

The Analysis of Photoelectrochemical Chemical Oxygen Demand (COD) Compared to Traditional COD and BOD



for Various Sample Matrices

## Introduction

Chemical Oxygen Demand (COD) is a measurement of the amount of oxygen required to chemically oxidize organic species in a sample. It is an important measure of organic matter in water, and is often used to estimate Biochemical Oxygen Demand (BOD). BOD is measured by the amount of oxygen consumed over five days, therefore it is unable to provide continuous monitoring of organic load.

The standard method for measuring COD uses



Dichromate and other hazardous chemicals at high temperature to digest organic carbon, and the analysis can take up to three hours.



**Figure 1.** Stand alone PeCOD Unit with sample port, blank port, and waste port.

MANTECH's PeCOD is a new technology that measures soluble COD using a photo electrochemical method. This unique approach utilizes UV activated Titanium Dioxide nanoparticles to oxidize soluble organics, and measure COD in real time. The Ontario Ministry of the Environment and Climate Change (MOECC) has published Method E3515, making the PeCOD technology an approved method for the determination of COD. All samples in Ontario requiring COD for compliance, enforcement and legal reasons now analyzed by PeCOD Method.

Sampling Location

Figure 3. Green Range PeCOD vs Low Range Dichromate Results for WWTP Samples from Primary Influent to Final Effluent

Municipal samples were collected from The City of Guelph WWTP. The PeCOD measures soluble COD, therefore the Dichromate method gave higher results for primary influent due to the digestion of insoluble organics that were not measured by the PeCOD, as seen in Figure 3. A strong correlation between PeCOD and Dichromate COD was observed at each sampling location. With the purchase of an automated PeCOD system, the City of Guelph WWTP has moved to 24 hour COD monitoring.

"The Laboratory Services Branch of the Ontario MOECC supports the development of new green technology. Analysis time was significantly reduced and the method *detection limit was 1 mg/L O2.*" - Vasile Furdui, Ph.D. Research Scientist, MOECC

Finished Floc Raw Filtered DOC—dissolved organic carbon, floc—flocculated water, peCOD—photoelectrochemical chemical oxygen demand, TOC—total organic carbon Error bars represent 95% confidence intervals with n = 3.

**Figure 5.** Comparison of PeCOD, TOC, and DOC during treatment of samples from Pockwock Lake in Halifax, Nova Scotia.

PeCOD has proven to be a useful tool for low COD surface and treated drinking water samples. The low detection limit of the PeCOD allows for comparisons to traditional natural organic matter (NOM) techniques such as total organic carbon (TOC) and dissolved organic carbon (DOC). Figure 5 demonstrates a higher resolution from the PeCOD, compared to TOC and DOC, due to the strong oxidizing potential of Titanium Dioxide.

""PeCOD routinely predicts major shifts (NOM, organics, DPB formation) through source water monitoring that is not seen with TOC or UV254." – Water Quality Analyst



## Industrial Waste Water



Figure 4. PeCOD vs Dichromate COD (CrCOD) for treated effluent samples from Clean Harbors WWTP

Clean Harbors is a waste water treatment facility that

## Conclusion

- PeCOD provides precise results when testing various sample matrices, and displays a strong correlation with traditional COD and BOD methods
- Results in 15 minutes
- Does not use Dichromate or other hazardous reagents
- Safe for the analyst and the environment
- MANTECH offers automated and online PeCOD systems for overall process optimization





Figure 2. Diagram of PeCOD sensor technology. UV activation causes TiO2 nanoparticles to become a powerful oxidant and react with organic species in the sample.

Various industries and sample types have been examined based on their applicability for use with the PeCOD, including influent and effluent waste from food and beverage manufacturers, pulp and paper mills, municipal waste water treatment, surface water, and drinking water.

generates safe effluent for discharge into municipal sewer systems. Figure 4 is data collected over a 3 month period from a variety of industries including automotive service industry, automotive manufacturing, primary steel industry, and chemical facilities. There is a strong correlation between the PeCOD technology and Dichromate COD for treated effluent samples. Clean Harbors also uses the PeCOD to estimate BOD to ensure they will meet the municipal requirements.

"Speed of results creates a more efficient process and really drives clean compliance for us which is critical." – Ian Culverwell, General Manager of Clean Harbors Guelph Facility



Figure 6. PeCOD online analyzer for direct connection to high flow water lines

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