Elemental Analysis
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Total Organic Carbon Analysis of Surface Water by USEPA Method 415.3

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source water, drinking water, total organic carbon, Tekmar Fusion UV/Persulfate TOC analyzer, Tekmar Torch Combustion TOC analyzer, US EPA 415.3

Introduction

Beginning in the late 1950s, environmental conservation was becoming a widely discussed topic in the United States. Concern about air and water pollution heightened in the 1960s, steadily increasing as numerous disastrous events were occurring across the country. Oil rig accidents fouled beaches, a heavily contaminated river in northern Ohio spontaneously burst into flames, and waste was being dumped unregulated into the Great Lakes. Occurrences such as these were becoming increasingly widespread. Public outcry for pollution regulation prompted action from the United States government.

In early 1970, President Richard Nixon presented his plan for protecting human health and the environment. By the end of the year the proposal was approved, and the United States Environmental Protection Agency (USEPA, EPA) was established. One of the many tasks of the EPA was to create regulations, guidelines, and methods for monitoring and controlling environmental pollutants. USEPA Method 415.3 - Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm in Source and Drinking water (Rev 1.2) is the USEPA sanctioned method for quantifying levels of Total Organic Carbon (TOC) in water.

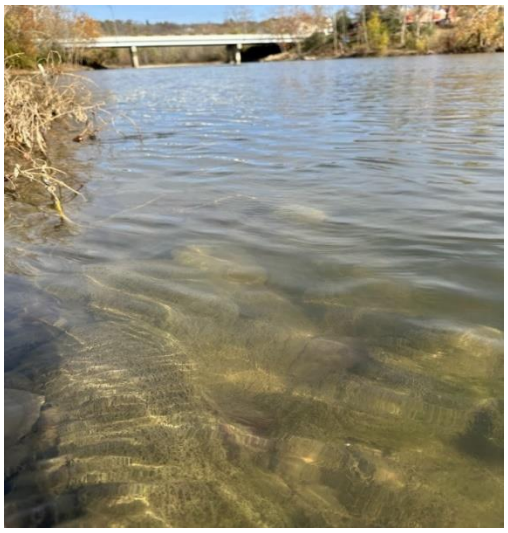


Figure 1 USEPA Method 415.3 measures Total Organic Carbon in water

Discussion

TOC analysis is a broad, nonspecific measurement of organic carbon. Organic carbon in a water sample can be comprised of carbon-based pollutants including volatile and semi-volatile organics, oils and greases, bacteria, living micro-organisms, and decaying matter. Regulatory agencies such the EPA and state level safety and health administrations have established TOC limits in drinking water, source water, wastewater, and sewage treatment effluent to maintain a level of cleanliness in these water types to help prevent harmful consequences on health and the environment.

Teledyne LABS offers an analytical instrument for each of the two methodologies approved for TOC analysis in USEPA Method 415.3. The Fusion uses ultraviolet promoted persulfate oxidation for TOC analysis and the Torch is a high-temperature combustion TOC analyzer.

Fusion Methodology

To achieve a TOC result using the Fusion UV/Persulfate TOC analyzer (pictured in Figure 2), the inorganic carbon (IC) fraction of the sample must be removed. IC removal occurs automatically inside the IC sparger. Phosphoric acid is added to the IC sparger along with the sample. The acidified sample is then sparged for a predetermined time, removing the IC from the sample. After IC removal, an aliquot of sample is transferred to the UV reactor.

With an addition of sodium persulfate along with sparging, the organic carbon is oxidized and converted into CO_2 and then swept into a non-dispersive infrared (NDIR) detector.

Torch Methodology

Like the Fusion, to achieve a TOC result, the inorganic carbon (IC) fraction of the sample must be removed. This is accomplished exactly as described above in Fusion methodology. After IC removal, an aliquot of sample is injected into a combustion tube containing platinum catalyst at a high temperature. The carbon in the sample is converted into CO_2 and then swept into a non-dispersive infrared (NDIR) detector.

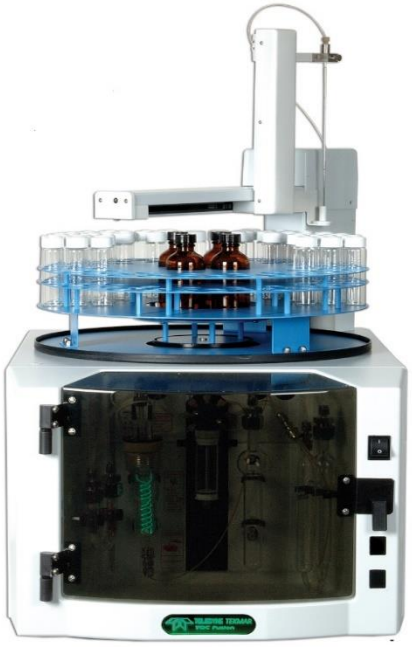


Figure 2 Fusion UV/Persulfate TOC Analyzer

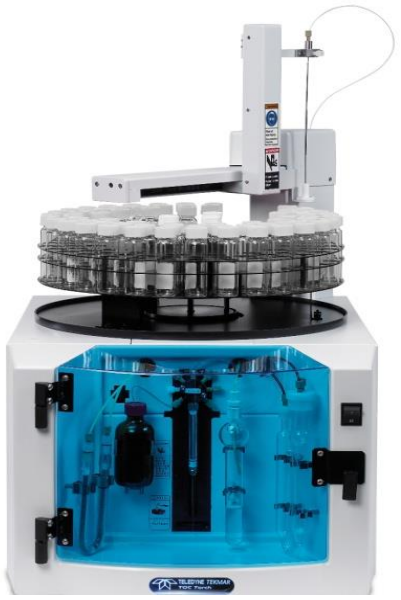


Figure 3 Torch Combustion TOC Analyzer

Demonstration

While both instruments, the Fusion and Torch, satisfy all guidelines and requirements presented by USEPA Method 415.3, this demonstration will focus on the requirements established for analyzing a set of environmental samples. The table below lists the commonly applied calibration elements for analyzing samples.

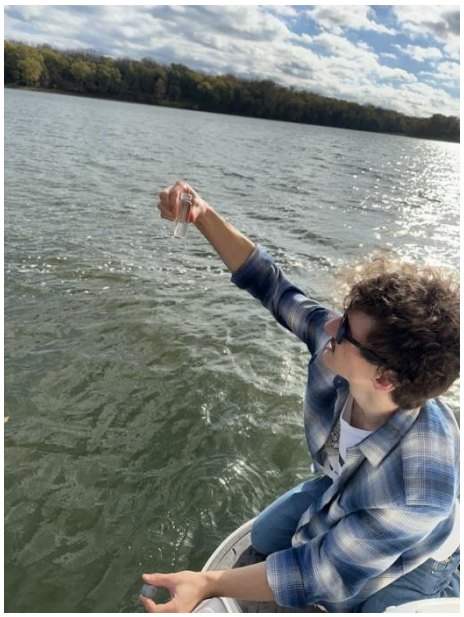
Table I Commonly applied calibration elements

Calibration Element	Acceptance Criteria
Initial Calibration (ICAL)	$r^2 \geq 0.995$
Reproducibility of replicates	< 10% RSD
Initial Calibration Verification (ICV)	± 10% from expected concentration
Continuing Calibration Verification (CCV) (after every 10 samples and at end of schedule)	± 10% from expected concentration
Duplicate Sample (Dup)	<20% Relative % Difference (RPD)
Matrix Spike (MS)	± 20% from expected value
Matrix Spike Duplicate (MSD)	± 20% from expected value and <20% RPD

For demonstration purposes, several sources of surface water were individually collected in 40 mL sample vials and analyzed on both the Fusion and the Torch. Comparative results from each instrument will be analyzed for accuracy equivalent to duplicate sample acceptance criteria.

Many types of surface waters are used as source water for drinking water utilities. The water sources that were collected are listed below.

Table II **Water sources**
Ohio River - near Cincinnati Water Works Inlet
Ohio River - near N. Kentucky Water Works Inlet
William H. Harsha (East Fork) Lake (W. Clermont WW)
Little Miami River
East Fork Little Miami River
Ohio River - near Cincinnati Water Works Inlet
Ohio River - near N. Kentucky Water Works Inlet



These samples were collected, preserved, and stored according to the guidelines in USEPA Method 415.3. The samples were acidified to pH ≤2 by adding 2 drops of concentrated acid. The samples were stored at ≤6 °C until analysis. Samples must be analyzed within 28 days from time of collection. Samples that are improperly collected cannot be used for compliance monitoring under the Safe Drinking Water Act (SDWA).

For both instruments, many method parameters are adjustable to tailor the methods for multiple sample types and concentration ranges. For this study, the methods used are detailed below.

Analysis Type (Complex):TOC Calibration: **TOC Drinking Water**
Optimal Sample Range: 0.0018 to 10.0 (ppm)

General | Advanced | Comments

Variables	TOC
Sample Volume (mL)	6.0
Dilution	1:1
Acid Volume (ml)	1.0
Reagent Volume (ml)	1.0
UV Reactor Prerinse	On
UV Reactor Prerinse Volume	5.0
Number of UV Reactor Prerinses	1
IC Sparge Time (mins)	1.00
Detector Sweep Flow (ml/min)	500
PreSparge Time (mins)	0.20
System Flow (ml/min)	350

Figure 5 Fusion method

Analysis Type (Complex):TOC Calibration: **TOC Surface Water**
Optimal Sample Range: 0.15 to 30.0 (ppm)

General | Advanced | Comments

Variables	TOC
Sample Volume (mL)	0.7
Water Chase Volume (mL)	1.50
Dilution	1:1
Number Of Injection Line Rinses	1
Injection Line Rinse	On
Injection Line Rinse Volume (mL)	0.50
Acid Volume (mL)	0.5
IC Sparge Flow (mL/min)	200
Carrier Gas Delay Time (mins)	0.40
IC Sparge Time (mins)	0.50
Detector Sweep Flow (mL/min)	500
Furnace Sweep Time (mins)	1.00
System Flow (mL/min)	200

Figure 4 Torch method

Calibration

A 1000 mg/L organic carbon stock solution was prepared by dissolving 2.125 g of potassium hydrogen phthalate (KHP) in 1.0 L of reagent water. From this stock solution, calibration standards were prepared. The working standard for each instrument is the high concentration calibration point for the calibration curve. The additional points for the calibration curve were made through the auto-calibration feature.

Calibration results are listed below.

Table III Fusion calibration

Calibration ID	Adj ABS	%RSD
0.0	4.94	3.41
0.5	24.82	1.50
1.0	45.75	0.81
2.0	91.76	0.22
5.0	219.1	0.82
10.0	417.3	0.58

r_2 = 0.99951
m = 40.01
b = 9.56

Table IV Torch calibration

Calibration ID	Adj ABS	%RSD
0.0	10.44	8.53
2.0	18.33	4.74
5.0	27.96	2.63
10.0	46.31	3.28
25.0	111.0	0.60
50.0	221.0	2.35

r_2 = 0.99964
m = 4.313
b = 6.679

Accuracy and Precision

To demonstrate the accuracy and precision of the Fusion and Torch, calibration points and check standards were analyzed in triplicate. The precision of each instrument is indicated as low percent relative standard deviation (%RSD) for each triplicate analysis. Accuracy is demonstrated by excellent percent recoveries for the check standards and matrix spikes as presented next in experimental data.

Experimental

For demonstrating the Fusion and Torch's ability to perform ICV, CCV, MS, and MSD adequately, the surface water samples collected were analyzed for TOC content. All samples, standards, and spikes were analyzed in triplicate to show precision of the results. See details in table below.

Table V Fusion - Surface water sample results with quality assurance controls

Sample ID	TOC Result (ppm)	%RSD	%Recovery	% Difference
ICV (5.0 ppm)	5.29	0.79	105.8	
ICV (10.0 ppm)	10.37	0.55	103.7	
Ohio River CWW Inlet	3.89	2.26		1.02
Ohio River NKYWW Inlet	3.93	1.04		
East Fork Little Miami River	5.99	3.35		
Little Miami River	3.27	6.06		
East Fork Lake	7.44	0.81		0.13
East Fork Lake Dup	7.45	0.86		
East Fork Lake MS (5.0 ppm)	12.63	1.09	103.6	0.08
East Fork Lake MSD (5.0 ppm)	12.62	0.18	103.4	
East Fork Lake MS (10.0 ppm)	18.62	2.39	111.7	0.43
East Fork Lake MSD (10.0 ppm)	18.70	0.87	112.5	
CCV (5.0 ppm)	5.26	0.14	105.2	
CCV (10.0 ppm)	10.25	0.30	102.5	

Table VI **Torch - Surface water sample results with quality assurance controls**				
Sample ID	**TOC Result (ppm)**	**%RSD**	**%Recovery**	**% Difference**
ICV (25.0 ppm)	24.6	0.68	98.4	
ICV (50.0 ppm)	50.6	0.42	101.2	
Ohio River CWW Inlet	3.72	3.59		1.88
Ohio River NKYWW Inlet	3.65	1.61		
East Fork Little Miami River	5.74	2.04		
Little Miami River	4.29	1.52		
East Fork Lake	6.85	3.01		4.06
East Fork Lake Dup	7.14	1.41		
East Fork Lake MS (5.0 ppm)	11.57	0.67	94.4	0.86
East Fork Lake MSD (5.0 ppm)	11.47	1.34	92.4	
East Fork Lake MS (10.0 ppm)	15.9	2.11	87.6	0.50
East Fork Lake MSD (10.0 ppm)	15.82	0.85	86.8	
CCV (25.0 ppm)	24.61	1.00	98.4	
CCV (50.0 ppm)	50.57	1.26	101.1	

As seen in the tables above, ICV and CCV accuracy is exceptional with low % RSDs indicating outstanding precision. Spike recoveries are well within acceptance limits, and duplicates show very low % difference.

Result Comparison of Instruments – Fusion versus Torch

The comparison of results from each instrument in the table below show very similar results. The percent differences of all but one comparison are well within the acceptance criteria of USEPA Method 415.3 regarding duplicate samples. The Little Miami River comparison is just outside the 20% acceptance limit. This is possibly the result of particulates within the sample being oxidized by the combustion analyzer. Regardless of instrumentation or oxidation methodology, precise and accurate TOC measurements are assured with either the Fusion or Torch.

Table VII **Comparison of instruments**			
Sample ID	**Fusion Result (ppm)**	**Torch Result (ppm)**	**% Difference**
Ohio River CWW Inlet	3.89	3.72	4.37
Ohio River NKYWW Inlet	3.93	3.65	7.12
East Fork Little Miami River	5.99	5.74	4.17
Little Miami River	3.27	4.29	23.8
East Fork Lake	7.44	6.85	7.93
East Fork Lake Dup	7.45	7.14	4.16

Conclusion

Teledyne LAB's Fusion UV/Persulfate TOC analyzer is an instrument of proven quality and performance. It can meet all guidelines and requirements presented in USEPA Method 415.3. The Fusion features an advanced syringe/multiport valve fluid management system and a robust built-in autosampler that enables calibration curves to be automatically diluted from just one standard. Should a sample exceed the calibrated range, the Fusion can apply Intellidilution which will dilute the sample to within the calibration range without interrupting the schedule. Additionally, TOC Teklink is a fully optimized user interface that simplifies operating and maintaining the Fusion. Predeveloped methods allow for quick start-up and variable parameters within methods permit for method development for analyzing uncharacteristic samples. The Fusion is an excellent choice for determining TOC levels in multiple water sources.

The Torch high-temperature combustion TOC analyzer's software is like the Fusion's and has all features mentioned above. The Torch is suitable for samples with higher TOC levels, such as wastewater. Wastewater can reach TOC concentrations exceeding 300 mg/L. Wastewater samples typically contain suspended organic carbon and halides, sample types that are typically not compatible with other types of TOC methodology. Combustion TOC analysis is routinely used to determine organic carbon levels for sample types that are hard to oxidize. The Torch can operate up to 1000 °C and will oxidize the most stubborn sample types. This makes it an ideal instrument for TOC determination in wastewater analysis. The Torch is also sensitive enough to determine TOC levels in all types of surface waters.