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PeCOD Application Note #1

Municipal Wastewater

Introduction:

Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) are important 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. The PeCOD® method for COD analysis is a new technology that uses photoactive TiO_2 nanomaterials that directly measures the amount of oxidizable material in a sample. Unlike the standard dichromate method for COD analysis, this new method is fast (5-10 minutes per sample) and it eliminates the need for hazardous chemicals, which helps ensure the safety of laboratory staff, reduces disposal costs, and helps companies meet green initiatives.

The PeCOD® method for COD analysis is well suited to the waste water industry since the fast results obtained helps provide information important for process monitoring and control. Constant COD monitoring can protect wastewater treatment plants from high COD events by providing advance notice of any problem streams. It also provides the opportunity for plant optimization. Aeration and power consumption used in the process for COD removal can be fine-tuned based on the requirements of the plant, rather than constantly running at a level higher than necessary to allow for the possibility of high COD loads. Event monitoring will also improve the environmental performance of a plant and lower discharge costs.

This document describes the application of the PeCOD® COD Analyzer for the wastewater industry, focusing on the City of Cincinnati who is a current PeCOD enduser. This particular municipality has a population over two million people and therefore is a good representation of other wastewater treatment plants.

Sample Matrix: Wastewater; various locations along the sewage treatment process.

Concentration Range: Variable; This enduser reports COD values ranging from 0 – 250mg/L.

Apparatus:

Note: Apparatus listed below is for a laboratory unit. Additional hardware can be added for a more automated COD solution. An online COD analyzer is also available for continuous monitoring of COD at specific process locations.

1. PeCOD® Laboratory/Portable COD Analyzer (L100)
2. MANTECH software and interface for complete control of PeCOD® L100.

Optional add-ons for COD automation:
1. MANTECH AutoMax73 sampler
2. Patented dosing pump for automatic electrolyte addition
3. PC-Titrate TitraSip for automatic sample pipetting and pH-adjustment
4. Reagent addition pump for automatic sample dilution

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Additional Equipment:
1. System controller with Labterm installed
2. Sensors for PeCOD® COD Analyzers, pack of 5.
3. Battery and carrying case for portable use.
4. PeCOD® Single Range Starter Kit, BLUE Range (<25mg/L)
5. PeCOD® Single Range Starter Kit, GREEN Range (<150mg/L)
6. PeCOD® Single Range Starter Kit, YELLOW Range (<1500mg/L)
7. PeCOD® Single Range Starter Kit, RED Range (<15000mg/L)

Reagents:

1. Premium Electrolyte solution – BLUE Range, 1L
2. Premium Electrolyte solution – GREEN Range, 1L
3. Premium Electrolyte solution – YELLOW Range, 1L
4. Premium Electrolyte solution – RED Range, 1L
5. Calibrant Solution – BLUE Range, 1L
6. Calibrant Solution – GREEN Range, 1L
7. Calibrant Solution – YELLOW Range, 1L
8. Calibrant Solution – RED Range, 1L
9. Deionized water for rinsing, dilutions and blank preparation

Procedure:

Note: The procedure listed below refers to a stand alone PeCOD® COD system. The MANTECH PC-Titrate automated COD system option eliminates many sample preparation steps and allows for multiple samples to be analyzed together in one batch without user intervention.

Calibration:

1. Pipette the appropriate amount of calibrant and electrolyte into a tube according to the desired analysis range. Swirl to mix.
2. Place the port A line into solution and prime a few times.
3. Run two calibrations to properly hydrate and calibrate the sensor. Results will be displayed on the screen when the calibrations are complete.

Sample Preparation:

1. If samples contain large particles, they should be filtered with a 50µm filter to avoid clogging the PeCOD® COD Analyzer.
2. If samples have been preserved with acid, they must be neutralized to a pH range of 4-10 with NaOH before analysis.
3. If necessary, samples can be diluted with DI water prior to analysis to allow for the measurement of extremely high COD samples, or to reduce the effects of interferences.

Sample Analysis:

1. Pipette the appropriate amount of sample and electrolyte into a tube according to the desired analysis range. Swirl to mix.
2. Place the port A line into solution and prime a few times.
3. Run the sample. Results will be displayed on the screen once oxidation is complete.

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Results and Discussion:

The City of Cincinnati uses the PeCOD® regularly as a BOD screening tool. They also have two MANTECH automated BOD systems which are used for reporting final numbers, but the ability to pre-screen their samples on the PeCOD® helps reduce the number of dilutions required. They have run a number of their samples through comparison studies alongside the dichromate COD test and have actually found that PeCOD® COD tends to correlate better with BOD than dichromate COD values.

Below are charts demonstrating the correlation observed between Dichromate COD, PeCOD® COD and BOD for influent, effluent, secondary combined and final samples analyzed by this municipality.

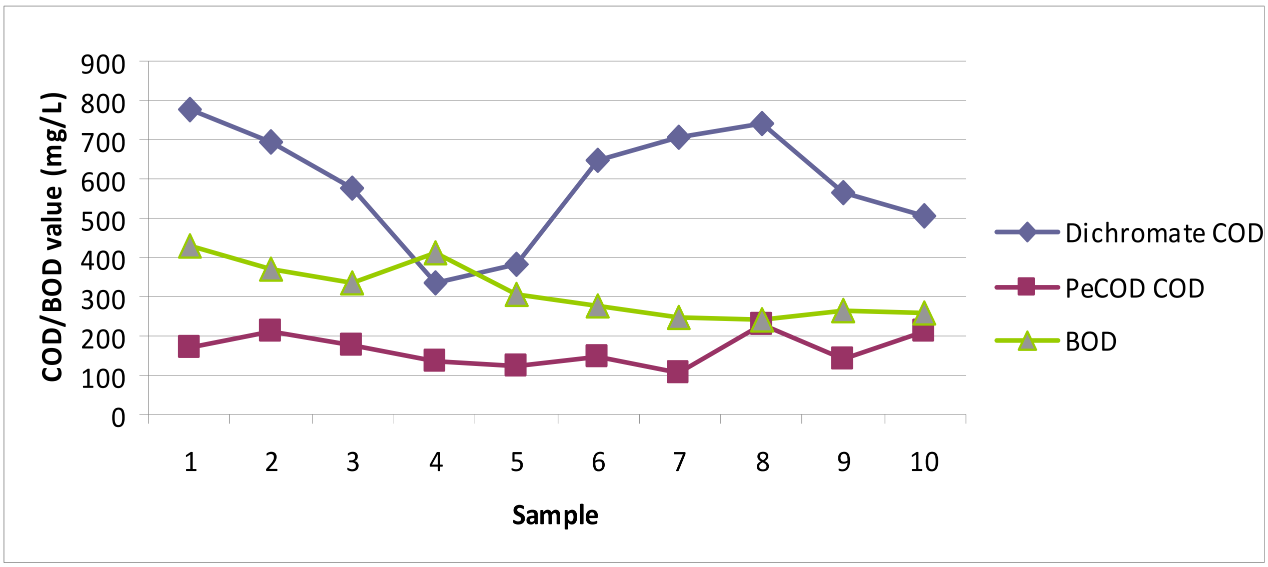

Figure 1: Plot of Dichromate COD, PeCOD® COD and BOD for a US Municipal Treatment Plant influent sample. A similar pattern should be observed for each trend line, which is apparent for PeCOD® COD and BOD, while Dichromate COD results are more variable.

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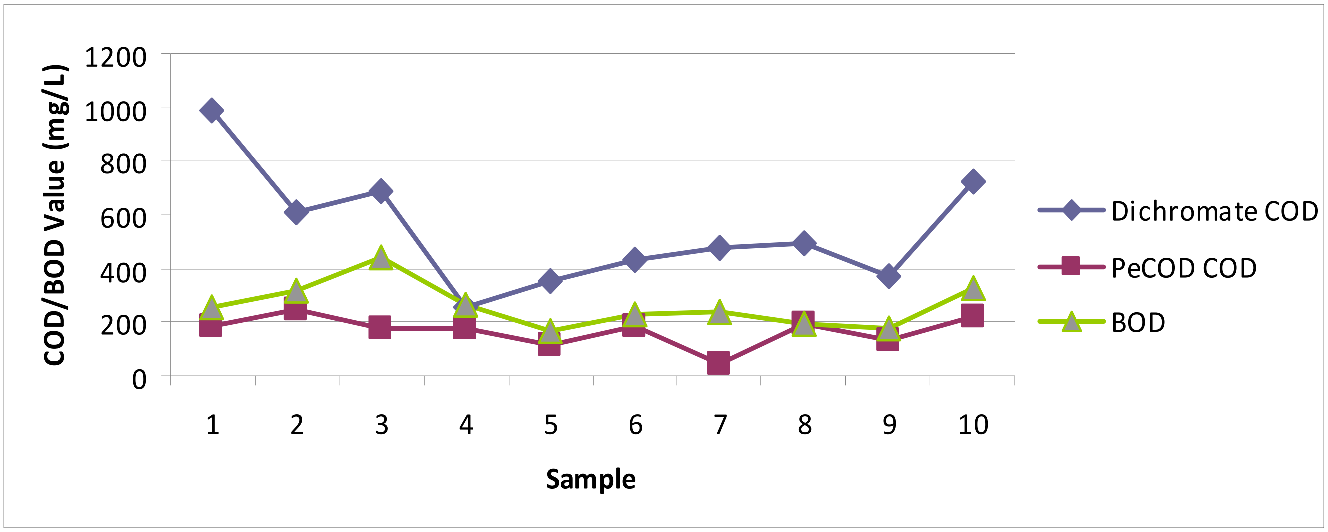

Figure 2: Plot of Dichromate COD, PeCOD® COD and BOD for a US Municipal Treatment Plant effluent sample. PeCOD® COD demonstrates a much stronger correlation to BOD than Dichromate COD values and in fact are almost equal.

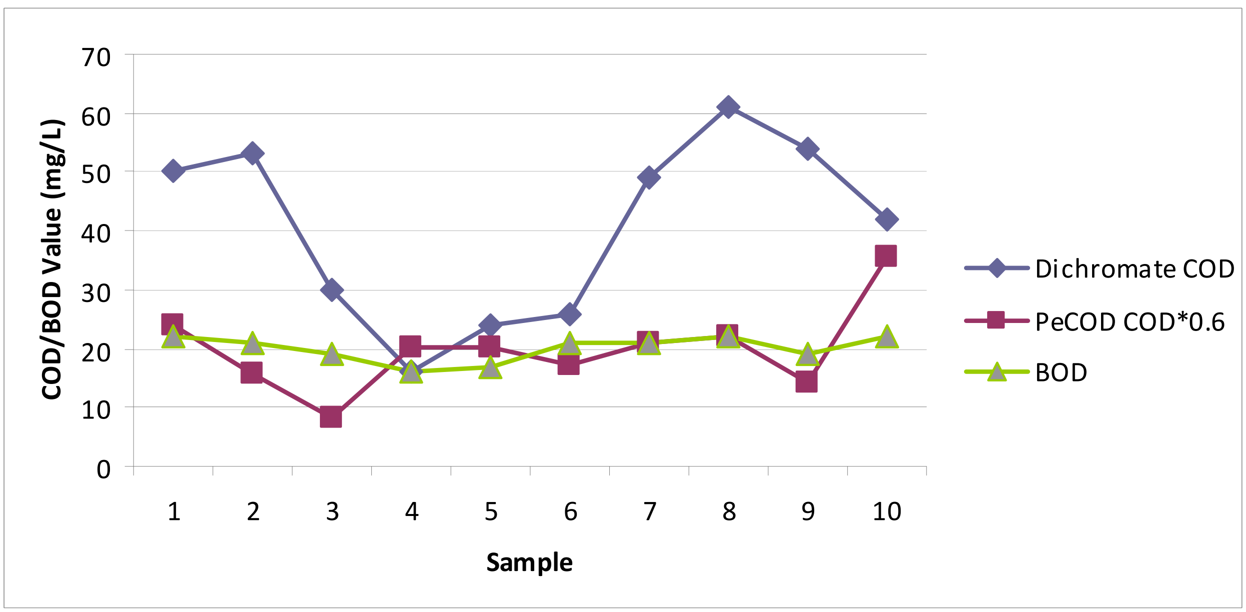

Figure 3: Plot of BOD, Dichromate COD and PeCOD® COD with a factor of 0.6 applied to PeCOD values for a secondary combined sample from a US Municipal Treatment Plant. This factor was applied to COD values as it provides very close estimations of BOD for most of the samples. As noted by the enduser, 2 small outliers may be observed in this data set because of extremely dark and turbid samples which may make representative sampling more difficult.

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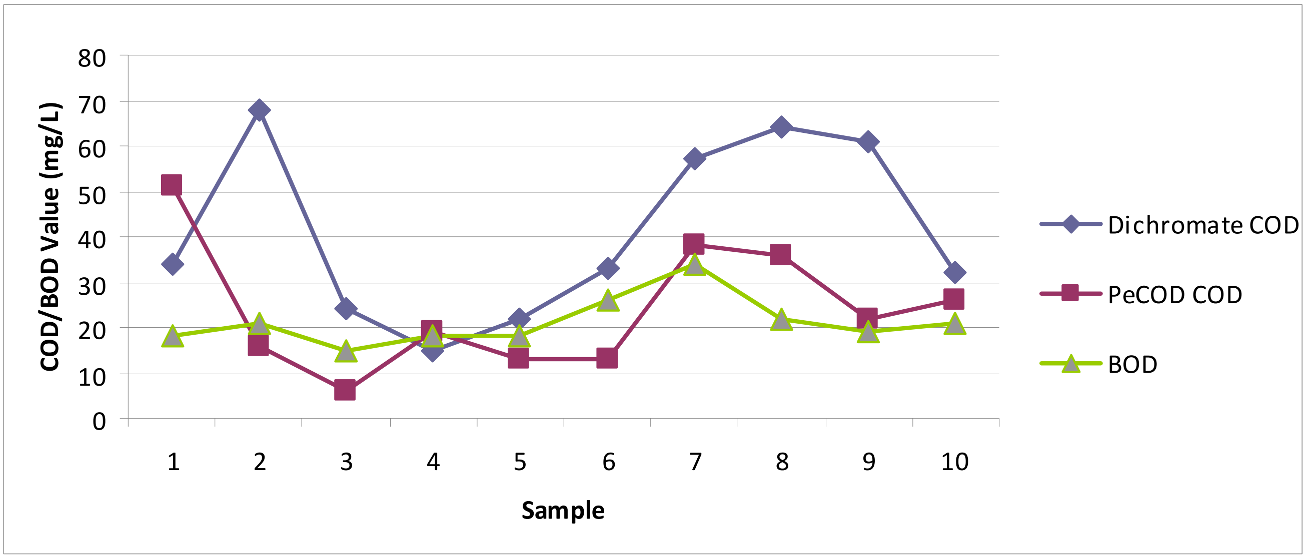

Figure 4: Plot of Dichromate COD, PeCOD® COD and BOD for a US Municipal Treatment Plant final sample. A good correlation is observed between all trends, with PeCOD® COD and BOD showing an excellent correlation.

These graphs demonstrate the excellent correlation observed between PeCOD® COD and BOD. In all cases, the correlation observed is stronger than that between dichromate COD and BOD. This means that the PeCOD® will give the treatment plant accurate and valuable process control information, and in a fraction of the time required for either the dichromate COD or BOD tests. It will also provide a more accurate estimate of BOD, meaning that fewer dilutions will be required.

As apparent from the curves, PeCOD® COD tends to report a lower value than dichromate COD. This is because PeCOD® COD reports soluble COD as opposed to total COD which is reported by the dichromate method. Raw wastewater samples may contain large amounts of solids which, when analyzed utilizing the dichromate method, are broken down during digestion and therefore end up contributing to the final COD. Since most of the solids are typically removed during the first stage of treatment, they actually have a low impact on the energy requirements of the secondary phase. This means that in the wastewater industry, soluble COD is actually a better indicator of the treatment process than total COD. It is also more representative of BOD since digestion steps are not required for BOD testing either. This is the reason behind the strong correlation between PeCOD® COD and BOD. Additionally, since the dichromate test is unable to differentiate between soluble and total COD, the PeCOD® is actually providing another valuable result that municipalities have never had access to before.

Conclusion

While both BOD and COD are core tests that are an integral part of all water quality management programs, waiting five days for BOD results is unrealistic for providing process control information. While the dichromate COD test is an improvement in speed over the BOD method, it still takes 2-3 hours to run and requires the use of hazardous chemicals. The cost of analysis is expensive and the requirement for hazardous waste disposals only adds to the expense. The PeCOD® requires only a simple electrolyte solution and sugar-based calibrant to run, consumable requirements are low and inexpensive, and accurate and precise results are generated in only 5-10 minutes. The PeCOD® is therefore ideal for the wastewater industry as it provides the benefit of more continuous organic monitoring, ensuring constant compliance with regulations. Additionally, its function as a BOD screening tool greatly reduces the number of dilutions required for BOD analysis.

Hints and Suggestions

1. The PeCOD® is also available as an online COD analyzer (P100 model) which is used for unattended monitoring. Results are communicated using a 4-20mA current loop that can interface to most control systems. The system is programmed to automatically calibrate and run samples at user defined intervals. It requires power, water and compressed air which is used to backflush the sampling probe (which has a 50um screen on the end to filter out solids) to keep it clear and unblocked. This is done automatically after every sample and ensures that the sample screen is kept clean and free of growths, which is especially important for extremely dirty samples like raw sewage.

2. The PeCOD® AssayPlus is a fully automated chemical oxygen demand system, ideal for those with higher sample loads. This utilizes the laboratory unit along with a 73-position AutoMax autosampler and a dosing pump for the automatic addition of electrolyte. Samples are loaded into the autosampler by the user and the system automates all sample preparation and analysis steps.

3. Upgrades to the PeCOD® AssayPlus include options for pH adjustment, auto-dilution of samples and multi-parameter analysis. The addition of a TitraSip module to the system means that preserved samples can be automatically adjusted to within the appropriate pH range, and high COD samples can be automatically diluted prior to analysis. Furthermore, if the initial COD result is reported beyond a predetermined value, the system is able to further dilute the sample and immediately re-analyse. In addition to COD automation, additional parameters such as pH, alkalinity, turbidity, etc. can be added to the system and analysed from the same sample tube if desired.

4. The PC-BOD/COD Duo is a dual platform system combining the PeCOD® AssayPlus with PC-BOD. This allows for both the automated analysis of chemical oxygen demand using the new PeCOD® technology, as well as biochemical oxygen demand analysis following 21st Edition Standard Methods. COD is analyzed first in order to obtain the estimated BOD values, which helps determine the appropriate dilution factor to use during BOD analysis. Following a simple swap of autosampler racks and probes, BOD analysis can then proceed. Rather than two separate systems, the PC-BOD/COD Duo combines these methods into one efficient automated system providing a more effective utilization of laboratory equipment.