Elemental Analysis
Application Note TOC-AN2401
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Standard Methods 5310C: TOC Determination by Persulfate-Ultraviolet Oxidation Method

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environmental, drinking water, total organic carbon, Tekmar Fusion UV/Persulfate TOC analyzer, SM 5310C

Introduction

The drinking water industry monitors Total Organic Carbon (TOC) concentrations not only in the final product, but in various stages of the water treatment process. TOC analysis is widely used to provide a value that indicates the amount of organic content in a water sample. Depending on geographical location, TOC concentrations in source water can vary greatly. The knowledge of organic content in water and its removal is valuable information for determining actions required for processing source water into drinking water. Analytical instruments that provide TOC results are regulated to adhere to specific methodologies. Standard Methods 5310C is a well-known and reliable method for determining TOC that complies with regulatory authorities. The Tekmar Fusion UV/Persulfate TOC analyzer designed by Teledyne LABs meets all the requirements presented by method 5310C.

Figure 1 shows the typical stages necessary to produce drinking water. TOC samples can be analyzed as the water moves through the different stages. Monitoring TOC values can assist in determining types and quantities of coagulants to add, time needed in sedimentation stage, effectiveness of the filtration system, and quantity of disinfectant addition.

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.

Many method parameters are adjustable to tailor the method for various sample types and concentration ranges. For this study the drinking water method is used and is detailed in Figure 3.

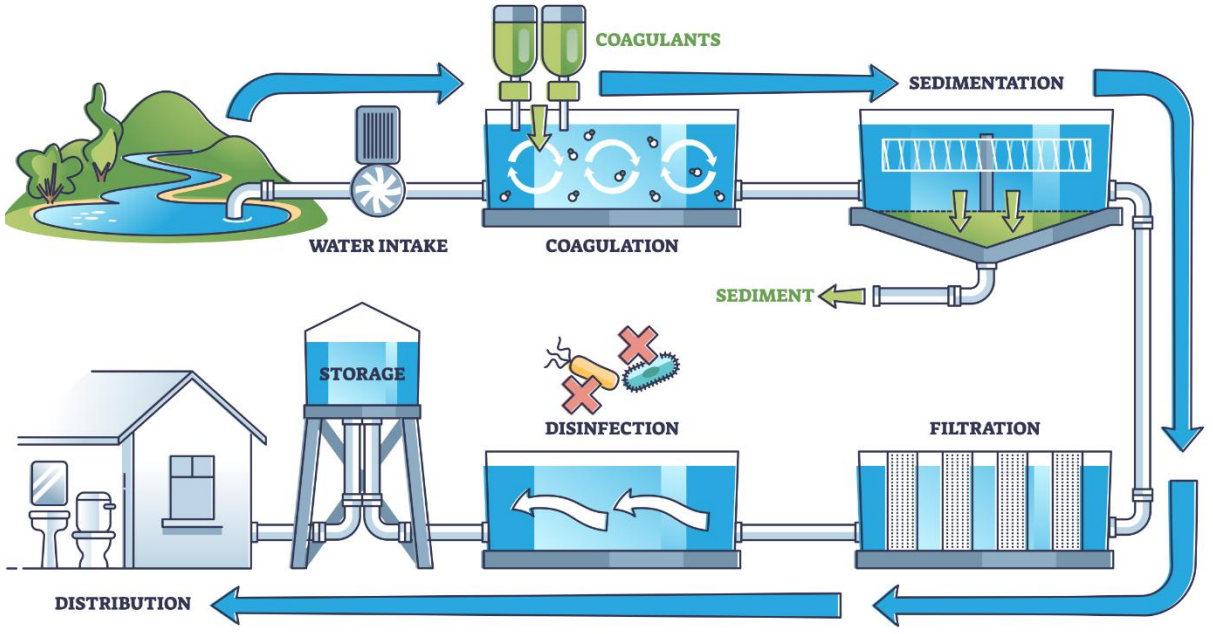

Figure 1 Typical Water Treatment Process for Drinking Water

Figure 2 Fusion – UV/Persulfate TOC Analyzer

Name: TOC Drinking Water (TOC)

Version: v2
Ver Creation: 2009/07/31 08:23
Comment: This method is designed to use the Non-Purgeable Organic Carbon (NPOC) method for TOC analysis on drinking water type samples.

Parameter	Value
SampleVolume	6.0 mL
Dilution	1:1
AcidVolume	1.0 ml
ReagentVolume	1.0 ml
UVReactorPrerinse	On
UVReactorPrerinseVolume	5.0
NumberOfUVReactorPrerinses	1
ICSpargeTime	1.00 mins
DetectorSweepFlow	500 ml/min
PreSpargeTime	0.20 mins
SystemFlow	350 ml/min

Figure 3 Drinking Water Method

Calibration

A common regulatory level set by city or county municipalities for TOC in drinking water is <2.0 mg/L. Considering the sample type as drinking water and assuming the regulatory limit is TOC < 2.0 mg/L, the Fusion TOC analyzer was calibrated to a range of 0.5 to 20.0 mg/L.

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, a calibration standard was prepared. The working standard is the high concentration (20.0 mg/L) calibration point for the calibration curve. The additional points for the calibration curve were made through the auto-calibration feature of the Fusion. A graphical representation of the calibration curve is shown in Figure 4.

The calibration performed on the Fusion was a six point calibration curve (not including the 0 point). The zero point was added to help anchor the calibration line to the point of origin. The points in the calibration were 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 mg/L. The resulting coefficient of correlation (r2) was 0.099951.

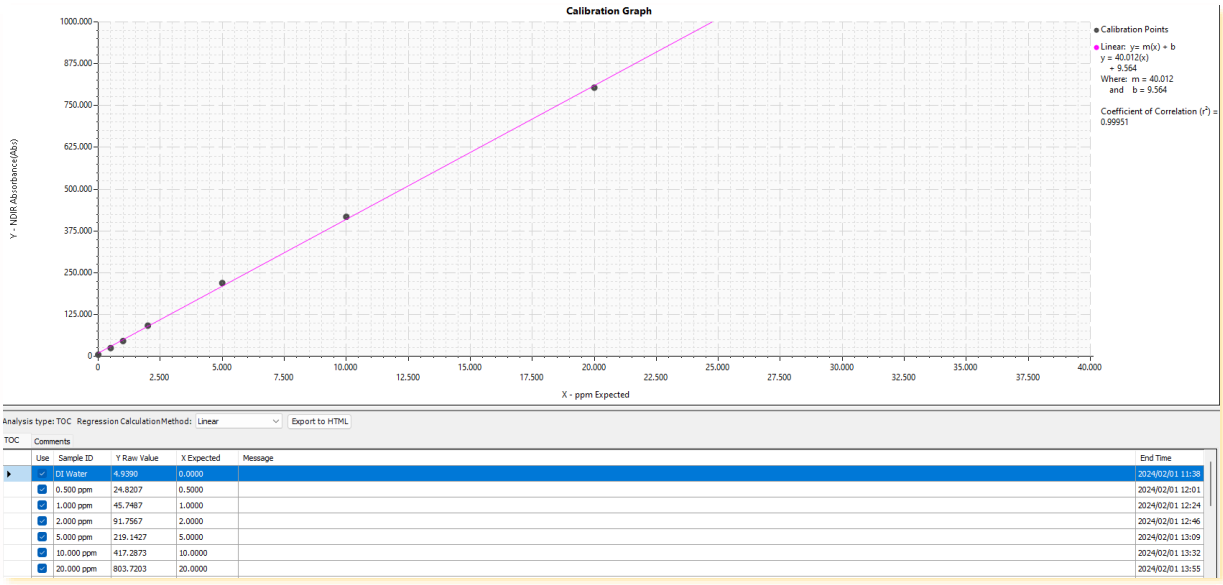

Figure 4 Drinking Water Calibration Curve

Accuracy and Precision

To demonstrate the accuracy and precision of the Fusion, calibration points and check standards were analyzed in triplicate. Table I exhibits the precision of the Fusion as low percent relative standard deviation (%RSD) for each triplicate analysis. Accuracy is demonstrated by excellent percent recoveries for the check standards.

Table I **CALIBRATION**

Concentration C (ppm)	Response (Abs.)	% RSD
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
20.0	803.7	3.89
CALIBRATION CHECK STANDARDS		
Concentration C (ppm)	Result (ppm)	% Rec.
5.0	4.96	99.2
10.0	9.58	95.8

Quality Assurance/Quality Control

Method Detection Level

According to Standard Methods 5020, Method detection level (MDL) determination is not required if data are not reported below the instrument's calibrated range, and the ability to provide quantitative data at the minimum reporting limit (MRL) is verified. For this study the MRL was 1.0 mg/L and MDL was not required. However, in the case that MDL was required, per Standard Methods 5020, seven replicates of a solution of a known TOC concentration (1.0 mg/L) was analyzed, and the MDL was calculated with results shown in Table II.

Table II **METHOD DETECTION LEVEL (MDL)**

Concentration C (ppm)	Result (ppm)
1.0	0.89
1.0	0.92
1.0	0.92
1.0	0.90
1.0	0.92
1.0	0.92
1.0	0.93
Mean (ppm)	**0.91**
Std Dev	**0.014**
MDL (ppm)	**0.044**

TOC Carryover Check

Immediately following the analysis of the highest calibration standard, a blank was analyzed. The result of the blank is required to be < ½ MRL (0.50 mg/L). The result was 0.07 mg/L.

Demonstration of IC Removal Efficiency

A 102.5 mg/L inorganic carbon (IC) standard was prepared from sodium bicarbonate. This IC standard was analyzed as TOC. The result is required to be < ½ MRL (0.50 mg/L). The result was 0.44 mg/L. If the result is > ½ MRL, method modifications can allow for additional acid to be combined with the sample or a longer sparge time can be used to increase the IC removal efficiency.

Continuing Calibration Verification (CCV), Matrix Spike (MS), and Matrix Spike Duplicate (MSD)

CCV, MS, and MSD procedures, frequencies, and acceptance criteria are included in Standard Methods 5020. Specific regulatory programs will determine what guidelines and/or requirements will be used, and individual laboratories will formalize these requirements in a written Quality Assurance Manual. For this study, the results for CCV, MS, and MSD are included next, in the experimental section.

Experimental

For the purpose of demonstrating the Fusion's ability to perform CCV, MS, and MSD adequately, a regional study of local drinking water sources were collected and analyzed for TOC content. All samples, standards, and spikes were analyzed in triplicate to show precision of the results. See details in Table III.

As seen in Table III, CCV accuracy is exceptional with low % RSDs indicating outstanding precision. Spike recoveries are spot on, and duplicates show very low percent difference.

Conclusion

The Tekmar Fusion UV/Persulfate TOC analyzer is an instrument of proven quality and performance. It can meet all guidelines and requirements presented in Standard Methods 5310C. 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 water treatment facilities for all the stages of treatment, from source water to treated water.

Table III Drinking Water Sample Results with Quality Assurance Controls

Sample ID	TOC Result (ppm)	% RSD	% Recovery	% Difference
CCV (5.0 ppm)	4.96	0.85	99.2	
CCV (10.0 ppm)	9.58	0.09	95.8	
Clermont County	1.15	5.69		2.61
Clermont County Duplicate	1.12	6.15		
Hamilton County	1.46	2.14		
Butler County	0.90	7.15		
Montgomery County	0.86	7.60		
Warren County	1.45	2.54		
Warren County MS (2.0 ppm)	3.55	0.55	105.0	0.84
Warren County MSD (2.0 ppm)	3.58	0.78	106.5	
Warren County MS (4.0 ppm)	5.49	0.50	101.0	0.90
Warren County MSD (4.0 ppm)	5.54	0.32	102.3	
CCV (5.0 ppm)	4.96	1.32	99.2	
CCV (10.0 ppm)	9.68	0.95	96.8	

Reference

American Public Health Association (APHA) 2022. *Standard Methods of Water and Wastewater*. 24th ed. American Public Health Association, American Water Works Association, Water Environment Federation publication. APHA, Washington D.C.