Supercritical Water Oxidation TOC Analysis

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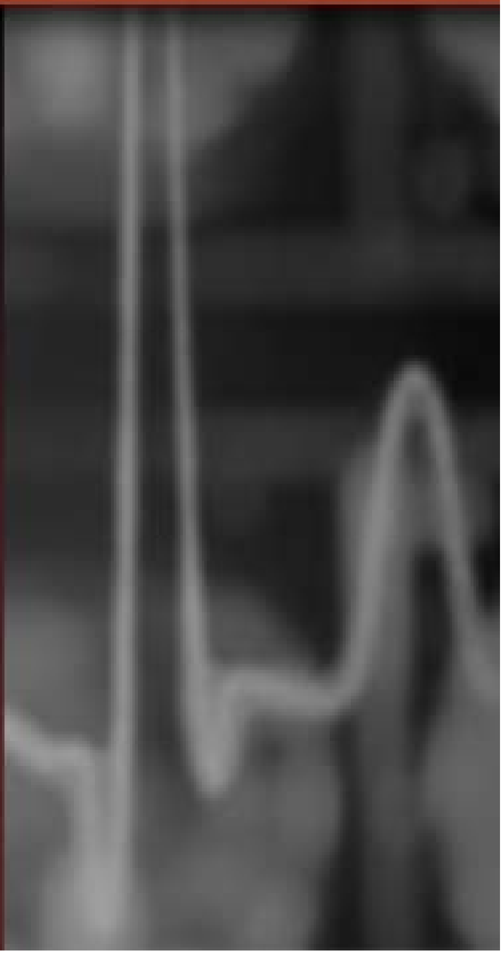
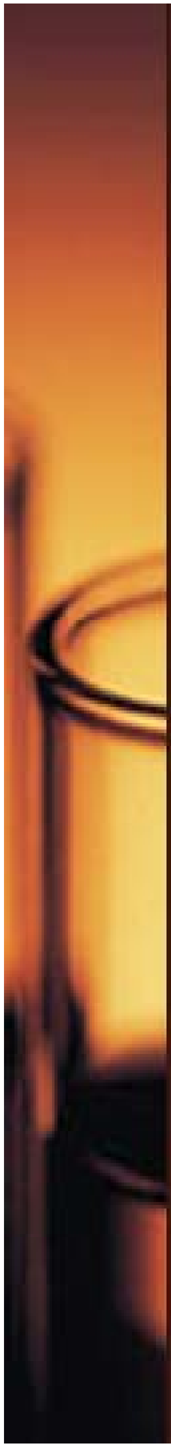


TOC Analyses

- When measuring Total Organic Carbon (TOC), several techniques are used to oxidize the organic carbon in the sample to form carbon dioxide.
- Once the CO_2 is formed it can be detected and quantified.

TOC Con't.

- The main problem facing TOC analysis is ensuring efficient oxidation of the organic carbon.
- The GE InnovOx TOC Analyzer uses the Standard Methods wet chemical oxidation technique. (5310-D.)
- The InnovOx is currently being utilized by TEEX, Global Petroleum Research Institute in a wide variety of research and applications projects.



Super Wet-Critical Oxidation Method

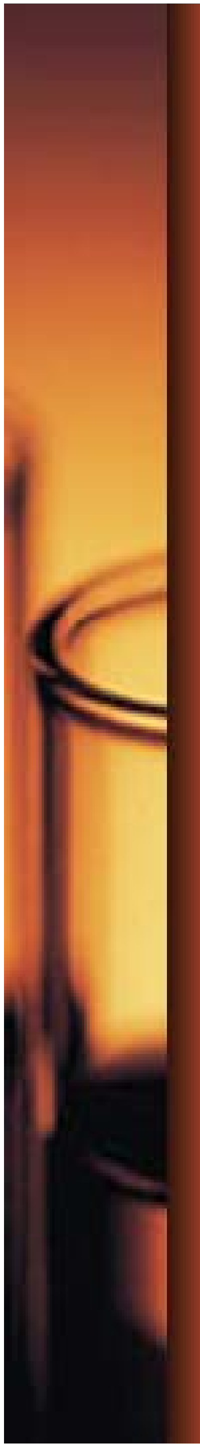
- Supercritical Water Oxidation (SCWO) was originally developed to treat large volumes of aqueous waste streams, sludges and highly concentrated brine/mineralized waters
- SCWO destroys organic wastes using an oxidant in water and temperatures and pressures above the critical point of water, 375 °C, and 3,200 psi.

SWCO Description

- 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.

Why SWCO ?

- 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 and accounting for difficult sample matrices.
- Numerous studies have demonstrated that the process achieves oxidation efficiencies of > 99% for residence times of 10 to 30 seconds.

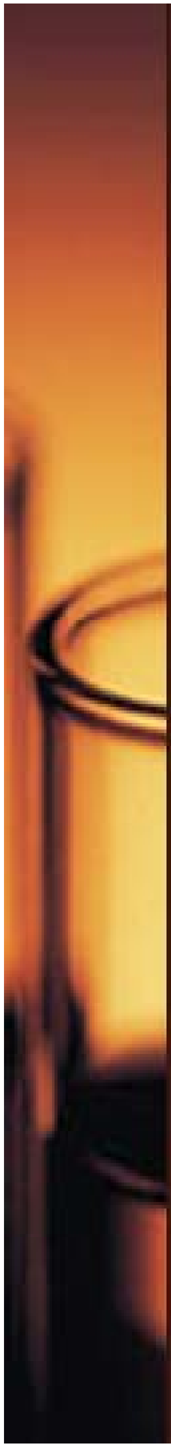


SWCO Chemistry

- When water reaches a supercritical state, organic material and gases become highly soluble, while inorganic salts become insoluble.
- Salts will typically scavenge the oxidizer, resulting in an incomplete organic carbon to carbon dioxide conversion.

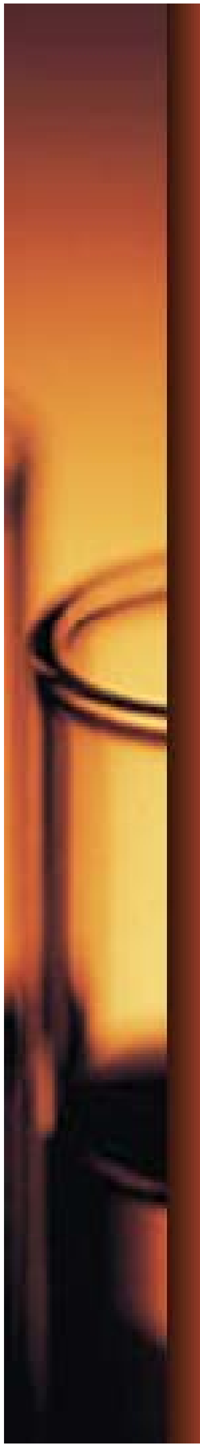
SWCO Chemistry Cont’d.

- The InnovOx takes the environmental sample to a supercritical state by increasing the temperature and subsequently the pressure within the reactor.
- The InnovOx uses a titanium oxidation chamber capable of withstanding excessive pressures.



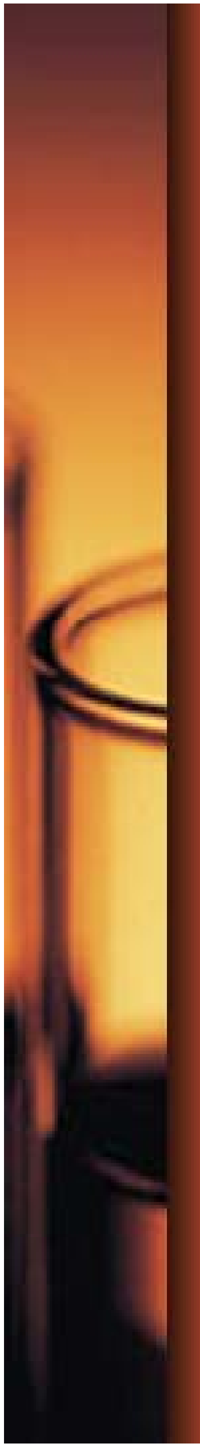
SWCO Is…In Short:

- The properties of supercritical water enable the ultra-efficient, rapid oxidation of organic carbon to CO2, even in the presence of chloride and other inorganic species that negatively interfere with non-SCWO wet chemical oxidation.



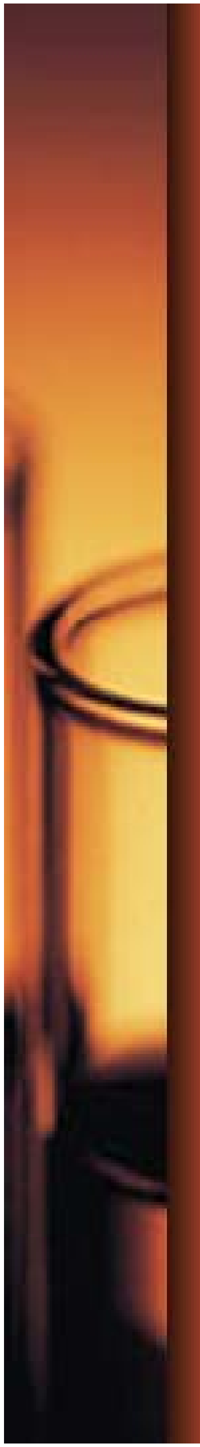
Meaning

- Environmental samples of various matrices can be analyzed without interferences.
- This application is an important protocol for the critical analyses of a broad range of very difficult samples.
- i.e.: oil-field wastewaters, frac-flow back and brine waste ponds.



TOC Detection in Environmental Matrices

- When testing for TOC in the detection range of 0.5 to 50,000 ppm, it is very common to have a complicated sample matrix.
- Specifically, in a UV- Nondispersive infrared (NDIR) type system, the aggressive sample matrix attacks the lamp and dramatically reduces its sensitivity to detection of TOC.

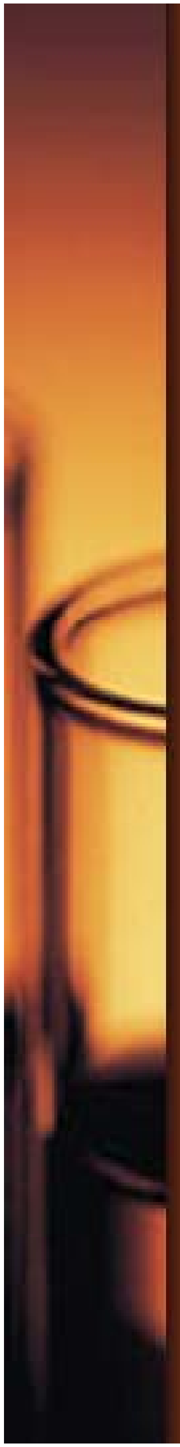


Detector

- The InnovOx uses a highly stable, nondispersive infrared (NDIR) detector.
- Unlike other NDIR detectors the InnovOx NDIR has no moving parts, and features tight temperature control of the IR source and detector.

Environmental Applications

- Flow-back waters in well fracing
- Brine retention ponds
- Wastewaters from petro,chemical production & gas condensate management sites.
- Groundwater monitoring



Current Research at TEEX & GPRI

- Frac-water analyses protocol developments
- Linear relationships of known “difficult” to analyze sample matrices against known standards
- Oil/gas produced wastewaters clean-up technology, organic monitoring

Samples Analyzed So Far

- Evaluations of a wide range of oil field waters in diverse matrices of sludges, liquids and glycol dehydrator condensates.
- Brine waters, treated/untreated flow-back & groundwater
- From these studies, protocols and methodologies can be designed for these applications.

Questions??

Thank you!

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Determination of Total Organic Carbons in Difficult Sample Matrices Utilizing the Supercritical Water-Oxidation TOC Procedure

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Abstract

The requirement for monitoring Total Organic Carbon (TOC) in oil/gas produced waters is inevitable. Most often, organics in these types of waters are volatiles, petroleum distillates, and natural organic acids or purposely added organic chemical compounds. These are generally difficult to analyze due to the presence of several interfering factors such as high turbidity, increased alkalinity, drilling mud additives and very high concentrations of various salts/minerals. Additionally, inorganic compounds in the waters (i.e.: brines, alkalinity) can give false high readings in traditional total organic analyses if not accounted for. The methodology of Supercritical Water Oxidation (SCWO) for monitoring TOC in oil/gas produced waters is being utilized and evaluated. The SCWO method has shown to be a robust procedure for analyzing TOC in otherwise difficult water matrices.

Introduction

An inherent issue with TOC analyses of oil/gas production water is the problem with difficult sample matrices. Produced waters contain a variety of organic and inorganic compounds which may be capable of exacerbating the chemistry mechanisms of analytical testing. Additionally, environmental monitoring of oil and gas produced wastewaters is dependent upon protocols that are robust enough to be of reliability. The work presented here is the evaluation of the modified wet-oxidation method described as Supercritical Water Oxidation (SCWO) for the analysis of TOC in very difficult oil/gas produced water sample matrices.

TOC Methodologies

TOC analysis is carried out through a choice of methodologies. Given that all TOC analyzers only actually measure total carbon, TOC analysis always requires some accounting for the IC that is always present. One analysis technique involves a two-stage process commonly referred to as TC-IC. It measures the amount of IC evolved from an acidified aliquot of a sample and also the amount of TC present in the sample. TOC is calculated by subtraction of the IC value from the TC the sample. Another variant employs acidification of the sample to evolve carbon dioxide and measuring it as IC, then oxidizing and measuring the remaining non-purgeable organic carbon (NPOC). This is called TIC-NPOC analysis.

A more common method directly measures TOC in the sample by again acidifying the sample to a pH value of two or less to release the IC gas to the atmosphere. Any remaining NPOC-CO_2 dissolved in the liquid aliquot is then oxidized releasing the gases. These gases are then transmitted to the detector for quantification.

TOC analysis does have intrinsic problems with difficult sample matrices. Turbidity, salinity, oils and other high mineral content samples can be problematic to adjust for and calibrate for in most traditional TOC methodologies. Concerns are environmentally controlled waters and oil/gas production wastewaters may not be monitored for TOCs' due to those issues.

If laboratories do have the capability to analyze difficult samples, they generally require more frequent maintenance, and weekly or daily recalibrations. To eliminate those issues, the SCWO was developed by GE Analytical Instruments (Boulder, CO.) to provide complete oxidation of organic carbons in complex sample matrices.

Supercritical Water Oxidation

By convention, there are three phases of matter; solid, liquid, and gas**.** Science has since shown that there are fifteen (15) states of matter, including super critical. When describing supercritical water, it is fundamental to understand the different phases of water. When liquid water is sitting in an open container at room temperature and ambient 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. 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 was attached on a container and the temperature rose to 130 °C, the liquid water would transition into the gas phase. Given that 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. As a result, 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.

At a specific 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 similar to a gas. Organic material and gases become highly soluble in SCW and, conversely, inorganic salts become insoluble. These conditions are ideal for SCWO reaction. The GE InnovOx (InO) TOC Analyzer employed in the study uses the wet chemical oxidation technique. This process seeds the solution with an oxygen donating reagent. The InO 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 SCWO is achieved. The increased pressure within the reaction cell noticeably enhanced the efficiency of the oxidation process, thus offering better recovery of CO_2 from difficult sample matrices. The CO_2 is then analyzed through a highly stable, non-dispersive infrared (NDIR) detector.

Noted in the current evaluation was the difference from the traditional Standard Methods for The Examination of Water and Wastewater (SM) 5310-D. Wet-Oxidation Combustion procedure, was that the SCWO process completely removed all by-products from the sample flow path between sample runs. This allowed for no carry over contamination from sample to sample. Analysis data from organic-free water blanks between sample runs, demonstrated this. Additionally noted was that as discussed previously, when water reaches a supercritical state, organic material and gases become highly soluble in SCW, while inorganic salts become insoluble. This concept is of importance, since salts will typically scavenge the oxidizer, resulting in an incomplete organic C to CO_2 conversion. This was of significance when analyzing the oil and gas produced wastewaters which were excessive in chlorides.

Evaluation of SCWO

The evaluation of the SCWO method employed the GE Analytical InO TOC Analyzer.

Water samples described in Table 8, were obtained from various sources that represented a spectrum of industries that may make use of the TOC results for organic loading monitoring into the environment, experimental TOC removal technology in the oil/gas industry, frac-water studies and raw water characteristics.

For this assessment, oil/gas produced and source waters that were to be treated by various membrane or chemical treatment systems were collected. The Global Petroleum Research Institute (GPRI) and the Membrane Separations Laboratory (MSL) at Texas A&M University (TAMU), College Station, Texas provided the samples and treatment technology. Samples were analyzed at The Texas Engineering Extension Service (TEEX) Water and Environmental Laboratory, College Station, Texas.

Table 8. Samples evaluated for SCWO-TOC

Sample Type	Industry
Brazos River	Source Water
Fractured Pond Waste	Gas Fracing Drilling
Brine Pond	Crude Oil Production
Glycol Condensate	Natural Gas Drying
Mixed Oil/Gas Wastewater	Environmental Monitoring

Table 9. Results of SCWO-TOC analyses

Raw Sample	TOC PPM	Dup. PPM	Blank PPM	%RSD	Cal. Range
Brazos	180.3	181.4	0.32	0.30	1000.0 PPM
Frac-Pond	83.2	82.5	1.90	.42	1000.0 PPM
Gly. Cond.	44.3	39.5	0.14	5.72	1000.0 PPM
Mixed WW	91.0	92.7	0.05	0.92	10000.0 PPM
Brine Pond	15.3	17.3	0.11	6.13	1000.0 PPM

Post Treated	TOC PPM	Dup. PPM	Blank PPM	%RSD	Cal. Range
Brazos	15.7	21.0	0.09	14.4	1000.0 PPM
Frac-Pond	22.3	19.2	0.12	7.4	1000.0 PPM
Gly. Cond.	40.0	33.1	0.11	9.58	1000.0 PPM
Mixed WW	15.7	19.2	0.01	10.0	10000.0 PPM
Brine Pond	16.0	19.1	0.94	8.83	1000.0 PPM

Raw Sample	Chloride PPM	Alkalinity PPM	Sulfate PPM	pH S.U.	Turbidity NTU
Brazos	33.4	162.9	3.1	7.44	775
Frac-Pond	25,492	427.0	67.8	8.01	360
Gly. Cond	10,041	34.7	273.8	9.05	12
Mixed WW	125	79.1	157.4	8.02	152
Brine Pond	31,202	519.0	6.81	7.73	88
Concentrate	**TOC PPM**	**Dup. PPM**	**Blank PPM**	**%RSD**	**Cal. Range**
Frac-Pond	59.3	58.2	0.32	0.94	1000.0 PPM
Brine Pond	2.44	2.42	1.01	0.41	1000.0 PPM

Observations

The InO and SCWO had performed well above expectations for this Phase I evaluation. The Brazos River sample containing the heavy silt was duplicated within a RSD of 0.30%. This was unexpected due to the high levels of solids. The brine pond water required no dilution, filtration or adjustments to the persulfate feed on the InO and primary standards ran after the analysis showed very good accuracy and no carry-over of contamination from the samples previously analyzed. Repeat samples of the frac-water had a precision of 7.4 %RSD, despite having a heavy black colored turbidity and strong sulfide odor. The glycol condensate water was clear but high in chloride. Organic-free water blanks ran between each sample repeat batch showed that the InO rinse cycles performed efficiently and no carry-over had occurred. The membrane concentrate wastes contained a heavy brine level and effectively, the SCWO method was able to compensate for those levels and still maintain RSDs' of 0.94 and 0.41 respectively.

The InO can determine Total Inorganic Carbon (TIC), NPOC, and TOC by difference (TC-IC). This allows for any combination of these modes in a single sample run or multiple duplicates on the same sample**.**

Conclusions

The Phase I evaluation of the SCWO-TOC Method had proved to be a robust and accurate method on otherwise difficult sample matrices. The SCWO methodology had demonstrated that at specific calibration levels, readings were analyzed without needed dilutions. Despite heavy solids loading and color in some samples, the InO was able to analyze the samples and provide proper line flushing and rinse cycles to prevent carry over. The analyst friendly software guided the technician through the step-by-step sample set-up and provided printer friendly reports. Calibration curves were not difficult to develop and the certified primary standards were delivered in a ready to analyze kit and there was no need to make-up laboratory standards. The portability of the analyzer was also a convenience as some samples were analyzed in different laboratory locations and outdoors during field trials. The InO required no carry gas cylinders making it an ideal analyzer for field analysis.

The SCWO methodology demonstrated to be a very robust method and had the ability to handle very difficult matrices and still provide accurate and precise results.