Application Note

Correlating Total Organic Carbon (TOC) to Biochemical (BOD_5) and Chemical Oxygen Demand (COD)

In all regions of the world, environmental agencies and academia are exploring and supporting measurement of total organic carbon (TOC), and its use in correlating to oxygen demand.

Background

Oxygen demand measurements, biochemical and chemical, have been used for over 100 years to qualify and quantify contamination in municipal and industrial wastewater. Biochemical Oxygen Demand, currently a five-day laboratory test labeled BOD_5, is one of the most broadly used parameters for wastewater quality in the world; the standard for municipal sewage treatment. Chemical Oxygen Demand, (COD), typically a two-hour test, is more widely used in industrial applications. Often, both of these laboratory methods are measured, recorded and compared over time (Citations 1, 2 and 3).

Total Organic Carbon, (or TOC), and is a well-known analytical method used in diverse water and wastewater quality applications, municipal and industrial. There are multiple methods and technologies available, in laboratory and online configurations. Typical analytical times are between 3 and 10 minutes, and varying by mode of analysis. The quick analytical cycle and online operation provide an advantage over oxygen demand, with real-time analyses for event detection and integrated process control.

Depending upon the wastewater composition and stability, a relationship or correlation can often be established between the organic carbon and the oxygen demand of the sample.

Regulatory Framework

In the U.S., pre-treatment standards are established for all industrial and publically-owned treatment works (POTWs). Under the authority of the Clean Water Act, and subsequent legislation, the National Pollutant Discharge Elimination System (NPDES) was established under the administration of the Environmental Protection Agency (EPA). With minimal exceptions, NPDES is the primary mechanism to set discharge limits or effluent limitations guidelines (ELG), for anyone releasing process effluent or wastewater to public waterways (Citations 4 – 7).

The U.S. Clean Water Act authorizes considerable civil penalties for all violators, up to US$25,000 per day per violation. (Citation 8). According to the U.S law, Code of Federal Regulations 403.12, POTWs over 5 million gallons per day (MGD) have to have their own pretreatment program. (Citation 9)

In Asia, Taiwan's EPA has guidelines to qualify river pollution based on concentration of BOD_5. They classify 5 to 15 mg/L as moderately polluted and > 15 mg/L as severely polluted (Citation 10).

In Europe, France has effluent discharge limitations in open waterways that are BOD_5 < 100 mg/L and COD < 300 mg/L (Citation 11). Germany allows a maximum COD value based on 4 x TOC – "a chemical oxygen demand (COD) level specified in the water discharge permit shall also be deemed to have been met provided the quadruple amount of total organically bonded carbon (TOC), specified in milligrams per litre, does not exceed this level." (Citation 12)

GE Power & Water
Water & Process Technologies
Analytical Instruments

Importance and Value of TOC to Oxygen Demand Correlation

The analytical method for TOC is faster and more accurate than either, oxygen demand method, and a direct measurement of the organic load. Both forms of oxygen demand are indirect measurements. TOC has an analysis time of 3 to 10 minutes, or 30 minutes for at least three (3) repetitions, compared to two hours for COD, or five days for BOD_5.

The NPDES system allows for "authorized alternatives", such as TOC measurement correlating to oxygen demand, as a means for operators to have faster and more accurate monitoring and process control. In this way, industrial facilities, "non-municipal dischargers", with wastewater treatment can often trend oxygen demand and anticipate excursions before exceeding their permit limits (Citation 13).

A pre-treatment facility should work with their state NPDES administrator to execute a long-term, correlation test and replace BOD or COD with TOC as the primary discharge parameter. 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, "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" (Citation 14).

Around the globe, municipal sewage and industrial wastewater plants can use short-term and long-term studies to determine the correlation between TOC and oxygen demand.

According to the Government of India, Central Pollution Control Board, under the Ministry of Environment & Forests:

"...based on the laboratory validation as regards to the observed ratio of TOC:BOD & TOC:COD a correlation factor is established... In the field TOC is monitored online... Based on repeatable empirical relationship established between TOC, BOD or COD for a specific waste water source accompanying BOD or COD can be estimated from the recorded TOC values." (Citation 15) The CPCB also specifies that the correlation must be established based on the sample matrix and validated periodically.

Since TOC and oxygen demand methods are inherently different, the historical concern over TOC: OD correlation is the stability of the relationship through time, due to any changes in the process stream(s). The variability of organics in time could alter the mathematical relationship to oxygen demand. The sample matrix, particulate or solids composition, viscosity and turbidity, can influence the correlation factor through time.

By measuring TOC once every ten minutes and applying the correlation factor:

- COD can be estimated as much as 12 times more frequently than the traditional test
- BOD_5 can be estimated 288 times per day, compared to the traditional test

How to Determine the Correlation Factor

There are a number of ways to properly determine the correlation factor between the TOC and Oxygen Demand parameter of choice, BOD_5 or COD. The method detailed in the ITA Test Report is very specific with corresponding statistical analyses; refer to the Implementation Protocol (Citation 14 pages 7, 30-31). ITA's suggested protocol specifies four steps with recommendations, references published analytical methods:

1. Long term sampling for TOC and BOD_5 analyses, of various points from influent to discharge
   - Recommends immediate BOD_5 analysis after collection
   - Recommends immediate TOC analysis after collection OR acidification and refrigeration
   - Recommends 10% of samples "used for quality assurance and quality control purposes"
2. Statistically analyze data for significant correlation between data sets
3. If correlation is confirmed, set correlation equation and calculate TOC equivalent to BOD_5 limit (Citation 14 pages 30-31)

Whether this procedure or another is followed, one should properly design, execute and analyze their experiment utilizing scientific method and current best practices to assure statistical validity, internal and external. Some validity considerations for statistical process control and analyses are: minimum number of data points in data set before determining process stability; normality of data; process capability; and criteria for determining inference to data correlation. Regarding Design of Experiments — Consult with quality and engineering personnel, applied statisticians, Six Sigma specialists and/or follow appropriate company processes and procedures.

The table below provides a few of the first order, correlation equations that were determined in the ITA Test Report (Citation 14 pages 10, 17, and 22). The report summarizes all of the correlation findings that the data were tested for statistically.

Location	Correlation Formula	R_2
Oceanside WPCP, San Francisco, CA Primary effluent and final effluent	TOC = 0.2326 (BOD_5) + 14.426	0.8138
Longwood Park Sewage Lagoon Town of Quispamsis, NB, Canada Combined raw sewage and final effluent	TOC = 0.4476 (BOD_5) + 23.787	0.703
City of Winnipeg, Manitoba, Canada North End Water Pollution Control Centre (NEWPCC) Combined raw sewage and final effluent	TOC = 0.5569 (BOD_5) + 11.38	0.8832

Conclusion

In Asia, Europe and the Americas, correlating TOC to BOD_5 is well-known and becoming a best practice in wastewater quality and treatment. Faster and more accurate TOC measurements can be used to improve process control, in addition to real-time discharge monitoring to decrease excursions. TOC analysis for BOD_5 can reduce operational costs, chemicals and energy, and help to avoid fines for exceeding effluent limits. There are established procedures and methods, analytical and statistical, to properly execute a correlation study, validate data and determine the equations. Universities, research institutions, environmental agencies and private industry are all learning the advantages of total organic carbon analysis to rapidly monitor and predict oxygen demand, improving wastewater quality, lowering cost and risk.

Works Cited

Format based on MLA Style Citations (Modern Language Association)

1. "Pacific Southwest, Region 9 – Quality Assurance." United States Environmental Protection Agency. Last updated 15 October 2014. 21 April 2015 <http://www.epa.gov/region9/qa/>
2. "BIOCHEMICAL OXYGEN DEMAND (BOD) – Standard Method 5210 B (5-day BOD Test)." United States Environmental Protection Agency. Last updated 15 October 2014. 21 April 2015 <http://www.epa.gov/region9/qa/pdfs/5210dqi.pdf>
3. ASTM D1252 – 06(2012) Standard Test Methods for Chemical Oxygen Demand (Dichromate Oxygen Demand) of Water
4. "NPDES Permit Program Basics." United States Environmental Protection Agency. Last updated 7 April 2015. 21 April 2015 <http://water.epa.gov/polwaste/npdes/basics/index.cfm>
5. "Water Permitting 101." United States Environmental Protection Agency – Office of Wastewater Management. Last updated 15 July 2014. 21 April 2015
6. "State Program Information." United States Environmental Protection Agency. Last updated 15 July 2014. 21 April 2015 <http://water.epa.gov/polwaste/npdes/basics/State-and-Tribal-Program-Authorization-Status.cfm>
7. "State NPDES Program Authority." United States Environmental Protection Agency. Last updated 15 July 2014. 21 April 2015 <http://water.epa.gov/polwaste/npdes/basics/upload/State_NPDES_Prog_Auth.pdf>
8. "Code of Federal Regulations (CFR) 40 Part 122 EPA ADMINISTERED PERMIT PROGRAMS: THE NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM." Subpart C – Permit Conditions 122.41 (a) (2). Office of the Federal Register (OFR) and the Government Publishing Office. Current as of 20 April 2015. 21 April 2015 <http://www.ecfr.gov/cgi-bin/retrieveECFR?gp=1&SID=b7eb72833b03e9e6690689db4517ac81&ty=HTML&h=L&mc=true&n=pt40.22.122&r=PART>

Works Cited continued

9. "Code of Federal Regulations (CFR) 403 Part 12 Reporting requirements for POTW's and industrial users." Office of the Federal Register (OFR) and the Government Publishing Office. Current as of 20 April 2015. 21 April 2015 <http://www.ecfr.gov/cgi-bin/retrieveECFR?gp=&SID=65573f195cbb8fc671687e3ada9c416f&mc=true&r=PART&n=pt40.29.403#se40.29.403_112>

10. "Environmental Water Information – Water Quality Standards – River Pollution Index (RPI)" Environmental Protection Administration, R.O.C.(Taiwan). 2010. 21 April 2015 <http://wq.epa.gov.tw/WQEPA/Code/Business/Standard.aspx?Languages=en>

11. "Arrêté du 26 mars 2012 relatif aux prescriptions générales applicables aux installations classées relevant du régime de l'enregistrement au titre de la rubrique n° 2710-2 (installations de collecte de déchets non dangereux apportés par leur producteur initial) de la nomenclature des installations classées pour la protection de l'environnement." Article 35: Valeurs limites de rejet. Current as of 26 March 2012. 21 April 2015 <http://legifrance.gouv.fr/eli/arrete/2012/3/26/DEVP1208907A/jo/article_35>

12. "Promulgation of the New Version of the Ordinance on Requirements for the Discharge of Waste Water into Waters." Article 6, section (3), page 5. Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, Germany. Current as of 17 June 2004. 4 June 2015 <http://www.bmub.bund.de/fileadmin/bmu-import/files/pdfs/allgemein/application/pdf/wastewater_ordinance.pdf>

13. "Central Tenets of the National Pollutant Discharge Elimination System (NPDES) Permitting Program." Page 2. United States Environmental Protection Agency. Last updated 7 April 2015. 21 April 2015 <http://water.epa.gov/polwaste/npdes/basics/upload/tenets.pdf>

14. Nutt, Stephen G. and Tran, John of XCG Consultants Ltd. "Addressing BOD_5 limitations through Total Organic Carbon Correlations: A Five Facility International Investigation." Pensacola, Florida: water & Wastewater Instrumentation Testing Association of North America (ITA). January 2013.

15. "Guidelines for Online continuous monitoring system for Effluents." Guidelines for Real-time Effluent Quality Monitoring System, Page 12. Delhi, India: CENTRAL POLLUTION CONTROL BOARD (CPCB) Delhi. 7 November 2014. 21 April 2015 <http://cpcb.nic.in/upload/Latest/Latest_67_guidemanualw&wwanalysis.pdf>

The Americas
GE Analytical Instruments
6060 Spine Road
Boulder, CO 80301-3687 USA
T +1 800 255 6964
T +1 303 444 2009
F +1 303 527 1797
geai@ge.com

Europe/Middle East/Africa
GE Analytical Instruments
Unit 3, Mercury Way
Urmston, Manchester
UK M41 7LY
T +44 (0) 161 864 6800
F +44 (0) 161 864 6829
geai.europe@ge.com

Asia Pacific
GE Analytical Instruments
7/F, Building 5, No.2 Hua Tuo Rd,
Zhang Jiang Hi-Tech Park,
Pudong
Shanghai, China 201203
T + (8621) 38777735
F + (8621) 38777469
geai.asia@ge.com

For more information, visit:

www.geinstruments.com/innovox

GE Power & Water
Water & Process Technologies
Analytical Instruments

300 00266 Rev. B MC15-017
GEA32049