

Choosing the appropriate TOC analyzer for your application?

ABSTRACT

In choosing a Total Organic Carbon (TOC) analyzer, among the many factors that need to be given consideration are not only the current instruments and their accessories available on the market, but specifically to their method of sample oxidation in relation to the sample matrix. Different oxidation techniques may affect the analytical data due to the components within the sample matrix. This article highlights some analytical differences and similarities between the two TOC analyzers utilizing Static Pressure Concentration (SPC), patent pending, for the analysis of surface water samples.

INTRODUCTION

Over the years many TOC analyzers have been introduced by various manufacturers that use various oxidation technologies. These various oxidation technologies were developed to exploit specific market segments. For example, the use of UV or UV/ Persulfate oxidation methodologies was determined to be best suited for the pharmaceutical and biotechnological industries. This is primarily due to low instrument background and the large sample volumes that may be tested for TOC content. Table 1 associates the oxidation methodologies with applications and official methods.

<u>Oxidation</u>	<u>Detection Technique</u>	<u>Analytical Range</u>	<u>Official Methods</u>	<u>Application</u>
Combustion	TCD	0.5% to 100%	AOAC 955.07	Drinking and Source waters
Combustion	Coulometric	1% to 100%	ASTM D4129	Drinking and Source waters
UV/Persulfate or UV	NDIR	0.002 to 10,000 ppm	EPA 415.3, 9060A Standard Methods 5310C ASTM D2579, ISO (Draft) 8245, AOAC 973.47, USP 643	Water for Injection, Purified water
Heated Persulfate	NDIR	0.002 to 1,000 ppm	EPA 415.1, 9060A Standard Methods 5310C ASTM D2579, ISO (Draft) 8245, AOAC 973.47, USP 643	Water for Injection, Purified water
SCWO	NDIR	0.002 to 30,000 ppm	Standard Methods 5310C	Industrial waste effluent; Salty waters; Drinking and Source waters;
Combustion	NDIR	0.004 to 25,000 ppm	EPA 415.3, 9060A Standard Methods 5310B ASTM D2579, ISO (Draft) 8245, AOAC 973.47, USP 643	Industrial waste effluent; Salty waters; Drinking and Source waters;
UV/Persulfate	Membrane/ Conductivity	0.0005 to 50 ppm	Standard Methods 5310C, USP 643	Water for Injection; Purified water; Drinking water
UV	Conductivity or NDIR	0.0005 to 0.5 ppm	USP 643	Water for Injection, Purified water; Semi Conductors

Table 1: Comparison of oxidation methods and associated application

EXPERIMENTAL

Two instruments that use Static Pressure Concentration (SPC) technology were configured for the analysis of TOC in samples collected from various lakes and ponds. The method parameters for drinking water analysis were employed in each instrument, respectively (Tables 2 and 3).

SPC technology is a process by which a single measurement of the CO₂ inside a pressurized non-dispersive infrared (NDIR) detector is taken. This is achieved by oxidizing the sample by either UV-Persulfate or High Temperature Combustion techniques. During the oxidation, the detector outlet is sealed allowing the CO₂ to be swept inside the detector to a predetermined pressure set-point. Once the pressure setting is achieved and all the CO₂ is pressurized inside the detector, a single CO₂ measurement is taken. The amount of CO₂ detected correlates to the amount of carbon in the sample.

General Parameters	Value
Sample Volume	6.0mL
Dilution	1:1
Acid Volume	1.0mL
Reagent Volume	1.0mL
UV Reactor Prerinse	On
UV Reactor Prerinse Volume	5.0mL
Number of UV Reactor Prerinse	1
IC Sparge Time	1.0 min
Detector Sweep Flow	500mL/min
Pre Sparge Time	0.50 min
System Flow	350mL/min

Advanced Parameters	Value
Needle Rinse Volume	5.0mL
Vial Prime Volume	2.0mL
IC Sample Prime Volume	2.0mL
IC Sample Rinse Volume	5.0mL
Baseline Stabilization Time	0.70 min
Detector Pressure Flow	300mL/min
Syringe Speed Waste	10
Syringe Speed Acid	4
Syringe Speed Reagent	4
Syringe Speed DI Water	4
NDIR Pressurization	50 psig
Syringe Speed Sample Dispense	7
Syringe Speed Sample Aspirate	4
Syringe Speed UV Dispense	7
Syringe Speed UV Aspirate	5
NDIR Pressure Stabilize	0.50 min
Sample Mixing	Off
Sample Mixing Cycles	1
Sample Mixing Volume	10.0mL
Low Level Filter NDIR	Off

Table 2: Fusion TOC Drinking Water Method parameters

General Parameters	Value
Sample Volume	0.5mL
Water Chase Volume	1.00mL
Dilution	1:1
Number of Injection Line Rinses	1
Injection Line Rinse	On
Injection Line Rinse Volume	0.5mL
Acid Volume	0.5mL
IC Spurge Flow	200mL/min
Carrier Gas Delay Time	0.4 min
IC Spurge Time	0.5 min
Detector Sweep Flow	500mL/min
Furnace Sweep Time	1.0 min
System Flow	500mL/min

Advanced Parameters	Value
Mixer Magnet Enable	On
Spurge In Vial Enable	Off
Needle Rinse Volume	2.0mL
Vial Prime Volume	2.0mL
IC Sample Prime Volume	2.0mL
Baseline Stabilization Time	1.25 min
Detector Pressure Flow	175mL/min
Syringe Speed Waste	10
Syringe Speed Acid	7
Syringe Speed DI Water	7
NDIR Pressurization	45 psig
Syringe Speed Sample Dispense	7
Syringe Speed Sample Aspirate	7
Syringe Speed IC Dispense	7
Syringe Speed IC Aspirate	5
NDIR Pressure Stabilize	0.75 min
Syringe Speed Furnace Dispense	5
Syringe Speed Furnace Aspirate	5
Furnace Temp	750° C
TN Expansion Stabilization Time	0.25 min
TN Detector Sweep Time	1.25 min

Table 3 Torch TOC Drinking Water Method parameters

<u>Results Comparison</u>				
	Fusion		Torch	
Sample ID	TOC (ppm)	STD Dev. (ppm)	TOC (ppm)	STD Dev. (ppm)
Landen Lake	2.6732	0.0293	6.9400	0.3390
Willow Pond North	7.0710	0.1436	6.6688	0.2674
Adena Pond	4.2060	0.0131	8.5805	0.2838
Lakeshore Lake	4.6946	0.0153	6.3122	0.1863
Water's Edge Pond	1.5809	0.0170	6.1773	0.1709
Water's Edge Reservoir	2.5003	0.1456	7.0599	0.0308
Water's Edge Lagoon	6.5141	0.0156	8.8207	0.1200
Willow Pond South	5.3605	0.0204	9.2184	0.4583
Willow Pond West	6.3582	0.1065	7.1822	0.0835

Table 4 Torch and Fusion sample results. The stirring option was enabled on the Torch High Temperature Combustion analyzer during the analysis of these water samples. This allows the particulates within the sample matrix to be analyzed resulting higher TOC results compared to the Fusion where the particulates settled and were not analyzed.

CONCLUSION

If particulate matter within the sample matrix is being considered in the overall TOC analysis scheme, differences in not only the oxidation techniques employed, but also the analytical method parameters may have large effects on sample recovery. As highlighted in Tables 2 and 3, each oxidation scheme uses different sample volumes for analysis since combustion oxidation inherently requires less sample volume. However, sample mixing and furnace temperature parameters were of greater influence when considering the higher TOC recoveries of the Torch results due to the particulate matter within the sample matrices. SPC technology, which is the use of a pressurized detector cell, enhances recoveries for each oxidation scheme and should be considered when optimizing method parameters for differing sample matrices.

As expected the level of precision was superior with the persulfate technique as a result of favorable sample instrument background ratios versus the combustion technique (Table 4). Although not presented here, combustion oxidation offers additional benefits of combining TOC analysis with nitrogen monitoring through chemiluminescence. Analytical parameters such

as sample recovery, detection limits, precision and particulates should be considered when determining which oxidation technique is best suited for a water type. Overall, both TOC oxidation technologies demonstrated excellent results for TOC analysis of the surface water.