GE
Water & Process Technologies
Analytical Instruments

White Paper

New Wet Chemical Oxidation Process for Total Organic Carbon (TOC) Analysis

imagination at work

Introduction

Sample matrices are known to create analytical obstacles during routine Total Organic Carbon (TOC) analysis. Until now, 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 novel approach to this wet chemical oxidation technique employs both heat and pressure. The increased pressure within the reaction cell 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. The data presented will show the Sievers InnovOx TOC Analyzer's calibration robustness and long-term stability.

What does Supercritical Mean?

Traditionally, we were taught that there are three phases of matter; solid, liquid, and gas. Scientific research now shows that 15 different phases of matter can be clearly identified. The one that is pertinent to this white paper is the "supercritical" phase.

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 32 °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. At the same weight, or mass, solid water and liquid water occupy about the same volume at atmospheric pressure. The equivalent weight of gaseous water occupies about 1,600 times the volume at atmospheric pressure. However, if a gas-tight lid were placed on a container and the temperature raised to 130 °C, the liquid water would transition into the gas phase. Since the volume needed for expansion is limited, the pressure in the headspace of the sealed container would begin to increase as more gas is formed.

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 shows 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).

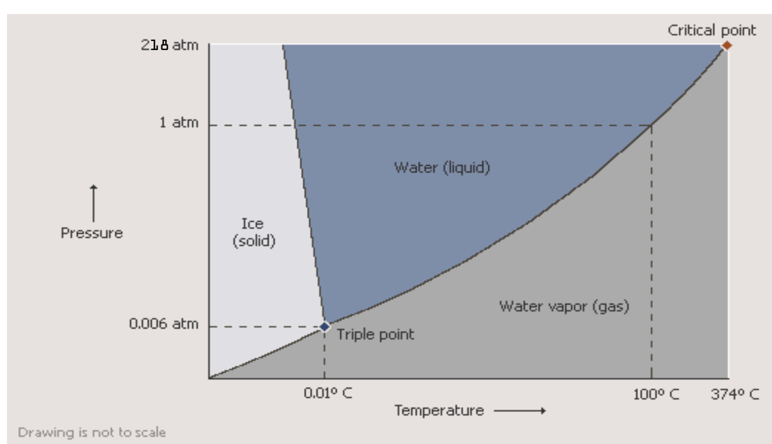

Figure 1. Phase diagram of water

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 (**Figure 2**).

Super Critical Water Oxidation (SCWO)

$$\text{Organic} + S_2O_8^{-2} + \text{heat} + \text{pressure}$$

$$\rightarrow CO_2 + H_2O + SO_4^{-2}$$

Figure 2. Supercritical Water Oxidation

What is SCWO and How Does it Help TOC Analysis?

When measuring Total Organic Carbon (TOC), several techniques are used to oxidize the organic carbon in the sample to form carbon dioxide (CO_2). Once the CO_2 is formed it can be detected and quantified. The main problem facing TOC analysts is ensuring efficient oxidation of the organic carbon. The InnovOx TOC Analyzer uses the wet chemical oxidation technique. This process seeds the solution with a oxygen donating reagent. The InnovOx employs a 30% weight/volume solution of sodium persulphate as the oxidizer. It then heats the sample and oxidizer in a sealed reactor past the critical point and Supercritical Water Oxidation (SCWO) is achieved.

Research performed in the 1970's found the SCWO technique to have many characteristics that were ideal for an analytical technique relying on efficient sample oxidation. Numerous studies have demonstrated that the process achieves oxidation efficiencies of > 99% for residence times of 10 to 30 seconds. The first patent for the technique was issued in 1985 to M. Modell. In addition to Modell, MIT Professor of Chemical Engineering, J. Testor, has published extensive research on SCWO and continues to promote the features and benefits this technology offers.

Figure 3. Sievers InnovOx Laboratory TOC Analyzer and Autosampler

As discussed previously, when water reaches a supercritical state, organic material and gases become highly soluble in SCW, while inorganic salts become insoluble. This is very important, since salts will typically scavenge the oxidizer, resulting in an incomplete organic carbon to carbon dioxide conversion. This SCW medium is the perfect environment for efficient sample oxidation.

Although showing great promise, the technique had to overcome many hurdles before it could be used commercially. One challenge was achieving the temperatures and pressures required to create supercritical water. Water enters the supercritical state at 374 °C and 218 atm (3200 psi). An apparatus must be able to handle the powerful SCWO behavior and any destructive sample by-products, such as inorganic salts and acids.

GE Analytical Instruments is the first company to successfully build a TOC analyzer based on the SCWO technique with commercial applications for aqueous samples. By combining the standardized wet chemical oxidizing technique and SCWO, TOC analysis has achieved new performance criteria that are unequalled by competing techniques.

Instrumentation

The Sievers InnovOx Laboratory TOC Analyzer (**Figure 3**), 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 for performing a Non-Purgeable Organic Carbon (NPOC) analysis.

1. Sample Handling and 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.

2. 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 4**).

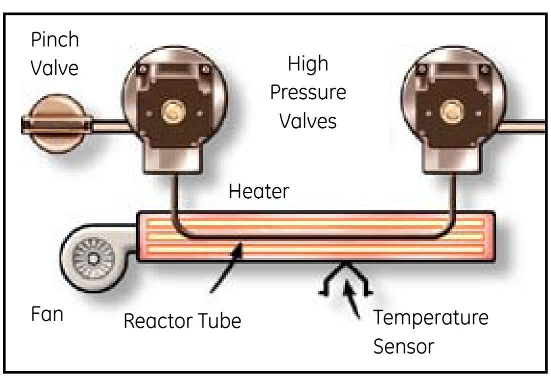

Figure 4. InnovOx Reactor Tube

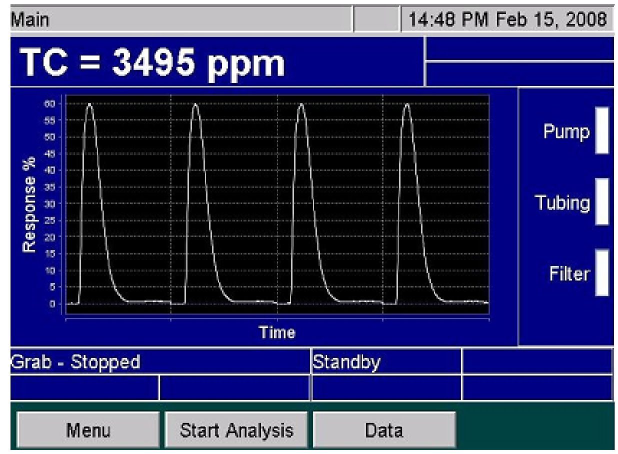

Figure 5. Peaks on the InnovOx Screen

3. 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 5**). 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 - Sample Preparation

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 6**).

Experimental Data/Results

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 7**). This test represents about thirteen hours of continuous analysis.

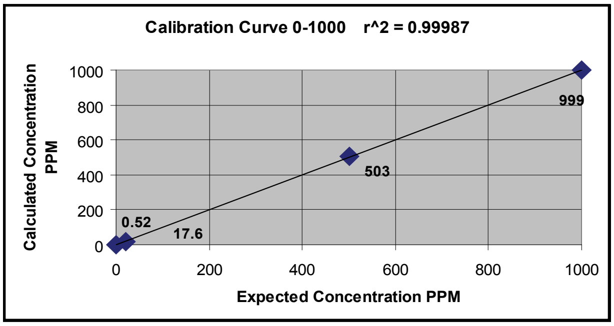

Figure 6. Calibration Curve Graph

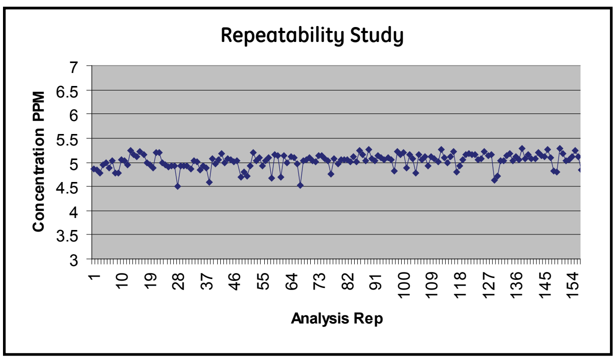

Figure 7. Repeatability Study Results

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. 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 the enhanced wet chemical oxidation and the methodology's ability to perform TOC analysis on what were once considered very difficult or impossible sample matrices.

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Patents pending.

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