

Overcoming Challenging SM 5310B TOC Determination of Municipal and Industrial Wastewater Samples

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Introduction

Total organic carbon (TOC) is often used as a non-specific indicator of water quality. In the natural process of our environment and the man-made processes of industry the ubiquitous nature of carbon provides a screening tool to determine the status of water quality. Customers need a reliable TOC system that can determine contamination from natural occurring compounds, man-made compounds, viruses, bacteria or biological growth. Total Organic Carbon analyzers determine the amount of total carbon in a sample aliquot. Total Organic Carbon is comprised of an Inorganic (TIC) and Organic fraction. The Inorganic fraction consists of the carbonate and bicarbonate compounds. In order to make an accurate determination of the Organic fraction, the analyzer must remove, or quantify, the Inorganic fraction of the sample aliquot.

Discussion

The determination of either TIC or TOC relies on the conversion of the carbon containing species to carbon dioxide. In the methodology for TOC determination, the sample is first acidified with acid that converts TIC to carbon dioxide (CO₂). If the determination of TIC is desired, the carbon dioxide generated in this step is directed to the Non-Dispersive Infrared Detector (NDIR); otherwise, it is directed to atmospheric vent. Once TIC is removed, the remaining TOC is oxidized to carbon dioxide and purged through the NDIR. TOC determination is applicable, and necessary, for both drinking water and wastewater.

Standard Method 5310B provides guidance on the determination of TOC by High-Temperature Catalytic Oxidation (HTCO) with Non-Dispersive Infrared Detection. The sample is homogenized and diluted, if necessary, and a pre-determined volume is injected into the combustion tube containing the catalyst. The sample is vaporized and organic compounds are converted to CO₂. The carbon dioxide generated from the oxidation of the TIC and TOC fractions is measured by the NDIR.¹

The USEPA has issued two rules regulating levels of disinfectants and disinfection by-products in drinking water. The Stage 1 Disinfectants and Disinfection Byproducts Rule (D/DBPR) was promulgated in 1998 and took effect on January 1, 2002.² This rule lowered permissible levels of trihalomethanes (THMs) to 80 µg/L and regulated levels for five haloacetic acids (HAAs), bromate and chlorite in drinking water for the first time.

The USEPA Stage 2 D/DBPR was promulgated in 2006.³ Compliance dates for the Stage 2 D/DBPR are phased in over time based upon the number of people served by a water system. The compliance date for systems serving over 100,000 people was April 1, 2012. Systems serving 10,000-49,000 people and less than 10,000 people had to be in compliance by October 1, 2013. TOC analysis is an indicator of NOM and THM levels in source water and finished drinking water.⁴

The rule only applies to systems treating surface water. A system measures the source water and finished water quarterly and calculates the percentage of carbon removal. Table 1 shows the percent TOC removal requirements as a function of TOC and alkalinity concentration.

Wastewater treatment plans (WWTPs) use the Biological Oxygen Demand (BOD) test to measure oxygen consumed by decomposition of organic matter in secondary wastewater treatment processes. Total organic carbon (TOC) analysis provides a direct quantitative measurement of organic contamination in water and wastewater, whereas, BOD tests provide an indirect, empirical estimation of organic contamination.

In 40 CFR 133.104 the USEPA allows wastewater treatment plants to substitute TOC analysis for BOD monitoring of oxygen-demanding substances. WWTPs seeking to substitute and report TOC values for BOD values must conduct a long-term correlation study and submit results to the regulatory body that issued the NPDES permit to their facility. Study data must be collected using USEPA-approved methods intended for NPDES permit compliance reporting.

Table 1. TOC Removal Requirements

	Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as CaCO ₃)	
	0-60	60-120	Greater than 120
2.0 - 4.0	35.0%	25.0%	15.0%
4.0 - 8.0	45.0%	35.0%	25.0%
Greater than 8.0	50.0%	40.0%	30.0%

Experimental

Instrumentation in this study included the Model 1080 TOC equipped with a Model 1088 Rotary Autosampler. SM 5310 requires an initial instrument calibration using a minimum of three calibration points for linear curves. The instrument was calibrated to cover the range of concentrations typically found in drinking water and wastewater samples.

A 1000 ppm stock solution was prepared by dissolving 2.125 g of potassium hydrogen phthalate (KHP) in one liter of water. From this stock solution, a series of standards were prepared at the following concentrations: 1, 10, 25, 50 and 100 ppm. The curve is shown in Figure 1 with a summary in Table 2. Method parameters are shown in Table 3.

The system was evaluated by running a sequence that is typically found as part of the Standard Operating Procedure for many laboratories. This sequence evaluates, in addition to representative samples, the Instrument Blank at different points in the sequence as required by 5310B, and check standards at different points in the calibration range.

Table 2. Calibration Summary

Calibration Standard	RSD Value
Reagent Water (0 ppm)	3.87
1 ppm	2.07
10 ppm	0.63
25 ppm	0.78
50 ppm	1.03
100 ppm	1.55
R-Squared Value	0.9995

Results and Discussion

Table 4 shows the results of a typical sequence that is required in many laboratories. First, the Instrument Blank must be demonstrated to be below the minimum detectable concentration as defined by 5310B. This is often referred to as the Reporting Limit, RL. Additionally, checks standards must be analyzed at different points in the calibration curve as defined by 5310B. In this study, one such check standard was analyzed the RL. After every tenth analysis, a blank and laboratory control sample prepared from a source of material other than the calibration standards, at a level similar to the analytical samples must be analyzed.

In this study, these checks were conducted at 1 ppm, 25 ppm and 75 ppm. In every case, the reported values were well within the precision and accuracy required by 5310B. The results are listed in Table 4.



Figure 1. Calibration Curve for 5310B Study (Drinking Water and Wastewater)

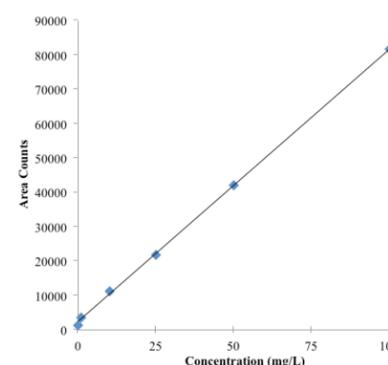


Table 3. Method Parameters

Setting	Value
Analysis Mode	NPOC
Sparging	Internal
Sample Volume	500 µL
Acid Volume	100 µL
Furnace Temperature	680 °C
Sample Sparge Time	1 minute
Reaction Time	1 minute
Detection Time	3 minutes (max)

Table 4. Sequence Results

Check Standard/Sample	Result (mg/L)	RSD
Instrument Blank	0.00	7.52
ICV (50 ppm)	49.85	0.98
Method Blank	0.010	9.91
RL (Reporting Limit)	0.95	0.64
469-12 (Wastewater sample)	91.27	2.02
438-20 (Wastewater sample)	42.84	2.70
438-21 (Wastewater sample)	39.13	1.19
600-1 (Wastewater sample)	14.21	2.54
10 ppm (in 3.5% NaCl)	10.78	2.91
CCV (75 ppm)	73.24	1.01

Conclusions

The OI Analytical Model 1080 Total Organic Carbon Analyzer is ideal for the TOC determination by Standard Method 5310B. The Model 1080 utilizes high temperature combustion on a platinum catalyst in a furnace operated at 680 °C. Moreover, the ability to create, calibrate, and validate one method and one calibration curve for the entire range of expected sample concentrations overcomes the demands of meeting the requirements of SM 5310B.

References

- Standard Methods for the Examination of Water and Wastewater, 21st Edition (2005), 5310C High-Temperature Combustion Method.
- Federal Register, Vol. 63, No. 24, December 16, 1998.
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