

Application Note

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Abstract

The typical disinfectants used in drinking water production – chlorine, hypochlorite, ozone, chlorine dioxide, chloramines – are potentially harmful to human health in the presence of Natural Organic Matter (NOM) forming Disinfectants/ Disinfection Byproducts (D/DBP). The United States Environmental Protection Agency (USEPA) created the D/DBPs rule – Method 415.3 – to assist laboratories conducting analyses of source and drinking waters using Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), and UV absorption at 254nm (UVA). The increased regulation is to reduce the levels of TOC in water prior to the disinfection processes lessening the formation of D/DBPs in drinking water production. This poster describes how a new TOC analyzer, using UV persulfate oxidation and Non-Dispersive Infrared (NDIR) detection, easily meets the new USEPA requirements for Method 415.3.

KEY WORDS:

Fusion, Total Organic Carbon (TOC), Total Carbon (TC), Inorganic Carbon (IC), TOC analyzers, Non-Dispersive Infrared Detection (NDIR), pharmaceutical, drinking water, waste water, USEPA 415.3

USEPA Method 415.3 Requirements

The method creates a formal quality control program for TOC analysis that 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)
- Filter Blanks (FB) for DOC analysis

Of these requirements, only the IDC applies directly to the instrument, as the rest are procedural, and will be of primary interest.

IDC requirements:

Each laboratory must meet eight specifications as part of the Initial Demonstration of Capability. The Initial Demonstration of Filter Membrane requirement does not directly affect the Fusion TOC analyzer, as the instrument has no filtration capabilities. The remaining seven requirements apply directly to the instrument.

Initial OC Flow Injection Memory

The Initial Organic Carbon (OC) Flow Injection Memory requirement specifies the analysis of the LRB directly following the analysis of the highest OC calibration standard. According to Method 415.3, if the LRB is > 0.35 mg/L OC, a carryover memory problem exists and a LRB may need to be placed between each sample. Teledyne Tekmar's Fusion TOC analyzer has automated rinses and cleaning procedures between samples that prevent carryover. The Fusion also uses a self-calibrating NDIR detector, which

never comes into direct contact with the sample – preventing contamination and carry over. Other TOC analyzers employing Membrane Conductivity Detection may experience problems meeting this carryover requirement due to detector contamination or carryover from the sample pathway.

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 $\pm 20\%$ of true value
Initial OC Flow Injection Memory	LRB injection after the highest OC-CAL Injections must be ≤ 0.35 mg/L TOC
Inorganic Carbon Removal	IC Test solution must result in ≤ 0.35 mg/L measured as OC
Initial Demonstration of Accuracy (n=5)	Spiked OC in reagent water (2-5 mg/L C) must be $\pm 20\%$ of true value
Initial Demonstration of Precision (n=5)	Spiked OC in reagent water (2-5 mg/L C) must have $\%RSD \leq 20\%$
Organic Carbon Detection Limit (OCDL) Determination (n=7 over 3 days)	OCDL < 0.35 mg/L OC Spiked OC in reagent water (0.1-0.5 mg/L C) used must be $\pm 50\%$ of true value
Initial Demonstration of Filter Membrane Suitability*	Filter Blank < 0.35 mg/L OC Sample filtrate OC $\pm 15\%$ of the unfiltered sample OC*

Table 1: IDC Requirements

* Filtration is a sample preparation process before TOC analysis.

Initial Inorganic Carbon (IC) Removal Efficiency

The IC removal requirement gauges the IC removal capacity of the TOC analyzer. It specifies TOC analysis of a solution containing approximately 100mg C/L IC. This sample simulates extreme IC concentrations analysts may encounter in the field. Inorganic Carbon is made of carbonates, bicarbonates, and dissolved carbon dioxide within a water sample. The IC Test solution is analyzed for TOC or DOC to determine the efficiency of removing IC interferences. Teledyne Tekmar's Fusion UV/Persulfate TOC analyzer has the capability to remove these IC interferences utilizing its default TOC methodology within a 1.5 minute IC removal time or less.

Experimental

All tests were completed in the order described in USEPA Method 415.3. The IC Test solution was prepared according to Section 7.82 of USEPA Method 415.3 that included various chlorides, sulfates, nitrates, silicates, and phosphates. Illustrated in Table 3, the Fusion easily exceeds all the method requirements.

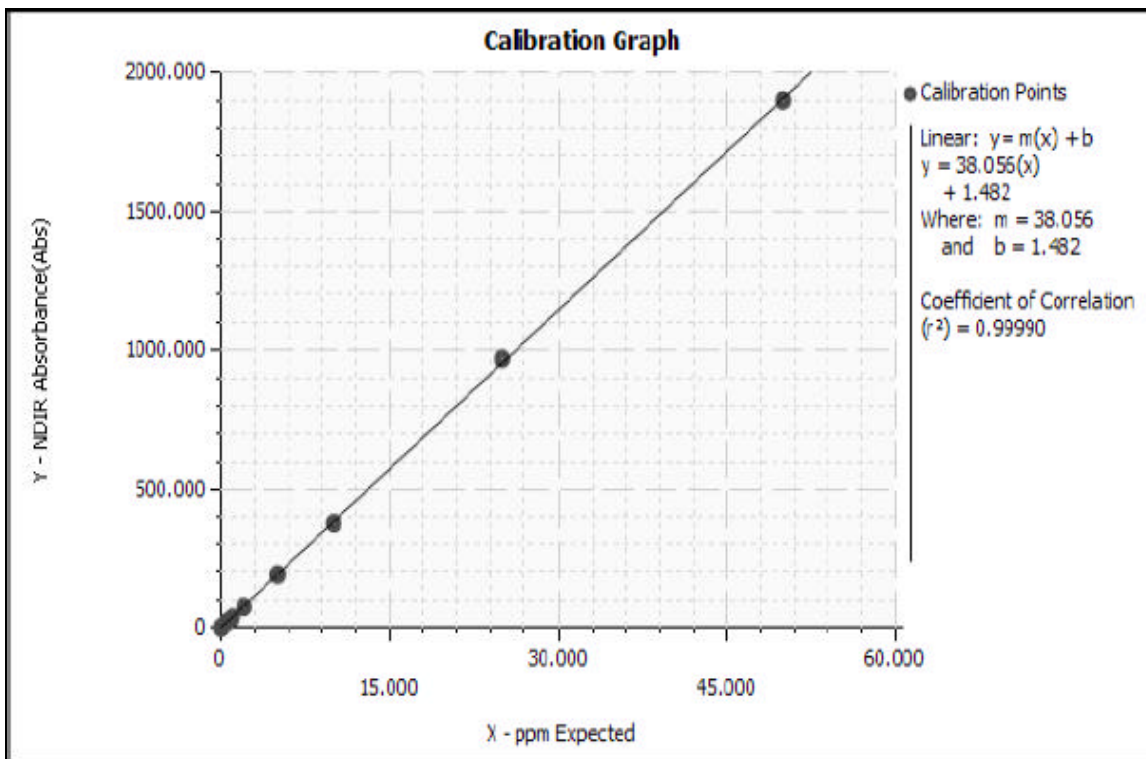


Figure 1. Multi-Point Calibration Curve of the Fusion TOC Analyzer

Sample ID	Y Raw Value	X Expected Value
DI Water	1.1600	0.0000
0.500 mg C/L	21.2833	0.5000
1.000 mg C/L	38.0233	1.0000
2.000 mg C/L	75.5133	2.0000
5.000 mg C/L	191.5967	5.0000
10.000 mg C/L	376.5000	10.0000
25.000 mg C/L	968.1200	25.0000
50.000 mg C/L	1897.8933	50.0000

Table 2. Linear Calibration Data of the Fusion TOC Analyzer (Absorbance vs. mg C/L)

USEPA Method 415.3 Tests	415.3 Requirement	Fusion TOC Analyzer Performance	Exceeds Method Specifications
Initial Demonstration of Low System Background	< 0.35 mg/L C	0.0120 mg/L C	✓
Initial Calibration Verification	+/- 20 % of true value	5.16% of true value	✓
Initial Organic Carbon Flow Memory Check	≤ 0.35 mg/L C	0.0444 mg/L C	✓
Inorganic Carbon Removal	≤ 0.35 mg/L C measured as OC	0.2465 mg/L C	✓
Initial Demonstration of Accuracy (n=5)	+/- 20 % of true value	4.23 % of true value	✓
Initial Demonstration of Precision (n=5)	% RSD ≤ 20 %	% RSD = 0.52 %	✓
Organic Carbon Detection Limit (OCDL) Determination *	OCDL ≤ 0.35 mg/L OC and +/- 50% of true value	OCDL = 0.0121 mg/L 0.20% of true value	✓
Highest Calibration Point	10, 25, or 50 mg/L C	50ppm mg/L C	✓
Calibration Curve	$r^2 \geq 0.993$	$r^2 = 0.99990$	✓

Table 3: Fusion TOC Analyzer Results for USEPA Method 415.3 Requirements

*(n=7 over 3 days)

Conclusion

The Fusion can effectively help your facility implement USEPA **Method 415.3's** new regulations by providing:

- **Low Instrumental Background with Minimum Carryover**
 - ✓ LRB's exceed requirement by more than 10 fold
 - ✓ < 1% Cross Contamination Carryover
- **Effective IC Removal**
 - ✓ Within 1.5 minutes using default TOC methods (other TOC analyzer that require up to 20 minutes for removal.)
- **Outstanding Precision and Accuracy**
 - ✓ +/- 1% RSD
 - ✓ Limit of detection: 0.2 ppb
- Easy, Fast and Linear Auto-Calibration and Auto-Calibration Verifications

The Fusion TOC Analyzer utilizes UV Persulfate oxidation and Non-Dispersive Infrared (NDIR) detection that directly and specifically measures CO₂ gas generated from the organic carbon in the sample. This method offers the only interference-free detection of TOC. Since the sample is in a gaseous form, no direct contact is made between the sample gas and the detector, adding years of life to the detector. Automatic calibration and a self-calibrating detector make the Fusion a great choice in analyzing TOC for USEPA Method 415.3.

Reference

1. 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.