Shimadzu Scientific Instruments, 7102 Riverwood Drive, Columbia, MD 21046
Tel: 800.477.1227/410.381.1227; Fax: 410.381.1222; www.ssi.shimadzu.com

The Effectiveness of Total Organic Carbon (TOC) as the Defining Test for Wastewater Treatment Plants

As urban communities continue to grow, wastewater treatment facilities must grow with them. To meet the demands of the 21st century, quicker, more accurate testing with fewer sources of error must be employed. Take the following scenario for example. A municipal wastewater treatment plant has just received a call from the local dairy that a slug of high-strength product has been accidentally lost to the sewer and is on its way. When this happened before, soluble organics upset the aerobic bacteria treatment process, resulting in high concentrations of solids and nutrients being released to the water environment.

Carbonaceous Biochemical Oxygen Demand (CBOD) results from samples confirmed five days later that the facility violated its state-operating permit. The facility was faced with fines and a loss of trust from the community. If Total Organic Carbon (TOC) instrumentation would have been employed, the plant influent samples, collected and analyzed within five minutes, would have shown when to start and stop diverting high strength wastewater to a containment basin. Collected wastewater could then be slowly fed to the aerobic treatment process at a rate that would not impact the bacterial efficiency as assessed before and after TOC analysis.

This example demonstrates the effectiveness of TOC testing and how TOC can enhance and may someday replace CBOD as the defining test for wastewater treatment plants. TOC can point out contamination in five minutes as opposed to five days for CBOD. All data used in this article was collected by Cedar Rapids Water Pollution Control Facility (CRWPCF) (1).

CBOD

Traditionally, CBOD has been the defining test to determine the efficiency of wastewater treatment. Aerobic bacteria are used to break down the carbon compounds in the sample, using it as an energy source. As the carbon is utilized, oxygen in the sample is decreased. If dissolved oxygen is low, the effluent water will adversely affect the aquatic environment.

Biodegradable Carbon Compounds in Sample + Oxygen (in the presence of the bacteria) → $CO_{2(g)}$.

The CBOD technique uses nitrification inhibitors that eliminate the use of nitrogen compounds by the bacteria for energy. Without these inhibitors, the measurement would be Biochemical Oxygen Demand (BOD). The amount of oxygen in the sample is measured before and after the five day incubation period. The decrease in oxygen is correlated to the amount of carbon in the sample.

Non-linearity of bacterial enzyme activities is a well-known fact and makes accurate measurement very hard to achieve. Also, if the sample contains organic compounds which cannot be utilized as an energy source by the bacteria or if large particulates are present, false low results will occur.

Laboratories process varying dilutions of a sample according to a set of prescribed steps so that analysis conforms to the standard method's fixed conditions. An aliquot of the sample is treated to neutralize interfering substances such as chlorine_ and pH. A seed culture of microorganisms is added to carry out the bioxidation of organics. Sufficient dissolved oxygen and micronutrients are added to insure that these are not rate limiting components. Incubation is done for five days in the dark at 20 degrees Centigrade.

CRWPCF analyzes up to 20 wastewater samples daily for CBOD. To improve sample throughput without sacrificing data quality, the lab employs advanced instrumentation such as a computerized bench sheet that takes raw data from an oxygen analyzer and performs the required calculations. Also, a Shimadzu TOC analyzes the samples beforehand so that a reasonable set of dilutions can be chosen based upon accurate organic carbon determinations.

TOC

Total Organic Carbon (TOC) is a direct measure of organic compound in samples. Carbon in samples can be broken down into two types: organic and inorganic carbon. The inorganic carbon in the sample is composed of carbonates, bicarbonates, and carbon dioxide. In many measurements these forms of carbon are not necessary to include in the measurement. When inorganic carbon is removed from the sample all that remains is organic carbon. This organic carbon is TOC. There are three methods for measuring TOC.

TOC Method 1: Direct Method NPOC = TOC

The Direct Method is the simplest and most commonly used technique. In this method the samples are acidified to a pH less than 3. This converts carbonates and bicarbonates to CO_2. After acidifying, air is bubbled through the sample which displaces the CO_2. This bubbling process is referred to as sparging. The CO_2 escapes to the atmosphere, which leaves only organic carbon. The sample now is ready for measurement. Subjected to oxidation either by chemicals or high temperature, the carbon in the sample is converted to CO_2 and water. The water is condensed at various stages in the flow path and removed by a dehumidifier. The CO_2 remains in a gaseous state and travels to the non-dispersive infrared (NDIR) detector where it is analyzed. Only the non-purgeable organic carbon (NPOC) is measured when using the direct method. This method can only be used if the volatile organic compounds do not constitute a significant amount of the total organic carbon. These compounds are referred to as purgeable organic carbons (POC).

TOC Method 2: Difference Method TC-IC = TOC

The Difference Method is also a commonly used technique for calculating TOC. This method measures the total carbon (TC) content then measures the inorganic carbon (IC) content. For TC measurement, the sample is oxidized the same way as for NPOC measurement in the Direct Method. However, the sample has not been sparged so the IC will be included in this measurement. After the TC is measured, another aliquot of the sample is taken and added to a high acid content solution. All carbonates and bicarbonates are converted to CO_2. The acid used is typically either phosphoric or hydrochloric. Air is bubbled through the solution and the CO_2 is displaced and travels though the flow path to the NDIR. This is the IC result. The IC is subtracted from the TC, which leaves only TOC.

TOC Method 3: Addition Method NPOC+POC = TOC

The Addition Method is the least commonly used method but gives the analyst the most accurate TOC value if POC contributes significantly to the TOC content. In this method a portion of the sample is injected into a high acid concentration solution. The acid is typically phosphoric or hydrochloric. The acid converts the carbonates and bicarbonates to CO_2.

Air is bubbled through the solution and the CO_2 and POC are displaced. A CO_2 scrubber is inserted into the flow path before the oxidation chamber. This scrubber contains lithium hydroxide. The CO_2 from the IC is removed and the POC flows through the oxidation chamber and is converted to CO_2 and water. The water is condensed and removed from the flow path and the CO_2 travels to the NDIR where it is measured. After the POC measurement is complete, NPOC is measured as in the Direct Method. The addition of POC and NPOC equals TOC.

TOC Instruments

TOC instruments can be divided into two main categories: online and laboratory. The online instrument can handle one or more streams and can periodically measure the TOC in these streams. Most laboratory instruments can be automated to analyze multiple samples by using an autosampler.

There are many different types of oxidation techniques used in these instruments. Typically, the combustion technique is employed for wastewater applications. The combustion technique thermally decomposes the sample to CO_2 and water. The temperature of the combustion chamber is usually in the range of 680°C and 900°C and may contain a platinum catalyst. The combustion technique offers complete oxidation of all organic compounds while· the chemical techniques cannot. Compounds such as halomethanes and long chain organics may not be completely broken down by the chemical techniques.

If large amounts of salts are present in the samples, these can adversely affect the higher temperature combustion techniques. Because of this, the 680°C catalyst aided combustion technique was developed. At 900°C the salts are decomposed. As the gas is cooled the salts reform and are deposited throughout the remainder of the flow path and in the NDIR. The salt deposits can clog flow lines and interfere with light reflection in the NDIR. The 680°C platinum catalyst aided combustion technique does not volatilize the salts so they are harmlessly deposited on the catalyst, which can be washed to remove the salts.

Most laboratory instruments can also be equipped with a solid sample accessory. This accessory is used when particulates in the sample exceed the smallest diameter in the flow path. Shimadzu's TOC instruments can handle particulates up to 0.8mm without the need for the solids module. With the solids module the TOC can measure up to 1g of solid sample.

The wastewater samples routinely tested by TOC instrumentation at the CRWPCF are exclusively composed of carbonates and nonvolatile (non-purgeable) organics. Therefore, diluted aliquots are acidified with hydrochloric acid and purged with ultrapure air to eliminate inorganic carbon (the Direct Method). After sparging is complete, a 40 µL portion of the sample is injected into the 680°C combustion tube that contains the platinum catalyst. The sample is immediately converted into CO_2 and water and swept through the flow path. The water is condensed and removed by the dehumidifier. Carbon dioxide peak area resulting from the oxidation of the (NPOC) compounds in the sample is compared to a three-point calibration curve.

TOC vs. CBOD

Claims that TOC can replace CBOD could not be substantiated without hard data. CRWPCF collected sample over a 65 day period from four different sampling points. The four streams were an industrial waste source, raw influent, post primary settling, and final effluent. Each sample was analyzed for CBOD and TOC. A Shimadzu TOC analyzer with an autosampler and suspended particles kit was used for all TOC testing. The suspended particles kit makes possible the analysis of samples with particulates up to 0.8 mm. The ratio of CBOD to TOC was calculated along with the mean, coefficient of variance and standard deviation. The first three sampling points were all untreated. The final effluent was a treated sampling point.

Figure 1 shows the results of the industrial waste source. The top line is CBOD and the bottom line is TOC. The y-axis shows the concentration in parts per million. The x-axis is the sampling event in days. The graph clearly shows that TOC results track the CBOD results throughout the sampling period: The average ratio of CBOD to TOC was 2.0 with a Coefficient of Variance (CV) of 11 for the industrial waste source. Notice that when CBOD increases so do the TOC values. The raw influent and post primary settling point produced similar results with mean ratio of 1.9 and 2.0 and CV's of 9.3 and 11.3 respectively.

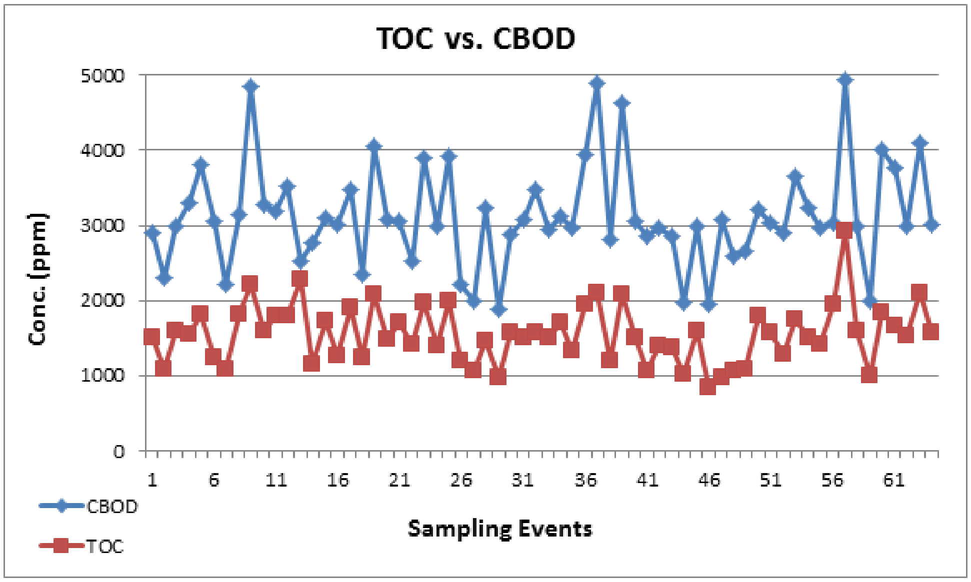

Figure 1: Results of TOC and CBOD from the Industrial Waste Source.

These results (CBOD being higher than TOC) are in direct conflict with some previously published articles. Bill Bornak (4) reported that TOC results are usually higher than BOD results. While that is not the case for these three sampling points, Mr. Bornak's (2) findings hold true for the much cleaner final effluent sampling point. It can be assumed that this is due to the fact that not all carbon compounds can be used as an energy source by any given bacteria when performing CBOD measurement.

Figure 2 shows the CBOD and TOC results for the final effluent. Here the top line is TOC and the bottom line is CBOD. The ratio of CBOD to TOC is a fraction. This point is treated hence the amount of carbon in the sample is going to be less than the other points. This is an example of how the bacteria will not completely utilize some of the compounds or could possibly be due to nonlinearity of the bacterial enzymes when performing CBOD measurement. Remember that TOC employing the 680°C catalyst aided combustion gives complete oxidation of all organic compounds.

More importantly, notice that sampling point 17 on *Figure 2* shows an increase in concentration of both TOC and CBOD. Due to a heavy infiltration of storm water, final stages of biological treatment were bypassed causing an influx of untreated water. The extent of the bypass on day 17 was noted in five minutes with TOC while the CBOD result took five days.

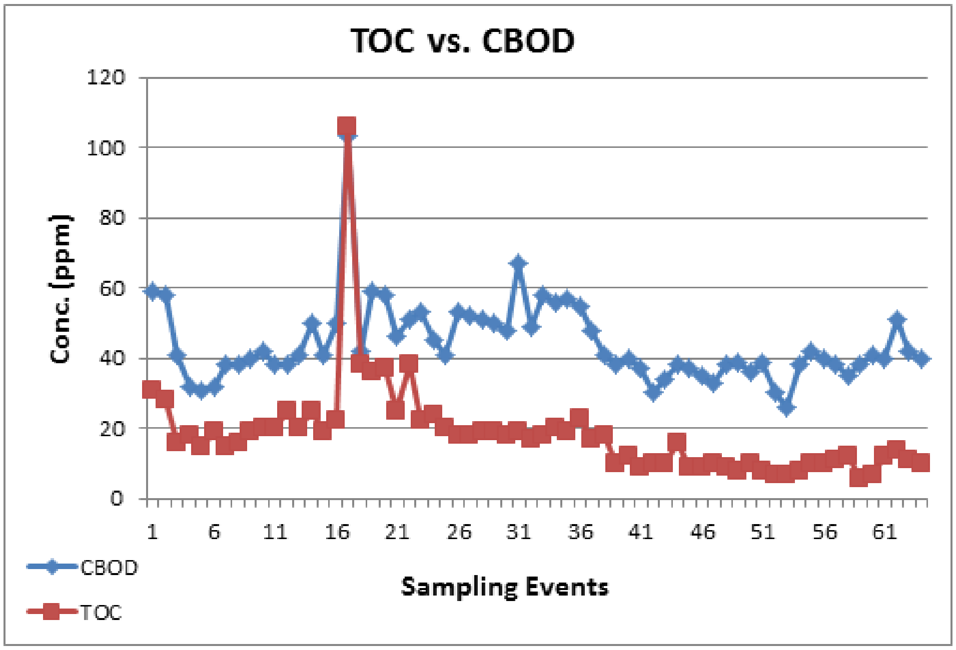

Figure 2: TOC and CBOD results for the final effluent sampling point.

Standard Methods For the Examination of Water and Wastewater (5) explains that if an empirical relationship is established between TOC and BOD (CBOD without the nitrification inhibitors), then TOC can be used to estimate the BOD results. This, however, must be done for each stream that has a different matrix. Once the relationship has been discovered, TOC can be used as the sole test for that stream totally replacing CBOD.

The results for TOC and CBOD for the four sampling points were presented at the Iowa Water Pollution Control Association Annual Conference (6). The title of the presentation was "TOC Instrumentation and Correlating TOC to CBOD". The purpose of the presentation was to inform treatment facility workers of the advantages of TOC as compared to CBOD. Also, the presentation outlined the flow path of Shimadzu TOC Instrumentation, which use the proven 680°C catalyst aided combustion technique. Details were given on the TOC methods used by water treatment facilities and on how different organic and inorganic compounds are classified for TOC measurement.

Conclusion

The data here shows that there is indeed a relationship between TOC and CBOD. More importantly, the data shows that TOC is capable of discovering contamination in the treated water. The most compelling reason for using TOC, as the data demonstrates, is that contamination can be discovered in five minutes as opposed to five days with CBOD. Also, TOC eliminates sources of error associated with CBOD analysis, such as nonlinear bacterial enzyme activities and the fact that certain compounds cannot be used as an energy source.

When using TOC instruments that employ the 680°C catalyst aided combustion technique, there are no expensive chemicals, such as various persulfate compounds and large quantities of ultrapure acids. When using TOC instrumentation employing the suspended particles kit, particulates are easily oxidized.

The speed, accuracy and precision displayed by Shimadzu's TOC instrumentation accompanied by the ability to handle particulate up to 0.8mm and the 680°C catalyst aided combustion technique make them ideal for water analysis. Shimadzu's TOC Instrumentation can provide fast, easy, and reliable results, satisfying the needs of water treatment facilities for the 21st century.

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SHIMADZU Corporation
www.shimadzu.com/an/

SHIMADZU SCIENTIFIC INSTRUMENTS
7102 Riverwood Drive, Columbia, MD 21046, USA
Phone: 800-477-1227/410-381-1227, Fax: 410-381-1222
URL: www.ssi.shimadzu.com