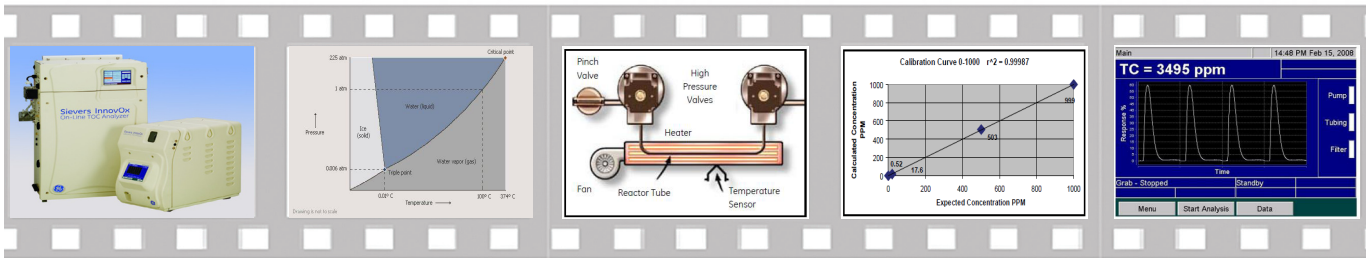


# New Chapter In TOC Analysis



**Online TOC monitoring at the primary effluent stage provides a feed-forward control strategy for managing plant waste loads and preventing plant upsets.**

By GE Analytical Instruments

Online Total Organic Carbon (TOC) analyzers can be used at wastewater treatment plants to monitor final effluent for regulatory reporting purposes and at various points throughout the treatment process for preventative control. Online TOC monitoring at the primary effluent stage provides a feed-forward control strategy for managing plant waste loads and preventing plant upsets.

## Technologies

Currently, there are several major types of instrument technologies used for online TOC analyzers:

- High Temperature Catalytic/Combustion Oxidation (HTCO)
- Supercritical Water Oxidation (SCWO)
- Heated Persulfate Ultraviolet (UV) Oxidation

Total Carbon (TC) of a wastewater sample is typically composed of a mixture of total organic carbon (TOC) and inorganic carbon (IC) or mathematically:  $TC = TOC + IC$  or  $TOC = TC - IC$ . Using these equations, there are two methods to determine TOC. One method is to measure TC and IC independently and subtracting the IC from the TC. The second method uses an acid to carbonate the sample to chemically remove the IC from the sample and leave only the TOC in the sample for analysis by the instrument.

All online TOC analyzer technologies oxidize the total organic carbon samples to break the sample's organic carbon down into a carbon dioxide (CO<sub>2</sub>) gas. The CO<sub>2</sub> gas is measured by a Nondispersive Infrared (NDIR) detector.

## Supercritical Water Oxidation

The sample matrices are known to create analytical obstacles during routine Total Organic Carbon (TOC) analysis. Interferences from sample matrices have caused calibration curve stability to be sacrificed. Some common aggressive matrices require frequent maintenance, and weekly or even daily recalibration. By re-engineering the sample flow path and the oxidation technique, GE Analytical Instruments developed a robust TOC analyzer to hold a calibration curve for up to six months for even the most troublesome brine matrices.

The process used in the Sievers InnovOx Laboratory TOC Analyzer is Supercritical Water Oxidation (SCWO). The Supercritical Water Oxidation online TOC analyzer uses a patented technique that exposes heat and pressure to a wastewater sample to bring the sample into a supercritical state (a state in which the sample is neither a liquid or a gas), and is based on wet chemical oxidation technique. First the sample is acidified and purged (sparged) with a carrier gas to remove inorganic carbon in the form of CO<sub>2</sub>. Then the sample is converted to a supercritical state. The supercritical sample is then oxidized to CO<sub>2</sub> gas using persulfate at elevated temperatures, and an

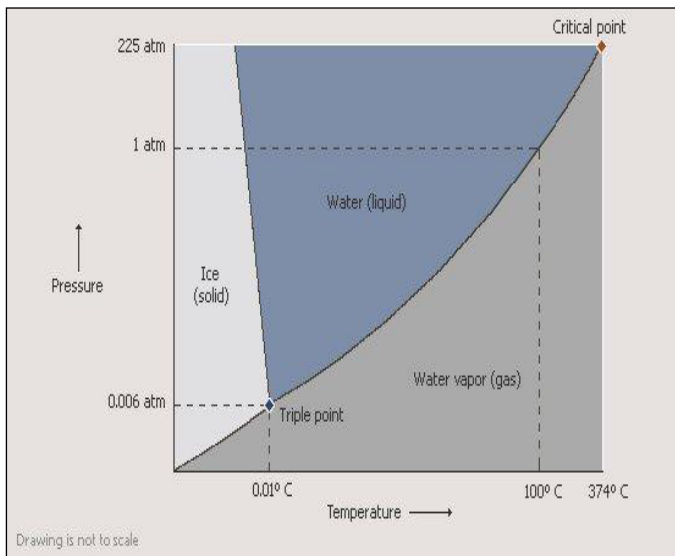


Figure 1: Supercritical Water Oxidation State

NDIR detector measures the concentration of CO<sub>2</sub> which is proportional to the concentration of the TOC in the sample

This novel approach to this wet chemical oxidation technique dramatically increases the efficiency of the oxidation process, thereby offering better recovery for difficult matrices. Unlike combustion techniques, this process completely removes all by-products from the sample flow path between sample runs offering calibration robustness and long-term stability.



Figure 2: The Sievers InnovOx TOC Analyzer

### What Does Supercritical Mean?

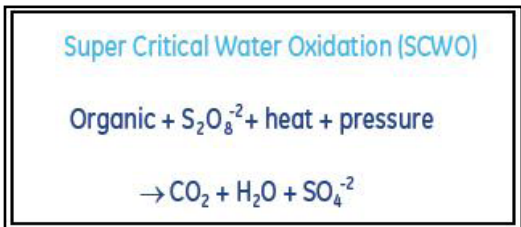
A transition point is when a compound changes phases. When discussing supercritical water, it is important to understand first the different phases of water. When liquid water is placed in an open container, at room temperature and atmospheric pressure, and then cooled to below 0°C, the water transitions from liquid phase to solid phase. If the temperature of the liquid water in the same open container is raised above 100°C, the water boils and transitions from liquid phase to gas phase.

This is normal behavior when atmospheric pressure is kept constant at ambient conditions. As shown in the phase diagram of water (Figure 1), an increase in head pressure raises the temperature at which all the liquid water would transition into the gas phase. Therefore, the liquid water can be heated to a higher temperature without boiling. In this example, the resulting pressure inside the container increases to nearly twice atmospheric pressure, similar to what occurs in a common pressure cooker.

Figure 1 also demonstrates that the more the liquid water temperature increases, the greater the corresponding pressure necessary to keep the water in a liquid phase. At a certain point, pressure can no longer be increased to maintain the liquid phase. Beyond 374 °C and 218 atm (3200 psi), the gas and liquid phases merge to form another phase of matter. This phase is called Supercritical Water (SCW).

When in a supercritical state, water exhibits the characteristics and benefits of both a liquid and a gas. The SCW has a density closer to that of a liquid, but can still diffuse like a gas. Organic material and gases become highly soluble in SCW and, conversely, inorganic salts become insoluble. These conditions are ideal for Supercritical Water Oxidation (SCWO) reactions.

### Supercritical Water Oxidation Reactions



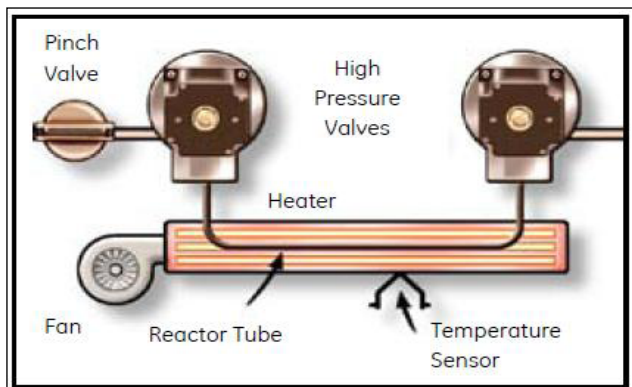


Figure 3: Reactor Tube

### Instrumentation

The Sievers InnovOx TOC Analyzer (Figure 2), has three basic steps of operation: (1) Sample handling and reagent mixing; (2) The SCWO reaction; and (3) Detection by non-dispersive infrared. These steps are discussed below:

#### Sample Handling & Reagent Mixing

The sample handling module automates several functions, including: sample delivery from the vial to the mixing chamber; dilution capabilities, if necessary; acid addition; oxidizer addition, if necessary; and mixture delivery to the reaction module.

#### SCWO Reaction

The effectiveness of sodium persulphate in oxidizing organic carbon increases as temperature is applied. Until recently, wet chemical oxidation chambers have been around 100 °C, depending on the heat source. The heat assistance could go no higher because of technology limitations in handling the increased pressure caused by the closed vessel heating. The InnovOx, however, uses a titanium oxidation chamber capable of withstanding excessive pressures with ease.

To maximize the wet chemical oxidation reaction, the sample and oxidizer are delivered to the reaction module and then heated to 375 °C, which allows the water to achieve its supercritical state. The superior reaction conditions create greater confidence for complete oxidation, regardless of sample matrix or impurity interference (Figure 3).

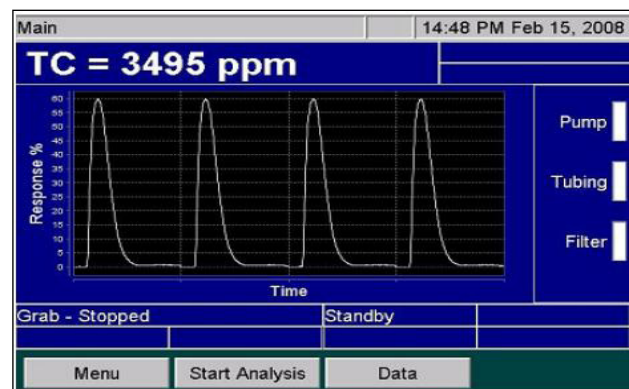


Figure 4: Peaks on Instrument Screen

### NDIR Detection

When completely oxidized, the sample is transferred to a gas/liquid separator and the isolated carbon dioxide is sent to a calibrated non-dispersive infrared (NDIR) detector for quantification (Figure 4). The NDIR detector used in the InnovOx offers a dynamic linearity range from 0.5 ppm to 50,000 ppm. Four ranges have been optimized: 0.5 to 1,000 ppm, 1,000 to 5,000 ppm, 5,000 to 20,000 ppm, and 20,000 to 50,000 ppm.

### Calibration & Experimental Data/Results

To demonstrate the effectiveness of SCWO, a study was conducted using the 0.5 to 1,000 ppm calibration range. A KHP standard was made at the 1,000 ppm total carbon concentration, and a calibration made using four points. Each point was analyzed with nine replicates, with the first three analyses discarded and the remaining results averaged (Figure 5).

The calibration curve was verified using a 5 ppm stock solution and running it continuously 157 times. The mean was 5.03 ppm, the standard deviation was 0.15, and the RSD was 3.04% (Figure 6). This test represents about thirteen hours of continuous analysis.

### Conclusion

By utilizing the fundamental supercritical properties of water, wet chemical oxidation has proven to be significantly more reliable and robust than the original combustion technique.

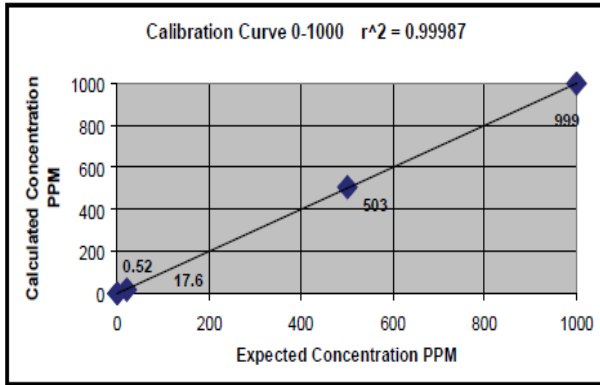


Figure 5: Calibration Curve

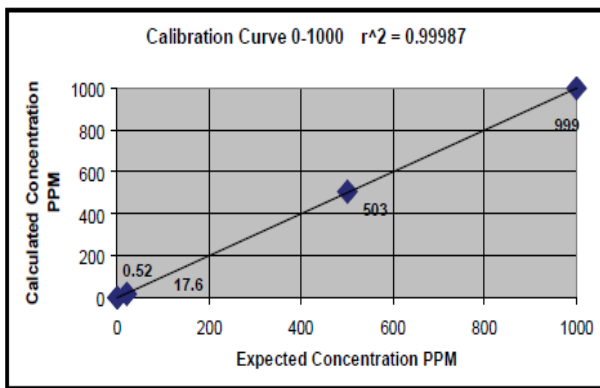


Figure 6: Repeatability Study

The 375 °C and 218 atm (3200 psi) combination have allowed the process to achieve ultra-efficient conversion of organic carbon to carbon dioxide. Controlling the purging of reaction by-products and matrix impurities between each analysis, the InnovOx offers something never available before: long-term system integrity. Each analysis starts with a clean sample path that ensures data accuracy, calibration robustness, and extended periods of time between routine system maintenance activities.

The data presented clearly shows the benefit of enhanced wet chemical oxidation and the methodology's ability to perform TOC analysis on what were once considered very difficult or impossible sample matrices.

#### About The Article

This article has been contributed by GE Analytical Instruments; the Company has more than 20 years' experience in TOC measurement technologies and offers a wide range of ultrapure water and wastewater Total Organic Carbon (TOC) analyzers and sensors, ready-to-use Sievers Standards and applications support. [www.geinstruments.com](http://www.geinstruments.com)

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