Background

In modern drinking water treatment facilities, the chemical process of treating source water - lake, river, reservoir, or groundwater, has nearly eradicated the spread of water borne diseases. Chlorine, hypochlorite, ozone, chlorine dioxide, and chloramines are the most often used chemicals in the disinfection process of source waters. These disinfectants will form other chemicals in the presence of natural organic mater (NOM) that are described as disinfection byproducts (DBP), which have been shown to cause adverse health risks to humans over time. In recent years there has been increased industry research and government regulation into the formation of DBPs. As NOM is a precursor to DBP formation and can be measured by Total Organic Carbon (TOC) analysis, TOC analysis was chosen as a readily identifiable parameter to determine the extent of DBPs precursors present in potable and source waters. In April of 2000, the USEPA published the Stage 1 Disinfectants/Disinfection Byproducts Rule (D/DBP) to standardize the monitoring and removal NOM as an indicator of DBP. The Stage 1 D/DBP rule calls for the use of Standard Method 5310 as the approved analytical method for TOC analysis.[1] All conventional public water systems using surface water as their source were required to monitor TOC by December 2003 and if necessary, lower the TOC level by enhanced coagulation and enhanced softening techniques within the treatment process. Accurate TOC analysis is crucial as inaccurately high TOC analysis measurements could potentially cost municipalities thousands of wasted monies on unnecessary water treatments. The USEPA Method 415.3 was created as a guideline for analysis of TOC, dissolved organic carbon (DOC), and Specific UV absorption at 254 nm (SUVA) in source and drinking waters. As of January 4, 2006, 415.3 became an official method within the Federal Register.

Source and Drinking Water Analysis

The basic process of TOC analysis involves conversion of carbon in the water sample to CO_2 gas and the subsequent detection of the CO_2 gas. As TOC monitoring has become critical in the processes of producing the effluents of wastewater, industrial and drinking water facilities, choosing the right instrument capable of analyzing the diverse samples within these processes is crucial. Teledyne's Phoenix 8000, utilizing the combined the oxidation benefits of Ultra Violet (U/V) radiation and persulfate chemical oxidation with non-dispersive infrared (NDIR) detection, is an all purpose TOC analyzer for source water, environmental and drinking water sample analysis. Teledyne's Phoenix 8000 meets Standard Method 5310C, EPA 415.1- 415.3 9060, and EN-1484 requirements for TOC analysis. Operating on a user friendly Windows based software environment, scheduling, method editing, instrument calibration, calibration verification, analysis mode selection, data processing and instrument monitoring can easily and efficiently be accomplished.

A comparison of TOC analyses taken from various water treatment facilities demonstrates the performance of the Phoenix 8000 on various environmental samples. These samples range from water treatment plant influents, to river and lake water, to various treatment plant locations. Each sample was analyzed in triplicate with a relative standard deviation (RSD) of less than 2% and combined average of less than 1%. The results are given in Table 1.

Table 1

Phoenix 8000 (UV/Persulfate)			
	Sample Location	**TOC mg/L C**	**% RSD**
Highlands Ranch, CO	Treatment Plant Influent	3.7000	0.55
		3.6542	0.74
		3.7063	0.78
	Treatment Plant Effluent	2.2538	0.22
		2.5242	1.10
		2.5546	1.15
Cincinnati, OH	Lake Water	5.769	0.77
	River Water	5.494	0.93
Passaic Valley, NJ	Basin 3&4	2.4393	0.4
	Wanaque North	2.1506	0.34
	LFWTP	2.1853	0.16
	Settling Tube Boiler	17.7839	0.81
Greenville, NC	Filtered	4.214	0.37
	Raw	8.6165	0.35
	Pre-Settled 1	9.6485	1.08
	Pre-Settled 2	9.6698	0.96
Average		N/A	**0.67**

Method 415.3

As stated previously, USEPA Method 415.3 was created as a guideline for analysis of TOC, DOC and UV absorption at 254nm (UVA) in source waters and drinking waters.[2]

Each laboratory using 415.3 must use a formal quality control program which includes:

- Initial Demonstration of Capability (IDC)
- Continuing Calibration Checks (CCC)
- Independent Quality Control Samples (OCS)
- Laboratory Reagent Blanks (LRB)
- Field Duplicates (FD)
- Laboratory Fortified Matrix (LFM)
- Filter blanks (FB) for DOC analysis

The IDC requirements and acceptance criteria are listed in table 2. These set of tests act as an operational qualification of a TOC analyzer for TOC and DOC analysis.

Table 2 Initial Demonstration of Capability (IDC) TOC & DOC Requirements

Requirement	Acceptance Criteria
Initial Demonstration of Low System Background	LRB must be ≤ 0.35 mg/L OC
Initial Calibration Verification	QCS from independent source (1 – 5 mg/L OC) must be +/- 20% of true value
Initial OC Flow Injection Memory	**LRB injections after the highest OC-CAL injection must be ≤ 0.35 mg/L TOC**
IC Removal	**IC-Test Solution must result in ≤ 0.35 mg/L measured as OC.**
Initial Demonstration of Accuracy (n= 5)	LFB must be +/- 20% of true value
Initial Demonstration of Precision (n= 5)	LFB must be % RSD ≤ 20%
OCDL Determination	The calculated OCDL ≤ 0.35 mg/L OC. The LFB used to determine OCDL must be +/-50% of true value
Initial Demonstration of Filter Membrane Suitability	FB ≤ 0.35 mg/L OC. Sample filtrate OC +/- 15% of unfiltered sample OC

The Initial Organic Carbon (OC) Flow Injection Memory Check requirement states that the LRB must be ≤ 0.35 mg/L OC after analysis of the highest OC-CAL standard (5ppm – 50ppmC). If the LRB > 0.35 mg/L OC, a carryover problem exists and a LRB may need to be placed between every sample. Instruments using membrane conductivity may experience this problem as the membrane is not specific for CO2 gas and is subject to other species interferences. Teledyne Tekmar's Phoenix 8000 UV Persulfate TOC analyzer® has automated rinses between samples that prevent carryover.5 In addition, if carryover persists, a default cleaning method may be used for a faster analysis instead of a LRB between each sample. The Inorganic Carbon (IC) Removal Sparging Efficiency Test uses an inorganic carbon mixture, IC-Test solution, containing ~100 mg/L C based on bicarbonate calculation and impurities. The ionic content of the mixture is designed to simulate extreme IC concentration and is analyzed for TOC or DOC to determine IC interferences. The IC-Test solution should be acidified and sparged with high purity nitrogen gas at approximately 200 mL/min prior to analysis. Teledyne's Phoenix 8000 UV Persulfate TOC analyzer® has the capability to remove these IC interferences with its default TOC methodology.

Experimental

- Section 7.82 of EPA 415.3
  - The IC-Test solution was prepared at ~100 mg/L C based on bicarbonate calculation and impurities
- Section 9.9 of EPA 415.3
  - Initial Organic Carbon Flow Memory Check requirement: ≤ 350 ppb
    - Actual LRB = 27 ppb
- Section 10.2.1 of EPA 415.3
  - Calibration Curve r^2 requirement ≥ 0.993
    - Actual r^2 = 0.99997
- Section 9.2.4 of EPA 415.3
  - 415.3 used a 10 run-time to achieve <0.1 ppm TOC
    - Phoenix 8000: 2 minute default run-time used and obtained comparable results in 1/5 of the run-time – see table 3.

Table 3

Study ID	TOC (ppm)	IC Concentration (ppm)
DI	0.0267	= LRB
DI	0.0021	
DI	-0.0016	
EPA 415.3	0.1128	~ 100 ppm IC
EPA 415.3	0.1357	~ 100 ppm IC
EPA 415.3	0.1325	~ 100 ppm IC
DI	0.0029	

Phoenix 8000 offers following benefits:

- Maximizes productivity of the TOC analysis – Direct analysis by NPOC instead of TC-IC.
- Cross contamination of ≤ 1%.
- Fast analysis times – completes TOC oxidation (excluding IC removal) in 2-3 minutes with as low as 13 minutes per triplicate.
- Priority samples can be inserted without stopping the analyzer. This feature allows additional time saving on the analysis.
- Faster analysis with minimal repairs (glassware and other parts are easily accessible, color-coded lines for quick identification), and minimizes downtime and cost of operation.
- Easy-to-run.

(“*TOC Analysis as a Precursor to Disinfection Byproducts”) Wallace, B., March 19, 2002;*
Total Organic Carbon (TOC) Analysis as a Precursor to Disinfection Byproducts (DBPs) Formation in Potable Water: Oxidation Technique Considerations, toc_appnote_091801_oct2001.dot. Wallace, B., Purcell, M., Furlong, J.

Potter, B. and Wimsatt, J. *USEPA Method 415.3 – Determination of TOC and SUVA at 254nm in Source Water and Drinking Water.* National Exposure Research Laboratory, Office of Research and Development, USEPA, Cincinnati, OH, June 2003.

1. *Phoenix 8000™ User Manual*, Teledyne Tekmar , Mason, OH, 2004.