Determination of Total Organic Carbon in Various Oil and Gas Produced Water Matrices Utilizing Supercritical Water Oxidation Procedure

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Abstract

- Total Organic Carbon (TOC) in oil/gas produced water
- Chemistry of produced water is varying
- Difficult matrices
- TOC analysis is very difficult to analyze for in produced waters
- Utilizing Supercritical Water Oxidation to elevate these issues

Introduction to R&D

- A Phase 1 approach to evaluate SCWO
- Produced waters can exacerbate the chemistry mechanisms of analytical testing
- Environmental monitoring of produced waters require protocols that are robust and dependable

TOC Methodologies

- All TOC methods only measure *Total* carbon (TC)
- Thus there must be some accounting for inorganic carbons (IC) that is present in produced water
- One way to account for this is TC minus IC
- Another way is acidification of sample to evolve carbon dioxide - CO_2 and measure as IC, then oxidize to non-purgeable organic carbon (NPOC)

Methods Cont'd.

- 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

SCWO Method

- 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

SCWO Description

- The InnovOx® analyzer utilized in the Phase 1 study 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
- Numerous studies have demonstrated that this process achieves oxidation efficiencies of > 99% for residence times of 10 to 30 seconds

SCWO Concept

- 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 conversion to CO_2
- CO_2 is then passed through a NDIR detector

Samples Evaluated

- Were obtained from various sources that represented a spectrum of industries that may make use of the TOC results for organic loading monitoring in the environment, experimental TOC removal technology in the oil/gas industry, frac-water reuse considerations and raw water fracturing fluids blending characteristics
- Samples treated by various research membrane or chemical treatment systems at separations lab

Samples Analyzed

Sample Type	Industry
Brazos River	Source Water
Fractured Well Pond Waste	Gas Fracing Drilling
Brine Pond	Crude Oil Production
Condensate	Natural Gas Drying
Mixed Oil/Gas Wastewater	Environmental Monitoring
Frac-Flowback Mixture	Gas Shale Fracturing

Wet Chemistry Evaluation

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
Condensate	14.8	4.7	273.8	6.05	12
Mixed WW	125	79.1	157.4	8.02	152
Brine Pond	31,202	519.0	6.81	7.73	88
Frac-Flow	85,000	34,050	1235.3	3.25	N/A

Raw Sample TOC

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
Condensate	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
Frac-Flow	1542.7	1554.3	0.29	0.37	25000.0 PPM

Post Treated TOC

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
Condensate	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
Frac-Flow	1327.2	1320.0	0.19	0.27	25000.0 PPM

Membrane Concentrate TOC

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 analyzer and SCWO had performed well above expectations for this Phase I evaluation
- Primary standards analyzed after the batch run, indicated acceptable accuracy and no carry-over of contamination from the samples previously tested
- Organic-free water blanks ran between each sample repeat batch showed that the analyzer rinse cycles performed efficiently and no carry-over had occurred

Analysis Observations

- Repeat samples of the frac flowback-water had a precision of 0.27 % RSD, despite having a heavy black colored turbidity and strong sulfide odor
- The Brazos River sample containing the heavy silt was duplicated within a RSD of 0.30%
- 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.

Conclusions

- 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 InnovOx was able to analyze the samples and provide proper line flushing and rinse cycles to prevent carry over
- Calibration curves were not difficult to develop and the certified primary standards were delivered in a ready to analyze kit

Additional Conclusions

- The InnovOx required no carry gas cylinders making it an ideal analyzer for field or lab bench usage
- 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 for this evaluation study of the various oil and gas produced water samples collected

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Questions? And Thank You

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