

Total Organic Carbon (TOC) Analysis Technique Comparison

A Practical Guide

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About This Guide

Total Organic Carbon (TOC) analysis is a means to determine water cleanliness and purity. TOC is used in variety of laboratories fields including:

- Environmental
 - Contract Laboratories
 - Municipalities
- Pharmaceutical
- Universities
- Petrochemical

The United States Pharmacopoeia (USP), European Pharmacopoeia (EP) and Japanese Pharmacopoeia (JP) all mandate TOC analysis as a required test. It can be used in a variety of applications including:

- Drinking Water
- Wastewater
- Soils

TOC has found wide acceptance in the **biotechnology/pharmaceutical industry** to assist in cleaning validation procedures, especially Clean-In-Place (CIP) procedures. TOC concentration levels can be used to track the success of these cleaning procedures to ensure there is no cross-contamination.

TOC is used to **monitor drinking water** safety. When high organic content water is subjected to the disinfection process during normal purification, it will create disinfection by-products, which are carcinogenic. It is important to make sure the TOC is low in water coming in and water leaving the water treatment facility to ensure public safety.

Total Organic Carbon (TOC) analysis grew from the need to analyze wastewater and municipal water for organic matter. The need to protect water quality and establish criteria for screening and measuring contaminant levels was recognized when Congress enacted the Resource Conservation and Recovery Act (RCRA) in 1976. This act requires operators of waste disposal sites to monitor their groundwater on a quarterly basis for organic carbon levels and organic halide levels.

This guide helps provide all the essential knowledge for TOC users and help recommend the best instrument for your application.

The History of TOC

Carbon analysis has been around for 100s of years, and periodically continues to improve. Carbon analysis began with the discovery in the 1630s by scientist Jan Battist Van Helmont when burning wood, the gas emitted was Carbon Dioxide. Later, in 1756, Joseph Black found a way to measure carbon dioxide by Loss on Ignition. In this method, samples were heated and when heated the samples loss mass. From this difference in mass, the amount of carbon could be determined.



The method became more refined in 1924, T.D. Yensen laid steel samples into a 1000 °C furnace along with oxygen, which combusted the carbon and then collected the CO₂ cryogenically. The infrared gas analyzer was born in 1948 by American Cyanamid, which leads to later use of NDIR detector for TOC analysis. Then in 1967, Dow Chemical patented, “Method and Apparatus for Determination of Total Carbon Content in Aqueous Systems.” This system manually injected aqueous samples directly into a gas stream of oxygen in a 700-900 °C furnace. The CO₂ produced during this process was measured with infrared absorbance. This was the first combustion TOC instrument produced. The analytical range, at that time, was 2-500 ppm and 98% combustion efficiency rate (Lipps, American Laboratory).

TOC analysis grew popular from the need to analyze wastewater and municipal water for organic matter. Criteria was established for screening and measuring contaminant levels when Congress enacted the Resource Conservation and Recovery Act (RCRA) in 1976.

Although the technology of TOC has been around for quite some time, TOC analyzers continue to improve to meet customers changing demands.

TOC Overview

TOC analyzers can measure:

- Total Carbon (TC)
- Total Organic Carbon (TOC)
- Inorganic Carbon (IC)
- Non-Purgeable Organic Carbon (NPOC)
- Purgeable Organic Carbon (POC)

TOC measurement involves:

- Oxidizing organic carbon in a sample
- Detecting and quantifying the oxidized carbon (CO₂)
- Presenting the results in units of mass of carbon per volume of sample

Definitions:

- **Total Carbon (TC)** – The measure of all the carbon in the sample, both inorganic and organic, as a single parameter. Generally, the measurement is made by placing the sample directly into the analyzer without pretreatment.
- **Total Organic Carbon (TOC)** - The sum of all the organic carbon in the sample.
- **Direct TOC Measurement (NPOC)** – In the direct approach, IC is first removed by acidification and sparging and the remaining carbon is measured as TOC. IC and POC are not recovered for further analysis in this approach. However, since POC generally represents 1% or less of total carbon in a sample, it is considered negligible.
- **TOC Measurement by Difference (TC-IC)** - This approach requires two analyses: one to measure TC, and one to measure IC. The difference between these two measurements is precisely TOC.
- **TOC Measurement by Sum** - This approach measures NPOC and POC. The sum of these measurements is precisely TOC.
- **Inorganic Carbon (IC)** - Includes carbonate, bicarbonate, and dissolved carbon dioxide. IC is analyzed in liquid samples by acidifying with an inorganic acid to pH 3 or lower, and then sparging with a stream of inert gas. The acidification converts carbonates and bicarbonates to carbon dioxide, which is then removed along with dissolved CO₂ by the gas stream and measured to provide an IC value.

Types of Oxidation Techniques

There are three primary oxidation techniques employed by TOC analyzers today: Catalytic, UV persulfate, and High Temperature Ceramic. A description of each oxidation method and the positive and negatives aspects of each oxidation method is discussed briefly below.

Catalytic Combustion



Catalytic Combustion system is where the sample is injected into a catalyst packed tube. The catalyst tube is enclosed in a furnace, which heats to 680 °C -1000 °C. The combination of temperature, an oxygen rich environment from the carrier gas (generally Ultra Zero Air or Oxygen), and a catalyst is used to oxidize the carbon in the sample to CO₂. The CO₂ is then swept to the Non-Dispersive, Infrared (NDIR) detector. Catalytic combustion is best used for wastewater applications with 10-20,000 ppm range. It is not sensitive enough for accurate low level analysis like drinking water. The catalyst will need to be replaced periodically which can be somewhat costly and will cause some downtime of the system. Salt will cause the catalyst to be spent more quickly. Some systems may require a different catalyst when analyzing salt samples.

High Temperature Ceramic

High Temperature Ceramic (HTC) system is where the sample is injected into a furnace up to 1800 °C with a stream of oxygen. There is no catalyst needed for this oxidation process. The CO₂ is then swept to the Non-Dispersive, Infrared (NDIR) detector. Most ceramic systems recommend concentrations above 50 ppmC.

HTC is also not recommended for low carbon samples such as drinking water or water for injection samples. It can only handle large amounts of carbon in the 10,000s ppm, so it is usually recommended for applications such as wastewater and soil analysis. There is not much information on HTC, and is not a commonly practiced method of oxidation, because there is no regulated method written around HTC.

UV Persulfate



UV Persulfate (UVP) system is where an aliquot of sparged sample is transferred to a UV reactor where the oxidation power comes from a combination of sodium persulfate (chemical oxidizer) and UV light. UV Persulfate systems are good for low level TOC analysis. These systems should not be used for samples that are hard to oxidize.

Factors that make a sample hard to oxidize for a UV Persulfate system include:

- Particulates
- High levels of carbon
- Oils
- Salts

Seawater samples should not be run on a UV Persulfate system. The salt will prevent the sample from fully oxidizing and could harm the detector.

UV Persulfate should only be used for samples less than 50 ppmC without dilution and contain no particulates. Dilution may cause this range to reach to 1000 ppm or above.

It is also important to note, that while combustion can be run on lab grade air, UV persulfate can only be used with nitrogen. Air or oxygen will create ozone from the chemical oxidization process, which causes respiratory issues. When making the sodium persulfate and acid reagent for this oxidation process, be careful cleaning glassware, so there is very little carbon contamination. Do not clean glassware with carbon containing cleaners.

Flow Control Systems

The gas flow through the system can be managed by a Mass Flow Controller (MFC) or by a gas pressure regulator. The MFC provides more accurate flow and variable flow conditions and can have features like automatic leak checking. A pressure regulator can only be set to one flow rate and can be turned on and off. If the flow needs to be reduced, a flow restrictor will be placed in the pathway. The benefit of the pressure regulator technique is it is less costly.

NDIR

Non-Dispersive Infrared (NDIR) detectors utilize infrared (IR) to detect the existence of CO₂. The IR beam is transferred through a chamber while the sample CO₂ gas fills it. The CO₂ measurement is a function of the absorption of IR energy as it travels through the optical path. Concentration measurements are based on the difference ratio in the IR absorption between a reference and sample signal. Reference and sample channels measure CO₂ in a single path through the use of narrow band optical filters with appropriately selected bands. The CO₂ sample channel uses an optical filter centered at 4.24 micrometers. This filter corresponds to the absorption band for CO₂. Concentrations of CO₂ present in the optical path will result in a reduction in IR energy as it traverses the optical path. The reference channel is established using a filter with a center wavelength at 3.95 micrometers. Examples of NDIR detectors are below:

Figure 1 Fusion / Torch NDIR Diagram

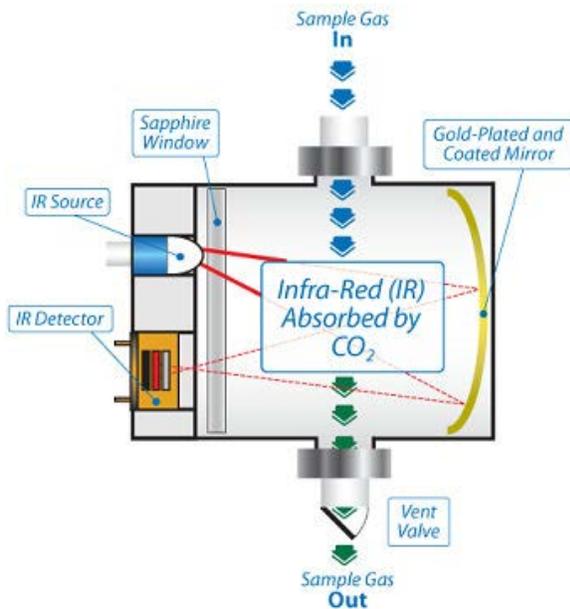
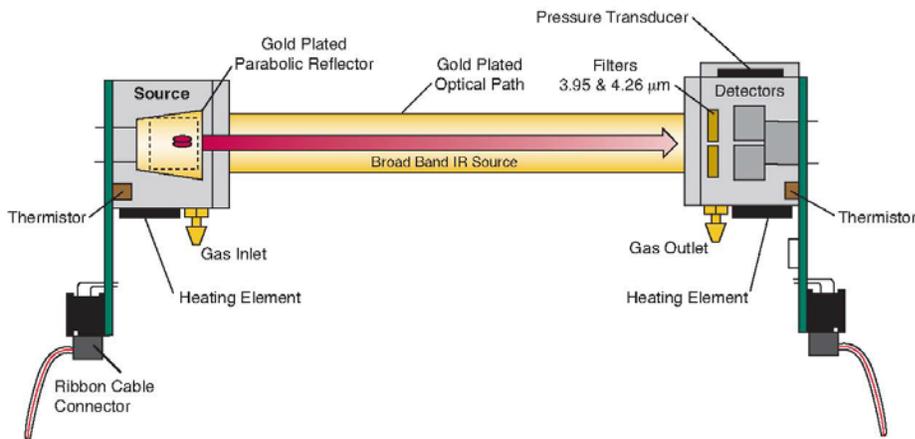


Figure 2 Lotix NDIR Diagram



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NDIR – Flow Through

Traditional flow-through detection is when the absorption of the infrared light is measured over time as the CO₂ is swept through the detector. The resulting measurement correlates to a peak, which can be integrated and calculated to a concentration. Flow-through detection can be done using a Mass Flow Controller or a pressure regulator. **The Lotix Combustion Analyzer is recommended for this detection scheme.**

NDIR - Static Pressure Concentration (SPC)

Static Pressure Concentration (SPC) allows for the specific carbon component to be oxidized and the resultant carbon dioxide swept into the detector using a non-interfering, inert gas, which is measured by a Mass Flow Controller. Once the gases inside the detector have reached equilibrium, the detector seals off. A single reading is used to determine the amount of CO₂ in the detector cell. The reading correlates directly to the concentration of the carbon contribution from the sample. The SPC is visually shown as a bar graph since it is a one moment in time reading. **The Torch Combustion Analyzer or Fusion UV Persulfate Analyzer is recommended for this detection scheme.**

NDIR Limitations:

Halogens

The NDIR has limitations, it cannot handle halogenated compounds. The most common halogen problem is salt in seawater samples. When looking to select a TOC analyzer, one will need to check with the TOC manufacturer on the amount of salinity the system can handle. Teledyne Tekmar suggests as little as possible, but realistically under 4% salinity is needed to not harm the NDIR detector. To help with this halogen problem, Tekmar includes halogen scrubbers. The tin in the scrubber collects the harmful halogen compounds and the copper turns dull to act as indicator. When one observes the copper turning dull and silver, it is time to replace the halogen scrubber. Make sure when purchasing a TOC analyzer with a NDIR detector that the system has some form of halogen removal in order to prevent harm to the NDIR.

Since halogenated compounds are harmful to the NDIR detector, never wash glassware or use with halogenated acids like Hydrochloric. We recommend only using phosphoric acid to preserve the samples and nitric acid to clean the glassware.

Figure 3 Halogen Scrubber



Water

Water is also harmful to the NDIR detector. Teledyne Tekmar employs a dual step moisture removal process, which includes a mist trap and a permeation dryer. After oxidation of the sample, carrier gas sweeps CO₂ and water vapor to the Mist Trap. During the transfer, some condensation occurs in the tubing. The tubing will need a cooling fan when using a combustion system to collect the water. Once in the Mist Trap, most of the condensate is removed.

Figure 4 Lotix Condensate Loop

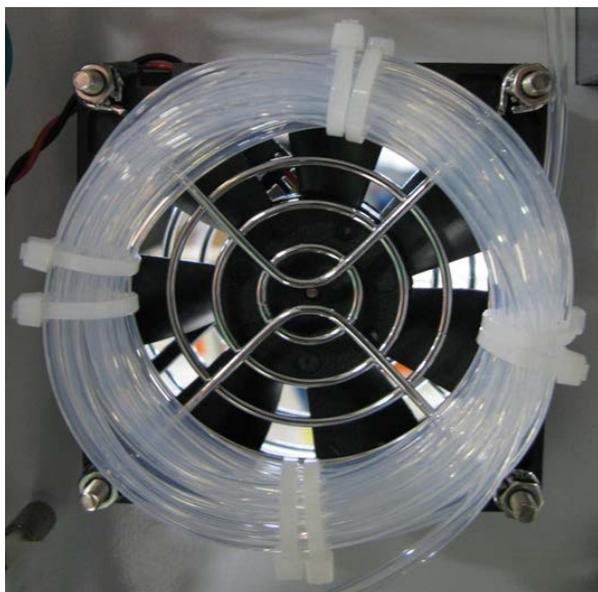


Figure 5 Mist Trap



The gases then travel to the Permeation Dryer, which removes the rest of the moisture from the sample gas. The permeation dryer is a tube inside another tube. The inner tube is made of a special membrane material that allows moisture to permeate. The outer tube has gas that sweeps in the opposite direction to remove the permeated moisture.

Figure 6 Fusion Permeation Dryer



At the completion of sample analysis, the condensate is sent to the waste container. Make sure when using a NDIR system that the instrument has a moisture removal process to ensure the life of the detector.

Other Detection Methods

Conductivity

Conductivity method measures the conductivity of the sample before and after oxidation the difference yields the amount of TOC. The sample, in the oxidation phase, forms dissolved CO_2 which acts as a weak acid, in turns, weakens the conductivity of the sample which is proportionate to the amount of TOC. This simple method may, depending on the chemical species of each individual sample and unique oxidation products, present a proportional positive or negative interference to the calculated TOC value. Conductivity detection limits are under 50 ppm, when carbon content is greater than 50 ppmC, the conductivity is no longer proportionate. This method works well for on-line applications in pharmaceutical industry.

Membrane Conductivity

The use of membranes was used to improve the accuracy of conductivity. It employs the use of hydrophobic gas permeation membrane which allows for greater discrimination for dissolved CO_2 over other chemical compounds. Although this membrane has the ability to differentiate, it can become clogged from microbes and other particulates. Membranes can also develop flow problems, dead spots, and micro leaks, which will affect the performance. Some amines still have the ability to pass through the membranes and add conductivity resulting in a false high concentration. Also, once the membrane is overloaded, it may take hours to before returning to working order. This method works well for on-line applications in the

pharmaceutical industry. This method is not recommended for concentrations above 50 ppm.

Conclusion

This guide provides the essential knowledge of Total Organic Carbon analysis which helps the user make more informed decisions when selecting the right best technique for their analysis. It is important to consider the oxidation technique and detection technique based on the users applications to select the best technique for TOC analysis.

About Teledyne Tekmar

At Teledyne Tekmar, we pride ourselves in designing and manufacturing quality environmental instrumentation. Our products include headspace autosamplers, purge and trap autosamplers for Volatile Organic Compound (VOC) analysis, an automated Quick-Easy-Cheap-Effective-Rugged-Safe (QuEChERS) extraction platform for pesticides analysis, and Total Organic Carbon (TOC) instruments.

We dedicate ourselves to resolving customer needs, concerns, and increase cost benefit within our products and services. We are driven to understand the latest customer needs and requirements and desires which directs our development process. We manufacture our products with the upmost attention to quality and are constantly improving all facets of our processes to ensure longevity and performance.

Our support does not stop once the customer invests in our products. We have a team of highly skilled technical support staff to aid our customer through the life of a Tekmar product supporting their needs including troubleshooting and application. By working closely with our customers, we are able to find key customer needs that we in return use to continuously improve our products for the future of environmental analysis. We find working closely together with our customers is the key to our success.

Figure 7 Teledyne Tekmar



Teledyne Tekmar TOC Analyzers

Fusion UV Persulfate - The Fusion was designed with the pharmaceutical and drinking water applications in mind. With its extremely low detection limit of 0.2 ppbC and its ability to handle high levels of carbon, acid, particulates, and salt, it is a very versatile analyzer for many sample matrices. The accuracy of the Fusion's UV/Persulfate oxidation is unmatched. UV/Persulfate has very little background carbon, lower than TOC combustion systems, making it the best choice for drinking water and ultra-pure water applications.

Figure 8 Fusion UV/Persulfate Analyzer



Torch Combustion - The Torch utilizes a patent pending Static Pressure Concentration (SPC) for the analysis of TOC/TN using high temperature combustion. The Torch Analyzer contains a built in autosampler with three vial rack choices and PC driven control. This features automated calibration and Intellidilution, which automatically dilutes over-range samples to within the working calibration range. Maintenance is simplified by design allowing easy access to all areas of the unit.

Figure 9 Torch Combustion Analyzer



Lotix Combustion - The Lotix TOC Combustion analyzer is designed to accurately measure carbon content in aqueous matrices down to the ppb level. With the vast detection range and robustness on the Lotix, dilution and filtration is no longer required for samples less than 20,000 ppmC and particles less than 0.8 mm in diameter. It uses proven high temperature combustion, oxidation of carbon material into carbon dioxide, and detection using a new Non-Dispersive Infrared (NDIR) detector. Lotix is the ultimate solution for wastewater, drinking and surface water, ground water, sea water, and other hard to oxidize matrices with an economical price to fit any budget.

Figure 10 Lotix Combustion Analyzer



For more information on the various TOC analyzer or to get additional help, please contact us at tekmar@teledyne.com or visit our website at www.teledynetekmar.com

Work Cited

1.) <http://www.americanlaboratory.com/913-Technical-Articles/186269-Measuring-Organic-Carbon-A-Brief-History-and-Discussion-of-Methodologies/>