbonate. The filter pore size defines different classes of dissolved organic matter (DOM) [Zsolnay, A. 2003]; sizes of 0.2 μm , 0.45 μm or 0.9 μm are commonly used. Tested for their qualitative and quantitative suitability before usage, the filters have to be rinsed with a part of the sample volume and the rinsing liquid has to be discarded. Glass-fiber filters (GFF) can be ignited before use to remove traces of potential carbon contamination, a great advantage of this material. The filtered sample can be filled into vials for analysis or storage. For carbon analysis, glass, high-density polyethylene or polypropylene bottles with tight caps are recommended for sample storage, thus avoiding impurities from the bottle wall or evaporation through the cap. The bottle size should closely match the sample size, keeping only a small head space. This helps to avoid CO_2 admixture upon opening the bottle to atmosphere.

The chemical preservation methods, the filtration- and the storage issues for liquid samples have been described in [de Groot, P.A. 2004, e.g. chapter 1.2, 15.3]

3 Preconditions for TOC measurement

Depending on sample properties, analytical requirements and technical equipment, the TOC can be determined either directly or indirectly. The direct quantification measures the parameter in question as such, a preferable method in many cases. In contrast, the indirect path obtains TOC values from calculation and needs an additional measurement: TC and TIC. The TOC is quantified subsequently as difference $\text{TOC} = \text{TC} - \text{TIC}$. Although the errors of TC- and TIC measurement are added for this method, the quantification of TOC using the indirect path can yield more accurate results than the direct determination, an effect of the applied techniques.

Independent of the chosen analysis mode, quantitative analysis is comprised of three principle steps (Fig. 1):

1. Separation of the sum parameter in question (TOC and / or TIC from the TC),
2. Conversion of the carbon containing compounds into a single stoichiometric species (e.g. carbon dioxide; CO_2),
3. Detection of the evolved reaction product in a direct or indirect way.

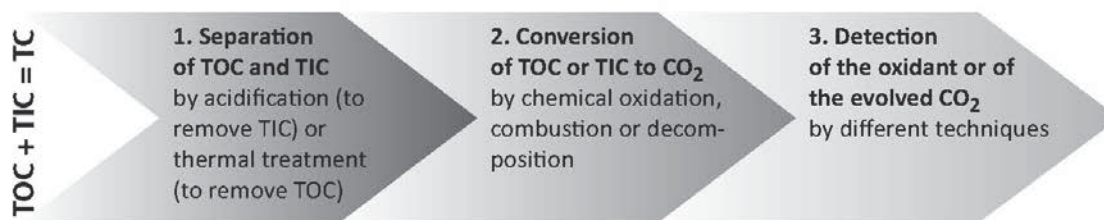


Fig. 1: Basic steps for analytical determination of the carbon sum parameters

4 Separation of TOC and TIC

Separation of the sum parameters can be carried out in a

- chemical or
- thermal pretreatment step.

In both cases, the treated sum parameter will be destroyed, i.e. it will be converted to CO₂. For some applications, the conversion product can be used directly for subsequent quantification (Fig 2). Both techniques, chemical and thermal pretreatment, allow direct or indirect quantification of TOC.

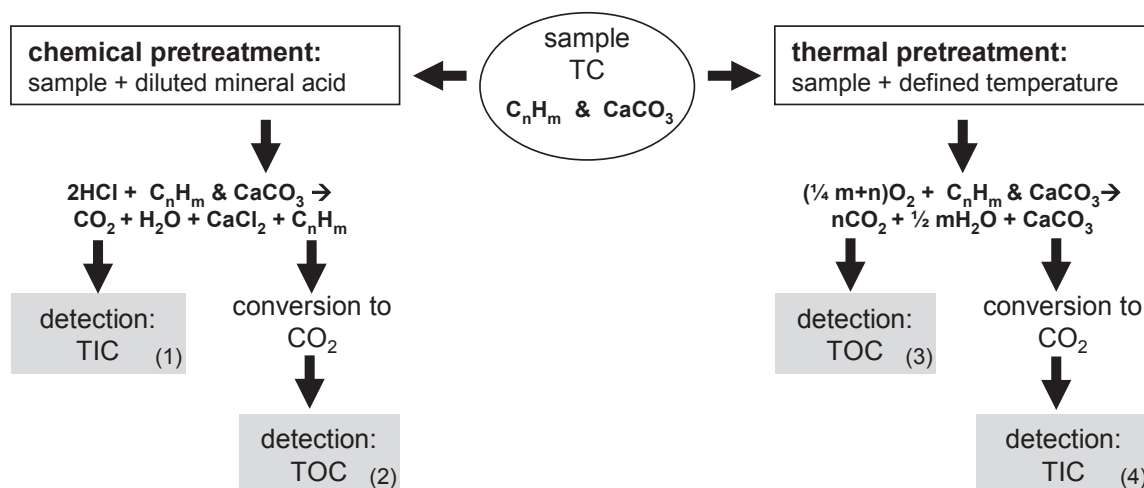


Fig. 2: Flow chart summarizing analytical procedures to separate the sum parameters TOC und TIC from TC in samples containing organic compounds and carbonates

Chemical pretreatment

The sum parameter separation via chemical pretreatment with mineral acid is used to destroy solid and dissolved inorganic carbon compounds, which react to carbon dioxide (CO₂).

In soils and sediments, the sum parameter TIC mainly consists of different, pedologically important carbonates [Bisutti, I. 2004, Schumacher, B. A. 2002, Schlichting, E. 1995, chapter 3.5.5]. Despite of this, the sum parameter TOC as part of SOM comprises carbon compounds in dead plant and animal tissues and in their transformation products as well as synthetics, organic carbon compounds derived from anthropogenic activities [Scheffer, F. 2002, chapter 3, Schumacher, B. A. 2002]. Soot, charcoal and other pyrolytic products named in literature as black carbon, form a part of organic matter, too [Scheffer, F. 2002, chapter 3], also referred to as elemental carbon, abbr.: EC [Schumacher, B. A. 2002].

From chemical point of view, TIC comprises elemental carbon, carbon oxides, carbon disulphide, and carbides as well as ionic cyanates, thiocyanates, and cyanides. Inorganic cyanide compounds found most frequently in soils or ground water are alkali cyanides and ferrocyanide species, commonly originating from industrial processes [Kjeldsen, P. 1998]. Cyanide contaminated samples require a separate treatment for analysis (release of toxic hydrocyanic acid (HCN)!). In calcareous soils, the dominating minerals for example are calcites and dolomites, whereas carbonic acid and its dissociation products (bicarbonate or carbonate) represent inorganic carbon in water [Bisutti, I. 2004].

The quantitative conversion of the carbonates to CO₂ depends on several factors. These are for example concentration and amount of the acid, reaction temperature and -time, kind of sample and composition, grain size in case of solid materials etc. The more information about the sample itself is available, the more specific the analytical procedure can be made, with procedural parameters varying with application areas and acid suitability (Tab. 2).

Tab. 2: Mineral acids used for TIC separation in solid or liquid samples [Bisutti, I. 2004, Brodie, C.R. 2011, Schlichting, E. 1995, chapter 5.5.4]

acid	field of application (+) advantages and (-) disadvantages
HCl	<p>in general used to quantify TIC in soils (DIN ISO 10693), as well as pretreatment agent for subsequent TOC measurements (DIN ISO 10694, DIN EN 13639), but also for sum parameter quantification of carbon in liquid samples</p> <p>(+) quantitative reaction with many carbonates (except siderite), variable in application (e.g. HCl concentration, techniques incl. time, temperature)</p> <p>(-) a) in situ-technique: possible overflow of material, CaCl₂ and / or HCl residues in the sample containers, risk of hydrolysis and CaCl₂-coating, high potential to damage components of analytical instruments</p> <p>(-) b) rinsing-technique: loss of SOM, depending on acid concentration, heating</p> <p>(-) c) fumigation: like in situ-technique, and inefficient TIC removal</p>
H ₂ SO ₃	<p>used for soil treatment, particularly for sample pretreatment in δ¹³C analysis as alternative to HCl</p> <p>(+) no or only small impact on SOM compared to HCl techniques</p> <p>(-) if heating is applied, decarboxylation can take place</p> <p>(-) not usable for samples containing dolomite or siderite, incomplete reaction</p> <p>(-) in situ-technique: overflow of material, hydrolysis, formation of SO₂ during subsequent elemental analysis</p> <p>(-) can be a source of TOC contamination</p>
H ₃ PO ₄	<p>preferred in water analysis as alternative to HCl to remove inorganic carbon and to determine NPOC subsequently (DIN EN 1484:1997-08)</p> <p>(+) limits the risk of material damage</p> <p>in soil analysis applied with heat</p> <p>(+) formation of sparingly soluble calcium phosphate can promote the reaction</p>
others	<p>HNO₃, H₂SO₄: not recommended, because of their oxidation potential;</p> <p>H₂SO₄ with FeSO₄: FeSO₄ is added to minimize oxidation and decarboxylation of organic matter; HClO₄: only for liquid samples. No heating! Otherwise oxidation of SOM, formation of perchlorates.</p>

Three different acidification techniques are commonly used to separate TOC in solid samples from TC and to determine it directly via dry combustion (Fig. 2, point 2). These preparation techniques can also be applied before isotopic measurements of $\delta^{13}\text{C}$:

- a) acidification in acid-resistant autosampler containers, e.g. in silver capsules or ceramic boots (in situ-technique)
- b) acidification in beakers with subsequent water rinsing steps (rinsing-technique)
- c) acidification with acid vapour (fumigation) [Brodie, C.R. 2011].

When the in situ technique is applied, the silver capsules additionally have to be wrapped with tin-foil before the measurement starts in order to ensure complete combustion [Brodie, C.R. 2011].

In general, mineral acids with low or non-oxidizing potential should be applied to prevent the oxidation and loss of organic carbon compounds. The latter is important for the rinsing-technique, where a possible loss of acid-soluble organic substances can appear. However, for all these techniques, the acid-resistance of the used lab devices and analyzers containing damageable components should be taken into account as well.

For liquid samples, an acidification at $\text{pH} < 2$ is necessary in order to convert all dissolved carbonates and bicarbonates into carbon dioxide (CO_2). Subsequent purging removes the inorganic CO_2 from the sample. NPOC can be measured directly, usually through combustion of the treated sample.

For TIC measurements of acidified solid or liquid samples (Fig. 2, point 1) the evolved CO_2 can be determined in several ways. When the TC value is available, TOC can be calculated as the difference $\text{TOC} = \text{TC} - \text{TIC}$. For the substance specific detection of the TIC-derived CO_2 , e.g. with infrared spectrometry, the mathematically obtained TOC value includes also potential VOC's. However, for very small differences, this indirect TOC method cannot be used.

Thermal pretreatment

The sum parameter separation via thermal pretreatment removes the TOC at a defined temperature in an oxic atmosphere and can be applied to solid samples. Using knowledge and experience from the Loss-on-Ignition method (LOI), this treatment is based on the assumption, that organic compounds are combusted quantitatively at a certain temperature, while carbonates remain unaffected. For applying this method, a muffle furnace or a special dry-chamber can be used. In contrast to LOI, the TOC in question is not calculated from the weight loss using individual conversion factors but as the difference between the directly estimated TC minus the directly estimated TIC, the latter received from the pre-treated subsample (Fig. 2 point 4). Although the method turns out to be a rather indirect way for TOC-quantification, the pros outweigh the cons. These are for example high precision and accuracy for suitable samples, high sample throughput, operator convenience and technical protection of analytical instruments [Hilke, I. 2003, Schreider, K. 2015]. Like the chemical pretreatment, the thermal pretreatment method has a number of factors which can influence the quantitative results. The most important factor is temperature, which needs to be high enough to oxidize the TOC, but not too high so that carbonates remain unaffected. Especially for magnesite, it is difficult to choose the correct temperature. The mineral starts to decompose at 350°C . At 500°C , the temperature at which most organic compounds will combust quantitatively, already 5 % of the magnesite carbon may be lost (Fig. 3).

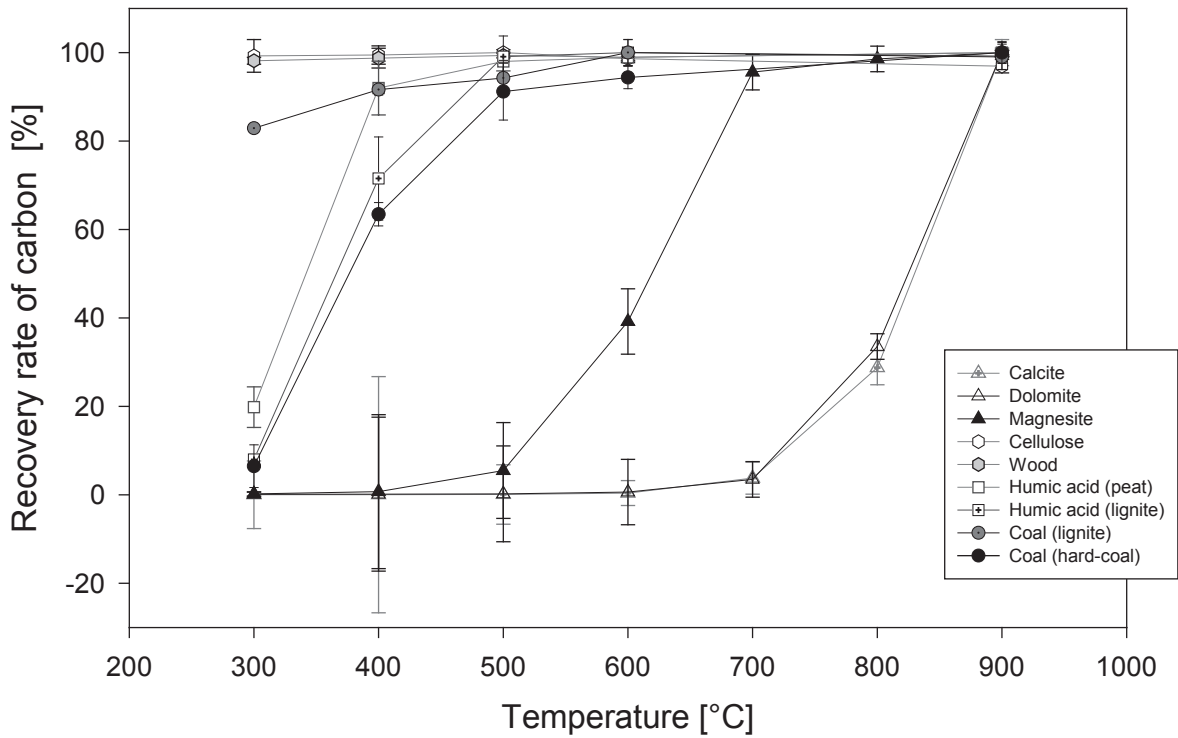


Fig. 3: Combustion and decomposition temperatures of different organic and inorganic carbon compounds [Bisutti, I. 2007]

Some elemental analyzers have the option to combust solid samples with a dynamic oven using a temperature program for one and the same sample. The lower temperature is applied to measure TOC, the higher to measure TIC. Also, some instruments allow simultaneous hydrogen measurements, an extra tool to check whether the organic carbon is quantitatively destroyed at the lower defined temperature. Combustion conditions for this direct method (Fig. 2, point 3) can differ compared to the thermal sample pretreatment in a muffle furnace or in an other extra device (Tab. 3), because the reaction time is restricted by the measuring process and -software. Total nitrogen measurements, which are often needed together with carbon measurements to characterize organic matter, can not be analysed simultaneously with this method.

Tab. 3: Examples for thermal pretreatment of solid samples (according to LOI-Method) [Bisutti, I. 2004]

samples	temperature and time to remove TOC
sandy soils	550 °C for 4 hours
arid zone soils	400 °C for 8 hours
mineral soils	450 °C for 12 hours
forest floor	450 °C for 12 hours
different loams	450 °C for 4 hours
sediments	450 ± 10 °C for 16 hours; 475 - 500 °C for 4-6 hours
particulate carbon	500 °C for 4 hours

5 Conversion methods to form CO₂

The conversion of carbon compounds into CO₂ can be achieved either by combustion of the sample material or by addition of oxidizing agents. The most commonly used method today is dry or Dumas combustion. In comparison to dry combustion, the wet combustion is a combined method, which needs both, addition of oxidants and heat. In all cases the reaction product CO₂ is measured for quantification of TOC. In addition, the remaining oxidant may be used as for quantifying the organic compounds. In the literature these methods are referred to as chemical oxidation procedures.

Dry combustion

The dry combustion method is based on the thermal oxidation of carbon compounds. It is applicable to solid and liquid samples. Depending on an eventual separation step before measurement, TOC, TIC, or the sum of both are converted to CO₂. Carried out as high-temperature technique, dry combustion is assumed to ensure a quantitative oxidation of organic carbon and therefore considered as the reference method. Most elemental analyzers are designed on the basis of this technique, varying in the use of different catalysts and their associated combustion temperatures (combustion in an empty tube with pure oxygen as carrier gas can be subsumed here as well). The most commonly used catalysts are tungsten(VI) oxide (WO₃), cerium dioxide (CeO₂), chromium(III) oxide (Cr₂O₃), copper(II) oxide (CuO) or platinum on carrier (Pt) using temperatures in the range of 1150 °C to 650 °C. Depending on detection techniques, different carrier gases are used, for example helium + oxygen, argon + oxygen, synthetic air, clean high-pressure air, pure oxygen etc. For solid samples, chemical additives such as WO₃ can support the oxidation process and prevent matrix effects.

Liquid samples are either directly injected into the combustion system or evaporated prior to injection. If directly injected, the evaporation step is critical for quantitative recovery. Because of flash evaporation, the sample will expand into a large volume immediately, pressure and gas flow increase in a step function. Minimal injection volume and gas flow regulation techniques prevent deviation in detection and quantification of the evolved CO₂.

Wet combustion

The wet combustion method is based on a rapid oxidation of organic matter with dichromate (Cr₂O₇²⁻), carried out in an acidic mixture with concentrated sulfuric acid (H₂SO₄) and heat. The evolved product CO₂ is measured (rather than the remaining oxidant in chemical oxidation methods). In general, the method is applied to sediment and soil analysis; it is also usable for samples with high chloride contents. Because of the subsequent CO₂ measurement, TIC has to be removed before TOC determination. However, detection of TIC and TOC from one and the same sample is possible too, for example by detecting TIC using decomposition with phosphoric acid before TOC oxidation. The method has the potential for automation, for example in combination with flow systems.

Chemical oxidation

Chemical oxidation usually is some form of wet combustion method or variations of it. The oxidation of organic carbon inside the liquid can be carried out with dichromate (Cr₂O₇²⁻), but also with peroxy-disulfate (S₂O₈²⁻), shortened to “persulfate” in the following). Sometimes, also UV radiation is applied to drive the oxidation to completion.

Dichromate oxidation is one of the best known techniques, comprising the Walkley-Black-method and its numerous modifications. The latter include a different temperature or reaction

time, or use of a suitable catalyst. Because oxidant loss is the measurand, no separation of TIC and TOC is needed prior to quantification of organic carbon. Therefore, the Walkley-Black-method has been used widely for soils, sediments and waste samples for a long time, also as reference method. In waste water analysis, the dichromate oxidation is used for estimating the quality parameter “Chemical Oxygen Demand (COD)”. However, there are some restrictions. Apart from the toxicity of dichromate, the TOC recovery yield (often < 1) and the cross-sensitivity to other oxidizable substances needs to be taken into account. In soils, oxidizable carbon (OXC) depends on the chemical behaviour of the organic compounds and on matrix properties like soil texture, clay content and pH. In soils of similar type, OXC can form an approximately constant fraction, generally 75–85% of the TOC [Bisutti, I. 2004]. A correction factor or equation, determined empirically for each soil type and origin may be used for quantifying OXC in such samples. Otherwise, interferences or cross-sensivities caused by chloride ions (Cl^-), ferric ions (Fe^{2+}) and manganese dioxide (MnO_2) for example, can pretend higher amounts of TOC because of their additional uptake of oxidant. To reduce interferences of Cl^- , either Ag_2SO_4 addition or a stoichiometric correction are needed, an oxidation of interfering Fe^{2+} can be achieved by drying the samples with air before measurement.

Oxidation with persulfate is generally used for determination of dissolved organic carbon (DOC) in water samples. DOC differs from TOC in particle size (see chapter 3.1.1.2). The use of silver ions as catalyst in an acidic medium has been described for the determination of soil organic carbon in various forms, but also for DOC. For direct quantification of organic carbon, the TIC has to be removed prior to the addition of the oxidant.

Persulfate oxidation can be accelerated either by heat or by UV. High chloride concentrations can interfere with the reaction, such as in sea-water samples. Using a higher concentration of the persulfate reagent, extending the reaction time or the addition of a sequestering agent can help. Persulfate, like dichromate, tends to decompose with increasing temperature. Because the decomposition can be faster than the rate of oxidation, the concentration of the oxidant should be increased rather than the temperature to accelerate the reaction. The combination of persulfate with UV increases the recovery of organic carbon compounds. This combined technique is employed in TOC-Analyzers for sum parameter detection in liquid samples; the separation of TIC and TOC is carried out by adding phosphoric acid prior to adding the oxidant. High-Performance Liquid Chromatography coupled with Isotope Ratio Mass Spectrometry (HPLC/IRMS) can be combined with the persulfate oxidation technique, for example to measure dissolved organic matter (DOM) in soil water samples and to determine the isotopic signature of the organic compounds [Scheibe, A. 2012].

Photooxidation

Oxidation with UV can be accomplished in automated systems as the liquid sample passes over an UV light and the organic carbon is converted into CO_2 . UV lamps providing two wavelengths enable both, the production of highly reactive radicals by water radiolysis as well as the oxidation of organic molecules. The technique is used to enhance performance in continuous flow systems [Federer, U. 2008]. TC and TIC are determined simultaneously in the acidified sample, which is split into two channels with and without additional UV-oxidation. The TOC is obtained indirectly as the difference between the two results.

The specified conversion methods in this chapter have been described and cited in a review paper [Bisutti, I. 2004].

6 Detection techniques

The detection techniques used in TOC analysis follow one of two principles: determination of the evolved CO₂ or measurement of the remaining oxidant.

The most commonly employed methods to detect the evolved CO₂ are:

- **Thermal conductivity detection (TCD):** Differences in thermal conductivity between the pure carrier gas (mostly helium) and the carrier gas containing the analyte are quantified. Some detectors can also be run with argon, although the TCD signal will be smaller owing to the lower relative difference in thermal conductivity. The TCD is universal detector; all substances passing through the measuring cell generate a signal at this detector. Hence, on top of CO₂, also nitrogen, sulfur dioxide and hydrogen dioxide (water-vapour) can be detected at no additional cost. Separation of the original sample gas mixture is required, the TCD is not selective for the different combustion gases. Gaseous components can be concentrated using purge and trap and separated on specific heatable adsorption columns, as is common in gas chromatography. The different adsorption columns can be operated chromatography-like; the different components from the combustion reaction (N₂, CO₂, SO₂ and H₂O) are released one after the other and detected accordingly, which (compared to uninterrupted chromatography) requires slightly enhanced analysis times. Interferences from other gases can cause errors in quantification. Typical examples are methane or carbon monoxide, both of which can arise from oxygen-deficient combustion. The TCD is characterized by a large dynamic range; it is linear over several orders of magnitude. However, because of its low sensitivity, it is not suitable for detecting trace amounts of material or compounds. Corrosive substances like hydrogen halides can affect the lifetime of the filaments inside the detector.
- **Non-dispersive infrared spectrometry (NDIR):** The concentration of the carbon dioxide in the combustion gas is measured electro-optically by absorption of a specific wavelength in the infrared spectrum. This kind of detector has high sensitivity and specificity, coupled with a low detection limit. Because of its specificity, combustion gases like carbon dioxide and sulphur dioxide can be detected simultaneously, which shortens the time required for analysis. Nitrogen, however, cannot be determined by this technique. There are no absorption lines available in the IR. In order to include nitrogen quantification, combinations of NDIR with TCD are available. Water interferes with the detection of CO₂, hydrogen halides can have a negative impact on the lifetime of the cuvettes in the detector.
- **Conductometry:** A conductometric instrument measures changes in electrolyte conductance. More specifically, the electric current through the analyte flow is observed, with a constant voltage applied between two electrodes inside the detector. CO₂ from the combustion reaction is dissolved into the liquid water flow. The resulting change in conductivity is measured and the carbon content can be calculated. Conductometric detection usually exhibits an extremely stable calibration and is not susceptible to significant drifts over time, compared to the NDIR technique. The performance can be enhanced by using a gas-permeable membrane preventing compounds such as acids, bases and halogenated compounds from interfering with the measurement of CO₂.
- **Manometry:** manometric detection is carried out either by gas volume- or by pressure measurement. The technique is often encountered in older lab-equipment such as the manually-operated Scheibler-devices for TIC-measurements in soil samples or the various Ströhlein instruments. After acid treatment, the evolved CO₂ volume is measured. Usually the gas volume is read by the user directly using a burette scale. The content of CO₂ has to be calculated from these observations using correction factors for temperature and air

pressure. The procedure is not very sensitive and operator-specific errors in reading the analog instruments cannot be avoided. Interferences may arise from sulfur dioxide, hydrogen sulfide and from organic compounds which can de-carboxylate (i.e. release CO₂).

Further detection techniques of CO₂ are turbidimetry, potentiometry, ion chromatography, flame ionization detection, often combined with gas chromatography.

The methods for oxidant determination are:

- **Titration:** This method is generally used after chemical oxidation of organic compounds and does not need the separation of inorganic carbon. For direct titration, the oxidant excess is detected. For back-titration, FeSO₄ is added and titrated with di-chromate following oxidation. Direct titration is the more reliable technique. Back-titration is prone to carbon over-estimation, because chromic sulfate has a catalytic effect on the decomposition of excess di-chromate.
- **Photometry:** The absorbance of green-colored chromium (Cr³⁺), generated during the oxidation of organic carbon compounds, is measured either at 600 or 625 nm. The method is suitable for automated routine analysis, for example in continuous flow systems.

The specified detection techniques in this chapter also have been described and cited in the review by Bisutti et.al. [Bisutti, I. 2004].

7 Applications

For selecting a suitable TOC determination method, the analytical goal and the physico-chemical properties of the sample material must be taken into account. The expected sample throughput and the kind of elemental analyzers are also important issues which have to be considered. Instruments of different manufacturers provide various options regarding a potential separation of TIC and TOC, the conversion of the carbon components to carbon dioxide, the detection of the evolved CO₂, and additional other combustion components. Options like a two-zone-oven with combustion and post-combustion unit, the use of a dynamic heater for the application of temperature gradients or the potential switch between oxidizing or inert gas conditions offer a thermal fractionation and separation of soil carbon components during analysis. However, neither for solid samples in general nor for soil samples a universal method covering the whole sample spectrum can be found. Additional information on soil type and parent material may be helpful. With this knowledge and with first test measurements, the relative proportion of TOC and TIC in a sample or the thermal and chemical behavior of these components may be assessed. This helps to decide, whether an acid or a thermal separation of TIC and TOC is more usable and whether the direct or the indirect quantification of the parameter in question should be chosen (Fig 2).

In order to validate the quantification results of organic and / or inorganic carbon in unknown samples it is recommended to use a second method as a reference. Chemical standards and certified reference materials should be used routinely in order to ensure the accuracy of the measurement results as well as the long-term performance of the instruments. Measurements obtained with a given instrument at specified conditions should be reproducible given the

same conditions. If a single parameter is changed, the user must check whether the method is still suitable.

For solid samples, the temperature-dependent separation of TOC and TIC can be influenced for example by the carrier gas (e.g. pure oxygen or an inert gas mixed with oxygen during the flush combustion), the catalyst, the sample weight and the sample containers (e.g. the geometrical shape and the heat conductance of the material are of importance), even when the predetermined temperatures are comparable. Sample additives have an influence on the reaction as well. Tungsten(VI)oxide (WO_3), for instance, enhances the combustion of organic compounds and acts as a slag former; adding silver foil to the samples can delay the thermal decomposition of magnesite considerably [Bisutti, I. 2007].

SRDTC Method

The Single Run Dual Temperature Combustion (SRDTC) was developed to determine TOC and TIC of a solid sample in a single step. The method is based on the assumption that organic carbon is combusted at lower temperatures (e.g. 515°C) and oxidized to CO_2 in an atmosphere of pure oxygen whereas substantially elevated temperatures (e.g. 925°C) are needed for the complete decomposition of inorganic carbon. For synthetic samples the results for TOC, TIC, and TC indicated good agreement with the theoretical values. However, significant differences in TOC and TIC contents were seen when samples contain low amounts of TOC ($\leq 0.25\%$) in addition to high amounts of TIC ($\cong 10\%$). Also the chemical characteristics of the carbonates became important. Addition of silver foil to the samples considerably reduced the thermal dissociation of magnesite and resulted in much better distinction between TOC and TIC [Bisutti, I. 2007]. The instrument used in the study is not available on the market anymore.

550°C Method

This method is being developed for determining organic carbon in mineral soils following the SRDTC Method. The samples are flush-combusted in an elemental analyzer at a temperature of 550°C , in presence of oxygen during the combustion process (e.g. helium + oxygen gas mixture). The use of sample containers made from steel instead of ceramic is highly recommended, to allow a fast heat transfer. The evolved CO_2 represents the content of organic carbon. It is separated from interfering combustion products and measured by thermal conductivity or infrared detection. By convention, inorganic carbon remains unaffected or can be neglected, respectively.

High-temperature Combustion (HTC)

The samples are combusted in presence of oxygen at a defined temperature between 900°C and 1500°C , depending on the analyzing system. To separate the carbon components, inorganic carbon compounds are destroyed prior to the HTC step by treatment with diluted non-oxidizing acid or determined in parallel using a subsample after thermal pretreatment. In the latter case, the TOC is determined indirectly and calculated by difference from TC minus TIC. This method is described as Muffle Furnace Method (MFM) [Hilke, I. 2003].

Muffle Furnace Method (MFM)

The MFM combines the decomposition of organic carbon as known from the loss on ignition procedure (LOI) with the precise measurement of the remaining inorganic carbon using high temperature combustion with an elemental analyzer. The pretreatment temperature of 450°C and a decomposition time of 16 h results in the best fit between measured and target values in synthetic samples with known contents of TIC and TOC [Hilke, I. 2003].

Chemical pretreatment + HTC versus Thermal pretreatment + HTC

In a comparative study the separation and measurement of TIC and TOC were carried out with two contrasting approaches:

- a) the direct measurement of TOC using high-temperature combustion after the removal of carbonates with a non-oxidizing agent (e.g. hydrochloric acid according DIN ISO 10694, named as HCl Method in the following) or
- b) the indirect determination of TOC as calculated from $TOC = TC - TIC$ after thermal decomposition of soil organic matter in a muffle furnace (450 °C, 16 h, MFM) and following measurement of the remaining TIC with high-temperature combustion [Hilke, I. 2003].

Both analytical approaches work reliably when soils contain low or intermediate contents of TOC and carbonates (Fig. 4).

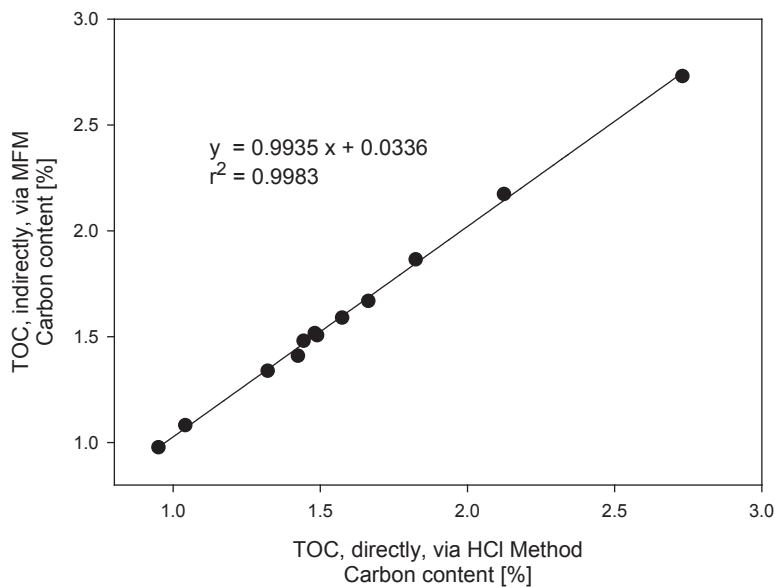


Fig. 4: Correlation between TOC determined directly (following DIN ISO 10694, HCl Method) and indirectly (Muffle Furnace Method, MFM) in samples from a calcareous soil profile containing < 4.5 % TIC in subsoil.

When a soil sample is rich in carbonates (> 6% TIC) however, the carbonate removal with acid can be incomplete, resulting in an overestimation of TOC. This effect suggests an increase of soil organic carbon in subsoil (Figs. 5, 6).

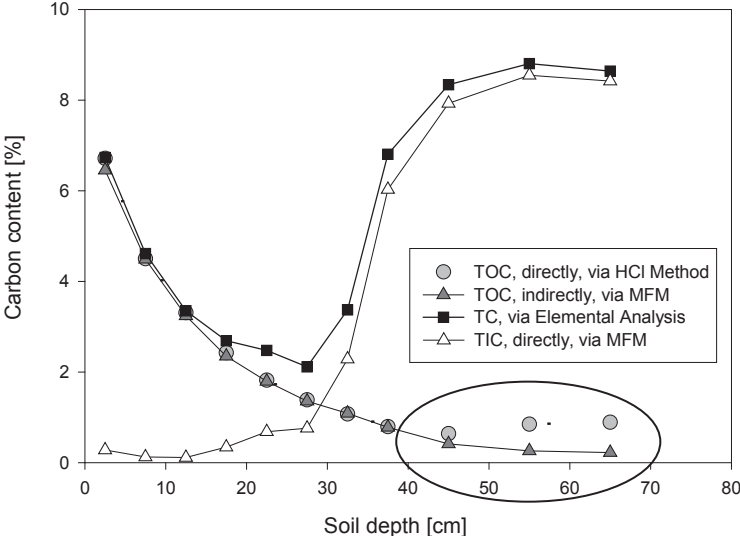


Fig. 5: TOC, TIC and TC from a calcareous soil profile with high TIC amounts. TOC is determined directly (following DIN ISO 10694, HCl Method) and indirectly (Muffle Furnace Method, MFM).

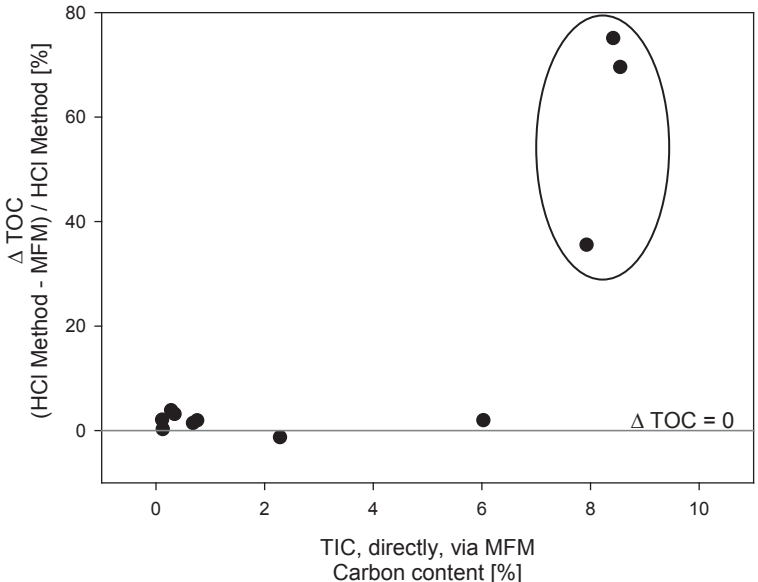


Fig. 6: Difference of TOC expressed as percentage in relation to TIC contents. TOC is determined directly (following DIN ISO 10694, HCl Method) and indirectly (Muffle Furnace Method, MFM). Results derived from samples of a calcareous soil profile with high TIC amounts in subsoil (Fig. 5). Solid line represents the target: $\Delta \text{TOC} = 0$; no deviation between the methods.

Because the HCl Method overestimates the TOC contents in soils containing high amounts of carbonate (> 6% TIC), the MFM should be applied as method of choice. The MFM provides reliable and precise results, although it needs two measurements for calculating the TOC compared to the HCl Method with a single, direct TOC determination [Hilke, I. 2003]. However, to test unknown samples, a reference method like an acid pretreatment should be used in addition in order to check whether the organic matter has been decomposed completely and to ensure that thermally instable carbonates are not present.

The high reliability and precision of TOC determination in soil samples using the MFM has been outlined in a study concerning soil carbon storage in experimental grasslands [Steinbeiss, S. 2008].

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