
THE IMPORTANCE OF MEASURING TOTAL ORGANIC CARBON

Organic carbon compounds vary greatly. In fact, one of the first lessons in most introductory Organic Chemistry courses explains that the number of possible carbon compounds is virtually infinite due to carbon's ability to form long, chain-like molecules. While chromatographic methods like gas chromatography (GC) or high-performance liquid chromatography (HPLC) are able to make quantitative determinations for specific compounds, the user must first know which specific compounds to look for.

Total organic carbon (TOC) is a non-specific test, which means TOC will not determine which particular compounds are present (most samples are complex mixtures which contain thousands of different organic carbon compounds). Instead, TOC will inform the user of the sum of all organic carbon within those compounds.

The reasons for measuring TOC vary across industries, but generally fall into two categories: process control, or regulatory compulsion. Some of the most common TOC measurement applications include:

Municipal Drinking Water: Organic carbon reacts with disinfection chemicals such as chlorine and forms disinfection byproducts (DBP), which may be carcinogenic. Reducing organic carbon prior to disinfection can significantly decrease harmful DBP exposure for the public.

Municipal Waste Water: Monitoring organic carbon of influent facilitates process controls for maximizing plant efficiency, while monitoring effluent is often a requirement for discharging into surface waters.
Industrial Waste Water: Industries which discharge liquid waste into a surface water body are required to monitor TOC.

Power Plants: Limiting potential sources of corrosive compounds can prevent costly damage to expensive equipment.

Pharmaceutical Manufacturers: Water is the most commonly used ingredient used to produce drugs. Regulations limit the concentration of organic carbon to prevent harmful bacteria from growing.

Electronics Manufacturers: Ultra-pure water is used in the manufacture of microprocessors and computer chips. As processors and circuits become smaller and smaller the water must be kept incredibly clean to prevent microscopic damage to these miniature circuits.

TOC Detection Methods

Several methods exist for measuring TOC, however each method has two common objectives: 1) Oxidize organic carbon to carbon dioxide, and 2) measure the carbon dioxide generated.

Common oxidation methods include chemical agents (such as persulfate), combustion (usually aided by a catalyst), exposure to ionizing radiation (such as ultra violet light), exposure to heat, or some combination of these methods.

There are fewer options for detecting carbon dioxide, two common methods are conductivity and non-dispersive infra-red (NDIR). Conductivity based detection methods work by sensing an increase in ion

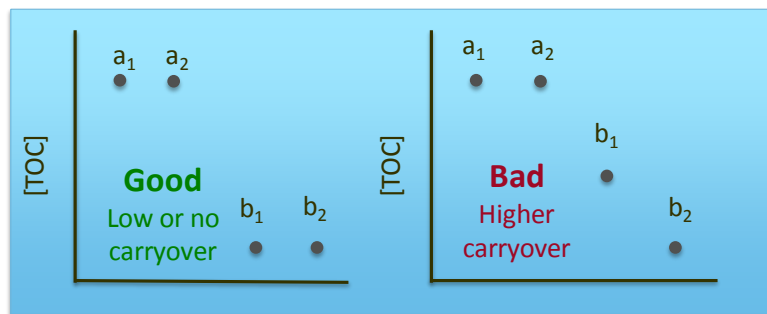
concentration which is attributed to the increased presence of bicarbonate and carbonate ions created from the oxidation of organic compounds. Non-dispersive Infra-red detectors measure carbon dioxide by determining the amount of infra-red light absorbed across a known distance.

Preventing Damage to the Instrument

Two common pitfalls that can damage TOC measurement instruments or produce erroneous measurement results include sample overload (running a sample which far exceeds the maximum analyte specification), and carryover (contamination from a previous sample).

Overload conditions are common when running unknown samples. Depending on the measurement technology used this condition can cause costly damage to an instrument. For example, a combustion-type instrument which uses platinum catalysts can very easily ruin the catalysts and require expensive replacements. Membrane-based TOC measurement instruments can also coat the surface of the membrane with organic carbon compounds from a high-concentration unknown sample. Such an event will leave the instrument out of operation while awaiting service.

Carryover results from residual sample left from a previous measurement. It is most often observed when multiple replicates of a sample are measured, and a high concentration sample is followed by a low concentration sample. The following equation calculates carryover as a percentage of the difference between the two sample concentrations:



$$\text{Carryover} = \frac{(b_1 - b_2)}{(a_2 - b_2)} \times 100\%$$

Methods of Calculating TOC

Inorganic carbon is bound only to oxygen, as in carbon dioxide, bicarbonate, or carbonate (for example: limestone is calcium carbonate which is a form of inorganic carbon). Organic carbon can be bound to a variety of other elements such as hydrogen, nitrogen, or other carbon atoms.

Other forms of carbon include purgeable versus non-purgeable carbon. Volatile organic compounds have a low boiling point, and can be purged from a solution by bubbling gas through a sample.

The following abbreviations are commonly used to describe various forms of carbon when measuring TOC:

TC: Total Carbon

TOC: Total Organic Carbon

TIC: Total Inorganic Carbon

POC: Purgeable Organic Carbon (also called VOC or Volatile Organic Carbon)

NPOC: Non-purgeable Organic Carbon

Calculating TOC can be done by subtracting the TIC from the TC. This method is described by the equation

$$\text{TC} - \text{TIC} = \text{TOC}$$

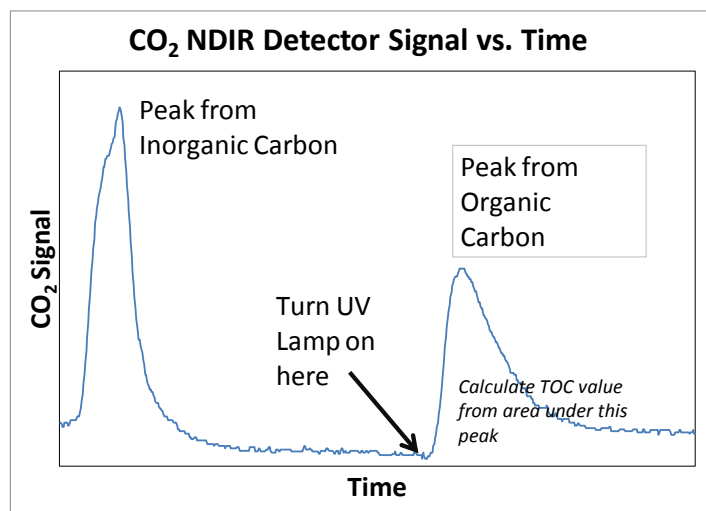
This method works well when there is a large difference between TC and TIC; however when TIC values are high the difference method can produce very erratic results because the margin of error for both the TC measurement and the TIC measurement must be added together.

In many TOC measurement applications it is reasonable to assume that the contribution of POC to the overall TOC value is negligible, and therefore the following approximation is used

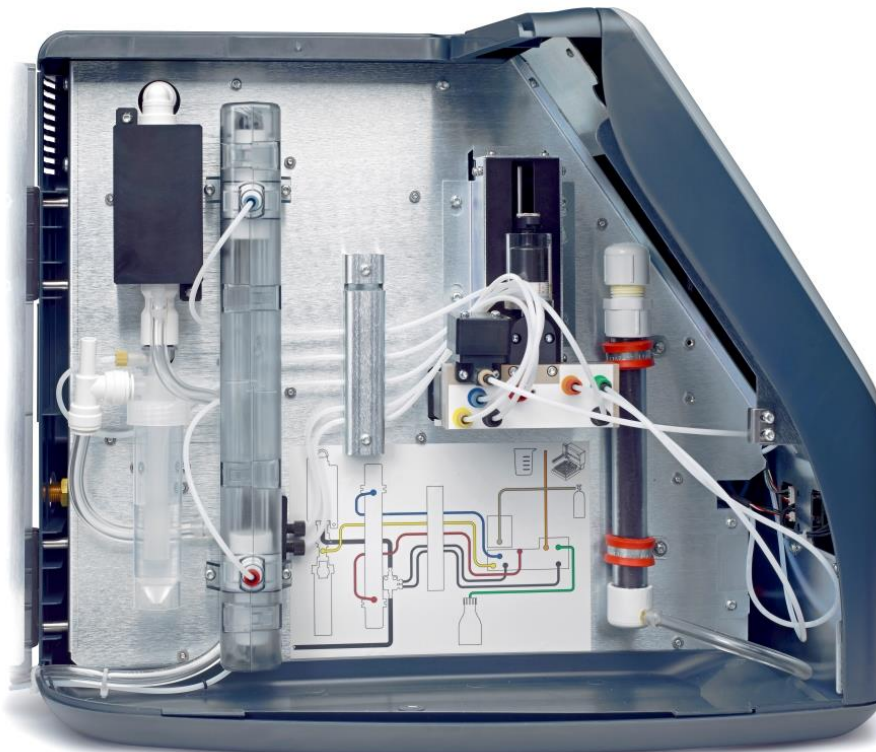
$$\text{NPOC} \approx \text{TOC}$$

This approximation is good for drinking water, where the largest contribution of organic carbon comes from humic acids which are non-volatile, high molecular weight compounds. Ultra-pure applications such as pharmaceutical, power, and semiconductor manufacturing also should expect to have negligible concentrations of POC present in the sample.

The NPOC methods usually employ NDIR measurement technology, which generates a signal that is recorded over time. When the signal is graphed two peaks are prominent. The first peak results from inorganic carbon (dissolved CO₂ already present in the sample). The second peak results from the organic carbon which is oxidized to CO₂.



Below are photos of the newest TOC instrument from Hach, the QbD1200



DOC040.52.10062.Jun15