



On-line TOC Analysis in the Drinking Water Treatment Process

Introduction

In 1974 the Congress of the United States passed Public Law 93-523; the Safe Drinking Water Act (SDWA) to protect public health by regulating the nation's drinking water supply and protecting sources of drinking water. The SDWA first went into effect on June 24, 1977 and has been amended multiple times.

The SDWA empowers the U.S. EPA to establish enforceable standards for contaminants in drinking water, along with monitoring requirements and analytical test methods. The U.S. EPA has set standards for 90 chemical, microbiological, radiological, and physical contaminants.

Total Organic Carbon (TOC) analysis measures organic contamination levels and is an important indicator of water quality throughout the drinking water treatment process.

Drinking Water Treatment

The SDWA defines two types of drinking water systems. A Public Water system (PWS) serves at least 25 persons or 15 service connections for at least 60 days per year. There are approximately 161,000 public water systems in the United States. A Community Water System (CWS) is a public water system that supplies drinking water to homes year-round. The majority of people in the U.S. (268 million) obtain their drinking water from one of the 54,000 community water systems.

Community water systems serving large populations generally rely upon surface water sources such as rivers, lakes, and reservoirs. The quality of water from these sources determines the treatment process employed. The basic steps of the drinking water treatment process are depicted in Figure 1 and described below.

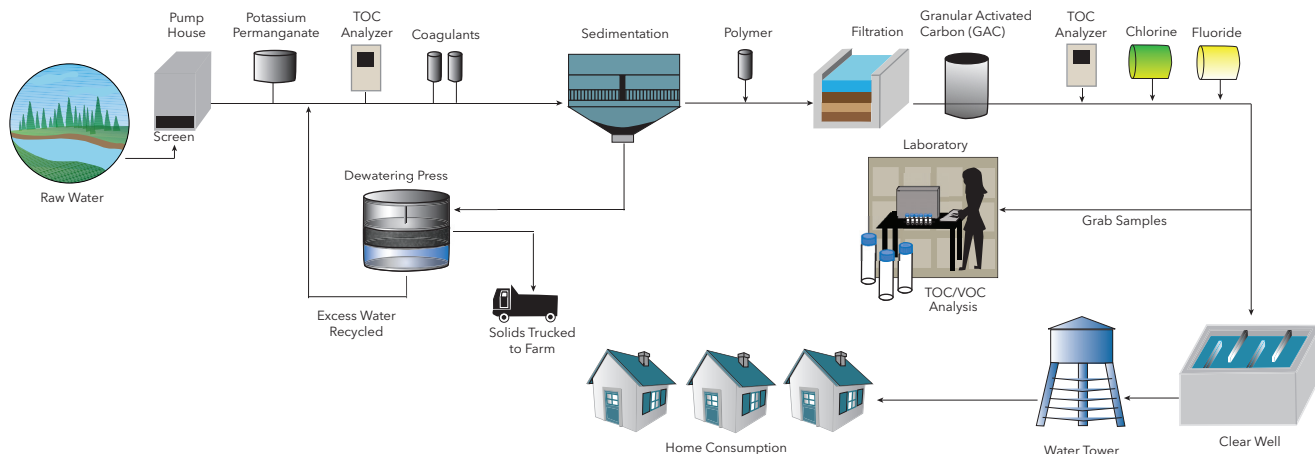


Figure 1. TOC Analysis in the Drinking Water Treatment Process

Raw source water is pumped through a screen to remove large debris. Potassium permanganate (KMnO_4) is a strong oxidizing agent that may be added to oxidize organic matter responsible for imparting undesirable tastes, odors, and colors. The U.S. EPA lists potassium permanganate as a substitute preoxidant to chlorine to control total trihalomethanes (TTHMs). The water is then clarified by flocculation and sedimentation. Alum, iron salts, or organic polyelectrolyte polymers are added to coagulate small particles into larger ones that settle out as sediment. The clear water is then filtered through a bed of sand and gravel to remove remaining particles and natural organic matter.

After filtration, water may also be directed through a bed of granular activated carbon (GAC) to adsorb and remove residual natural organic matter (NOM) and disinfection by-product precursor compounds such as humic and fulvic acids. The efficiency of post-filtration GAC treatment is monitored by TOC analysis. Reducing the TOC content enables a utility to reduce the formation of trihalomethanes (THMs) and haloacetic acids (HAA5) and comply with the Disinfectants and Disinfection Byproducts Rule (D/DBPR).

Before drinking water is released into a distribution system, it is disinfected by either chlorination or ozonation to kill dangerous microbes. Chlorine (Cl), chloramines (NH_2Cl), and chlorine dioxide (ClO_2) are highly effective disinfectants. Ozone (O_3) and ultraviolet radiation are effective in treating relatively clean water, but are not relied upon to control microbial contaminants throughout a distribution system.

Disinfectants and Disinfection Byproducts Rule (D/DBPR)

The U.S. EPA 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⁽¹⁾ and took effect on January 1, 2002. This rule lowered permissible levels of trihalomethanes (THMs) to $80 \mu\text{g/L}$ and regulated levels for five haloacetic acids (HAAs), bromate and chlorite in drinking water for the first time.⁽²⁾

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 must

be in compliance by October 1, 2013.⁽⁴⁾ TOC analysis is an indicator of NOM and THM levels in source and finished drinking water.

Drinking Water Security

The U. S. Government has passed legislation and issued directives to protect the nation’s water supply infrastructure.⁽⁵⁾ Title IV of the Public Health Security and Bioterrorism Preparedness and Response Act requires drinking water systems serving more than 3,300 people to develop response measures to incidents that could disrupt the supply of safe drinking water, or pose serious public health concerns.⁽⁶⁾ Under Homeland Security Presidential Directive 9, the USEPA is responsible for developing a “robust, comprehensive surveillance and monitoring program to provide early warning in the event of a terrorist attack using biological, chemical, or radiological contaminants”.⁽⁷⁾

On-line TOC monitoring of drinking water supply systems provides warning of organic chemical contamination from accidental or intentional incidents. TOC is an effective monitoring parameter because it responds to all types of organic carbon dissolved or suspended in water including compounds without a chromophore.

TOC Analysis

The OI Analytical 9210p On-line TOC Analyzer (Figure 2) employs the heated persulfate oxidation technique in USEPA-approved methods 415.3⁽⁸⁾ and SM 5310C⁽⁹⁾ for analysis of source water and finished drinking water.

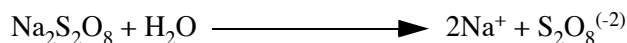


Figure 2. 9210p On-line TOC Analyzer

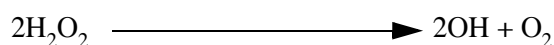
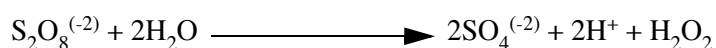
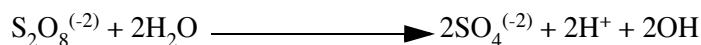
Principle of Operation

In operation, samples are drawn into the 9210p On-line analyzer at programmed time intervals from a fill and spill sampling system. Phosphoric acid is introduced to the syringe to sparge and remove the inorganic carbon (TIC) content. The TIC-free sample is then transferred into a reaction chamber to be oxidized by heated sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) at a programmed temperature up to 100 °C.

Sodium persulfate is highly soluble in water:



When heat is applied sulfate and hydroxyl radicals are formed by the following reactions:



Oxidation of organic molecules requires 2.5 - 3 sulfate or hydroxyl radicals per carbon atom.⁽¹⁰⁾ Virtually all organic compounds dissolved in water can be oxidized by this technique. Concentrated solutions (1 or 1.5 M) can effectively oxidize organic matter present in the form of colloids, macromolecules, and suspended solids.⁽¹¹⁾

Organic compounds in the sample are oxidized and converted to CO_2 , which is measured by a solid state non-dispersive infrared (SSNDIR) detector to calculate and report the TOC content. Results for each sample are shown on the touch-screen display and can be output to a Supervisory Control and Data Acquisition (SCADA) system, PC via ethernet connection, relay / alarm closure, or as a 4-20 mA analog signal.

Correlation of Laboratory and On-line TOC Analysis

Test methods for regulatory compliance reporting are currently based upon laboratory TOC analysis. On-line TOC analyzers are generally used for process control and need not operate under the quality assurance requirements specified in USEPA methods. Nonetheless, on-line TOC analyzers must be calibrated periodically to ensure accuracy, minimize drift, and verify oxidation efficiency.

OI Analytical Application Note #3945⁽¹²⁾ presents comparative data obtained on raw and finished drinking water samples using laboratory and on-line TOC analyzers employing the heated sodium persulfate oxidation technique in USEPA-approved methods 415.3 and SM 5310C. A synopsis of this study and its findings follows.

Instruments used in this study included an Aurora 1030W laboratory TOC analyzer equipped with a model 1088 autosampler and a 9210p on-line TOC analyzer equipped with a process gas module to deliver CO_2 -free air. Instrument operating parameters, reagent conditions, and calibration settings used in the study are summarized in Table 1.

Table 1: Instrument Operating Conditions

Parameter	9210p	Aurora 1030W
Analysis Mode	NPOC	NPOC
Sample Volume	2 mL	2 mL
Phosphoric Acid Volume	1.0 mL	0.5 mL
Persulfate Volume	1.2 mL	1.2 mL
TIC Reaction Time	0.5 min	1.30 min
TOC Reaction Temperature	98 °C	98 °C
TOC Reaction Time	0.5 min	2.30 min
TOC Detection Time	1.45 min	3.0 min
Calibration Standard	KHP - C ₉ H ₈ O ₄ K	KHP - C ₉ H ₈ O ₄ K
Calibration Points	0, 1, 5, 10, 25 ppmC	0, 1, 5, 10, 25 ppmC
Calibration Blank	0 ppm	0 ppm
Cal 1	1 ppm	1 ppm
Cal 2	5 ppm	5 ppm
Cal 3	10 ppm	10 ppm
Cal 4	25 ppm	25 ppm

Operating conditions of the analyzers were adjusted to obtain the Safe Drinking Water Act (SDWA) minimum required reporting limit of 0.35 mg/L but also allow for accurate quantitation of storm or terrorist events that may yield TOC values much higher than the average values of 2 - 10 ppm. Calibrated in this way, the 9210 on-line analyzer provides process control capability for TOC removal to minimize DBP formation, and also provides an early warning of organic contamination in the drinking water supply system.

A PotableWatr™ Quality Control Sample obtained from Environmental Resource Associates (ERA)⁽¹³⁾ was analyzed on each instrument in quadruplicate. Table 2 summarizes the data. Both instruments obtained values very near the certified value of 8.53 mg/L and were well within the 7.21 - 9.85 mg/L acceptable range. Notice that the precision of the 9210p on-line analyzer exceeds that of the 1030W laboratory instrument.

Table 2. TOC Data from Analysis of Potable Watr™ Quality Control Standard

9210p (mg TOC/L)	1030W (mg TOC/L)
8.68 (1.03)	7.92 (0.20)
8.75 (0.82)	8.67 (0.06)
8.76 (0.75)	8.56 (0.63)
8.73 (0.86)	8.41 (3.62)

%RSD in parentheses n=3

The 40 CFR part 136 Appendix B method detection limit was determined on each analyzer using a 0.2 mg/L TOC standard. The 9210p method detection limit (MDL) was 0.05 mg/L and the MDL for the 1030W was 0.07 mg/L. The accuracy of the 9210p and the 1030W MDL standard was 127% and 75% respectively. Each was well within the ±50% EPA 415.3 method requirement. An upper limit of linearity was verified on the 9210p only. Results from a 50-mg/L carbon and a 100-mg/L carbon standard obtained 49.9 mg/L and 98.4 mg/L respectively.

A Suwannee River NOM reference material (1R101N) with known organic carbon content was obtained from the International Humic Substances Society.⁽¹⁴⁾ The entire portion of humic material supplied was transferred to a 1000-milliliter volumetric flask and diluted to the mark with reagent water to prepare a 52-ppm TOC humic acid quality control standard. This standard was diluted further to 1.04 mg/L TOC and 5.2 mg/L TOC and the solutions

were analyzed on each analyzer. Table 3 provides a summary of the results for Suwannee River NOM reference material. The 9210p on-line TOC analyzer obtained better recovery and precision at the higher humic acid concentration.

Table 3. Recovery of Suwannee River NOM Reference Material

9210p (mg TOC/L)	1030W (mg TOC/L)
1.19 (1.15)	1.13 (1.38)
4.55 (0.85)	4.34 (1.55)

%RSD in parentheses n=3

Six surface waters with unknown TOC concentrations were obtained from a local commercial laboratory (Accutest, Bryan, Texas) and analyzed on each instrument. One of the samples was chosen at random as a duplicate resulting in a total of seven samples each analyzed in triplicate. Figure 3 plots the correlation of these unknown samples between the two analyzers. The correlation of 0.99747 demonstrates that the results between the two instruments are statistically the same.

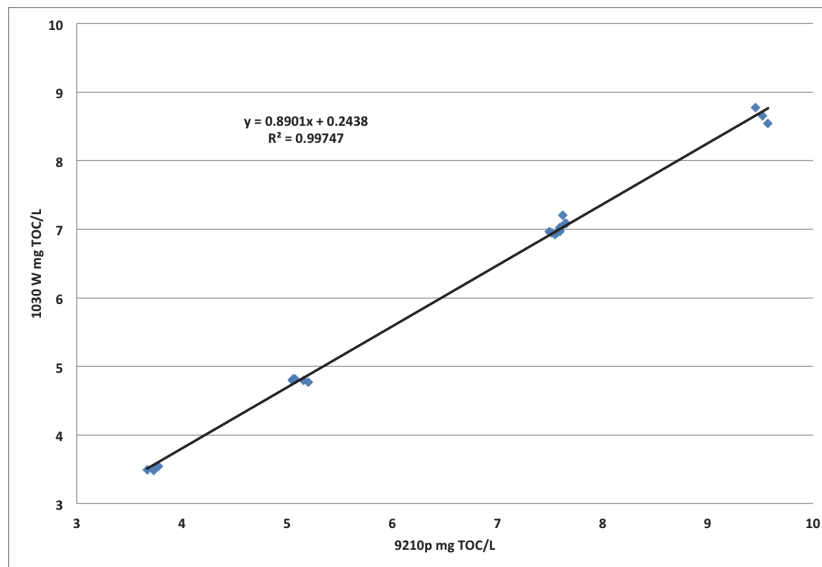


Figure 3. Correlation of Results Obtained on Unknown Samples Between 9210p On-line and the 1030W Laboratory TOC Analyzers

Summary and Conclusions

Results of this study indicate that the 9210p On-line TOC Analyzer and Aurora 1030W Laboratory TOC Analyzer obtain comparable data on drinking water samples. The 9210p On-line TOC Analyzer is capable of providing continuous real-time TOC data that can be used for routine monitoring of TOC removal and DBP reduction, detecting high TOC events, and drinking water security monitoring.

The 9210p is fully compliant with calibration, oxidation, detection, and QC verification criteria required in U.S. EPA approved methods 415.3 and SM 5310C. Accordingly, the results obtained by continuous TOC monitoring should be reportable for compliance purposes.

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