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Real Time BOD Estimations by Automated COD Analysis Using the PC-BOD/COD Duo

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ABSTRACT

Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) are among the most diagnostic parameters for the determination of water quality in natural waterways and waste streams. The standard BOD test requires five days to complete, and is therefore unable to provide continuous monitoring of organic load. COD is therefore often used for BOD screening, however the standard dichromate method is slow, limited in sensitivity and oxidizing power, and requires the use of toxic chemicals. A rapid COD method for BOD estimations is therefore highly desirable. This paper discusses the new rapid COD technology as well as the new PC-BOD/COD Duo, a completely automated dual platform system that can be used to analyze both COD and BOD using one efficient system.

INTRODUCTION

Chemical oxygen demand (COD) and biological oxygen demand (BOD5) are two of the most common generic indices used to assess aquatic organic pollution. BOD5 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 BOD5 readings will generally report as lower than COD. This is due to differences in the methods of oxidation of the samples. While BOD5 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 analysis of organic load becomes a desirable option as opposed to a 5 day test as is the case with BOD5. Subsequently the ability to relate COD to BOD5 proves as a useful tool to give a good representation of biogeochemical interactions, while still providing real time, *in situ* analysis. Additionally, the utilization of Man-Tech's PC-BOD/COD Duo system to obtain both rapid COD and BOD5 results provides further advantages such as automatic sample preparation, analysis and reporting.

PROCEDURE

Aqua Diagnostic has developed a new, rapid, sensitive and green alternative to measuring COD employing recently developed photoactive titanium dioxide (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.

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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

In co-operation with Aqua Diagnostic, Man-Tech has taken this new technology and integrated it with their fully automated PC-Titrate software-controlled system, the PeCOD Assay Plus (see Figure 1). The new PC-BOD/COD Duo (Figure 2) is a dual platform system that allows for both the automated analysis of COD using this new green technology, as well as BOD following 21st edition Standard Methods. Rather than two separate systems, the PC-BOD/COD Duo combines these methods into one efficient system providing a more effective utilization of laboratory equipment.

Figure 1: The PeCOD Assay-Plus

Figure 2: PC-BOD/COD Duo

COD is analyzed first in order to obtain the estimated BOD values, which can help determine the appropriate dilution factor to use during BOD analysis. After samples are placed into the autosampler

rack and the system is started, the sample line is automatically rinsed with deionized water and the blank solution line is automatically primed to ensure fresh solution is used. If desired, the initial pH of the sample can be measured and adjusted if required - a useful step for samples that have been treated with sulfuric acid in the field. Depending on the expected COD range of the sample, the appropriate electrolyte solution is then pipetted into the sample and automatically mixed via a paddle stirrer before being pumped into the PeCOD and analyzed. When completed, the COD value is reported along with the estimated BOD result.

Following a batch of COD samples, the analyst simply removes the COD-configured autosampler rack and replaces it with the BOD rack which can accommodate up to twenty four 300mL bottles. The probe holder is also changed to include the dissolved oxygen probe, tips and the BOD stirrer. BOD analysis then proceeds following 21st Edition Standard Methods. The Man-Tech PC-BOD system includes the automatic addition of dilution water, seed and inhibitor (if required), along with all rinsing and dissolved oxygen measurements that can be viewed in real-time. The software also includes the ability to re-analyze samples during or following the completion of a run and reprocess data as necessary. Due dates and times of finals to be run are also quickly and easily viewed. Both BOD and COD methods also include a full quality control tracking database, audit trail and exporting capabilities.

RESULTS

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 analyzer and relating the accrued values back to the relevant BOD5 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 analyzed for COD by the PeCOD technique and for BOD5 by an independent laboratory using the standard 5 day BOD method. The COD data obtained was greater than the BOD5 data, as is typical for industrial and municipal effluent. The data collected from the PeCOD COD analyzer was compared to the BOD5 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 3.

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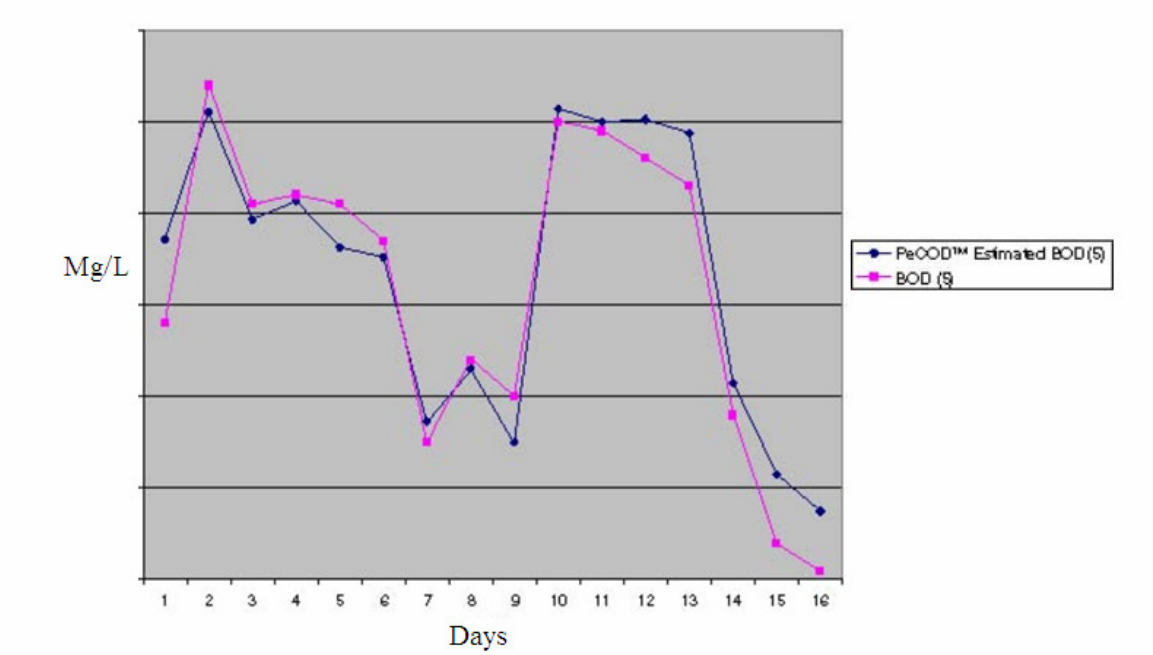

Figure 3: Comparative concentration data at a brewery for BOD5 and Estimated BOD5 using PeCOD COD analysis

By applying the constant offset factor to the PeCOD COD the estimated BOD5 showed excellent correlation with the BOD5 results. A paired t-test performed on the BOD5 and estimated BOD5 data set for the brewery showed no significant difference at the critical $\alpha = 0.05$ level between the concentrations observed from the estimated BOD5 based on the PeCOD COD method and the standard reference method for BOD5 ($t = 2.13$, $P = 0.19$), implying a good relationship between estimated BOD5 and BOD5.

In addition, a regression test showed a significant correlation at the $P < 0.05$ level (by testing the fully fitted model; Estimated BOD5 = m [BOD5] + [Estimated BOD5]; $F = 242$, $P = < 0.001$, $r = 0.97$) implying there is a significant correlation between estimated BOD5 and standard BOD5 methods.

Sugar Mill Study

The study employed a PeCOD online COD analyzer (P100) set to measure effluent samples at 15 min cycles. “Grab samples” were collected during this trial period where samples were analyzed by the PeCOD method for COD and then externally measured for BOD5 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 BOD5 and the externally measured standard BOD5 method for a lower concentration range (see Figure 4).

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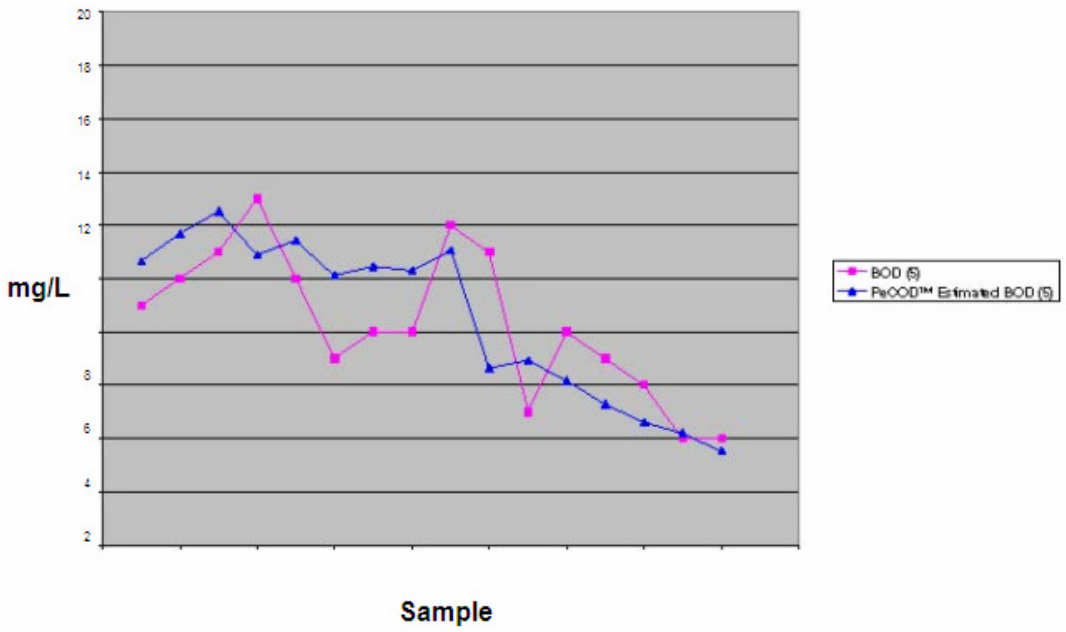

Figure 4: Comparative concentration data at a Sugar Mill for BOD5 and Estimated BOD5 using PeCOD COD analysis

Statistical analysis performed on the sugar mill BOD5 and estimated BOD5 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 BOD5 based on the PeCOD COD method and standard reference method for BOD ($t = 2.14$, $P = 0.84$) implying a good relationship between estimated BOD5 and BOD5. 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 BOD5.

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 BOD5. 'Grab samples" were collected and analyzed for COD using The PeCOD COD analyzer and then externally measured for COD by the dichromate method and for BOD5**.** 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

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By minimizing the sum difference between estimated and laboratory tested BOD5 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 5). 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 BOD5 data.

The correlation between the PeCOD estimated BOD and BOD5 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 BOD5 and BOD5. 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 BOD5 and standard BOD5 methods.

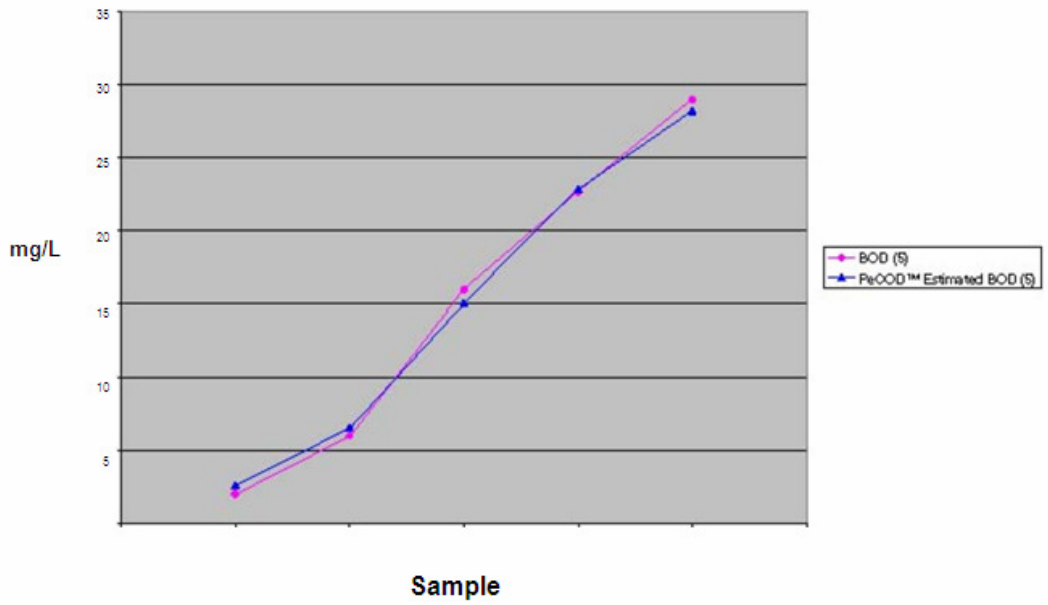

Figure 5: Comparative concentration data at a Sugar Refinery for BOD5 and Estimated BOD5 using PeCOD COD analysis

CONCLUSIONS

The ability of the PeCOD analyzer to reliably relate COD to BOD5, 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 and has been shown to provide a good representation of the organic load for both total organics and the organics available for biological consumption. This rapid COD method therefore provides the benefit of more continuous organic monitoring to ensure constant compliance with regulations, and its function as a BOD screening tool greatly reduces the number of dilutions required for BOD analysis. Additionally, utilizing Man-Tech's fully automated PC-BOD/COD Duo system offers a simple and efficient way to obtain results for COD, estimated BOD, and BOD5 faster than ever before.

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