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.

"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)."

Mira Kovacheva
HACH LANGE GmbH
Willstaetterstr. 11
40549 Duesseldorf
Germany
Tel: +49 211 5288 358
Email: mira.kovacheva@hach.com
Web: www.de.hach.com

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.

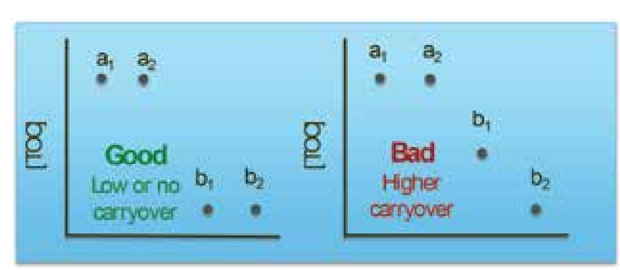
There are fewer options for detecting carbon dioxide, two common methods are conductivity and non-dispersive infra-red (NDIR). Conductivity based detection methods work by sensing an increase in ion concentration which is attributed to the increased presence of bicarbonate and carbonate ions created 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

TC – TIC = TOC

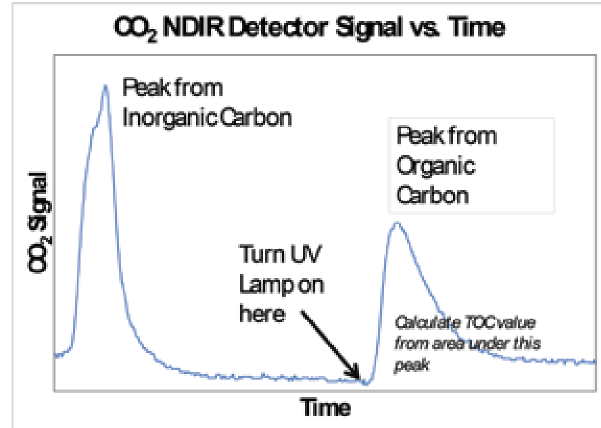
This method works well when there is a large difference between TC and TIC; however when TIC values are high the difference method can produce very erratic results because the margin of error for both the TC measurement and the TIC measurement must be added together.

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

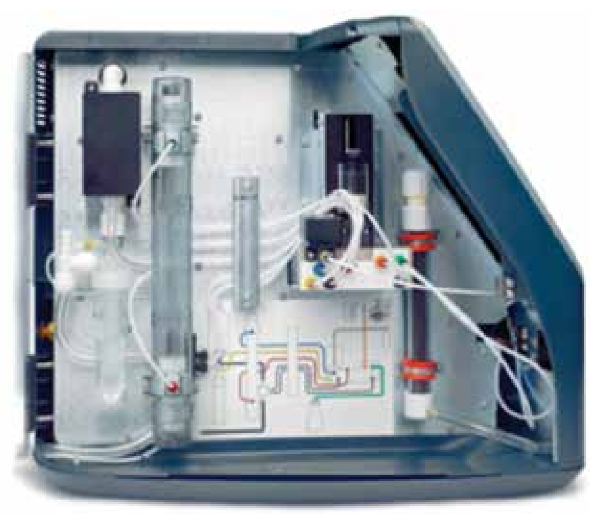
NPOC ≈ TOC

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 CO_2 already present in the sample). The second peak results from the organic carbon which is oxidized to CO_2. The graph below illustrates an NPOC measurement cycle.



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



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Global Ultrasonic Capability the Key to Major Australian Contract

Watercorp, Australia's largest water company, manages the water and wastewater needs of the whole of Western Australia, an area more than a quarter of the size of the USA. After trials and long experience of a wide variety of both contacting and non-contacting alternatives, Watercorp have chosen UK manufacturer **Pulsar Process Measurement** (UK) to supply their level measurement and control requirements; they will use hundreds of Pulsar's specialist non-contacting ultrasonic sensors and controllers, with technical and sales support from Pulsar's regional office and Australian distributor.

From their main office in Perth and centres throughout the State, Watercorp's 3000 staff look after more than 100 wastewater treatment plants and over 700 pumping stations. Since 2012, Watercorp have installed over 200 Pulsar ultrasonic units, and have purchased a further 330 to install throughout their network. Pulsar's Australian distributor Bintech are supplying both equipment and know-how through their Western Australian representative Gateway Technical Services.

With such an extensive network operating in the often extreme conditions of Australia, equipment has to work reliably; Watercorp have seen issues including pumps running dry and pumping stations occasionally overflowing. They undertook a detailed investigation of all the equipment in use throughout all their sites, reviewing and comparing performance. They were able to identify Pulsar equipment as consistently the most reliable systems they used.

As Paul Jacobs, Watercorp's Supervising Engineer, put it: "Due to the large area we cover, it is critical that we can offer our customers the highest quality and reliability. With Ultrasonics we look at ease of installation, set up requirements, reliability, accuracy and product support. With the experience from our use of other suppliers for Ultrasonics, Radar, Hydrostatic, electrodes and ball floats, it was obvious that there was a major cost and support advantage to using Pulsar, ensuring our needs were met".

The support point is crucial. Pulsar has grown to the point that the company is now the leading specialist ultrasonic manufacturer in the world, with non-contacting measurement systems working successfully from the heat of Australia to the steppes of Russia, from China to the United States. With regional offices strategically positioned around the world working with an extensive network of trained and accredited distributors, Pulsar can confidently supply and support equipment anywhere in the world.

Colin Murphy, Pulsar's Regional Manager Asia Pacific, comments: "Watercorp's choice of Pulsar equipment demonstrates the lower support costs and high reliability that we offer, and we are delighted to be able to help them to solve technical issues and provide a high standard of service to the people of Western Australia. Our policy of strongly supporting national specialists such as Bintech means that users can be absolutely confident of great on-going advice and training wherever they are."

For More Info, email: 34965pr@reply-direct.com

email: 4933ad@reply-direct.com