Challenge
Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) are traditional parameters analyzed in the laboratory to determine organic matter in water and wastewater. Wastewater facility operators need to have constant data to monitor their discharges and optimize treatment processes (biological treatment, chemical dosing, etc.). The requirements of BOD and COD analysis prevent them from being implemented as control parameters, however. The BOD five-day analysis time requirement does not allow an operator to use the data for process optimization and, although COD requires less time than the BOD, its analysis includes the use of hazardous chemicals and has no constant analysis capability.

Business Impact
GE Analytical Instruments’ InnovOx On-Line Total Organic Carbon (TOC) Analyzer provides a continuous analysis of TOC. The TOC values can be correlated with BOD or COD values, and provide the opportunity to use the regulatory data requirement for process optimization. In addition, the operator can retain, divert, or dilute discharges prior to causing damage.

Industry and Regulatory Guidance
The TOC and BOD or COD correlation procedure has been becoming commonly accepted protocol in wastewater operations. In January 2013, the Instrumentation Testing Association (ITA) published the study, Addressing BOD limitations through Total Organic Carbon Correlations: A Five Facility International Investigation, to promote the protocol development. In recent years, TOC analysis has been gaining recognition internationally, particularly in European communities, as a substitute for BOD and COD analysis in regulatory requirements [e.g. The Council of European Communities Directive 91/271 EEC dated May 21, 1991, and the German Wastewater Law (AbwV) dated June 17, 2004].

Case Study
To help demonstrate the effectiveness of constant TOC monitoring, Figure 1 shows the calculated COD values taken from the InnovOx TOC Analyzer and the actual COD measurements made by an engineer in a US wastewater facility. The fluctuations in the day-to-day (or even hour-to-hour) operation are not being properly tracked. The green overlaid line shows what the facility perceives as the current state. The blue line represents the actual influent which needs additional treatment. From this data, it is apparent that several events are unknowingly entering this treatment facility and ultimately being discharged to the municipality. This shows that continuous TOC monitoring can provide valuable insight on organic loading fluctuation and optimize the treatment performance.

Procedure
The following procedure describes how to use a TOC analyzer to measure BOD or COD continuously. The procedure follows the ITA Study Report’s recommendations and is adapted based on our customer feedback and other industry case studies. To complete the procedure, you will need our TOC and BOD/COD Correlation Tool (GE document #303 00267) created in an Excel spreadsheet.

1. Collect a one-liter water sample from the target stream, split the sample into two, label as YYYYMMDD-T and YYYYMMDD-B (e.g. 20130601-T, 20130601-B).
2. YYYYMMDD-T will be analyzed by the TOC analyzer as a “Grab” analysis. In the “Correlation Tool” spreadsheet, enter the sample date in the “Date” column and the TOC result into the “TOC (mg/L)” column.
3. Send YYYYMMDD-B to a lab for BOD or COD analysis. Enter BOD or COD values into the “Correlation Tool” spreadsheet (BOD or COD mg/L column) upon receiving the lab results.
4. Repeat Steps 1 through 3 for additional samples. We recommend that a number of samples should be taken over a 30-day period for best results.

5. The “Correlation Tool” spreadsheet will run regression analysis once a number of TOC and BOD or COD values are entered. The chart will display the linear regression equation as:

\[ Y = \text{slope} \times X + \text{intercept}, \text{ where } Y = \text{BOD or COD}, X = \text{TOC} \]

The slope typically ranges from 0.5 to 5. The Pearson Correlation value is shown in Cell F13 of the “Correlation Tool.” A value approaching 1 indicates a strong, positive linear correlation. If no significant correlation is observed, further sample analysis is recommended.

6. Use the equation to enter the conversion factor in the InnovOx touchscreen display:

Intercept + Slope \times C

Go to “Menu”->“Maintenance”->“Conversion Factor” (Figure 2) ->“Factor 1 Equation” (Figure 3). One or two conversion factors may be input.

7. Change the setup of the sample protocol to display results using the Conversion Factor. Go to the analysis protocol setup menu: “Menu”->“Setup”->“Grab”->“Analysis Protocol.” Select the protocol to be modified, then press “Modify.” Select the “Conversion Factor” button, then choose either Factor 1 or Factor 2.

8. Thereafter, organic values are displayed in the units of choice: TOC, BOD, or COD.

Notes:
1. Regulatory agencies (e.g. USEPA, state DEPs) may have specific requirements on the number of samples and test period. As indicated by ITA Study Report,1 weekly sample analysis for a minimum of one year to include seasonal variations is recommended for municipal wastewater plant in order to obtain discharge permit (e.g. City of Santa Cruz WWTP NPDES permit).

2. In addition to the simple Pearson Correlation value, a statistical two-tailed t-test could also be used to determine if a correlation exists between TOC and BOD or COD. For the purpose of the analysis, if the t-test falls a 95 percent confidence interval, then null hypothesis of no relationship cannot be rejected (i.e. no relationship exists). A trend-line should be added to the graph with the equation and correlation coefficient \(R^2\) identified. Based on the \(R^2\) value and the number of data pairs (n), the test value (t) is calculated from the following formula:

\[ t = R \times \sqrt{n-2/(1-R^2)} \]

The calculated value of t can then be compared with standard t-tables to determine the statistical significance at the 95 percent confidence interval for a two-tailed t-test.\(^1\)

References


3. Evaluation of Total Organic Carbon as a Reliable Technique to Predict the Biochemical Oxygen Demand in Wastewater at the Clark County Water Reclamation District, June 22, 2006.