Real-time Biological Oxygen Demand (BOD_5) Measurements by Correlation with Rapid PeCOD™ Chemical Oxygen Demand (COD) Measurements

Keywords: *Biological Oxygen Demand (BOD_5); Chemical Oxygen Demand (COD), Estimated BOD_5*

Abstract

BOD_5 is an important standard parameter commonly used to monitor organic load for environmental and process control in a vast range of industries. Using the Aqua Diagnostic PeCOD™ COD analyser to determine COD in a brewery, sugar mill and sugar refinery it has been shown that a scaling factor can be applied to COD measurements to determine an estimated BOD_5 concentration in a range of saline conditions that was well within the 95% confidence level when compared to the standard BOD_5 test.

Introduction

Chemical oxygen demand (COD) and biological oxygen demand (BOD_5) are two of the most common generic indices used to assess aquatic organic pollution. BOD_5 is often used to evaluate the biodegradable fraction, and COD the total organic pollution load of waters contaminated by reductive pollutants[1-4].

Concentrations of BOD_5 readings will generally report as lower than COD. This is due to differences in the methods of oxidation of the samples. While BOD_5 provides a good approximation of the biologically consumable organic fraction in waterways, the test takes 5 days. Alternatively, COD is able to provide a rapid and reliable estimate of the biogeochemical interactions in waterways.

In the industrial world the continuous monitoring of organic load becomes essential to comply with regulatory requirements. Therefore a rapid method as presented by COD for online analysis of organic load becomes a desirable option as opposed to a 5 day test as is the case with BOD_5. Subsequently the ability to relate COD to BOD_5 proves as a useful tool to give a good representation of biogeochemical interactions, while still providing real time, *in situ* analysis.

The Aqua Diagnostic PeCOD System

Aqua Diagnostic has developed a new, rapid, sensitive and green alternative to measuring COD employing recently developed photoactive TiO_2 nanomaterials combined with photocatalytic technologies. The standard dichromate COD test is currently registered as the standard method; however, this dated method is slow, limited in sensitivity and requires the addition of toxic chemicals (i.e. mercury) to eliminate interferences such as for chloride.

Based on the oxidative degradation principle, the innovative aspects of the PeCOD™ method lie in the novel approach to generate and quantify the useful analytical signals[5] with a sensitivity and speed far greater than any standard method (minutes compared to hours and µg/L compared to > 10 mg/L) as shown in Table 1.

Table 1 – Analytical Figures of Merit and System Requirements

Linear Range (mg COD/L)	0-300 R^2 = 0.9992
Sample throughput	Up to 20 analyses hr^{-1}
LOD (mg COD/L)	0.1*
Sample Volume	10 µL $analyses^{-1}$
Supporting Electrolyte	2M $NaNO_3$

* Calculated based on particular instrument set-up

System Performance

It is essential for process control and environmental monitoring to observe concentrations of organic load in wastewater discharges. A trial performed at three different locations in a variety of industries was undertaken to measure the COD using the PeCOD™ analyser and relating the accrued values back to the relevant BOD_5 concentration. This included studies at a brewery, sugar mill and sugar refinery.

Brewery Study

A comparison of measurements on 24 hour composite wastewater samples from a brewery plant was analysed for COD by the PeCOD™ technique and for BOD_5 by an independent laboratory using the standard 5 day BOD method. The COD data obtained was greater than the BOD_5 data, as is typical for industrial and municipal effluent. The data collected from the PeCOD™ COD analyser was compared to the BOD_5 results and an average factor was determined between the two data sets. The resulting factor was 1.83 which is equivalent to a multiplier of 0.55 ±0.02 required to convert COD values to a 5-day BOD estimate. The results are shown in Figure 1.

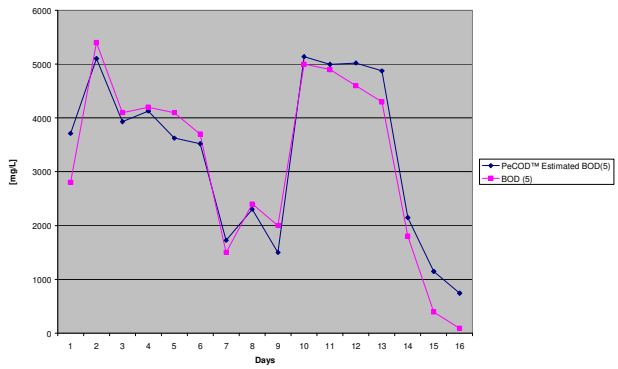

Figure 1 – Comparative concentration data at a brewery for BOD_5 and Estimated BOD_5 using PeCOD™ COD analysis

By applying the constant offset factor to the PeCOD™ COD the estimated BOD_5 showed excellent correlation with the BOD_5 results. A paired t-test performed on the BOD_5 and estimated BOD_5 data set for the brewery showed no significant difference at the critical $\alpha = 0.05$ level between the concentrations observed from the estimated BOD_5 based on the PeCOD™ COD method and the standard reference method for BOD_5 ($t = 2.13$, $P = 0.19$), implying a good relationship between estimated BOD_5 and BOD_5.

In addition, a regression test showed a significant correlation at the $P < 0.05$ level (by testing the fully fitted model; Estimated $BOD_5 = m\ [BOD_5] + [\text{Estimated } BOD_5]$; $F = 242$, $P = < 0.001$, $r = 0.97$) implying there is a significant correlation between estimated BOD_5 and standard BOD_5 methods.

Sugar Mill Study

The study employed a PeCOD™ online COD analyser (P100) set to measure effluent samples at 15 min cycles. “Grab samples” were collected during this trial period where samples were analysed by the PeCOD™ method for COD and then externally measured for BOD_5 concentrations. Applying the same method of scaling as determined with the brewery data, a multiplier of 0.55 was again achieved resulting in a good correlation at this site between the estimated BOD_5 and the externally measured standard BOD_5 method for a lower concentration range (see Figure 2).

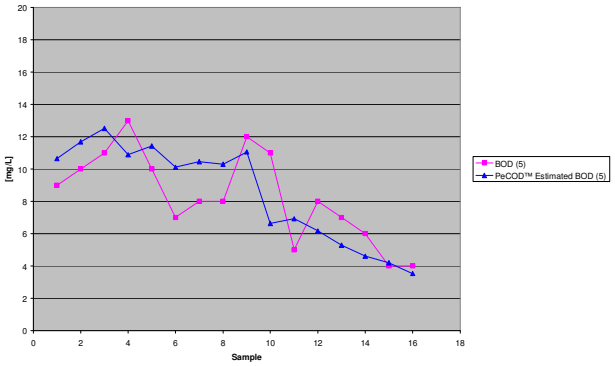

Figure 2 – Comparative concentration data at a Sugar Mill for BOD_5 and Estimated BOD_5 using PeCOD™ COD analysis

Statistical analysis performed on the sugar mill BOD_5 and estimated BOD_5 data set using a paired t-test showed no significant difference at the critical $\alpha = 0.05$ level between the concentrations observed from the estimated BOD_5 based on the PeCOD COD method and standard reference method for BOD ($t = 2.14$, $P = 0.84$) implying a good relationship between estimated BOD_5 and BOD_5. Further regression analysis showed a significant correlation at the $P < 0.05$ level ($F = 16.2$, $P = 0.001$, $r = 0.79$) further validating the relationship between PeCOD™ COD and BOD_5.

Sugar Refinery Study – Monitoring Oxygen Demand in Seawater

The use of seawater in cooling towers is a commonly used practice providing significant cost savings. However, until now, monitoring of seawater discharge has been limited due to the presence of high chloride concentrations. A sugar refinery employing seawater in its cooling water was used as a trial site to monitor COD

and BOD_5. 'Grab samples" were collected and analysed for COD using The PeCOD™ COD analyser and then externally measured for COD by the dichromate method and for BOD_5**.** The results are presented in Table 2.

Table 2 – Results for oxygen demand measurements taken at a Sugar Refinery

Sample	Spiked concentration[+]	BOD*	PeCOD™ *	COD*
A	Sea water blank	2	3.8	633
B	11.2	6	9.6	260
C	22.4	16	22.1	47
D	33.6	22.7	33.5	163
E	44.9	29	41.4	77

[+] Expected COD concentration (mg/L) after blank correction
* Concentrations reported as mg/L post blank correction

By minimizing the sum difference between estimated and laboratory tested BOD_5 data a multiplier of 0.68 was achieved to convert COD values to a 5-day BOD estimate. The difference in the scaling factor between the results obtained at the brewery and sugar mill is believed to be due to the presence of high chloride concentrations, which have altered the scaling factor. Nonetheless, an excellent correlation was observed (see Figure 3). As can be seen in Table 2 the standard dichromate COD method was unable to accurately measure COD in such a high chloride background and it subsequently struggled to produce any meaningful relationships with BOD_5 data.

The correlation between the PeCOD™ estimated BOD and BOD_5 concentration measured in a seawater background was further validated by statistical analysis via a paired t-test and regression analysis performed at the critical $\alpha = 0.05$ level. The t-test showed no significant difference between the PeCOD™ estimated BOD and standard reference method for BOD ($t = 3.18$, $P = 0.52$) implying a good relationship between estimated BOD_5 and BOD_5. While the regression analysis showed a significant linear relationship ($F = 523$, $P = 0.002$, $r = 0.99$) implying there is a significant correlation between Estimated BOD_5 and standard BOD_5 methods.

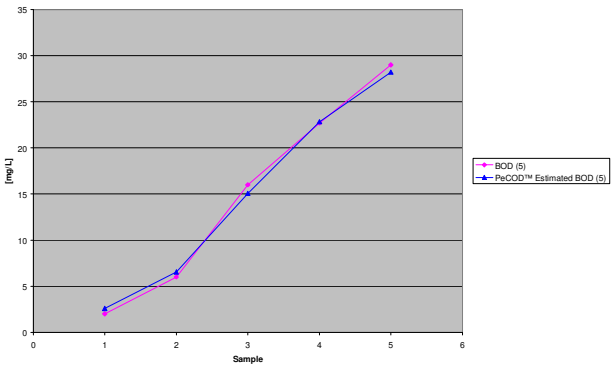

Figure 3 – Comparative concentration data at a Sugar Refinery for BOD_5 and Estimated BOD_5 using PeCOD™ COD analysis

Conclusions

The ability of the PeCOD™ analyser to reliably relate COD to $BOD_{5,}$, producing an accurate estimate of BOD has been clearly demonstrated at the 95% confidence level. The PeCOD™ system can accurately monitor in real-time a wide range of concentrations down to the sub ppm level. It has been shown to provide a good representation of the organic load for both total organics and the organics available for biological consumption.

References

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