

Water Analysis: Organic Carbon Determinations

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The determination of total organic carbon and dissolved organic carbon (TOC and DOC) is one of the most important parameters in water quality and environmental analysis today. TOC is composed of particulate organic carbon, DOC and volatile organic carbon, (POC, DOC and VOC). In most waters, DOC is the dominant component of TOC. POC consists of living and nonliving organic particles and can occasionally become quantitatively important. POC, DOC and VOC are operationally defined by the methods used to separate them. POC and DOC are usually separated from each other by filtration, which can introduce errors due to contamination and filter clogging. Other major errors in TOC and DOC analyses are related to contamination and losses during sampling, sample storage and sample manipulation. In particular, removal of inorganic carbon by either acidification with sparging or by acidification with evaporation to dryness results in variable loss of VOC.

Commonly used TOC and DOC methods fall into two approaches: wet oxidation and high-temperature combustion (HTC). In both approaches, organic matter is oxidized to CO₂, which is then usually determined by nondispersive infrared (NDIR) absorbance. Two wet

oxidation methods are in common use: wet chemical oxidation (WCO) and ultraviolet oxidation (UVO). In WCO, a strong chemical oxidant, usually persulfate, is added to the aqueous sample and the digestion is usually carried out batchwise in a reactor at an elevated temperature. In contrast, UVO digestion is commonly carried out in a quartz coil surrounding a mercury vapor lamp. Thus, UVO methods can be readily automated using flow-injection systems. Two types of HTC methods are currently in use: dry combustion and direct aqueous injection. In dry combustion methods, the sample is acidified, dried and the residue is combusted at high temperature in a sealed tube, usually in the presence of a catalyst. This method is advantageous for the analysis of large samples. In direct aqueous injection HTC methods, samples are injected into a high-temperature column (600–900 °C), which usually contains a catalyst. In recent years, the latter method has become widely used for the analysis of seawater and other waters because it appears to have a greater oxidation efficiency and precision than most of the other methods, and it can be readily automated. However, automated HTC instruments have problems in the analysis of saline samples, in particular, salt deposits in the sample injection system, memory (or carry-over) effects, and system blank evaluation. Recently, improvements in the HTC injection system and column design have addressed these problems.

1 INTRODUCTION

The determination of TOC and DOC is an important and routine measurement in environmental, industrial and regulatory studies. It is used for estimating chemical oxygen demand (COD) resulting from anthropogenic activities, including dispersal of municipal sewage effluents, industrial wastes, agricultural runoff, and eutrophication of water bodies. TOC and DOC analyses are also used for monitoring organics in process water (i.e. cooling water, condensate and boiler-feed waters in power plants), in high-purity water generating systems, in drinking water, in desalination plants, in contaminated groundwater near waste-disposal sites, in sterilization water used in biotechnology and pharmaceutical processes, in semiconductor reclaim water, in raw and processed effluent water from food, paper and textile plants, and in a variety of regulatory and remediation operations. TOC and DOC are also important components of the global carbon cycle. Accurate measurements of these carbon pools are critical in oceanic and climatic models, as well as in evaluating food-web dynamics. For many of the above applications, real-time or near real-time evaluation of the organic carbon (OC) content of the water is often essential. Owing

to the heterogeneity and structural complexity of natural organic matter, its quantification has mainly relied on the determination of the OC content (DOC or TOC, if unfiltered).

Carbon constitutes about 50% of most organic molecules and it is usually determined by oxidation to CO₂ by various techniques. The techniques that have been employed to determine TOC or DOC in fresh and seawaters, include WCO, photo-oxidation, dry combustion, and direct injection-HTC. Although the oxidation of organic matter to CO₂ would seem to be straightforward, all current techniques have problems.⁽¹⁾ For example, there are differences in the oxidation efficiencies (i.e. the ability to oxidize completely OC to CO₂) as well as the ease of automation among these different techniques. There is also a lack of certified standards and accepted recalcitrant reference compounds for interlaboratory comparisons and for assessing oxidation efficiencies of the techniques. For most techniques, it is difficult to assess the blank, both instrumental and method. Improper assessment of the blanks, together with blank variability, adversely affect the precision and accuracy of TOC and DOC analyses. Poor reproducibility and poor accuracy can also arise from contamination during sampling, sample manipulations (e.g. transfers, filtration and acidification), incomplete sparging of inorganic carbon and sample storage.⁽²⁾ In this article, both sampling and instrumental aspects of TOC and DOC analysis are discussed.

2 OPERATIONAL DEFINITIONS AND ARTIFACTS

The commonly used units for TOC and DOC are mg L⁻¹, ppm, and μM, where 1 mg L⁻¹ is about 1 ppm (w/w), and 83 μM. In this article, the ppm and μM notations are used.

The total carbon content of a sample is the sum of all forms of dissolved inorganic carbon (DIC) and TOC. DIC is composed of the dissolved species within the carbonate system, i.e. carbon dioxide, carbonic acid, bicarbonate ion and carbonate ion. The relative proportion of these species depends on pH and on biological and physical processes. TOC is composed of POC, DOC and VOC matter. In most natural waters, DOC is the dominant component of TOC, usually 50 to >95%. POC consists of living and nonliving particles and can become quantitatively important (e.g. 10% or more of TOC) in surface waters during periods of high biological activity, in lakes and rivers during periods of high land runoff, and in sewerage and industrial effluents.

POC, DOC and VOC are operational definitions since their relative abundance depends on the physical methods used to separate them. POC and DOC are

usually separated from each other by filtration. However, filtration can introduce major errors. The pore size range most frequently used is 0.2–1.0 μm. Consequently, varying amounts of submicron detritus, microalgae, bacteria, viruses and colloidal substances pass through the filter and are measured as DOC. For samples containing a high particle load, the effective pore size may dramatically decrease during filtration as the pores become progressively clogged. Clogging results in a change in the size distribution of particles retained and passed by the filter and also in an increase in back pressure with time. Too large an overpressure (or underpressure) during filtration will lead to disruption of particles and fragile organisms with the concomitant leaching of their organic-rich dissolved contents into the filtrate. Other sources of error from filtration include adsorption of DOC onto the filter pad and contamination from the air and the filter itself, if inadequately cleaned.^(1,3,4) To avoid filtration problems, the filtration step is sometimes omitted and only TOC is analyzed. As POC often represents <5%, and usually <1%, of the TOC in many types of water samples (e.g. seawater, lake water, drinking water, cooling water, high-purity water, etc.), TOC is often equal to DOC within the analytical precision.

Two approaches are commonly used to separate TOC from DIC.⁽⁵⁾ In one approach, TOC is calculated as the difference between total carbon and DIC, the latter being determined as CO₂ released by the sample by either acidification followed by vigorous bubbling with organic- and CO₂-free gas (sparging) or by acidification and gentle heating. This approach for estimating TOC is best suited to freshwater samples where the carbonate concentration is low enough (i.e. similar to the TOC concentration) to ensure good accuracy and precision. However, in the case of seawater and alkaline lake water, DIC is present at about 15–50 times higher concentration than TOC. Thus, for these samples, determination of TOC by difference usually leads to a large analytical error. In the other approach, DIC is removed as above and the remaining TOC in the aqueous sample is determined by oxidation to CO₂, i.e. TOC is determined “directly” as opposed to “by difference”. For both approaches, complete removal of DIC is critical to obtain accurate and precise TOC values.⁽⁶⁾

Removal of DIC by either acidification with sparging or, in the case of dry combustion techniques, by acidification with evaporation to dryness (in an oven, desiccator, or freeze-drier), results in loss of VOC. The extent of this loss depends on the intensity of the DIC elimination step, with the least loss (usually <1% of TOC) with quick sparging and the most loss (about 5–15% of TOC) by oven drying.⁽¹⁾ Thus, the VOC fraction is operationally defined by the analytical procedure used to strip or remove it from the sample, as opposed to that fraction

which is volatile under ambient environmental conditions (wind and turbulence). A few commercial TOC systems are designed to trap and analyze the VOC fraction.

Because some (usually unknown) fraction of VOC is lost during the DIC removal step, TOC is also operationally defined, and is equal to DOC plus POC plus residual VOC. However, since the VOC fraction lost is usually minor (<1% of TOC), the error introduced by this loss is also usually minor. For humic-rich waters, an additional problem resulting from the acidification step is precipitation of humic acid, which may result in an underestimation of the DOC content.^(5,7)

3 SAMPLING PRECAUTIONS

Probably the largest source of error in TOC and DOC analyses is related to sampling and sample storage.^(1,2,8) In addition to the errors discussed in the previous section (i.e. from filtration and DIC removal), contamination during sampling and analysis is a major concern.⁽⁹⁾ Contamination can arise from incompletely cleaned samplers and sample bottles or from leaching of organic substances (e.g. plasticizers) from new plastic or PVC (polyvinyl chloride) sampling and storage bottles.^(4,10) In sampling of water bodies, samplers are often used that, by design, are initially open and then are closed at the desired sampling depth. As these samplers are lowered, they pass through the organic-rich surface microlayer and this material can become strongly adsorbed onto the inside walls of the sampler and contaminate the sample. Thus, samplers that are initially closed, then opened at depth are preferred.

After the sample is retrieved, subsequent sample handling steps are also critical, especially for low TOC samples. All transfers should be performed in an organic-free atmosphere or at least upwind from any major airborne contamination sources, in particular the operator and fumes. The latter is especially a problem when sampling from research vessels which are notoriously rich in exhaust and galley fumes. After collecting the uncontaminated sample, it must be stabilized as soon as possible, since biological processes can cause large changes in the DOC concentration even within the first hour of collection.⁽¹¹⁾ Stabilization is usually performed by quick freezing followed by storage at -20°C , acidification (pH 2–2.5) followed by refrigeration at $<4^{\circ}\text{C}$, or addition of a strong bacteriostatic agent (e.g. HgCl_2). Of course, any chemical addition made to the samples increases the risk of contamination. Thus, considerable care is required to obtain reliable DOC and POC results. The specific precautions and guidelines needed to overcome sampling and preservation artifacts vary with the sampling protocol used and the type of samples being studied. Detailed

studies of some of these precautions can be found in the literature.^(2,8,11–15) Some specific recommendations and procedures are given in Table 1.

4 MEASUREMENT OF ORGANIC CARBON

Attempts have been made to use the innate ultraviolet (UV) absorption (250–400 nm) of organic matter to estimate DOC, but this approach appears to be limited to specific geographic areas or water bodies where the organic composition of the sampled water does not change appreciably;^(16,17) that is, the fraction of non-UV absorbing DOC remains approximately constant.^(18,19) Another approach to measuring the organic content of water involves estimating its oxidizability, i.e. COD and total oxygen demand (TOD). However, these methods are mainly useful for organic-rich wastewaters and freshwaters, and are not suitable for uncontaminated drinking water and most natural waters.⁽²⁰⁾

The most commonly used TOC and DOC methods fall into two general approaches: wet oxidation and HTC. In both approaches, the organic matter is oxidized to CO_2 which is then determined by any number of techniques: ion chromatography-conductometry, coulometry, titrimetrically using a pH-sensitive indicator, potentiometrically using a CO_2 electrode, gravimetrically, pyrolysis-GC/MS (gas chromatography/mass spectrometry), inductively coupled plasma atomic emission spectrometry (ICP/AES), by conversion to CH_4 followed by flame ionization detection (FID), and by NDIR absorbance. The last technique is most widely used because it is sensitive and interferences can be readily eliminated. Details of CO_2 detection techniques are not addressed in this article.

4.1 Wet Oxidation Methods

Two wet oxidation methods are in common use: WCO and UVO. In WCO, a strong chemical oxidant is added to the aqueous sample after the DIC had been removed by acidification and sparging. Oxidants used include potassium peroxide, dichromate in sulfuric acid, silver-catalyzed dichromate (Walkey–Black method), perchlorate, silver-catalyzed persulfate (also called peroxydisulfate), platinum-catalyzed persulfate, and potassium persulfate. Persulfate-based methods are the most commonly used. The oxidative digestion of OC is usually performed batchwise using either a sealed glass ampoule or a reusable reaction chamber. Reaction times and temperatures are usually in the range of 0.1–4 h and 90 – 160°C , depending on the nature of the sample and oxidant. The CO_2 formed is measured in several ways (see above), but most frequently by NDIR.

Table 1 Recommended sample handling and treatment procedures prior to TOC and DOC analysis

Parameter	Recommendation
1. Sampling	Sampling should avoid contamination, for example, from contaminated air from exhaust stacks, automobile fumes, etc. Always collect and handle samples upwind from possible contamination sources. The precleaned sample container and cap should be rinsed at least three times with sample before filling.
2. Sample container type	Use precleaned borosilica glass bottles, or Teflon TM -coated plastic bottles to collect and store samples. Some types of plastic containers (e.g. high-density polyethylene) may also be used if carefully cleaned. ⁽¹⁵⁾
3. Cleaning glass sample containers	Muffle glassware for about 8 h at 450 °C. When cool, store in a sealed, clean container. Prior to use, rinse inside with 10% HF using a squirt bottle (and using gloves and goggles). Thoroughly flush out the HF with fresh low-carbon deionized water (i.e. direct from deionized water source). Fill the glassware to rim with fresh low-carbon deionized water and cover with caps or aluminum foil. The glassware can be stored this way at least 2 days. Decant the deionized water just before use.
4. Cleaning Teflon TM -coated plastic sample containers	Wash inside of the Teflon TM -coated plastic bottle with acetonitrile. Thoroughly flush out the acetonitrile with the fresh low-carbon deionized water and dry at 40–60 °C in a clean oven. (This is a critical step as any trace of acetonitrile left will contaminate samples and result in an elevated DOC concentration). Fill the washed plastic bottles to rim with fresh low-carbon deionized water and cap them, decanting the deionized water just before use.
5. Sample storage	Samples in glass bottles should be acidified and stored at 2–4 °C. Samples in plastic bottles should be stored at –20 °C or colder. For the latter, acidification is not necessary during storage, but highly recommended immediately after thawing.
6. Sample acidification	Use low-carbon or carbon-free 20–40% H ₃ PO ₄ (~85% H ₃ PO ₄ diluted by low-carbon deionized water) to acidify samples to a pH between 2–2.5.
7. Cleaning autosampler vials	Glass vials are cleaned as in step 3 above. If Teflon TM or Teflon TM -backed silicon rubber septa are used, they should be cleaned as in step 4 above. The cleaned septa should be stored in a sealed clean container.
8. Sample sparging	Sparging is needed to completely remove DIC from the acidified sample. This step is critical for accurate determination of TOC and DOC. The sparging gas should be carbon free, such as “zero” air, ultrahigh purity oxygen or nitrogen etc. The sparging time depends on gas flow rate, bubble size and sample volume. For example, for a 100 mL sample and a gas flow rate of 100–150 mL min ⁻¹ , the sparging time may be 8–10 min. For an automated HTC analyzer (such as the MQ1001 TOC analyzer, MQ Scientific), sparging is performed with the carrier gas automatically just before the sample is injected into the combustion column.

The advantages of WCO are that it is analytically simple and relatively inexpensive. However, WCO has some problems. For example, manual WCO methods are relatively labor-intensive and time-consuming. In addition, WCO has been reported to have a lower oxidation efficiency (usually 5–15% lower) compared to other methods, for example photooxidation and HTC.^(21–24) Several possibilities have been proposed to explain this apparent incomplete oxidation. For example, because samples are processed in batches, the reagent concentration and strength decrease during the course of the digestion as the easily oxidized substances are converted to CO₂. Consequently, the oxidative strength of the residual reagent may become too low to completely oxidize the remaining, more resistant carbon fraction in the sample.⁽²⁵⁾ In the case of seawater and estuarine water, chloride interferes strongly with persulfate methods, greatly lowering the oxidative strength of the reagent.⁽²⁶⁾ Thus, in either case, very high levels of oxidant must be added in order to ensure maximal oxidative efficiency and

maximal CO₂ production.⁽²⁶⁾ But large reagent additions can cause high and variable blanks due to contamination, which in turn leads to lowered precision and higher detection limits, especially for manual WCO methods. One study indicated that at least some of the apparent discrepancy in oxidation efficiency for WCO methods is probably due to improper assessment of the blanks, especially for earlier studies.⁽²³⁾ Another possible cause of the lower oxidation efficiency of WCO methods is the production of volatile reduced organic compounds during the digestion step. These compounds would be lost to the gas phase and go undetected by most CO₂ detection techniques.⁽²⁷⁾

Many of the problems associated with WCO are overcome by using UVO methods. Most of these methods rely on flow-injection analysis, as opposed to batch digestion used in WCO. Acidified and sparged samples are injected into an aqueous carrier stream, which is usually buffered and contains an oxidant (e.g. persulfate) and sometimes a catalyst (e.g. titanium dioxide, Hg(II)),

or platinum) that greatly enhances the UV oxidation rate and efficiency. The digestion is usually carried out in a quartz coil surrounding a medium-pressure mercury vapor lamp. Since oxidative free radicals are continuously produced by photochemical reactions in the UV-irradiated reaction coil, loss of oxidative efficiency during digestion is not a serious problem, as is possible with WCO. The reaction time is typically 5–30 min at 40–90 °C. The CO₂ produced is stripped from the flow stream, dried and detected (usually by NDIR).

In general, UVO instruments are more complex than WCO set-ups. However, since UVO methods can be readily automated, sample manipulation is greatly reduced, which in turn reduces the potential for contamination and improves the sample throughput and precision relative to manual WCO methods. Automation also facilitates near real-time analysis of TOC and DOC in field and industrial applications. Problems in UVO methods can result from a decrease in UV output due to lamp aging, and from differences in lamp-to-lamp performance. Also, ozone venting of the lamp can be a problem for some experimental set-ups. The oxidation efficiency of most UVO methods (about 95%) appears to be between that of WCO and HTC, with the latter assumed to be 100%. Colloidal material such as complex polysaccharides⁽²¹⁾ and algal exudates,⁽²²⁾ particulate matter, and some sulfur- and nitrogen-containing organic compounds have been reported to be incompletely degraded by UVO methods, with the apparent exception of the titanium dioxide-catalyzed UV oxidation method.⁽²⁸⁾ The latter, although promising, has not been widely tested.

4.2 High-temperature Combustion Methods

Two types of HTC method are currently in use: dry combustion and direct aqueous injection. In dry combustion methods, the sample is acidified, dried and the residue is combusted at high temperature in a furnace or in a sealed tube, with or without the presence of a catalyst, such as copper oxide or platinum.⁽¹⁰⁾ The CO₂ formed is purified in a series of traps prior to quantification. The initial drying step is critical and has been performed in several ways: oven drying at 60 °C, vacuum drying at room temperature, and freeze-drying.^(1,10) The dry combustion method has several major disadvantages. In particular, the volatile organic fraction is completely lost. Furthermore, the method is time-consuming and does not lend itself to automation or field use. Contamination is a major problem as the dry salts are strong absorbers of organic vapors. To avoid the latter problem, specially designed freeze-dryers must be used and sample transfer steps must be conducted in a clean environment and by an experienced analyst.^(1,10) The main advantage of this method is that large samples can be analyzed resulting in a large

analytical signal. This method is particularly useful for stable-isotope analysis of DOC because large samples are needed to obtain a sufficiently large analytical signal.⁽¹⁰⁾

The disadvantages of dry combustion methods are largely overcome by using direct aqueous injection HTC methods. Acidified and sparged samples (Table 1) are injected into a high-temperature column (e.g. 600–900 °C), which usually contains catalytic materials such as platinum, cobalt oxide, copper oxide or silver oxide. It is generally believed that a catalyst is needed to ensure complete conversion of reduced carbon, including carbon monoxide, to CO₂. At the time of injection, the aqueous sample is rapidly volatilized creating a momentary pressure pulse in the system which needs to be damped.⁽²⁹⁾ The combustion products are swept through the column with a carrier gas, usually high-purity oxygen, although other gases can also be used.⁽²⁹⁾ The CO₂ that is produced in the combustion column is then purified and dried through a series of traps prior to detection, usually by NDIR.

4.3 Problems Associated with High-temperature Combustion Methods and Applications to Seawater

DOC is the largest pool of reduced carbon in the sea (about 10¹⁸ g-C), a mass comparable to the total mass of carbon in the atmospheric CO₂ reservoir, or to that stored in terrestrial forests or soil humus matter.⁽³⁰⁾ Despite the large size of the DOC pool in the oceans, the concentration of DOC is low, about 40 μM (0.5 ppm) in deep waters and 80–90 μM (about 1 ppm) in surface waters. As a result of both this low concentration and the high salt content, the accurate, precise and artifact-free determination of DOC and TOC in seawater has been a major problem despite over 30 years of effort.⁽¹⁾ The necessity for accurate and precise determination of DOC in natural waters has increased sharply over the last few years because several large-scale models and major field studies of marine systems have focused on carbon cycling and its relation to global fluxes, climatic fluctuations and food-web dynamics. This need has been partly met through recent concerted efforts, which involved several workshops and community-wide interlaboratory comparisons.^(12,31)

Direct injection high-temperature catalytic oxidation has become widely used for the analysis of TOC and DOC in seawater and other natural waters because this method appears to have greater oxidation efficiency, accuracy and precision than most of the other methods.⁽¹⁾ A large number of experimental HTC systems have been built and several commercial instruments are available.^(6,12) However, many of these instruments have problems, particularly in the analysis of seawater. These problems are mainly related to salt deposits in the sample injection

system, memory (or carry-over) effects, system blank evaluation, and motion and vibration sensitivity of NDIR detectors.

The autosampler and injector components of most commercial systems are generally not designed to work with samples with high salt concentrations (e.g. seawater and brines). Many of these injection systems use a sliding metallic or Teflon™ valve, which is susceptible to salt abrasion. In addition to this problem, the high salt content of seawater and brines can cause mechanical and clogging problems in other components of some fully automated TOC instruments. As a consequence, the autoinjection features have sometimes been bypassed or avoided in favor of more reliable manual syringe injection techniques,⁽⁶⁾ which are more labor-intensive. Most shipboard TOC analyses are currently being performed by manual injection, often requiring two or three operators working in shifts.

Manual injection systems also have some problems. Most manual systems employ a septumless injection port. The use of this semi-open injector can result in a major disturbance in the gas flow and an increased potential for contamination (e.g. from a contaminated needle). Using a septum-type injector does not solve these problems, as the septum itself can introduce contamination.⁽³²⁾ Another potential problem with manual injection arises from variations in the injection delay interval (i.e. the time between injections), which results in blank variability and consequently in poor precision and accuracy.^(33,34) Thus, for manual injection systems, obtaining high precision for very-low-carbon samples depends on the skill level of the operator. The reason for the injection delay effect is not known. However, this problem can be minimized with the use of an autosampler and autoinjector that employs a short and reproducible injection delay time. In addition, most TOC and DOC analyzers use an autosparking system with a constant sample sparging time to ensure complete DIC removal, which is critical. The use of a constant sparging time also ensures that any minor organic contamination that might be present in the sparging gas would be incorporated reproducibly within the blank.⁽⁶⁾

Memory effects may arise because most HTC column designs have a “cold” zone at the top, where vaporized OC together with sea salts can deposit on the wall in the dead volume above the column packing.^(33,35) During subsequent injections, these deposits may wash off or “flake off” randomly and become oxidized, giving rise to an unusually large peak.⁽³⁵⁾ Owing to the random nature of this memory effect, it is difficult or impossible to correct for it since it may affect standards and samples differently. Discarding unexpectedly small or large peaks will improve the precision, but this may have a negative impact on the accuracy, especially if the large peaks are

due to residual OC deposits from prior samples. Thus, the overall impact may be lowered recoveries and less than 100% oxidation efficiencies for even thermally labile standards.^(34,35)

Problems arising from sample injection and memory effects have been recently addressed through major improvements in the HTC injection system and column design.⁽³⁴⁾ The improvements include coupling a self-rinsing, loop autoinjector directly to the HTC column via a platinum tube so that the injection process is closed to the atmosphere, thereby increasing the precision and eliminating potential contamination during manual injection. In order to address memory effects, the cold zone at the top of the column was essentially eliminated, which allowed the sample injection to take place entirely within the column’s “hot” zone. This modification eliminated effects due to deposits “flaking off” from the walls. In addition to this modification, a small amount of deionized water was automatically injected immediately after each sample injection to keep salt deposits from building up in the connecting tubing. The deionized water injection also helped to reduce memory effects from sample-to-sample carry-over and to increase the lifetime of the autoinjection valve by washing out residual salts.

The accuracy of TOC and DOC analyses is strongly dependent on evaluation of the system blank, which in turn is dependent on conditioning of the instrument, especially the HTC column. Column conditioning is often accomplished with repeated injections of low-carbon distilled water. Hundreds of injections have been reported to be required to obtain a low and stable blank for Pt-based HTC columns,^(29,36) which is problematic using manual injection. Once the HTC column is conditioned, accurate assessment of the instrument blank depends on the purity of the injected “zero” carbon water. Of the various methods that have been used for producing “zero” carbon water,⁽²⁵⁾ closed loop injection of the condensed water that is trapped after the HTC column appears to be the most effective.⁽³⁶⁾

Most HTC columns are packed with alumina beads containing Pt, supposedly to catalyze the complete oxidation of OC to carbon dioxide. However, these columns are relatively expensive and the catalytic sites may be subject to poisoning or deactivation by salt deposition.^(33,37) It is not clear what function, if any, the catalyst plays in the oxidation process. In fact, several recent studies have shown that complete oxidation can be achieved with HTC columns without a catalyst, for example using pure quartz beads.^(14,34) The latter is less expensive and has a lower blank.⁽³⁴⁾

From the above, it is apparent that the precision and accuracy of HTC methods are affected by various factors including the presence or absence of a cold zone (and dead volume) at the head of the column,

Table 2 Advantages and disadvantages of TOC and DOC methods for aqueous samples. Modified from MacKinnon⁽³⁸⁾

Parameter	Manual WCO (persulfate)	Automated WCO (persulfate)	UV oxidation (persulfate enhanced)	Dry or sealed tube combustion (Pt catalyzed)	Direct injection HTC
Oxidation efficiency (relative to HTC)	Generally 85–95%, but may be close to 100% depending on proper blank evaluation and sufficient reagent excess	Generally 85–95%, but may be close to 100% depending on proper blank evaluation and sufficient reagent excess	About 95%, but may be close to 100% if TiO ₂ catalyzed, (Abdullah and Eek ⁽²⁸⁾)	100%	100%
Changes in oxidation efficiency with time	Oxidative efficiency can decrease during digestion, especially for high TOC or chloride-containing samples	Oxidative efficiency can decrease during digestion, especially for high TOC or chloride-containing samples	Possible, due to degradation of lamp	No	No
Precision	Variable	Good	High	High with proper precautions	High with precautions taken to eliminate memory effects
Blank	High and difficult to assess	High and difficult to assess	Low	Low with proper precautions	Difficult to assess, but low after column conditioning;
Contamination	Variable	Low	Low	Low with proper precautions	Low
Interferences with oxidation	Chloride	Chloride	None	None	None
Memory or carry-over effects	None	None if reaction vessel is properly rinsed	None	None	None if injection system and column are properly designed
Sample preparation	Extensive	Minimal	Minimal	Extensive	Minimal
Automation	Possible	Yes	Yes	No	Yes
Real-time analysis	No	Yes	Yes	No	Yes
Shipboard use	Possible, but not recommended	Yes	Yes	No	Yes
Complete oxidation of colloids and particles	Yes	Yes	No	Yes	Yes
Loss of volatile organics	Moderate	Moderate	Minor	Complete	Minor
Cost of equipment	Low	High	High	Moderate	High

memory and carry-over effects, contamination and salt deposition during injection, variable injection delay time, and sample sparging time.^(20,33,34) In addition, variations in carrier gas flow rate and column temperature can have a strong impact on the precision.⁽³⁴⁾ Most of these sources of error are eliminated or minimized by using a closed self-rinsing autoinjection and autosparging system

directly coupled to a noncold zone, low dead volume combustion column.⁽³⁴⁾ These recent improvements in HTC instrument design should benefit other fields besides oceanography, especially where high precision, low detection limits, salts, or field portability are important. A summary of the advantages and disadvantages of the major TOC and DOC methods is given in Table 2.

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ABBREVIATIONS AND ACRONYMS

COD	Chemical Oxygen Demand
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
FID	Flame Ionization Detection
GC/MS	Gas Chromatography/Mass Spectrometry
HTC	High-temperature Combustion
ICP/AES	Inductively Coupled Plasma Atomic Emission Spectrometry
NDIR	Nondispersive Infrared
OC	Organic Carbon
POC	Particulate Organic Carbon
PVC	Polyvinyl Chloride
TOC	Total Organic Carbon
TOD	Total Oxygen Demand
UV	Ultraviolet
UVO	Ultraviolet Oxidation
VOC	Volatile Organic Carbon
WCO	Wet Chemical Oxidation

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