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Mantech PeCOD

Athabasca River

Analysis of Surface Samples for Chemical Oxygen Demand via the PeCOD Method as Compared to Traditional Dichromate Method

Abstract

Water samples in the Athabasca watershed are regularly monitored to ensure water safety across the watershed. In this study, chemical oxygen demand (COD) was monitored to evaluate organic matter and to enhance current monitoring programs. Over an eight-month period, Mantech worked with Environment Canada's National Laboratory of Environmental Testing (NLET) to study a new automated innovation, the PeCOD, developed by MANTECH. This COD method utilizes a new technology, PeCOD, which is a photoelectrochemical technique that directly measures dissolved COD in a sample in approximately ten minutes, without the need for any hazardous chemicals[1]. Results obtained by the automated PeCOD system demonstrate that the COD measured using the PeCOD method validated a strong correlation to the COD measurement obtained by the traditional dichromate method.

Introduction

Between August 1 2012 and March 31 2013, Mantech collaborated with NLET on a project involving the analysis of river and pond water in the Athabasca watershed. There is concern over environmental pollution in this area, due to hydrocarbon-associated contamination arising from rivers flowing through natural bitumen deposits and from anthropogenic activities such as oil sands mining[2]. Results were compared for chemical oxygen demand (COD) when analyzed via the automated PeCOD system versus traditional dichromate method. The PeCOD is a new innovation manufactured by Mantech which enables the measurement of COD, from a single sample, in fifteen minutes or less. Due to the nature of the traditional COD method, this rapid capability has never been an option before.

COD is used as a measure of organic pollution, along with Biochemical Oxygen Demand (BOD)[3]. However, the standard BOD test requires five days to complete, and is therefore unable to provide continuous monitoring of organic load[3]. COD is therefore often used for BOD screening or as an alternative measure of organic pollution[3]. However, the traditional dichromate COD method utilizes hazardous and toxic materials, and has an analysis time of approximately three hours[3]. Additionally, the dichromate method struggles with samples with low COD. Most Standard Methods have a minimum detection limit of 50mg/L, although a detection limit of 5mg/L may be obtained utilizing method 5220B.4b with reduced levels of accuracy[3]. The PeCOD analyzes COD via the PeCOD COD method, which eliminates the need for hazardous chemicals, has a reporting limit of less than 1mg/L, and results can be obtained in approximately ten minutes[4].

The PeCOD COD method relies on green chemistry and nanotechnologies for determining dissolved COD in natural and wastewater samples in a simple, rapid, and direct way[1]. The PeCOD COD method utilizes the charge originating from oxidizing organic species contained in the sample to measure COD[1]. The core of the PeCOD technology is the sensor, which consists of a UV-activated nano-particulate titanium dioxide (TiO2) photocatalyst coupled to an external circuit[1].

When a sample analysis is initiated, the sample is introduced into the sensor, the TiO2 is irradiated by UV light, and a potential bias is applied[1]. The UV light creates a positive photo hole in the TiO2 sensor which is a very powerful oxidizing agent (+3.1 V) that will readily lead to the transfer of electrons from organic species in the cell[1]. TiO2 has a much higher oxidizing power compared to dichromate (the chemical potential of dichromate is E° = 1.6V), meaning that TiO2 is better able to break the bonds contained within difficult organic compounds and liberate electrons[1]. Since

dichromate has less energy available to it to perform this function, the method relies on additional help in the form of heat, pressure and sulfuric acid. It is because of this increased oxidizing power that PeCOD is better able to measure a number of important organics such as nicotinic acid, benzene, diethylamine, certain carboxylic acids, alcohol, and more[5].

The goal of this project was to compare the results of the accredited analysis for COD utilized within the laboratory (the dichromate method) to the PeCOD COD results, and evaluate the correlation of the PeCOD measurement to the measurement of BOD.

Materials and Methods

During the study period, surface water samples from the Athabasca region were regularly sent to NLET and given unique sample identification numbers. These samples were analyzed by both NLET in the laboratory by dichromate and PeCOD techniques for comparison.

The PeCOD system included an AutoMax122 autosampler with a 47-position 125mL cup rack, two TitraSip modules used for automatic pipetting of sample, rinsing and draining, two 48,000-step burettes, for automatic pH adjustment of preserved COD samples, two dosing pumps, including one for deionized (DI) water for automatic sample dilutions and one for electrolyte addition for the PeCOD COD test, as well as a PeCOD COD analyzer.

COD was measured at NLET colorimetrically following digestion with potassium dichromate according to Standard Method 5220 D. Particles were allowed to settle out of solution prior to sampling in order to obtain a soluble COD result that can be correlated to the PeCOD COD result.

Samples were also thoroughly shaken prior to a duplicate sample to obtain a total COD result. Soluble COD was also determined photoelectrochemically utilizing the PeCOD COD analyzer connected to the Mantech PeCOD Multi automated system.

The PeCOD analyser can be run in one of four COD concentration ranges, including blue (<25mg/L), green (<150mg/L), yellow (<1500mg/L) and red (<15000mg/L), chosen according to the estimated COD concentration of the sample. The surface water samples were determined to be in the 100mg/L range, so the green range was selected for regular daily measurements.

The PeCOD COD analyser was calibrated twice daily with a 120mg/L sorbitol solution mixed in a 1:1 ratio with electrolyte. Quality control checks were performed both prior to and at the completion of a run of samples to verify accuracy. Sample bottles were shaken thoroughly before being poured into beakers and particles were allowed to settle out of solution to avoid clogging the sample needle, TitraSip pumps and PeCOD analyser fluidics.

Results

Surface water samples were collected between August 2 2012 and October 18 2012, with each sample analyzed utilizing the PeCOD method on the automated system, and via the traditional dichromate method in the NLET laboratory. For comparison purposes, results for soluble dichromate COD were also plotted against total COD. Results for each parameter were compared, and all data obtained is presented in Figures 1 to 4.

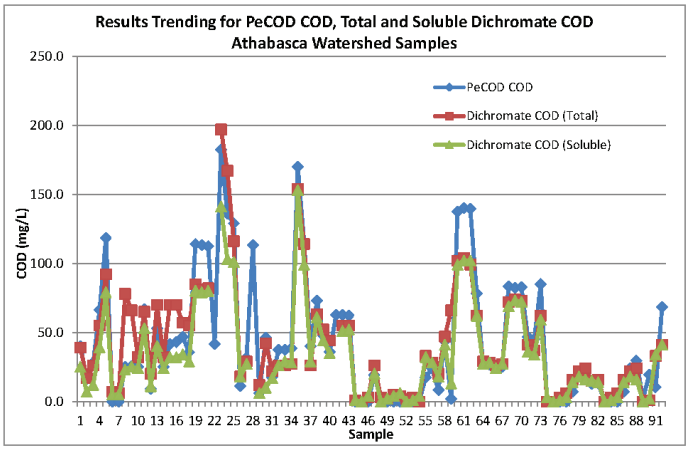

Figure 1: Plot of PeCOD COD, Soluble Dichromate COD, and Total Dichromate COD for various Athabasca samples collected between August 2 2012 and October 18 2012

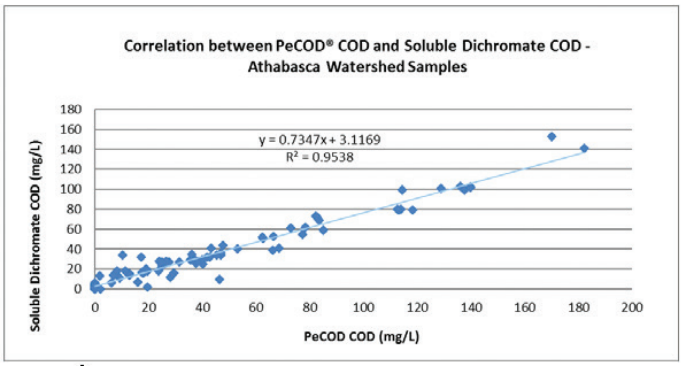

Figure 2: Scatter Plot of PeCOD COD against Soluble Dichromate COD for Athabasca samples analyzed between August 2 2012 and October 18 2012

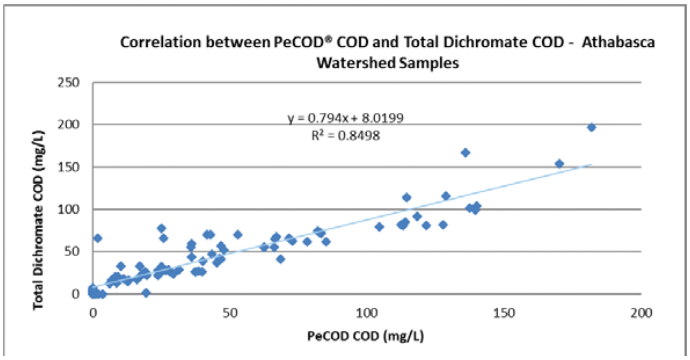

Figure 3: Scatter Plot of PeCOD COD against Total Dichromate COD for Athabasca samples analyzed between August 2 2012 and October 18 2012

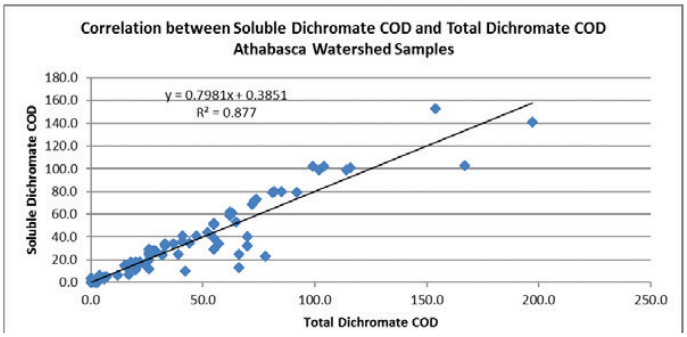

Figure 4: Scatter Plot of Total Dichromate COD against Soluble Dichromate COD for Athabasca samples analyzed between August 2 2012 and October 18 2012

Discussion

As evident from Figures 1 through 4, a strong correlation is evident between PeCOD COD and dichromate COD. While the soluble results correlated more closely (as expected), a reasonable correlation is also observed between PeCOD COD and total COD, with outliers due mainly to sampling differences. The PeCOD COD Method measures soluble COD. As demonstrated in Figure 4, this difference can also be seen when comparing the soluble dichromate COD results against the total COD.

This means that the PeCOD will provide important information on the quality of surface waters, and in a fraction of the time required for either the dichromate COD or BOD tests, without the need for any hazardous chemicals.

It was noted that the PeCOD often reported higher results than the dichromate method, especially when comparing the PeCOD results against soluble dichromate COD. To test the significance of the differences, paired t-tests were performed based on the null hypothesis that there was no significant difference between the data sets. The t-test comparing the PeCOD results against the total dichromate results produced a t-value of 0.7 on 96 degrees of freedom. This resulted in a p-value of 0.4856 indicating that there is no statistically significant difference observed between the two data sets. In other words, the PeCOD and total dichromate results produced equivalent results.

The t-test comparing PeCOD COD against soluble dichromate COD resulted in a t-value of 5.3 on 86 degrees of freedom, producing a p value of <0.0001. This indicates that there is a statistically significant difference between the two sets of data, so the PeCOD is in fact reporting higher results. For comparison purposes, a t-test was also performed to compare the significance of differences observed between the total and soluble dichromate COD results. The t-value obtained was 5.3 on 85 degrees of freedom, resulting in a p value of <0.0001 indicating that there is a statistically significant difference between the two sets of data. While it is expected that there would be a difference between soluble and total COD results, it was not expected to see a difference between soluble dichromate COD and PeCOD COD.

As outlined earlier, the PeCOD COD method utilizes a titanium dioxide based sensor which has a higher oxidation potential (3.1V) than dichromate (1.6V), meaning that some difficult organics may be oxidized more efficiently by the PeCOD method than by the dichromate method. Not surprisingly, the PeCOD COD results are reporting higher than soluble dichromate COD but equivalent to total dichromate COD.

Since the PeCOD measures soluble COD it would be expected that total dichromate COD results would report higher results than the PeCOD, especially considering that a significant difference was observed between soluble and total dichromate COD results. As evident from the results of the paired t-test for PeCOD against total dichromate however, this is not the case.

One explanation for this is that whatever the reason for the soluble dichromate results reporting lower than expected is causing the total dichromate COD results to report lower as well, bringing it closer in line with the PeCOD results. The key factor however is that high and low patterns are still observed (confirmed from Figure 1) and the PeCOD can accurately correlate to dichromate COD results with a high degree of certainty. With an R2 value of 0.9491 (1.0 is a perfect relationship) for soluble COD and 0.8270 for total COD, it is evident that this is the case.

Conclusion

The PeCOD system has demonstrated its ability to reliably analyze surface waters in the Athabasca Watershed for PeCOD COD. It provides the same accurate and precise results as manual methods, with the advantages that it also allows the laboratory to analyze multiple samples unattended, including blanks and QC checks, at user-specified intervals. It also frees up operator time and automatically logs sample results, exporting to laboratory information management systems if required. Furthermore, the PeCOD COD method is ideal for measuring COD in surface waters as it provides the benefit of continuous organic monitoring, providing crucial information on the presence of potential environmental contamination much faster and safer than ever before. This allows for faster response times if a spill is detected, allowing action to be taken before groundwater is contaminated. Additionally, the PeCOD method has a lower detection limit than the dichromate COD method, making it ideal for analyzing the low levels of COD that are typically present in surface waters, and it does not require the use of any hazardous materials. As a result of these advantages, the PeCOD technology is available for laboratory, field (portable) and online testing environments. The method is now supported by the Ministry of Environment and Climate Change's method

E3515vi and was recently approved as an alternate method in the updated MOECC's effluent protocol Titled the Municipal/Industrial Strategy for Abatement7 (MISA – May 2016).

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