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**Application Note 40230114**

# A Comparative Study of Online and Laboratory TOC Analyzers for Analysis of Municipal Wastewater


**Keywords**
Aurora 1030W TOC Analyzer
9210p Online TOC Analyzer
NPDES Permit
USEPA Method 415.3
Standard Method SM 5310C


## Introduction

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.

Test methods for regulatory compliance reporting are currently based upon laboratory analysis. This includes both TOC and BOD. Once the correlation between BOD and TOC results is established, the TOC in wastewater streams can be accurately and quickly determined by an online TOC analyzer.

This application note presents comparative data obtained on influent and effluent wastewater samples using laboratory and online TOC analyzers employing the heated sodium persulfate oxidation technique in USEPA-approved methods 415.3[(1)] and SM 5310C[(2)].

### *Heated Persulfate Oxidation*

Virtually all organic compounds dissolved in water can be oxidized by heated sodium persulfate ($Na_2S_2O_8$) oxidation. Concentrated solutions (1 or 1.5 M) can effectively oxidize organic matter in the form of colloids, macromolecules, and suspended solids[(3)].

Sodium persulfate is highly soluble in water:

$$Na_2S_2O_8 + H_2O \longrightarrow Na^+ + S_2O_8^{(-2)}$$

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

$$S_2O_8^{(-2)} + 2H_2O \longrightarrow 2SO_4^{(-2)} + 2H+ + 2OH$$

$$S_2O_8^{(-2)} + 2H_2O \longrightarrow 2SO_4^{(-2)} + 2H+ + H_2O_2$$

$$2H_2O_2 \longrightarrow 2OH + O_2$$

Oxidation of organic molecules requires 2.5 – 3 sulfate or hydroxyl radicals per carbon atom.

A previous study conducted on drinking water samples demonstrated that laboratory and online TOC analyzers using the heated persulfate oxidation technique obtained comparable results.(4)

## Experimental

Instrumentation used in this study included an OI Analytical Aurora 1030W laboratory TOC analyzer equipped with a model 1088 rotary autosampler (Figure 1) and a 9210p On-line TOC analyzer equipped with a process gas module (PGM) to deliver $CO_2$-free air (Figure 2). Instrument settings used in this study are summarized in Table 1.


Figure 1. Aurora 1030C Laboratory TOC Analyzer with 1088 Rotary Autosampler

The Aurora 1030W and 9210p TOC analyzers both remove inorganic carbon internally by acidification followed by purging with nitrogen (1030W) or air (9210p). Once inorganic carbon is removed, the persulfate reagent is added and the sample is quantified by a non-dispersive infrared detector (NDIR) and the result reported as TOC content in both mass and concentration.


Figure 2. 9210p Online TOC Analyzer

Table 1. Instrument Operating Conditions

| Parameter | 9210p | Aurora 1030W |
|---|---|---|
| Analysis Mode | NPOC | NPOC |
| Sample Volume | 1.5 mL | 1.0 mL |
| Phosphoric Acid Volume | 2.0 mL | 2.0 mL |
| Persulfate Volume | 3.0 mL | 3.0 mL |
| TIC Reaction Time | 2.0 min | 1.5 min |
| TOC Reaction Time | 1.5 min | 2.5 min |
| TOC Detection Time | 3.0 min | 3.0 min |
| Calibration Standard | KHP - $C_9H_8O_4K$ | KHP - $C_9H_8O_4K$ |
| Calibration Points | 0 and 100 ppmC | 0, 1, 10, 50, 100 ppmC |

*Calibration*

The same analyst using the same source of neat material prepared reagents for each analyzer. Low TOC laboratory reagent water was used to prepare rinse water and reagents. Certified calibration standards were obtained from ULTRA Scientific and are available from OI Analytical. Both instruments were calibrated using Potassium Hydrogen Phthalate (KHP) as a carbon standard. Carbon free water was used as a zero standard and for the preparation of reagents.

## Results and Discussion

This study was conducted with the cooperation and assistance of Kiran Makanji, Laboratory Manager for PALS (Pre-treatment and Analytical Services) and staff of the Dallas Central Waste Water Treatment Plant (CWWTP) Process Laboratory in Dallas, TX. One-liter samples from the plant were collected on a weekly basis (Monday through Friday), preserved with sulfuric acid, and stored in the plant laboratory coolers until they were transported to the OI Analytical laboratory for analysis. In most cases, the samples were analyzed at OI Analytical on the same day that they were collected from the plant laboratory. Samples, which were not analyzed on the same day that they arrived at OI Analytical, were stored at $\leq$ 4 °C in a refrigerator until they were analyzed.

CWWTP is comprised of two plants that receive wastewater influent from the Dallas area. They are designated as the Dallas Plant and the White Rock Plant. Each plant utilizes the steps that are found in conventional wastewater treatment plants. The influent treatment utilizes “trickling” filters that remove solid material and treat the influent through microbial action. This is followed by aeration, clarification, chlorination, de-chlorination and discharge.

The CWWTP Process Laboratory performs TOC determinations on samples from eight points in the process which are designated:

DPI Dallas Plant Influent

WRI White Rock Influent

DPE Dallas Plant Effluent

WRE White Rock Effluent

T1 Combined DP and WR Effluent

T2 Post Aeration (Activated Sludge Plant)

T3 Post Chlorination

PEFF Plant Effluent (Combined Treated Water from DP and WR)

Historical data indicated that rather large swings, as well as disparity, in TOC concentration could occur in the influents of both plants. Therefore, the influents and effluents from both plants were included in this study instead of the intermediate points of T1, T2, and T3. Of particular interest was the final plant effluent, PEFF, as this is the water that is ultimately released into the local aquifer.

The samples did contain solid matter, in particular, the influent and effluent samples. The identity of this material was not known, and no attempt was made to identify it. The samples were not filtered prior to analysis on either instrument. Aliquots from the 1-L containers were poured directly into 40-ml vials and placed into the Model 1088 autosampler tray for TOC determination on the Model 1030W. An external, six-port stream selector was employed with the 9210p. The individual sample lines were placed directly into the 1-L vessels and the 9210p sequence was programmed to sample each vessel in succession.

A mid-point concentration, 50-ppm, check was made prior to analysis on each instrument (not shown). The result had to be within ± 2% of the target value before proceeding with the analysis.

TOC results from on-line and laboratory analysis of Dallas CWWTP wastewater samples over a 4-week period are presented in Tables 2 - 5.

In most cases, the difference between the two results was not greater than 10%. In fact, the results differed only by 2- 5% for the majority of the samples. Exceptions did occur on occasion and generally for the influent samples. As previously mentioned, these samples were not filtered prior to analysis. It is possible that introduction of a particle of organic nature could be responsible for this observation.

No bias, positive or negative, was observed for either of the two analyzers. In other words, neither analyzer produced results that were either higher, or lower, than the other on a consistent basis.

Table 2. Week 1 TOC Results from Online and Laboratory Analysis of Dallas CWWTP Wastewater Samples

| | | 1030W (mg TOC/L) | 9210p (mg TOC/L) |
|---|---|---|---|
| **Week 1** | | | |
| Day 1 | PEFF | 7.53 (1.35) | 7.94 (2.69) |
| | DPI | 73.01 (1.08) | 72.92 (1.45) |
| | DPE | 20.74 (1.26) | 19.94 (0.18) |
| | WRI | 68.15 (0.01) | 66.89 (3.26) |
| | WRE | 26.33 (3.26) | 26.75 (2.69) |
| Day 2 | PEFF | 8.08 (0.77) | 9.07 (2.63) |
| | DPI | 90.67 (1.09) | 92.04 (0.64) |
| | DPE | 32.16 (1.20) | 29.94 (4.45) |
| | WRI | 67.23 (0.18) | 64.00 (1.85) |
| | WRE | 38.60 (0.54) | 35.70 (2.69) |
| Day 3 | PEFF | 8.43 (0.91) | 8.76 (1.84) |
| | DPI | 57.19 (2.23) | 64.82 (4.55) |
| | DPE | 22.29 (1.24) | 22.69 (4.45) |
| | WRI | 66.13 (1.54) | 71.80 (0.82) |
| | WRE | 39.57 (0.37) | 38.51 (3.73) |
| Day 4 | PEFF | 7.72 (0.11) | 8.31 (2.33) |
| | DPI | 68.20 (2.13) | 71.46 (1.16) |
| | DPE | 19.38 (1.65) | 19.49 (2.60) |
| | WRI | 69.40 (1.07) | 71.35 (0.68) |
| | WRE | 33.25 (0.01) | 35.43 (0.73) |
| Day 5 | PEFF | 8.42 (1.37) | 8.73 (0.54) |
| | DPI | 80.88 (0.44) | 78.98 (2.33) |
| | DPE | 26.31 (1.07) | 25.85 (1.56) |
| | WRI | 66.29 (0.67) | 68.92 (2.41) |
| | WRE | 38.45 (0.51) | 36.87 (0.80) |

Table 3. Week 2 TOC Results from Online and Laboratory Analysis of Dallas CWWTP Wastewater Samples

| | | 1030W (mg TOC/L) | 9210p (mg TOC/L) |
|---|---|---|---|
| **Week 2** | | | |
| Day 1 | PEFF | 8.31 (0.54) | 8.62 (3.56) |
| | DPI | 76.23 (1.16) | 77.57 (1.34) |
| | DPE | 28.04 (0.31) | 26.13 (1.25) |
| | WRI | 64.36 (1.04) | 64.18 (4.57) |
| | WRE | 36.37 (0.08) | 34.40 (2.24) |
| Day 2 | PEFF | 8.66 (1.54) | 9.09 (3.48) |
| | DPI | 43.12 (1.67) | 45.73 (3.83) |
| | DPE | 25.07 (0.41) | 26.02 (0.76) |
| | WRI | 63.77 (0.67) | 67.67 (3.19) |
| | WRE | 38.02 (0.67a0 | 36.91 (1.22) |
| Day 3 | PEFF | 8.45 (0.98) | 8.95 (2.56) |
| | DPI | 55.13 (1.99) | 56.03 (1.42) |
| | DPE | 18.42 (3.46) | 17.21 (1.36) |
| | WRI | 72.05 (0.67) | 70.67 (0.81) |
| | WRE | 54.63 (0.67) | 56.44 (2.88) |
| Day 4 | PEFF | 7.69 (1.37) | 8.76 (0.46) |
| | DPI | 60.85 (1.86) | 60.77 (4.66) |
| | DPE | 68.98 (0.36) | 77.50 (1.64) |
| | WRI | 18.73 (3.21) | 22.34 (2.41) |
| | WRE | 42.86 (0.41) | 41.83 (5.49) |
| Day 5 | PEFF | 7.616 (1.75) | 8.046 (1.16) |
| | DPI | 55.15 (0.81) | 58.28 (3.21) |
| | DPE | 14.87 (1.76) | 18.09 (1.05) |
| | WRI | 58.04 (0.29) | 59.17 (3.13) |

Table 4. Week 3 TOC Results from Online and Laboratory Analysis of Dallas CWWTP Wastewater Samples

| | | 1030W (mg TOC/L) | 9210p (mg TOC/L) |
|---|---|---|---|
| **Week 3** | | | |
| Day 1 | PEFF | 7.53 (0.97) | 8.70 (4.07) |
| | DPI | 84.29 (0.38) | 90.34 (3.74) |
| | DPE | 27.96 ((0.02) | 28.28 (3.52) |
| | WRI | 70.52 (5.82) | 72.89 (2.53) |
| | WRE | 37.65 (2.15) | 38.33 (2.16) |
| Day 2 | PEFF | 8.04 ((0.97) | 8.30 ((0.36) |
| | DPI | 88.99 (3.86) | 88.28 (0.25) |
| | DPE | 27.08 ((0.30) | 27.46 (1.88) |
| | WRI | 60.95 (0.71) | 63.56 (1.73) |
| | WRE | 49.29 (0.60) | 50.78 (1.54) |
| Day 3 | PEFF | 7.76 (0.01) | 8.70 (1.48) |
| | DPI | 45.43 (1.68) | 51.61 (4.38) |
| | DPE | 45.05 ((0.52) | 47.76 (1.81) |
| | WRI | 53.30 (0.78) | 54.54 (3.34) |
| | WRE | 33.13 (0.16) | 34.72 (0.99) |
| Day 4 | PEFF | 8.53 ((0.65) | 9.21 (1.23) |
| | DPI | 60.89 (1.56) | 61.38 (1.28) |
| | DPE | 19.71 (0.45) | 20.51 (1.78) |
| | WRI | 65.38 (0.81) | 70.06 (1.34) |
| | WRE | 51.52 ((1.06) | 56.61 (0.99) |
| Day 5 | PEFF | 7.81 (0.08) | 8.65 (1.08) |
| | DPI | 78.69 (0.26) | 80.52 (2.92) |
| | DPE | 23.81 (0.02) | 26.04 (2.58) |
| | WRI | 60.20 (0.63) | 60.74 (1.45) |

Table 5. Week 4 TOC Results from Online and Laboratory Analysis of Dallas CWWTP Wastewater Samples

| | | 1030W (mg TOC/L) | 9210p (mg TOC/L) |
|---|---|---|---|
| **Week 4** | | | |
| Day 1 | PEFF | 8.06 (1.34) | 8.58 (0.76) |
| | DPI | 55.45 (1.31) | 57.13 (0.77) |
| | DPE | 19.57 (1.39) | 20.18 (3.36) |
| | WRI | 61.48 (1.47) | 67.68 (1.15) |
| | WRE | 36.52 (0.19) | 38.04 (1.07) |
| Day 2 | PEFF | 7.89 (3.06) | 8.74 (0.78) |
| | DPI | 59.56 (1.15) | 61.38 (1.16) |
| | DPE | 18.58 (2.58) | 18.36 (3.95) |
| | WRI | 69.59 (0.30) | 70.26 (0.22) |
| | WRE | 55.11 (0.45) | 56.24 (1.40) |
| Day 3 | PEFF | 8.57 (0.31) | 8.95 (1.27) |
| | DPI | 112.4 (1.32) | 109.68 (1.25) |
| | DPE | 38.52 (0.08) | 36.22 (4.25) |
| | WRI | 82.21 (0.64) | 84.03 (3.15) |
| | WRE | 73.13 (0.12) | 76.97 (2.07) |
| Day 4 | PEFF | 7.57 (0.76) | 7.81 (0.36) |
| | DPI | 52.62 (1.89) | 51.61 (0.69) |
| | DPE | 27.81 (2.34) | 26.19 (1.68) |
| | WRI | 62.83 1.47) | 61.43 (1.47) |
| | WRE | 55.28 (1.80) | 52.58 (3.27) |
| Day 5 | PEFF | 7.79 (0.51) | 8.92 (0.84) |
| | DPI | 56.05 (1.36) | 58.68 (3.21) |
| | DPE | 26.16 (1.56) | 26.82 (1.85) |
| | WRI | 54.87 (2.08) | 55.68 (1.46) |

Figure 3 shows the correlation of the wastewater samples between the two analyzers. The correlation of 0.9901 demonstrates that he results between the two instruments are statistically the same. No additional statistical tests were performed on the data. The slope of near 1.000 indicates that no bias (high or low) in the results existed for the 9210p.

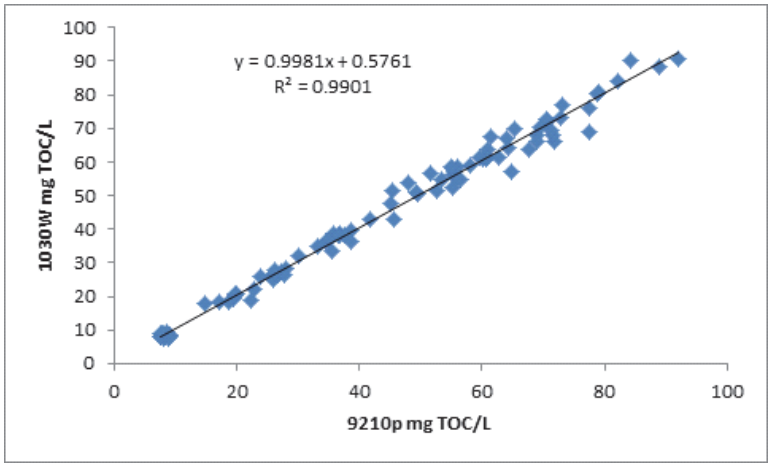


Figure 3. Correlation of TOC Results between the 9210p Online Analyzer and Aurora 1030W Lab Analyzer

## Summary and Conclusions

A 9210p online analyzer configured to analyze TOC by heated persulfate oxidation with NDIR detection was evaluated. Results of this study indicate that the 9210p online analyzer and Aurora 1030W laboratory TOC analyzer obtain comparable data on influent and effluent municipal wastewater samples.

Wastewater treatment plants seeking to substitute and report TOC values for $BOD_5$ values must conduct a long-term correlation study and submit the results to the regulatory body that issued the NPDES permit for their facility. A long-term TOC:BOD correlation study involves compiling data over a period of one year or more to account for seasonal, climatic effects on the secondary treatment efficiency. Study data from $BOD_5$ tests and TOC tests must be collected using USEPA-approved methods intended for NPDES permit compliance reporting.

The TOC results obtained on influent and effluent wastewater samples over a 4-week time period indicate a long term TOC:BOD correlation study conducted with a 9210p On-line TOC analyzer would enable a wastewater treatment plant to substitute and replace TOC values for $BOD_5$ values.

## References


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## Acknowledgments


OI Analytical would like to acknowledge the following individuals for their contributions to this study; Kiran Makanji, Laboratory Manager for PALS, and Laboratory Analysts; April West, Linda Lawrence, Kimberly Richenberger, Yi Zhang, and John Mangham.



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**Publication 40230114**