

## City of Cincinnati Case Study – An Effective and Reliable BOD Estimate with a New, Rapid COD Measurement



***ManSci Inc.***

The City of Cincinnati, a current PeCOD user , utilizes the system for fast and reliable BOD estimations

# INTRODUCTION

## Objectives

This paper describes the relevancy of the PeCOD COD Analyzer for the wastewater industry. PeCOD is an alternative means to standard COD methods based on photoelectrochemical oxidation in a microcell. The paper focuses on the City of Cincinnati, a current PeCOD user who utilizes their system for fast and reliable BOD estimations.

## Background

### BOD vs. COD

- Both BOD and COD are ubiquitous measurements of overall water quality
- Among the most diagnostic parameters for the determination of water quality in natural waterways and waste streams.

#### Chemical Oxygen Demand (COD)

- Measures the equivalent amount of oxygen required to chemically oxidize the organic compounds in water

#### Biological Oxygen Demand (BOD)

- Measures the equivalent amount of oxygen required to biologically (microbes) oxidize the organic compounds in water

### Regulatory Uses

- Both COD and BOD are among the most common generic indices used to assess aquatic organic pollution, with BOD often being used to evaluate the biodegradable fraction, and COD the total organic pollution load of waters contaminated by reductive pollutants.
- EPAs regulate environmental compliance of industry and public utilities (WWTPs) to water pollution limitations using COD or BOD<sub>5</sub>.

### Non-Regulatory Uses

- Industry uses COD & BOD<sub>5</sub> internally for process monitoring and process refinement

### The Measurement of COD & BOD

Both COD & BOD involve a 2 step process;

#### Step 1 - Oxidation of organic matter

- BOD – 5 days with biological matter
- COD – 2 hr Wet chemistry (acid, heat, pressure, catalyst with  $E^{\circ} = +1.9\text{v}$ )
- PeCOD COD – 5 to 10 min Photocatalyst (UV excited semiconductor with  $E^{\circ} = +3.2\text{v}$ )

#### Step 2 - Measurement of extent of oxidation

- BOD<sub>5</sub> – Direct measurement of uptake of O<sub>2</sub> by micro-organisms over 5 days
- COD – Wet Chemistry – indirect measurement of OD via electrons consumed in reducing Cr<sup>6+</sup> to Cr<sup>3+</sup>
- PeCOD COD – Electrochemistry – direct measurement of OD via in situ measurement of electrons generated during oxidation process

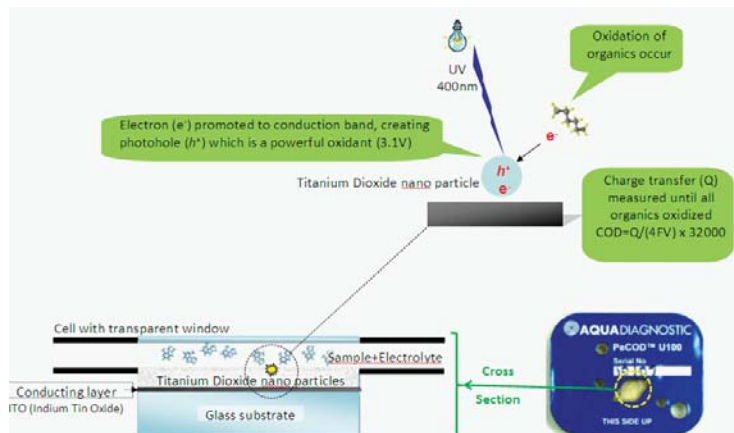
### PeCOD Method for COD Analysis

PeCOD<sup>®</sup> is a new technology

- Oxidant = UV-illuminated titanium dioxide
- Green & Safe : uses only an electrolyte
  - no silver, mercury, dichromate or concentrated acid
- Fast : 8-10 minute analysis
- Accurate : uncertainty typically < 5%
- Low Cost : \$1.00 - \$1.50/analysis, no disposal costs

Fast, Green, Accurate, Inexpensive

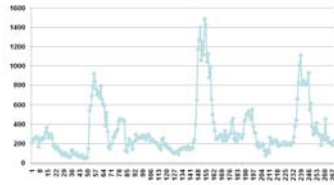
### PeCOD Sensor Technology



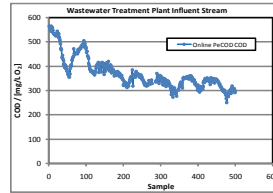
# APPLICATIONS

## Process Control: WWT Plant Protection & Optimization

- Constant COD monitoring can protect wastewater treatment plants from high COD events by providing advance notice of any problem streams
- Provides the opportunity for plant optimization as 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 improves the environmental performance of a plant and may help lower discharge costs.



Online monitoring of COD in 15 minute cycles in the primary clarifier effluent at a WWTP. Major fluctuations in COD would be hard to see without continuous monitoring.



Online Monitoring of COD in 15 minute cycles over 6 days at the secondary stage influent of a WWTP. The expected regular diurnal variations are apparent, however it started high and then declined which was the result of someone illegally dumping high COD industrial waste into a public drain

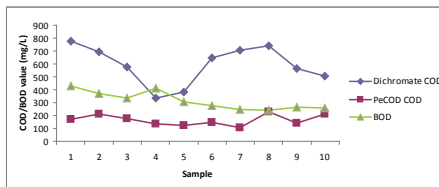
## BOD Screening:

- The continuous monitoring of organic load is becoming essential to comply with regulatory requirements. The standard BOD test requires five days to complete and is therefore unable to provide this information in a timely manner, so COD is often used to provide an estimate of the biogeochemical interactions in waterways.
- The dichromate COD method is not without its limitations as it is expensive, slow, and requires the use of hazardous chemicals.
- The PeCOD method for COD analysis therefore becomes a desirable option for estimating BOD as it is fast & requires only a simple electrolyte solution (i.e. no hazardous chemicals needed).

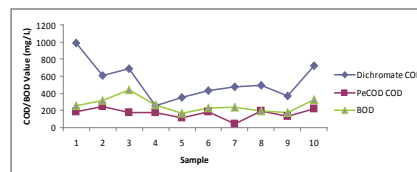
The City of Cincinnati, a municipality serving > 2 million people, is a current PeCOD enduser utilizing the system regularly as a BOD screening tool:

- The ability to quickly pre-screen their samples on the PeCOD reduces the number of dilutions required.
- Have two MANTECH automated BOD systems to report final numbers

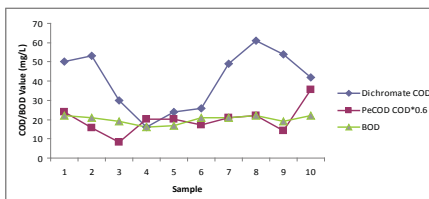
Comparison studies have been conducted for a number of samples (see graphs following)



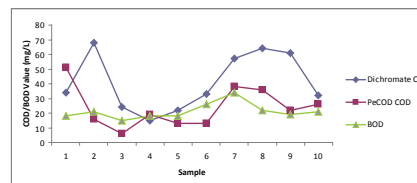
Plot of Dichromate COD, PeCOD COD and BOD for an influent sample. A similar pattern should be observed for each trend line, which is apparent for PeCOD COD and BOD, while Dichromate COD results are more variable.



Plot of Dichromate COD, PeCOD COD and BOD for an effluent sample. PeCOD COD demonstrates a much stronger correlation to BOD than Dichromate COD values and in fact are almost equal.



Plot of BOD, Dichromate COD and PeCOD COD with a factor of 0.6 applied to PeCOD values for a secondary combined sample. 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 makes representative sampling more difficult.



Plot of Dichromate COD, PeCOD COD and BOD for a final sample. A good correlation is observed between all trends, with PeCOD COD and BOD showing an excellent correlation.

- This study demonstrates the excellent correlation observed between PeCOD COD and BOD as evident from the graphs. In all cases, the correlation observed is stronger than that between dichromate COD and BOD.
- PeCOD COD is a better estimator of BOD since neither method requires the digestion step needed for dichromate COD analysis.
- PeCOD will give the treatment plant accurate and valuable process control information in a fraction of the time required for either the dichromate COD or BOD tests. With more reliable estimates of BOD as provided by the PeCOD, fewer dilutions are required.
- PeCOD COD tends to report a lower value than dichromate COD because PeCOD COD reports soluble COD as opposed to total COD.
- Raw wastewater samples may contain large amounts of solids which are broken down during the digestion step for dichromate analysis 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. Therefore, in the wastewater industry, soluble COD is actually a better indicator of the treatment process than total COD.
- The dichromate method is unable to differentiate between soluble and total COD, so the PeCOD is actually providing another valuable result that municipalities have never had access to before

# PRODUCTS

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- Laboratory Analyzer – Stand Alone
- Portable Field Analyzer
- On-line Analyzer
- Automated PeCOD, including the PC-BOD/COD Duo

## Laboratory/Portable Unit: L100

- Stand Alone unit
- Useful for smaller laboratories for quick sample analysis or on-the-spot checks in the field.
- Add a battery and carrying case for field use.



## On-line Unit: P100

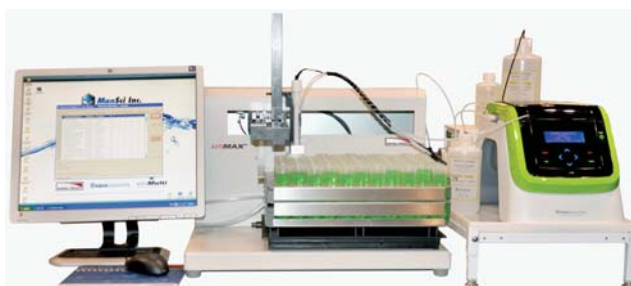
- Used for unattended monitoring; uses a 4-20mA current loop that can interface to most control systems
- Automatic regular calibration and sampling (user-defined intervals)
- Only requires replenishment of electrolyte reservoirs, and occasional replacement of sensor
- Requires power (110-240VAC), water and compressed air - used to backflush sampling probe to keep it clear and unblocked.



## Automated PeCOD: The PeCOD AssayPlus

- The PeCOD AssayPlus utilizes PC-Titrate software for all control and analysis functions, including sample preparation, analysis, reporting, and routine maintenance
- Combine the MANTECH automated PC-BOD system with the PeCOD AssayPlus = PC-BOD/COD Duo

- Allows for both the automated analysis of COD using the new PeCOD technology, as well as BOD following 21st Edition Standard Methods



- COD is analyzed first in order to obtain the estimated BOD values - determines the appropriate dilution factor to use during BOD analysis
- Following a batch of COD samples:
  - The COD-configured autosampler rack is replaced with the BOD rack which can accommodate up to twenty four 300mL bottles
  - The probe holder is swapped to include the dissolved oxygen probe, tips and the BOD stirrer
- BOD analysis can then occur:
  - Automatic addition of dilution water, seed and inhibitor (if required)
  - All rinsing and dissolved oxygen measurements are automated and can be viewed in real-time.
  - 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 quickly and easily viewed.
- The PC-BOD/COD system combines COD and BOD analysis into one efficient system providing a more effective utilization of laboratory equipment and bench space.

# SUMMARY

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Benefits of PeCOD Analysis Include:

- Low Analysis costs
- No use/disposal of toxic & hazardous reagents
- Protect regional WWTPs from high COD loads
- Save energy in WWTPs
- Fast and accurate BOD screening tool