United States EPA Method 415.3

Application Note

Abstract

In order to ensure drinking water is safe for human consumption, water treatment plants often add disinfectants to drinking water. The disinfectants, such as chlorine, protect drinking water from pathogens, disease causing organisms, but can react with naturally occurring materials in the water to form byproducts that may be harmful for consumption. The United States Environmental Protection Agency (USEPA) has developed Method 415.3, Determination of Total Organic Carbon and Specific Absorbance at 254 nm in Source Water and Drinking Water, as a way to determine and monitor the amount of disinfection byproducts (DBP) in Source and Drinking Water.

This study will demonstrate that Teledyne Tekmar's Fusion TOC UV/Persulfate system (Figure 1) easily meets the Initial Demonstration of Capability (IDC) requirements of USEPA Method 415.3.

Figure 1: Fusion UV/Persulfate TOC Analyzer

Introduction

While it is vital for human health and safety to remove pathogens from drinking water, disinfectants react with naturally occurring materials in water to form byproducts including trihalomethanes, haloacetic acids, bromate, and chlorite. Some of the possible health effects from exposure to these compounds include liver, kidney, and central nervous system problems and an increased risk for cancer. For this reason, the USEPA has developed the Disinfectant and Disinfectant Byproduct Rule to reduce exposure of D/DBPs in drinking water. Total Organic Carbon (TOC), determined using methods such as USEPA 415.3, can be used to gauge the amount of organic material available to form these DBPs.

The presence of salt in waters being analyzed for carbon presents problems when the method uses low temperature oxidation of carbon-to-carbon dioxide. The chloride ions scavenge the free radicals that are the principal agents of oxidation, markedly reducing oxidation efficiency and prolonging oxidation time. The Fusion is able to handle samples containing <0.8% salt.

The USEPA has several requirements to ensure an instrument's capability to run Method 415.3. The formal quality control program for TOC analysis includes: Initial Demonstration of Capability (IDC), Independent Quality Control Samples (QCS), Continuing Calibration Checks (CCC), Laboratory Reagent Blanks (LRB), Field Duplicates (FD), Laboratory Fortified Matrix (LFM), and Filter Blanks (FB) for TOC analysis. Only the IDC requirements apply directly to the instrument and will be the focus of this study.

For the Initial Demonstration of Capability, seven specifications must be met in compliance with USEPA Method 415.3. Table 1 outlines these requirements.

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Requirement	Success Criteria
Initial Demonstration of Low System Background	LRB must be ≤ 0.35 ppmOC
Initial Instrument Calibration Verification	Independent QCS (1-5 ppmOC) must be ± 20% of true value
Initial OC Flow Injection Memory	LRB after highest calibration point must be ≤ 0.35 ppmOC
Inorganic Carbon Removal Sparging Efficiency Test	IC-Test Solution must be ≤ 0.35 ppmOC
Initial Demonstration of Accuracy (n=5)	2-5 ppmOC samples must be ± 20% of true value
Initial Demonstration of Precision (n=5)	2-5 ppmOC samples must be ≤ 20% RSD
Organic Carbon Detection Limit Determination (n=7 over 3 days)	0.1-0.5 ppmOC, OCLD must be > 0.35 ppmOC

Table 1: Requirements for the Initial Demonstration of Capability for USEPA Method 415.3

This study will demonstrate the suitability of Teledyne Tekmar's Fusion TOC analyzer to meet the performance criteria of Method 415.3. Calibration data and detection limits will also be presented.

Experimental-Instrument Conditions

This study was performed using the method parameters found in Table 2. The optimal sample range for this method is 0.0053 to 30.1 ppmOC.

Parameters		Advanced Parameters	
Variable	**Value**	**Variable**	**Value**
Sample Volume	4.0 mL	Baseline Stabilization Time	0.70 min
Dilution	1:1	Detector Pressure Flow	300 mL/min
Acid Volume	1.0 mL	NDIR Pressurization	50 psig
Reagent Volume	3.0 mL	NDIR Stabilize	0.50 min
IC Sparge Time	1.00 min	Low Level Filter NDIR	Off

Table 2: Fusion Default TOC Drinking Water Method parameters

Sample Preparation

All glassware must be meticulously cleaned and all Lab Reagent Water (LRW) must be organic carbon free. The maximum amount of OC allowed in the LRW for this method is 0.35 mg/L[2].

The Organic Carbon Primary Dilution Standard (OC-PDS) was prepared by diluting 1.063 g KHP and 1 mL phosphoric acid in 1 L of deionized water for a final organic carbon concentration of 500 ppmOC. From this OC-PDS, a 50 ppmOC standard (1:10 dilution) was made and used to prepare the calibration curve using the Fusion's autodilution feature. The results of this calibration are presented in Figure 1.

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Using the 50 ppmOC stock solution, standards were prepared at 0.5 ppmOC for OCLD determination and at 2.5 ppmOC for the calibration verification, the accuracy demonstration, and the precision demonstration.

Another requirement to demonstrate the capability of this instrument is the inorganic carbon (IC) sparging efficiency. If inorganic carbon is not completely removed from the water sample, it will result in a positive or negative bias depending on the way the instrument system calculates TOC. When inorganic carbon (IC) is removed from the sample prior to the TOC assay, as required in the method, TOC = TC and the method bias is minimized[2].

For this analysis, the method prescribes an IC-Test solution at 100 ppmIC be prepared with the solutions found in Table 3. Once solutions A-D are prepared, 10 mL of each are added to a 40 mL vial, producing a turbid solution. Then, 40 µL of phosphoric acid is added and the solution returns to a clear, colorless solution with a concentration of approximately 100 ppmIC. This solution represents a sample with high levels of inorganic carbon, so meeting this requirement will validate the instrument's capability to efficiently remove IC from a sample to ensure accurate results.

Flask (1L)	Salt	Weight (g)
A	Magnesium sulfate heptahydrate, $MgSO_4 \cdot 7H_2O$	2.565
B	Ammonium Chloride, NH_4Cl	0.594
	Calcium chloride dehydrate, $CaCl_2 \cdot 2H_2O$	2.050
	Calcium nitrate tetrahydrate, $Ca(NO_3)_2 \cdot 4H_2O$	0.248
	Potassium chloride, KCl	0.283
	Sodium chloride, NaCl	0.281
C	Sodium phosphate dibasic heptahydrate, $Na_2HPO_4 \cdot 7H_2O$	0.705
	Sodium bicarbonate, $NaHCO_3$	2.806
D	Sodium-metasilscate nonahydrate, $Na_2SiO_3 \cdot 9H_2O$	1.862

Table 3: Solutions for the IC-Test Standard

Results

The IDC was performed to demonstrate the suitability of the Fusion TOC Analyzer to perform USEPA Method 415.3. Figure 2 shows the initial seven-point calibration curve at 0.0(reagent water), 0.5, 1.0, 2.0, 5.0, 10.0, and 25.0 ppmOC from a 50 ppmOC stock. The curve was prepared using the TekLink autodilution feature.

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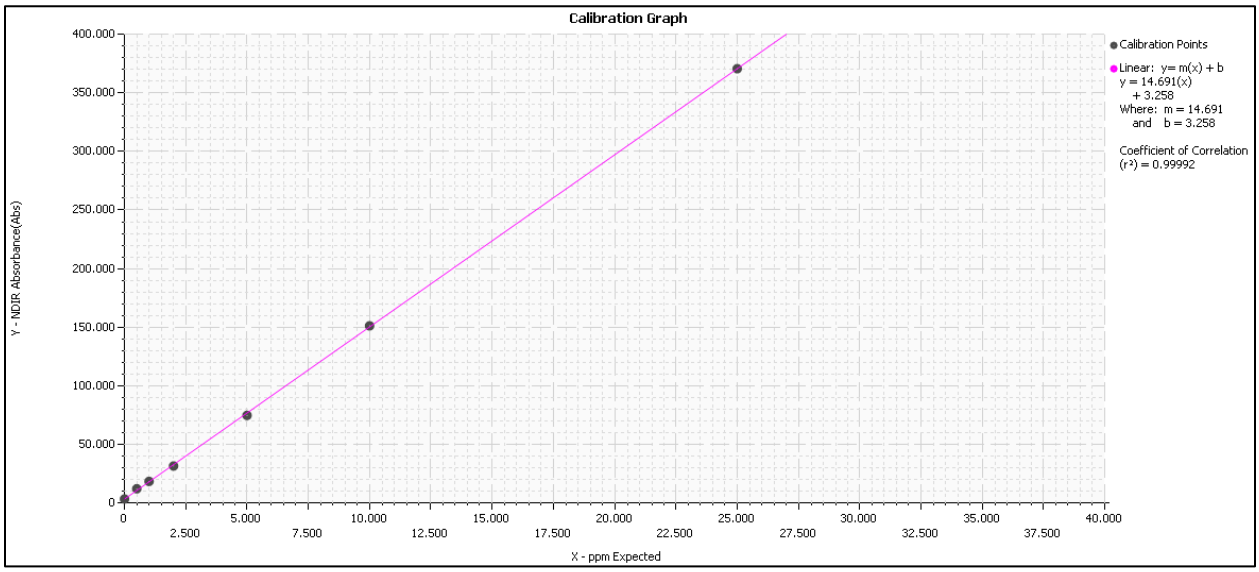

Figure 2: Calibration Curve for Standard Method 415.3 Analysis

Requirement	Success	Results
Initial Demonstration of Low System Background	≤ 0.35 ppmOC	0.0680 ppmOC
Initial Instrument Calibration Verification	± 20% of true value (2.0-3.0 ppmOC)	2.6363 ppmOC, 5.45% of true value
Initial OC Flow Injection Memory	≤ 0.35 ppmOC	0.1276 ppmOC
Inorganic Carbon Removal Sparging Efficiency Test	≤ 0.35 ppmOC	0.2450 ppmOC
Initial Demonstration of Accuracy (n=5)	± 20% of true value (2.0-3.0 ppmOC)	2.6029 ppmOC, 5.17% of true value
Initial Demonstration of Precision (n=5)	≤ 20% RSD	0.44% RSD
Organic Carbon Detection Limit Determination (n=7 over 3 days)	< 0.35 ppmOC	0.034 ppmOC

Table 4: Initial Demonstration of Capability Results

As seen in Table 4, Teledyne Tekmar's Fusion UV/Persulfate TOC Analyzer easily meets the requirements set forth in USEPA Method 415.3. A blank water sample was evaluated prior to analysis to demonstrate initial low system background. The corresponding TOC concentration was 0.0680 ppmOC, well below the method requirement of ≤ 0.35 ppmOC.

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Although it is not stated in the IDC, the method states that a calibration curve is considered suitable for analysis if the linear regression factor (r^2) ≥ 0.9930 or ≥ 0.9995 for best results. This calibration yielded an r^2 of 0.99992, well above the required value, demonstrating ideal analysis conditions. To validate the curve, an independent sample, 1-5 ppmOC, must be analyzed and return a TOC value within 20% of the true value. Table 4 shows that a 2.5 ppmOC sample returned a concentration of 2.6363 ppmOC, within 5.45% of the true value.

Directly following the highest point of the calibration curve, a LRB was analyzed to determine the Initial OC Flow Injection Memory. The resulting TOC value was 0.1267 ppmOC, less than half of the 0.35 ppmOC criteria. Teledyne Tekmar's Fusion TOC analyzer has automated rinses and cleaning procedures between samples to reduce carryover.

Using the IC-Test mix, prepared as prescribed in the method, the Inorganic Sparging capability was evaluated. The test mix concentration of approximately 100 ppmIC is representative of an extreme inorganic carbon sample, and should return a TOC value of less than 0.35 ppmOC. The IC test mix was found to have a TOC concentration of 0.245 ppmOC, well below the method requirement.

To meet the IDC requirements for accuracy and precision, five separate 2.5 ppmOC samples were analyzed. To demonstrate acceptable accuracy, the TOC values for the five samples have to be within 20% of the true value for samples between 1-5 ppmOC. Since 2.5 ppmOC samples were evaluated, TOC values must fall between 2.0 and 3.0 ppmOC to be considered accurate. To demonstrate acceptable precision, the %RSD of 5 replicate samples must be less than 20%. The Fusion proved to be both extremely accurate and precise, with an average concentration of 2.6029 ppmOC for the five samples at 2.5 ppmOC and %RSD of 0.44%.

The final component of the IDC, the OCDL, must be < 0.35 ppmOC after analysis of seven replicates over 3 days of a sample 0.1-0.5 ppmOC. For this evaluation, samples at 0.5 ppmOC were analyzed over three days and returned an OCDL of 0.034 ppmOC using the calculation below, given in the method. The determination of OCDL is dependent on the analytical instrument's system precision, the purity of the laboratory reagent water, and the skill of the analyst. Different TOC instrument systems may produce significantly different OCDLs[2].

OCLD= (Standard Deviation)*(Student's t value for 99% confidence level)
T value for 7 replicates = 3.14

Conclusions

Drinking water quality is vital for health and safety. Treatment plants add disinfectants to ensure water free of pathogens and other harmful substances. However, if water contains organic carbon the disinfection process can produce byproducts that can cause potential health issues including increased risk for cancer. For this reason, it is essential to screen water for TOC before treatment, and have instruments that can precisely and accurately detect and measure TOC. The USEPA established method 415.3, Determination of Total Organic Carbon and Specific Absorbance at 254 nm in Source Water and Drinking Water, as way to detect and measure TOC in water. This study demonstrates the suitability of Teledyne Tekmar's Fusion TOC Analyzer for this analysis by meeting and surpassing all performance criteria outlined in the method.

References

1. USEPA Drinking Water Contaminants: http://water.epa.gov/drink/contaminants/index.cfm
2. USEPA Method 415.3, "Determination of Total Organic Carbon and Specific Absorbance at 254 nm in Source Water and Drinking Water," Revision 1.1, February 2005.

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