

## Simple, Accurate Total Organic Carbon (TOC) Analysis of Complex, Challenging Environmental Water Samples

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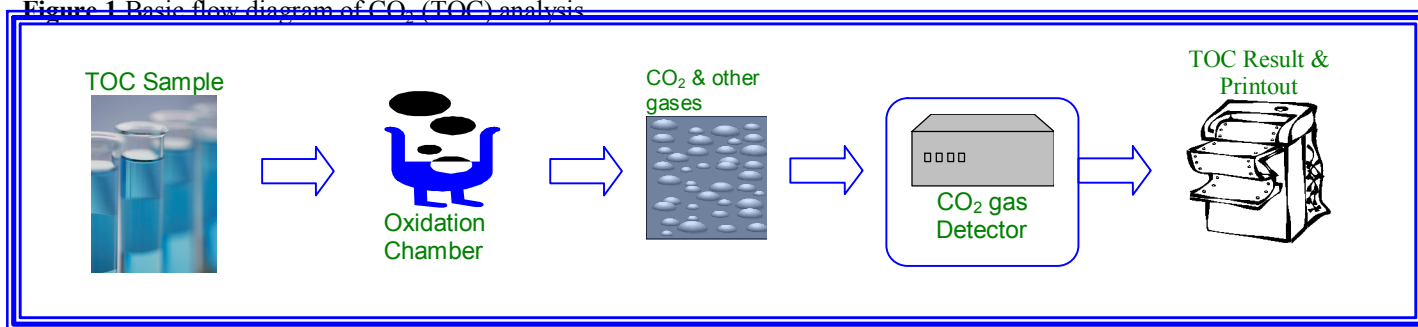
There are a number of approaches that can be taken to analyzing water samples for TOC, but not all of them afford accurate results, especially when samples are particulate or brackish. This study examines UV-Persulfate (UV-P) and High Temperature Combustion (HTC) oxidation techniques as well as sample-handling systems designed for challenging aqueous matrices. Results for a large collection of samples are presented and discussed for both UV-P and HTC along with results with and without sample-handling. The result of the study is a road map that helps guide analysts through the process of selecting the most appropriate method based on some basic sample characteristics. Using the information extracted from the results, laboratories can have complete confidence in their TOC results regardless of interfering species and components.

### Background (TOC-P-005)

The fundamental mechanism that all TOC analyzers use for TOC analysis maybe separated into two basic units, the oxidation chamber and the CO<sub>2</sub> gas detector. The components utilized within these units define the accuracy and precision of the TOC analysis. The use of thermal oxidation, chemical oxidation or ultraviolet radiation is used within the oxidation chamber to convert the organic carbon in the sample to CO<sub>2</sub> gas. The amount of CO<sub>2</sub> gas generated in the oxidation chamber is measured by the CO<sub>2</sub> gas detector. Precise analytical results are dependent on the effectiveness of the oxidation method employed within the oxidation chamber to convert all organic carbon in the sample to CO<sub>2</sub> gas and the ability of the detector to measure all of the CO<sub>2</sub> gas generated without inferences. TOC samples can vary from ultra pure to brine to industrial effluent. With several types of oxidation processes and CO<sub>2</sub> gas detectors available in the market, it is critical to match up the correct combination of oxidation reaction chamber and CO<sub>2</sub> detector with the type of TOC sample to be analyzed to achieve optimal accuracy and precision.

There are four common techniques currently in use within the oxidation chamber and all come with benefits and limitations. These are high temperature combustion, chemical oxidation aided by heat, ultraviolet oxidation only, and ultraviolet oxidation aided by chemical oxidation. High temperature combustion and U/V oxidation are summarized in the table below. (TOC\_AP-10)

Figure 1 Basic flow diagram of CO<sub>2</sub> (TOC) analysis



**Table 1** Benefits and limitations of oxidation techniques.

	<b>High Temperature Combustion (HTC)</b>	<b>U/V Oxidation only</b>	<b>U/V Oxidation aided by chemical oxidation</b>
<b>Benefits</b>	Better suited for challenging matrixes – acids, brines, particulates, high carbon content samples, sea water, and wastewater. Not affected by other species.	Allows a large volume of sample to be analyzed improving the lower limit of detection. Low blank values. Better suited for samples with low level carbon content.	Improved oxidation over U/V only and heated persulfate only methods by simultaneous ionization of dissolved organics and production of highly reactive sulfate and hydroxyl free radicals.
<b>Limitations</b>	Not suited for ultra-pure water analysis due to higher instrument background. Short lifespan of catalysts. High maintenance of high temperature components.	Not suited for samples with carbon content greater than 1 ppmC. System needs to be optimized for different types of samples – longer exposure times to U/V light	Addition of a foreign substance (persulfate) to analyte increases inaccuracies.

Poor accuracy and reproducibility, clogging of lines and valves in contact with the sample and increased instrument maintenance are all inherent problems when analyzing samples of a particulate matrix. Although these can be minimized by sample pretreatment through a 0.45 µm membrane filter, as stated in Standard Method 5310C, added sample preparation steps are time-consuming. Teledyne’s Apollo 9000® has a unique [ATLAS VALVELESS SAMPLE HANDLING SYSTEM](#) option designed specifically to minimize particulates from settling in the syringe, sample lines and valves without sample filtration or pretreatment. The [ATLAS VALVELESS SAMPLE HANDLING SYSTEM](#) uses less sample volume and an automatic rinse of the syringe after every injection ensuring an uncontaminated sample pathway and better reproducibility. Using Teledyne’s Apollo 9000® with the [ATLAS VALVELESS SAMPLE HANDLING SYSTEM](#), particles with 0.8 mm diameter or lower can now be analyzed accurately without prior homogenization or filtration. Samples containing particulates that have a larger particle size still need to be homogenized prior to analysis.

A study comparing the results of some historically difficult to oxidize compounds is summarized in Table 2. Each instrument was run under its normal operating parameters for TOC (NPOC). Statistically, there are few differences in recovery between Teledyne’s HTC Apollo 9000® and UV/P Phoenix 8000® as each instrument’s performance was of high-quality at better than 97%. Also precision in general was quite good. As expected the using potassium acid phthalate (KHC8H4O4 or “KHP”), showed better precision - relative standard deviations of less than 2% were observed on all compounds - as compared to the HTP Apollo 9000® at less than 3%.

To simulate the potentially high levels of inorganic carbon in groundwater samples (as carbonate), TOC standards ranging from ~2.0 – 100 ppm as carbon were prepared using potassium acid phthalate (KHC8H4O4 or “KHP”), and spiked with varying levels of IC from ~2.0 – 400 ppm as bicarbonate (NaHCO3) and analyzed on Teledyne’s Phoenix 8000®. The results are summarized in Table 3. There was no observable effect on TOC analyses at elevated levels of IC as demonstrated by a lack of trending in background TOC error with successively higher IC concentrations. The Phoenix 8000’s® linearity was excellent with a calibration curve slope of ~ 1, a y-intercept in the range of DI water blanks and a R<sup>2</sup> value of 0.9998. All of these samples were analyzed with a single method and a single calibration curve demonstrating Teledyne’s Phoenix

8000's versatility and performance range. The Percent error would likely be decreased substantially by using two methods/calibration curves and applied to two TOC ranges (low and high).

**Table 2** Comparison data of historically difficult to oxidize compounds at 10 mg/L C levels analyzed by HTC and UV/P TOC analyzers.

Compound (n = 3 replicates)	Apollo 9000HS (HTC)			Phoenix 8000 (UV/Persulfate)		
	Result (mg/L C)	%Recovery	% RSD	Result (mg/L C)	%Recovery	% RSD
Humic Acid <sup>†</sup>	10.02	100.20	2.01	9.93	99.30	0.95
Isonicotinic Acid	9.750	97.50	2.75	9.92	99.20	0.06
Sodium Hexane-1-Sulfonate	9.840	98.40	0.84	9.73	97.30	0.22
Glutaric Acid	9.660	96.60	0.77	9.78	97.80	0.33
Citric Acid	10.05	100.50	1.41	9.81	98.10	0.65
Lignosulfonic Acid	9.550	95.50	0.48	9.47	94.70	0.18
L-Tryptophan	9.640	96.40	2.44	9.70	97.00	1.45
1,4 -Benzoquinone	10.08	100.80	2.70	9.92	99.20	0.96
Lauric Acid	10.21	102.10	2.82	9.56	95.60	1.52
Nicotinic Acid	10.05	100.50	2.35	9.94	99.40	1.29
<b>Average Recovery</b>		<b>98.85 %</b>	<b>1.86</b>		<b>97.76 %</b>	<b>0.76</b>

**Table 3** Comparison of TOC (NPOC) samples spiked with various concentrations of IC.

Actual (expected) TOC ppm C	IC spike ppm HCO <sub>3</sub>	Avg. measured TOC ppm C	% error
0.9995	0	0.9946	1
99.95	0	106.62	6.6
199.9	0	208.89	4.4
1.999	50	1.91	4.0
1.999	100	1.98	0.5
1.999	200	1.92	3.5
1.999	400	2.07	4.0
1.999	2	1.89	5
9.995	10	10.08	0.8
24.98	25	26.02	4.2
49.97	50	53.20	6.5
99.94	100	105.21	5.3

## **SUMMARY**

The TOC instrument to meet your laboratory needs should have the accuracy, precision, and wide analytical range to meet the demands of the sample type. For high throughput automated TOC analysis of difficult or particulate matrices, the Apollo 9000 with the Atlas Sample Handling System is the system of choice. Whether it source waters, drinking waters, brines, particulate samples or ultra-pure waters, Teledyne's UV-Persulfate Phoenix 8000<sup>®</sup> or High Temperature Combustion Apollo 9000<sup>®</sup> TOC analyzers are well suited to handle your analysis needs.