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**METHODS FOR THE DETERMINATION OF TOTAL ORGANIC  
CARBON (TOC) IN SOILS AND SEDIMENTS**

by

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## **1. INTRODUCTION**

Organic matter in soils and sediments is widely distributed over the earth's surface occurring in almost all terrestrial and aquatic environments (Schnitzer, 1978). Soils and sediments contain a large variety of organic materials ranging from simple sugars and carbohydrates to the more complex proteins, fats, waxes, and organic acids. Important characteristics of the organic matter include their ability to: form water-soluble and water-insoluble complexes with metal ions and hydrous oxides; interact with clay minerals and bind particles together; sorb and desorb both naturally-occurring and anthropogenically-introduced organic compounds; absorb and release plant nutrients; and hold water in the soil environment. As a result of these characteristics, the determination of total organic carbon (a measure of one of the chemical components of organic matter that is often used as an indicator of its presence in a soil or sediment) is an essential part of any site characterization since its presence or absence can markedly influence how chemicals will react in the soil or sediment. Soil and sediment total organic carbon (TOC) determinations are typically requested with contaminant analyses as part of an ecological risk assessment data package. TOC contents may be used qualitatively to assess the nature of the sampling location (e.g., was it a depositional area) or may be used to normalize portions of the analytical chemistry data set (e.g., equilibrium partitioning).

The purpose of this document, as defined by the Ecological Risk Assessment Forum, is to answer the question of "What is the most appropriate method for soil and/or sediment TOC analyses and what factors should be considered when selecting the method?"

## **2. SOURCES AND FORMS OF CARBON IN SOILS AND SEDIMENTS**

In soils and sediments, there are three basic forms of carbon that may be present. They are: (1) elemental C, (2) inorganic C, and (3) organic C. The quality of organic matter in sediments is critical to the partitioning and bioavailability of sediment-associated contaminants. For example, Talley et al., 2002, demonstrated that although the majority of PAHs in a dredged sediment were found preferentially on coal-derived particles, the PAHs on the clay/silt sediment fraction were more mobile and available, and thus potentially of greater concern.

### **2.1. ELEMENTAL CARBON FORMS**

Elemental carbon forms include charcoal, soot, graphite, and coal. The primary sources for elemental carbon in soils and sediments are as incomplete combustion products of organic matter (i.e., charcoal, graphite, and soot), from geologic sources (i.e., graphite and coal), or dispersion of these carbon forms during mining, processing, or combustion of these materials.

## **2.2. INORGANIC CARBON FORMS**

Inorganic carbon forms are derived from geologic or soil parent material sources. Inorganic carbon forms are present in soils and sediments typically as carbonates. The two most common carbonate minerals found in soils and sediments are calcite ( $\text{CaCO}_3$ ) and dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ] although other forms may be present (e.g., siderite,  $\text{FeCO}_3$ ) depending on where the soils were formed or where the sediment source was located. It should be noted that calcite and to some extent, dolomite, may also be present in soils and sediments due to agricultural input (i.e., liming practices).

## **2.3. ORGANIC CARBON FORMS**

Naturally-occurring organic carbon forms are derived from the decomposition of plants and animals. In soils and sediments, a wide variety of organic carbon forms are present and range from freshly deposited litter (e.g., leaves, twigs, branches) to highly decomposed forms such as humus.

In addition to the naturally-occurring organic carbon sources are sources that are derived as a result of contamination through anthropogenic activities. The spills or releases of contaminants into the environment increase the total carbon content present in the soil or sediment. In general, though, the total carbon contribution from contaminants (typically measured in the  $\mu\text{g}/\text{kg}$  to  $\text{mg}/\text{kg}$  concentration range) to the total organic carbon content (measured in the % range) of the soil or sediment is relatively small to negligible unless a fresh spill has occurred, pure product is present, or a hot spot is sampled.

In contrast to spilled contaminants, various sites may contain discrete organic carbon-bearing particles such as wood fibers from pulp mill wastes or leather scraps from tannery wastes. At these locations, the total carbon content contribution of these wastes may be a significant to dominant fraction of the TOC determined for the sample. It should be noted that the methods for determining total organic carbon and total carbon contents generally do not distinguish between the sources of the organic carbon forms. Nonetheless, there are two methods noted below that are capable of qualitatively identifying carbon forms in the soil/sediment, and two methods that analyze specific fractions of the TOC.

## **3. SAMPLE COLLECTION AND HANDLING**

Prior to any analyses for TOC, the soil or sediment sample must be collected and properly handled. During the collection and handling of the samples, losses of organic compounds may occur due to: microbial degradation, sample drying, oxidation, volatilization, and sample processing biases (e.g., selective removal of carbon-bearing components). Soil and sediment samples can be collected by numerous different tools but once collected, the samples are

typically stored at 4°C and have a holding time of up to 28 days. While microbial degradation is greatly reduced at 4°C, it is not completely stopped leading to some potential loss of organic materials. Prior to analysis, some methods may require or recommend drying (either air drying or oven drying) of the sample. Samples that contain volatile organic compounds and those that have been in an anaerobic environment will undergo some loss of organic compounds when exposed to the atmosphere during drying. Volatilization losses may also occur due to poor sealing of the sample container. While these losses are generally small (probably <1% of the TOC content in a non-contaminated soil or sediment), they are noted here to inform the reader of these potential sources for carbon loss.

The collection and subsampling of a representative sample can be an area where organic matter is selectively removed from the soil or sediment and thus, the resultant TOC concentration will be affected. The main concern in obtaining the representative sample for analysis is what to do when there are large, discrete particles of organic matter present in the sample. For example, a sediment sample might contain part of a tree branch or a soil sample might contain wood chips. The larger particles may be removed by physically pulling the particles out of the sample or by sieving the sample. Typically, the larger particles are relatively inert chemically and thus do not contribute significantly to the soil or sediment's capacity to sorb or release contaminants. Removal of the larger organic particles, therefore, may lead to a more accurate assessment of the sample's TOC fraction that does interact with the contaminants and biota in the soil or sediment. In cases where the discrete particles of organic matter are believed to be either chemically or biologically active (i.e., they could affect contaminant concentrations through degradation, sorption, or similar processes), they should remain in the sample for analysis. Any decision to selectively remove particles from the sample should be made in conjunction with the data quality objective process and should receive approval from all parties involved in the program.

#### 4. ANALYTICAL METHODS FOR TOC DETERMINATION

In soils and sediments:

$$\text{Total Carbon} = \text{Inorganic Carbon} + \text{Organic Carbon} \quad (1)$$

TOC content can be measured directly or can be determined by difference if the total carbon content and inorganic carbon contents are measured. For soils and sediments where no inorganic carbon forms are present, Equation 1 becomes:

$$\text{Total Carbon} = \text{Organic Carbon} \quad (2)$$

Typically this is the case so methods described as quantifying total or organic carbon should produce the same result. However, in geographic areas where the parent material/geology is limestone, dolomite, or another carbonate-bearing mineral, inorganic forms of carbon may be

present in the samples. In arid regions, soils and sediments may have greater concentrations of carbon being derived from inorganic carbonates than from organic carbon sources.

The basic principle for the quantitation of total organic carbon relies on the destruction of organic matter present in the soil or sediment although there are a few non-destructive techniques identified in the literature that are currently under development. The destruction of the organic matter can be performed chemically or via heat at elevated temperatures. All carbon forms in the sample are converted to CO<sub>2</sub> which is then measured directly or indirectly and converted to total organic carbon or total carbon content, based on the presence of inorganic carbonates. These methods can either be quantitative or semi-quantitative depending on the process used to destroy the organic matter and the means used for detecting/quantifying the carbon present. In conjunction with the quantitative or semi-quantitative methods, there are also methods that are qualitative and can accurately identify the type of carbon compounds (e.g., sugars, carbohydrates, lignin, etc.) in the sample but are not far enough along in their development to quantitate the carbon content of the sample.

There are several factors that one must consider when selecting a method for the determination of total organic carbon. These factors include the ease of use, health and safety concerns, cost, sample throughput, and comparability to standard reference methods. These factors are a concern for both the sample preparation and sample quantitation phases of TOC determinations. Each of these selection factors will be discussed in more detail in the following sections.

Sample preparation techniques can range from simply weighing the sample prior to analysis through wet chemistry digestion with strong acids. Nearly all of the sample preparation methods are easy to perform following good laboratory practices. However, where sample preparation uses wet chemistry techniques, these operations should be carried out in a well ventilated area and protective clothing must be worn when handling concentrated acids. Another health and safety concern is that when preparing and using some of the indicator solutions in the wet chemistry techniques, these indicators may be carcinogenic (e.g., diphenylamine indicator) and should be handled with extreme caution. Costs associated with sample preparation are generally low and consist mainly of replacing consumable chemicals. Sample preparation throughput for typical wet chemistry techniques is around 25 minutes per sample. The use of a multiple extraction apparatus can increase the throughput by concurrently extracting multiple samples although the extraction time will remain about 25 minutes. Information on comparability of sample preparation techniques to standard reference methods will be more thoroughly presented in latter sections when each sample preparation technique is discussed and in the section on comparative studies.

Quantitation methods are as varied as the sample preparation methods. Some quantitation methods are based on titrations which rely on color changes of an indicator solution while others use gravimetric, volumetric, spectrophotometric, or chromatographic methods for carbon quantitation. As the detection and quantitation systems get more complex, the skill (and

knowledge) level of the operator increases. Typically, titrimetric, gravimetric, and volumetric techniques are relatively easy to perform implementing good laboratory practices. Spectrophotometric and chromatographic techniques require more skill in operating the instrument, interpreting the results, and trouble shooting should system problems arise. Health and safety concerns are generally negligible for the quantitation method except where the sample is combusted at high temperatures. These samples must be handled with care to avoid severe burns. Another important consideration is whether the quantitation method is manual or automated. It has been shown that the automated methods yield more precise results than methods quantitated manually (Soon and Abboud, 1991). However, automated methods tend to be more expensive due to the initial purchase of the instrument which can range up to \$20,000 or more. Manual methods can be performed with generally available laboratory glassware and equipment. The rate of sample throughput during carbon quantitation can range from a matter of seconds for gravimetric measurements to minutes for the other techniques. Sample throughput can be greatly enhanced using automated systems, especially where a multi-sample autoloader is available which allows the analyst to load a batch of samples, start the analyses, and then perform other sample preparations while the first batch of samples is being analyzed. Information on analytical comparability to standard reference methods will be more thoroughly presented in latter sections where each sample quantitation technique is discussed and in the section on comparative studies.

#### **4.2. QUALITATIVE METHODS FOR THE DETERMINATION OF ORGANIC CARBON**

There are two methods in the literature for the structural characterization of organic carbon forms in soils and sediments. One of these qualitative methods is based on nuclear magnetic resonance (NMR) spectroscopy and the other on diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. A brief synopsis of these qualitative techniques is presented here because research is ongoing to improve the techniques' qualitative identification capabilities and to advance the science into the area of quantitative determinations of the carbon forms in soils and sediments.

NMR is a valuable tool for the characterization of soil organic matter and humification processes in soils (Kögel-Knaber, 1997). NMR spectroscopy works on the principle of measuring the characteristic energy absorbed and re-emitted or dispersed by atomic nuclei that are placed in a static magnetic field and subjected to an oscillatory magnetic field of known radio-frequency. One specialized form of this technique is cross-polarization magic angle spinning (CPMAS)  $^{13}\text{C}$  NMR (Rumpel et al, 1998). CPMAS  $^{13}\text{C}$  NMR is capable of distinguishing chemical structures that are characteristic of recently formed organic matter as well as those organic carbon forms derived from the soil's parent material/geology, elemental carbon forms derived from ash, and even, carbonaceous particles from airborne lignite-derived contamination in soils. The advantage of NMR techniques is that no extraction of organic matter is needed. However, the NMR methods are expensive and time-consuming (Rumpel et al., 2001).

DRIFT spectroscopy, when used in conjunction with multivariate data analysis (i.e., partial least squares), provides a rapid and inexpensive means of differentiating carbon forms in soils and sediments (Rumpel et al., 2001). Carbon compounds are identified by assignment of the main infrared absorption bands to the bonds being stretched or deformed at that particular frequency. Both inorganic and organic forms of organic compounds may be identified using this technique (Nguyen et al., 1991). In initial experiments, Rumpel et al., (2001) were able to identify and quantify the lignite contribution to the TOC content of soil samples; however, TOC determination was performed by a dry combustion technique (to be discussed).

#### **4.3. SEMI-QUANTITATIVE METHODS FOR THE DETERMINATION OF ORGANIC MATTER**

There are two primary methods for the semi-quantitative estimation of organic matter in soils and sediments. Organic matter content can be used as a rough estimate of the total organic carbon content. Semi-quantitative methods are based upon the indiscriminant removal of all organic matter followed by gravimetric determination of sample weight loss. The two primary semi-quantitative methods are: (1) loss-on-ignition and (2) hydrogen peroxide digestion.

The loss-on-ignition (LOI) method for the determination of organic matter involves the heated destruction of all organic matter in the soil or sediment. A known weight of sample is placed in a ceramic crucible (or similar vessel) which is then heated to between 350° and 440°C overnight (Blume et al., 1990; Nelson and Sommers, 1996; ASTM, 2000). The sample is then cooled in a desiccator and weighed. Organic matter content is calculated as the difference between the initial and final sample weights divided by the initial sample weight times 100%. All weights should be corrected for moisture/water content prior to organic matter content calculation.

LOI method temperatures should be maintained below 440°C to avoid the destruction of any inorganic carbonates that may be present in the sample. One concern with this technique is that some clay minerals will lose structural water (i.e., water that is part of their matrix) or hydroxyl groups at the temperatures used to combust the samples. The structural water loss will increase the total sample weight loss leading to an overestimation in organic matter content. One possible means to avoid this concern is through the pre-treatment of the sample via removal of the mineral matter using HCl and HF acids (Rather, 1917). However, the use of HCl may dissolve part of the organic matter leading to an underestimation of the organic matter content and the potential use of a correction factor. Interestingly, ASTM method D 2974 allows for ashing the sample at 750°C for peats and other organic soils, such as organic clays, silts, and mucks (ASTM, 2000), presumably based on the assumption that no carbonates and little to no mineral matter are present in the sample that could influence the resultant organic matter content.

The hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) digestion method destroys the organic matter in the sample through oxidation. The hydrogen peroxide digestion involves the addition of concentrated hydrogen peroxide (30% or 50%) to a known weight of soil or sediment. H<sub>2</sub>O<sub>2</sub> is



continually added to the sample until sample frothing ceases. The samples may be heated to 90°C during peroxide addition to increase the speed and completeness of the peroxide digestion. Care must be taken to avoid excessive frothing and sample loss over the lip of the digestion container. Once the digestion process is completed, the sample is dried at 105°C, cooled in a desiccator, and weighed. Organic matter is determined gravimetrically and calculated as the difference between the initial and final sample weights divided by the initial sample weight times 100%. All weights should be corrected for moisture/water content prior to organic matter content calculation.

The hydrogen peroxide digestion method has several limitations that markedly reduce its effectiveness to quantify organic matter and TOC and, as such, the method is semi-quantitative at best. The major limitation of the peroxide digestion technique is that the oxidation of the organic matter is incomplete and the extent of oxidation varies markedly from one soil or sediment to another (Robinson, 1927). Another potential source for error with this method is the loss of volatile organic compounds if samples are air- or oven-dried prior to digestion. It should be noted that this method is a common pre-treatment during the determination of particle-size distributions in soils and sediments since organic matter is known to bind particles together.

Since these two methods determine the organic matter content in the soil or sediment, it is necessary to convert the organic matter content to total organic carbon content. Traditionally, for soils, a conversion factor of 1.724 has been used to convert organic matter to organic carbon based on the assumption that organic matter contains 58% organic C (i.e., g organic matter/1.724 = g organic C)(Nelson and Sommers, 1996). However, there is no universal conversion factor as the factor varies from soil to soil, from soil horizon to soil horizon within the same soil, and will vary depending upon the type of organic matter present in the sample. Conversion factors range from 1.724 to as high as 2.5 (Nelson and Sommers, 1996; Soil Survey Laboratory Methods Manual, 1992). Broadbent (1953) recommended the use of 1.9 and 2.5 to convert organic matter to total organic carbon for surface and subsurface soils, respectively.

#### **4.4. QUANTITATIVE TECHNIQUES FOR THE DETERMINATION OF TOTAL ORGANIC CARBON**

Both destructive and non-destructive techniques are available for the determination of TOC and total carbon in soils and sediments. The destructive techniques are by far the most common techniques in use today and generally involve some form of sample preparation or pre-treatment followed by sample extraction and quantitation. The three basic principles of the destructive techniques are: (1) wet oxidation followed by titration with ferrous ammonium sulfate or photometric determination of  $\text{Cr}^{3+}$ , (2) wet oxidation followed by the collection and measurement of evolved  $\text{CO}_2$ , and (3) dry combustion at high temperatures in a furnace with the collection and detection of evolved  $\text{CO}_2$  (Tiessen and Moir, 1993). An innovative non-destructive technique using non-elastic neutron scattering is also being developed for TOC determination (Wielopolski et al., 2000).

**4.4.1. Sample Preparation and Pre-Treatment.** Sample preparation for soil or sediment samples for the determination of TOC generally involves the removal of large particles (generally those particles greater than 2-mm in diameter) and sample homogenization. It should be noted that the removal of the large particles changes the particle-size distribution of the sample and thus, may affect the data quality objectives of the program. Large inorganic particles, such as gravel, pebbles and rocks, are generally removed with little concern due to their lack of contribution to TOC and their chemical inertness. The percentage of large inorganic particles can be determined visually or gravimetrically and is recorded for completeness of sample characterization. Removal of large organic particles, such as twigs, roots, stems, wood chips, branches, etc., will affect sample TOC concentrations. In some cases, their removal is warranted due to their relative chemical inertness (as compared to the finer, more highly decomposed forms of organic matter) or their lack of representativeness of the sample (e.g., anthropogenic additions versus naturally-occurring organic matter). Selective removal of the large organic particles should be based on the data quality objectives of the program. The presence of the large organic particles should be recorded for completeness of sample characterization. Samples should be stored at 4°C when not in use.

Sample pre-treatment generally involve the removal of interferents or water (in the case of the dry combustion technique). The primary interferent in the determination of TOC is the presence of inorganic carbonates in the soil or sediment. If the samples are left untreated, depending upon the method used, the carbonate minerals (e.g., calcite and dolomite) will be destroyed along with the organic matter and in the process additional CO<sub>2</sub> will be evolved and measured. The additional CO<sub>2</sub> will lead to a falsely elevated TOC content. None of the methods available for the determination of TOC are capable of distinguishing between inorganic or organic derived CO<sub>2</sub>.

A simple test can be performed to determine if carbonates are present. The test involves adding a few drops of HCl (1N to 4N HCl are often cited) and observing if the sample effervesces. Careful observations need to be made in cases where dolomite is present since it does not rapidly effervesce like calcite. Alternatively, the pH of the soil or sediment may be determined and if the pH is 7.8 to 8.2, then calcium carbonates are indicated in the sample (McLean, 1982). However, as a safety factor to account for possible isolated pockets of carbonates, a pH of 7.4 has been used as the pH above which the sample is treated to remove carbonates.

If carbonates are present, the most common method for their removal is the addition of an acid or a combination of acids. Two acids are commonly cited for carbonate removal, namely, HCl and H<sub>2</sub>SO<sub>4</sub>. HCl (1N) is added to the sample in small increments until effervescence stops. Two concerns with the use of HCl (to be discussed) are that the HCl will destroy some organic carbon compounds leading to a carbon loss prior to sample quantitation and Cl<sup>-</sup> is an interferents for the wet oxidation techniques. Alternatively, a combination of H<sub>2</sub>SO<sub>4</sub> and FeSO<sub>4</sub> may be used (with sample drying if the dichromate method is used, see interferents below). Typically, 3 mL of 2N H<sub>2</sub>SO<sub>4</sub>-5%FeSO<sub>4</sub> is added to the sample to remove inorganic carbonates (Nelson and

Sommers, 1996). The  $\text{FeSO}_4$  is added to minimize oxidation and decarboxylation of organic matter by the  $\text{H}_2\text{SO}_4$  or by  $\text{MnO}_2$  that may be present in the soil or sediment (Allison, 1960). If the soils or sediments are suspected of containing large amounts of carbonates (>10% calcium carbonate equivalent), then the  $\text{H}_2\text{SO}_4$  strength should be increased to 3N or 4N.

Removal of carbonates for samples undergoing dry combustion quantitation is more problematic than for those undergoing wet chemistry techniques (Nelson and Sommers, 1996). HCl may be used in a manner similar to that used for the wet chemistry techniques but the samples must be at least air-dried prior to analysis and there is the concern about the loss of organic matter due to its decomposition by the HCl. Alternatively, Bremner (1949) proposed using a mild  $\text{H}_2\text{SO}_3$  solution to remove the carbonates but Allison (1965) found it difficult to tell whether the treatment was complete especially if dolomite was present in the sample. It should be noted that the removal of carbonates for samples undergoing dry combustion is not necessary if TOC is going to be determined by difference (see the Analytical Methods for TOC Determination section).

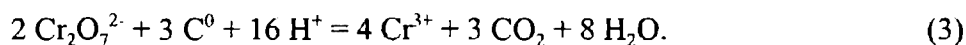
Other interferences for the wet chemistry techniques include  $\text{Fe}^{2+}$  and  $\text{Cl}^-$  which lead to positive errors (i.e., overestimation) in TOC determinations, and  $\text{MnO}_2$  which leads to a negative error (i.e., underestimation) of TOC contents (Schumacher et al., 1995). In a routine sample, both  $\text{Fe}^{2+}$  and organic matter are oxidized in the dichromate digestion solution (to be discussed) leading to a positive sample bias in TOC content.  $\text{Fe}^{2+}$  may be removed from the sample by oxidation (i.e., air-drying) at the risk of loss of any volatile organic compounds present in the sample. Excess  $\text{Cl}^-$  in a sample interferes through the formation of chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ). The consumption of the dichromate ions leads to a positive bias in TOC content. Excessive  $\text{Cl}^-$  may be removed by leaching the sample or through precipitation, as  $\text{AgCl}$ , by adding  $\text{AgSO}_4$  to the  $\text{H}_2\text{SO}_4$  used during the digestion process. In contrast,  $\text{MnO}_2$  in the sample will actively compete with the dichromate for any oxidizable carbon and thus, lead to negative bias during subsequent quantitation. If large quantities of  $\text{MnO}_2$  are present, pretreatment of the sample with  $\text{FeSO}_4$  will remove this interference (Walkley, 1947; Jackson, 1958).

The removal of water from the sample is essential during the determination of TOC by the dry combustion methods. While water passing through the system is removed from the gas flow by a sorbent, this sorbent is generally placed in the system to handle the removal of water created during the combustion process. The free water associated with the sample prior to combustion can be removed by the system sorbent but this will result in the more frequent replacement of the sorbent leading to instrument downtime (for sorbent replacement and gas flow line purging), excessive sorbent chemical loss, and unnecessary expense. Excessive water can be simply removed by air drying or oven-drying the sample at  $105^\circ\text{C}$  overnight. One concern about drying the samples prior to analysis is the loss of volatile organic compounds. For the wet oxidation methods, water removal is not essential but the analyst will have to determine the moisture content on a separate subsample to accurately correct the resultant data to an oven-dried basis.

**4.4.2. Wet Chemistry Techniques for the Determination of Total Organic Carbon.** Wet chemistry techniques can be divided into two phases, namely, sample extraction and sample quantitation. The extraction technique employed is essentially the same for all methods in the literature with variations existing only in the strength and combination of reagents used during extraction. Quantitation techniques associated with the wet chemistry determination of TOC either rely on titration (manual or automated), colorimetric, gravimetric, or manometric techniques.

**4.4.2.1. Sample Extraction** — The standard wet chemistry technique for the sample extraction involves the rapid dichromate oxidation of organic matter. Perhaps the best known of the rapid dichromate oxidation methods is the Walkley-Black procedure which has been the “reference” method for comparison to other methods in numerous studies. In this procedure, potassium dichromate ( $K_2Cr_2O_7$ ) and concentrated  $H_2SO_4$  are added to between 0.5 g and 1.0 g (although the range may be up to 10g depending on organic carbon content) of soil or sediment. The solution is swirled and allowed to cool (note: the sample must be cooled as a result of the exothermic reaction when the potassium dichromate and sulfuric acids are mixed) prior to adding water to halt the reaction. The addition of  $H_3PO_4$  to the digestive mix after the sample has cooled has been used to help eliminate interferences from the ferric ( $Fe^{3+}$ ) iron that may be present in the sample although in most cases, this step is not necessary (Tiessen and Moir, 1993).

The chemistry of this extraction procedure is as follows:



It should be noted that the concentrations of the reactants and volumes of solutions are not presented in this text due to the numerous variants available in the published literature, all of which are based upon the Walkley-Black procedure.

The Walkley-Black procedure is widely used because it is simple, rapid, and has minimal equipment needs (Nelson and Sommers, 1996). However, this procedure has been shown to lead to the incomplete oxidation of organic C and is particularly poor for digesting elemental C forms. Studies have shown that the recovery of organic C using the Walkley-Black procedure range from 60 to 86% with a mean recovery being 76% (Walkley and Black, 1934). As a result of the incomplete oxidation and in the absence of a site-specific correction factor, a correction factor of 1.33 is commonly applied to the results to adjust the organic C recovery.

To overcome the concern of incomplete digestion of the organic matter, the Walkley-Black procedure was modified to include extensive heating of the sample during sample digestion (Mebius, 1960). In this variation of the method, the sample and extraction solutions are gently boiled at 150°C for 30 minutes, allowed to cool, and then water is added to halt the reaction. The addition of heat to the system leads to a complete digestion of the organic C in the sample; therefore, no correction factor is needed. The temperature of this method must be

strictly controlled because the acid dichromate solution decomposes at temperatures above 150°C (Charles and Simmons, 1986).

**4.4.2.2. Sample Quantitation** — Upon completion of the sample extraction phase, the quantity of organic carbon present in the soil or sediment can be determined through a variety of different techniques. These techniques include: manual titration, automated titration using potentiometric determination, colorimetry, gravimetric determination, or volumetric/manometric measurement. Each of these techniques will be briefly discussed.

Upon examination of Equation 3, the three measurable products of the acid dichromate digestion process are the excess/unused  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{Cr}^{3+}$  and  $\text{CO}_2$ . Both the  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{Cr}^{3+}$  will remain in solution and can be measured titrimetrically or colorimetrically while the evolved  $\text{CO}_2$ , in its gaseous state, can be measured gravimetrically or manometrically.

To perform manual titrimetric quantitation, an indicator solution is added to the digestate. The most common indicators used are ortho-phenanthroline ferrous complex (commercially available as “Ferrouin”), barium diphenylamine sulfonate, and N-phenylanthranilic acid (Nelson and Sommers, 1996). The excess  $\text{Cr}_2\text{O}_7^{2-}$  is titrated with ferrous ammonium sulfate [ $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ] or ferrous sulfate ( $\text{FeSO}_4$ ) until color change occurs in the sample. Color changes associated with these indicators are: (1) green to reddish brown for the ortho-phenanthroline ferrous complex, (2) purple/blue to green for the barium diphenylamine sulfonate, and (3) dark violet-green to light green for the N-phenylanthranilic acid. The primary concern with the manual titration technique is the low visibility or subtlety of color changes during titration. Color changes may also be obscured by naturally-occurring high chroma soils.

The use of an automated titrator eliminates the need for indicators to be added to the digestate. Similar to manual titrimetric quantitation, excess  $\text{Cr}_2\text{O}_7^{2-}$  is titrated with ferrous ammonium sulfate or ferrous sulfate. However, the endpoint is not a color change but is determined potentiometrically. In this technique, a simple calomel electrode or platinum electrode is placed in the digestate, and the titer is added until a fixed electrical potential endpoint is reached. The endpoint is dependent upon the type of electrode used. For example, the National Soil Survey Center (Soil Survey Laboratory Methods Manual, 1992) uses a platinum electrode and sets the end point at 600 mV. Once the endpoint is reached, the titration is stopped and the TOC content calculated. The automated titration technique has the distinct advantage over manual titration since the endpoint is not dependent upon operator optical determination of exactly when the color changed. The only disadvantage of the automated technique is the necessity to purchase (i.e., cost) an automated titrator and suitable electrodes.

Colorimetric quantitation of TOC is performed through the measurement of the color change that results from the presence of  $\text{Cr}^{3+}$  in solution. After sample digestion, the digestate is centrifuged or filtered to remove any suspended particles and then placed in a colorimeter set to measure the light adsorbance at a wavelength of 600 nm. Quantitation is performed by comparison of the results against a standard curve. The colorimetric technique has the same

advantages (i.e., a measurable fixed endpoint with no human interpretation) and disadvantages (i.e., primarily initial cost) as the automated titration technique.

In contrast to the three prior techniques, determination of TOC content can also be determined by measuring the evolved CO<sub>2</sub>. The evolved CO<sub>2</sub> can either be absorbed on Ascarite (or similar adsorbent) or collected in a Van Slyke-Neil apparatus (Nelson and Sommers, 1996). Absorption of the evolved CO<sub>2</sub> by Ascarite causes a weight change in a tared weighing bulb. Once the digestion is completed, the weighing bulb is reweighed and the weight difference is converted to TOC content. This gravimetric technique has good accuracy, can be performed with readily available equipment. However, this method requires careful analytical techniques in which a CO<sub>2</sub> free gas flow system is maintained throughout the digestion and CO<sub>2</sub> collection process.

The use of a Van Slyke-Neil apparatus involves the collection of the CO<sub>2</sub> in its gaseous phase and measuring the change in pressure with a gauge (i.e., a manometric technique). While this technique is relatively simple to conduct and doesn't have the concern of maintaining a CO<sub>2</sub> free atmosphere as in the gravimetric technique, great skill is needed to operate the equipment and the initial expense of purchasing the apparatus is somewhat high (Nelson and Sommers, 1996). Additionally, the Van Slyke-Neil apparatus is easily damaged.

**4.4.3. Dry Chemistry Techniques for the Determination of Total Organic Carbon.** Dry chemistry techniques can be divided into two phases, namely, sample combustion and sample quantitation. The sample combustion technique consists of burning the sample in an oven at elevated temperatures. The end product of the combustion is CO<sub>2</sub> which is quantitated by titrimetric, gravimetric, manometric, spectrophotometric, or gas chromatographic techniques. Dry chemistry techniques are typically cited as total carbon techniques but in the absence or removal of inorganic carbonates, these techniques can be used to quantify TOC.

**4.4.3.1. Sample Combustion** — Soil or sediment samples are combusted at elevated temperatures in a resistance or an induction furnace in the presence of a stream of pure oxygen. Combustion temperatures generally exceed 1000°C and are dependent on oven type. Resistance ovens heat the sample to between 900 and 1000°C while induction ovens reach temperatures of between 1300 and 1500°C (Nelson and Sommers, 1996). It should be noted that combusting the sample at 1350° C or higher will allow for the complete destruction of any inorganic carbonates present in the sample. Therefore, it is essential to ensure that all carbonates have been removed from the sample prior to TOC determination.

The typical sample combustion train consists of a pure oxygen gas source; the oven; various traps and scrubbers to remove dust, particulate matter, halogen gases (especially important in the case of soils or sediments with high salt contents and in particular Cl contents), and water vapor; and a catalyst furnace to convert any CO to CO<sub>2</sub> prior to collection and detection of the evolved CO<sub>2</sub>.

Typical analyses consist of placing several hundred milligrams of soil or sediment in an inert boat (e.g., platinum, porcelain, or ceramic). To ensure complete combustion of the sample, a pure oxygen stream is used as well as various catalysts or accelerators. Typical catalysts and accelerants include: vanadium pentoxide, Cu, CuO, and aluminum oxide (LECO, 1996). Through the use of the accelerants, actual temperatures in the sample may temporarily reach up to 1650° C or greater as the accelerants melt and fuse with the sample. The accelerators/catalysts are sprinkled on top or mixed into the sample and the sample is then pushed into the oven. After several minutes of combustion in the pure oxygen stream, a carrier gas (typically He) is turned on, the combustion chamber is swept clean, and the evolved gases are carried through the traps and scrubbers to the detector.

The two main advantages of using a dry combustion method are that the elevated temperatures ensure combustion of all carbon forms present in the sample and that sample preparation is minimal. The two main disadvantages of using a dry combustion method are that a leak-free gas flow path must be maintained, else a false positive value will be obtained due to cross-contamination with atmospheric CO<sub>2</sub>, and the initial expense of purchasing the equipment may be high, especially if an automated system is used (Nelson and Sommers, 1996).

**4.4.3.2. Sample Detection and Quantitation** — Upon completion of the sample combustion phase, the quantity of organic carbon present in the soil or sediment can be determined through a variety of different techniques. These techniques include titration, gravimetric, manometric, spectrophotometric, or gas chromatographic techniques. The titration, gravimetric, and manometric techniques for quantifying TOC contents are the same as described previously for the wet chemistry techniques and thus, won't be discussed here. The remaining two detection techniques will be briefly discussed.

For each of the remaining two detector systems, both a constant flow of the evolved gases and carrier gas are passed through the detection cell. Analyses are stopped after a known volume of gas has been collected or after a given amount of time has passed and the TOC content determined. The % C should be reported on an oven-dry basis so adjustments for moisture content will be necessary if the samples are only air-dried prior to analysis.

Spectrophotometric detection techniques quantify the evolved CO<sub>2</sub> using either thermal conductivity or infrared detectors. Thermal conductivity detectors measure the difference between the thermal conductivity of the gas evolved from the sample and a reference gas (usually the pure carrier gas) and convert the temperature difference to % C in the sample. CO<sub>2</sub> has a thermal conductivity of  $(3.3 \text{ calories/cm}\cdot\text{sec}\cdot^{\circ}\text{C}) \times 10^5$  (LECO, 1996).

Infrared detectors rely on the absorption of infrared energy by CO<sub>2</sub> at a very precise wavelength (LECO, 1996). As CO<sub>2</sub> enters the infrared detector cell, the measured energy level decreases and the detector system converts the cumulative energy decrease to %C. CO<sub>2</sub> absorbs infrared radiation at a wavelength of 2.6 microns and 4 microns.

TOC may also be quantified using a gas chromatograph (GC) attached to either a thermal conductivity detector or a flame ionization detector (Nelson and Sommers, 1996). For use of the flame ionization detector (FID), the CO<sub>2</sub> must first be converted to CH<sub>4</sub> by passing the evolved gases through a heated alumina coated with nickel in a H<sub>2</sub> enriched atmosphere. These methods are expensive and make poor use of a GC system; however, the FID system can be purchased attached to individual automated carbon analyzers.

**4.4.4. A Non-Destructive Technique for TOC Determination in Soils.** An innovative non-destructive technique for TOC determination in soils is currently under development by Wielopolski et al. (2000). This technique involves inelastic neutron scattering and bears mentioning since it is non-destructive and can be performed *in situ*. This technique is based on the detection of 4.44 MeV gamma rays that result from the bombardment of carbon atoms with 14 MeV neutrons and the subsequent emission of gamma rays from the excited carbon. The gamma rays are then detected, quantified, and converted to % C content. Current drawbacks to the system are that it is in the preliminary stages of development and it requires a radioactive neutron generator be used and taken to the field for analysis.

**4.4.5. Fractional Analysis of Carbon Forms in Soils and Sediments.** Determining *only* TOC may not be sufficient for explaining contaminant bioavailability. The quality of the organic matter in sediments is critical to the partitioning and bioavailability of sediment-associated contaminants. Although it is beyond the scope of this report, it should be noted that there are methods available that look at specific fractions of the TOC in soils and sediments. Two examples of fractional analytical methods include SW-846 Method 9071B (U.S. EPA, 1992) and the soot quantification method of Gustafsson et al. (1997). SW-846 Method 9071B entitled, "n-Hexane Extractable Material for Sludge, Sediment, and Solid Material," is used to quantify the oil and grease fraction in soils and sediments. The Gustafsson et al. (1997) method was developed to quantify sedimentary soot since soot may significantly affect the environmental speciation of polycyclic aromatic hydrocarbons. Interestingly, the Gustafsson et al. method follows the same basic principles of inorganic carbon removal, organic matter removal, and dry combustion for carbon quantification as described in this report.

#### **4.5. PROGRAMMATIC REQUIREMENTS FOR TOC METHODOLOGIES**

Numerous programs require the analysis and determination of total carbon and total organic carbon as standard characterization parameters for soils and sediments. Additionally, there are published methods for general use and although they are perhaps, not program specific, they are included in this text. While the programs and methods presented in Table 1 cover a majority of the large-scale EPA programs, this list does not purport to be complete and is presented here for informational purposes.

Table 1 presents a listing of the methods available for the determination of total carbon (TC) and TOC listing the source (or reference) for the method, the basic principle of the method, and a brief listing of any aspects that are unique to the method/program. Please note that if the



principle of operation seems vague, it is because the reference method leaves the choice of specifics up to the user. Additionally, if there are multiple options allowed under the same reference method, all methods will be presented in the table.

#### 4.6. COMPARATIVE STUDIES

Numerous comparison studies have been performed examining the efficiency of TOC methods (Nelson and Sommers, 1996). In nearly all of these studies, the standard method to be compared against was the Walkley-Black dichromate extraction with titrimetric quantitation method. In general, nearly all of the newer methods having comparable or greater TOC recoveries and greater precision than the Walkley-Black method. For example, Bremner and Jenkinson (1960) showed that the TOC contents determined by the Tinsley method (heated dichromate/titration) were approximately 30% greater than those values determined by the Walkley-Black method. Further, when compared to "known" TOC concentrations (as determined by an independent wet combustion method), the corrected Walkley-Black TOC concentrations ranged from 73-119% of the known TOC concentration. In contrast, the Tinsley method (heated dichromate/titration) yielded recoveries of 88 to 106% for the same soils. These results show the greater precision obtained using the Tinsley method than using the Walkley-Black method.

In a large scale comparison study by Soon and Abboud (1991), three dichromate extraction procedures with titrimetric quantitation, one dichromate extraction method with spectrophotometric quantitation, LOI, and a dry combustion procedure were compared. The three dichromate/titration methods used were the Walkley-Black, the modified Tinsley method (a heated dichromate extraction with  $H_3PO_4$  as part of the extraction solution), and the modified Mebius (a heated dichromate extraction method). The spectrophotometric method involved a heated dichromate extraction with quantitation by colorimetric detection of  $Cr^{3+}$  at a wavelength of 600 nm. The LOI method heated the sample to 375°C overnight and measured gravimetric weight loss while the combustion method heated the sample at 1371°C and used infrared detection of the  $CO_2$  generated. The percent coefficient of variation among replicate samples ranged from 2.7% to 5.6%. The most precise method was the spectrophotometric method. The LOI method had the worst precision among replicate samples and was generally deemed unreliable for soils with low TOC contents. The Walkley-Black method with a correction factor of 1.40, instead of the traditional 1.33 value, yielded comparable TOC contents (correlation coefficients = 0.979 to 0.996) to the other methods tested. Relative to the combustion method, the modified Tinsley method and the modified Mebius method slightly underestimated the soil organic carbon content (slopes  $\pm$  standard errors were  $1.05 \pm 0.02$  and  $1.04 \pm 0.02$ , respectively). The spectrophotometric method yielded the same recoveries as the combustion method within experimental error (slope  $\pm$  standard error =  $0.98 \pm 0.02$ ). The automated quantitation methods were found to be more precise than those methods in which manual titration was necessary.

TABLE 1

Programmatic Requirements for TOC Methodologies

Reference Method	Principle of Operation	Method Specifics/Miscellaneous
SW-846 Method 9060 (U.S. EPA, 1992)	(a) automated combustion for TOC (b) automated wet chemistry for TOC	- infrared detection or FID - pretreat to remove of carbonates with acid
Methods of Chemical Analysis of Water and Wastes (U.S. EPA, 1974)	(a) automated combustion for TOC (b) automated wet chemistry for TOC	- infrared detection or FID - pretreat to remove carbonates with HCL or H <sub>2</sub> SO <sub>4</sub>
Procedures for Handling and Chemical Analysis of Sediment and Water Samples (Plumb, 1981)	(a) combustion for TC (b) differential combustion for TC and TOC (c) dichromate extraction and titration	- HCl pretreatment for carbonate removal - differential combustion at two temperatures to remove different carbon fractions
Contract Laboratory Program Organic SOW (ILM05.1)	(a) combustion for TOC	- detection and quantification by thermal conductivity, differential thermal conductivity, infrared, aqueous conductivity, or titrimetry - pretreat with phosphoric acid and heat to remove carbonates
Methods for Soil Analysis, Part 2 - Chemical and Microbiological Properties (Nelson and Sommers, 1996)	(a) combustion for TC with gravimetric quantitation (b) dichromate extraction for TC and TOC with titration	- procedures for resistance and inductive ovens presented - good overview of multiple methods

Reference Method	Principle of Operation	Method Specifics/Miscellaneous
Soil Survey Laboratory Methods Manual (1992)	(a) dichromate extraction with automated titration for TOC (b) automated combustion for TC with infrared detection and quantification	- heated dichromate method for TOC - TOC method assumes no carbonates present in sample
Soil Sampling and Methods of Analysis (Tiessen and Moir, 1993)	(a) dichromate extraction with titration for TOC (b) combustion with titration for TOC and TC	- Canadian method manual - removal of carbonates with H <sub>2</sub> SO <sub>4</sub> /FeSO <sub>4</sub> or HCl
Laboratory Methods for Soil and Foliar Analysis in Long-Term Environmental Monitoring Programs (Schumacher et al., 1995)	(a) combustion with infrared or thermal conductivity detection for TC (b) dichromate extraction with titration for TOC	- joint EPA and Environment Canada method
Puget Sound Estuary Program (1986)	(a) combustion with gravimetric quantitation for TOC	- induction furnace recommended - HCl removal of carbonates
Method 440.0 - Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis (Zimmerman et al., 1997)	(a) combustion with thermal conductivity detection for TC	
Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual (U.S. EPA, 2001)	(a) no method specified although combustion is presumed	- 18 hour pretreatment of sediments with non-oxidizing acid to remove carbonates - samples desiccated prior to analysis

Reference Method	Principle of Operation	Method Specifics/Miscellaneous
Standard Methods for the Examination of Water and Wastewater - Method 5310B (1992)	(a) combustion with infrared detection for TOC	- method modified for sediments (Michelson and Bragdon-Cook, 1993)
Handbook of Methods for Acid Deposition Studies, Laboratory Analyses for Soil Chemistry (Blume et al., 1990)	(a) combustion with thermal conductivity or infrared detection for TC	- also has organic matter by LOI method

## 5. SUMMARY AND RECOMMENDATION

The determination of total organic carbon is an essential part of any site characterization or ecological assessment since its presence or absence can markedly influence how chemicals will react in the soil or sediment. Numerous methods are available for the determination of TOC in soils and sediments. Carbon can be present in elemental, inorganic, or organic forms. Carbon is usually derived from weathering of the parent material/geology, the decomposition of plant and animal matter, or by addition through anthropogenic activities. There are numerous methods and variations of the methods for the identification and quantitation of TOC. These methods may be qualitative, semi-quantitative, or quantitative depending upon the technique used. Quantitative methods generally involve some form of sample preparation to remove water and/or inorganic carbonates, where present. After sample preparation is complete, either wet chemistry digestion or combustion techniques are used to convert the organic matter in the sample to CO<sub>2</sub> which is then quantified. Quantitation techniques range from simple gravimetric determinations through volumetric and manometric measurements through the more complex spectrophotometric and chromatographic methods.

For the purposes of determining TOC, the author would recommend the use of a high temperature, automated, dry combustion technique after pre-testing and pre-treatment to remove inorganic carbonates, when present. Pre-testing should be performed using a 1 to 4 N HCl drop test followed by observation for effervescence to determine if carbonates are present. Alternately, the pH of the sample may be determined and if the pH is below 7.4, then the sample should be free of all carbonates. If carbonates are present, they should be removed using a 2N H<sub>2</sub>SO<sub>4</sub> - 5% FeSO<sub>4</sub> solution followed by sample drying prior to sample analysis. Combustion of the sample should be at temperatures  $\geq 1350^{\circ}\text{C}$  and be performed in a pure oxygen atmosphere to ensure complete combustion of all carbon forms in the sample. Detection of the evolved CO<sub>2</sub> should be accomplished using either IR or thermal conductivity detectors (i.e., spectrometric determination). Both detector systems produce comparable and reproducible results. The availability/choice of detectors is usually based upon which instrument is purchased.

The advantages of the automated dry combustion technique are that: (1) minimal sample preparation is required other than drying the sample, (2) destruction of all carbon form is ensured at temperatures in excess of  $1350^{\circ}\text{C}$ , (3) actual sample analysis time is short, usually in the range of 5-7 minutes per sample, (4) the automated systems have been shown to be more precise than manually operated determinations, (5) the high temperature, dry combustion technique has been shown to produce comparable TOC concentrations when compared to the standard wet chemistry technique (i.e., the Walkley-Black technique), (6) the automated systems are capable of determining total H, S, and N, simultaneously with the TOC; thereby, providing additional information about the characteristics of the organic matter from a single sample analysis [Note: multiple instrument configurations are available on the commercial market with the most common configurations being the CN, CNS and CHN analyzers], and (7) the newer automated systems can be purchased with a sample autoloader allowing the analyst to load batches (up to 49

or more) of samples, standards, and blanks for analysis freeing the analyst to perform other work while the samples are being analyzed.

The disadvantages of the high temperature, automated, dry combustion technique recommended are: (1) initial expense to purchase the unit is high but as sample numbers increase the overall cost per sample markedly decreases, (2) a leak-free gas flow system must be maintained or false positive TOC contents will be reported, (3) pure oxygen and carrier gases must be purchased for the analysis, and (4) drying of the sample or pre-treatment to remove carbonates may result in the loss of volatile organic compounds or the decomposition and loss of other organic compounds present in the sample.

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<p>16. Abstract Organic matter in soils and sediments is widely distributed over the earth's surface occurring in almost all terrestrial and aquatic environments (Schnitzer, 1978). Soils and sediments contain a large variety of organic materials ranging from simple sugars and carbohydrates to the more complex proteins, fats, waxes, and organic acids. Important characteristics of the organic matter include their ability to: form water-soluble and water-insoluble complexes with metal ions and hydrous oxides; interact with clay minerals and bind particles together; sorb and desorb both naturally-occurring and anthropogenically-introduced organic compounds; absorb and release plant nutrients; and hold water in the soil environment. As a result of these characteristics, the determination of total organic carbon (a measure of one of the chemical components of organic matter that is often used as an indicator of its presence in a soil or sediment) is an essential part of any site characterization since its presence or absence can markedly influence how chemicals will react in the soil or sediment. Soil and sediment total organic carbon (TOC) determinations are typically requested with contaminant analyses as part of an ecological risk assessment data package. TOC contents may be used qualitatively to assess the nature of the sampling location (e.g., was it a depositional area) or may be used to normalize portions of the analytical chemistry data set (e.g., equilibrium partitioning).</p> <p>The purpose of this document, as defined by the Ecological Risk Assessment Forum, is to answer the question of "What is the most appropriate method for soil and/or sediment TOC analyses and what factors should be considered when selecting the method?"</p> <p><i>Mention of trade names, corporate names or commercial products does not constitute endorsement or recommendation by EPA for use.</i></p>			
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