Photo

Name of the presenting author:
Company:
Address:
Postcode/Town:
Country:
Email:

Analysis of peCOD Technology and Comparison to Dichromate Method

Abstract

The main objective of this report was to determine if a correlation exists between peCOD technology and the dichromate method of estimating Chemical Oxygen Demand (COD). Additional investigations described in this report were: to identify whether particle size in water samples affects the estimate of COD obtained by peCOD analysis and, to identify whether peCOD analysis is accurate when testing COD standards. Various wastewater samples were collected and tested using the peCOD and dichromate COD methods; additionally, COD standards were prepared and tested to ensure precision of the estimation methods. The peCOD COD procedure does not require the use of any hazardous materials and disposal methods are inexpensive and straightforward.

After the wastewater samples were tested and analyzed, it was discovered that a relationship exists between estimates of COD obtained using peCOD when compared to dichromate. Therefore, it was determined that peCOD is a suitable technology for the analysis of wastewater samples. Many of these wastewater samples tested using peCOD contained a large solids content, and it was concluded that peCOD cannot test any water samples with large solids content, or containing large particles, without prior filtration. In regard to the analysis of COD standard solutions, peCOD is more accurate and precise than the dichromate method at estimating the value of COD.

TABLE OF CONTENTS

INTRODUCTION

Oxygen demand is an important measure of organic matter in water. There are multiple methods of estimating oxygen demand, including BOD, COD and TOC. Since Total Organic Carbon (TOC) can only measure oxygen demand indirectly, it is difficult to relate TOC findings to BOD or COD. Biochemical Oxygen Demand (BOD) is determined by measuring the amount of oxygen consumed by microorganisms in a water sample. The amount of oxygen consumed is measured over a five day period, which means the results of a BOD test cannot accurately assess the water quality at a given instant in time. The standard Chemical Oxygen Demand (COD) test, typically analyzed via the dichromate method, uses strong chemicals to oxidize organic carbon in water into CO_2 and H_2O. The oxygen demand is determined by the amount of oxidant consumed, using a spectrophotometer or titration method. The dichromate test requires approximately three hours for completion and uses many hazardous chemicals.

PeCOD is a new technology which measures soluble COD (sCOD) in various water samples. The name peCOD originates from the photo-electrochemical method by which the device measures COD. peCOD was developed as a rapid, easy-to-use, and environmentally friendly technology which could replace dichromate as the standard method of measuring COD. peCOD utilizes a calibrant solution prepared with sorbitol and an electrolyte prepared with lithium nitrate. Used in sample preparation these chemicals are safe to handle and can provide a true soluble COD result in less than 15 minutes.

MANTECH INC, the manufacturer of the peCOD, loaned a standalone, manually operated laboratory unit (L100) to the University of Guelph for the analysis of various water and waste water samples. The peCOD device was installed in Room 1105 in the Thornborough building. This peCOD device has the ability to measure groundwater, surface water and waste water samples in four different ranges - blue, green, yellow and red range. The blue range measures COD from 0 to 25mg/L, the green range measures from 0-150mg/L, the yellow range measures 0-1500mg/L, while the red range measures 0-15000mg/L.

The principal purpose of this project was to determine if a correlation between peCOD COD (measures soluble COD only), and dichromate COD (can measure total or soluble COD), could be developed. Soluble COD (sCOD) is the COD value for a sample that has been filtered, meaning the COD of suspended solids is not taken into account, while total COD (tCOD) includes the soluble portion plus the oxygen demand of suspended solids present in the water sample that can be chemically oxidized. The other component of this project was to identify whether particle size in the water samples affect the estimate of COD provided by the peCOD device. This correlation would allow an estimate of tCOD to be made from sCOD, obtained rapidly and safely, from a peCOD device. In order to satisfy the scope of investigations involved in this project, various wastewater samples were tested in the green and yellow ranges for peCOD, as well as low and high ranges of dichromate COD test vials.

REVIEW OF PREVIOUS STUDIES

In 2008, Aqua Diagnostic conducted a study[1] comparing their peCOD technology with 5-day Biochemical Oxygen Demand (BOD_5) measurements. BOD_5 measures the oxygen demand over a five day period as exerted by organic pollutants present in water. A correlation often exists between COD and BOD, with BOD usually equating to between 0.4 – 0.6 that of the COD value. The actual factor observed however depends heavily on sample matrix. The peCOD testing was conducted using an electrolyte solution consisting of 2M $NaNO_3$ and a sample volume of 10µL to be analysed. According to the report, 20 peCOD analyses per hour could be conducted. The first test was performed on wastewater samples from a brewery, where it was found that when COD values are multiplied by 0.55, an estimate of BOD_5 can be determined with 95% confidence. The second round of testing was performed at a sugar mill where, once again, a multiplication factor of 0.55 to convert COD to BOD_5 was observed. The final oxygen demand testing was performed on water samples from a sugar refinery, which contained a high chloride content. In this case it was found that COD values provide an estimate of BOD_5 when multiplied by 0.68. The difference observed between the correlation factors may be related to the high chloride content in the sugar refinery waste, or may simply be due to a difference in sample matrices. It was also found that dichromate COD values could not be related to BOD values when samples contained high chloride content. The conclusions were that the peCOD technology can accurately measure oxygen demand in real-time and detect concentrations lower than 1ppm. Additionally, it was found that peCOD COD correlated well with biological consumption of organics (BOD) in a water sample when chloride content was low.

The Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) is a regulation which works in tandem with the European Chemicals Agency (ECHA), to improve protection of human health and the environment from chemical risks[2]. REACH applies to all chemical substances used in the European Union (EU), and if a chemical is determined to be hazardous to a certain extent, that chemical is known as a Substance of Very High Concern (SVHC). SVHCs often are included in the ECHA Authorisation List. When a chemical is placed on an authorisation list, it means that any manufacturer, importer or downstream user of the chemical within the EU has to fill out an application for authorisation in order to use the chemical. The European Commission makes the decision whether the application for authorisation is accepted or not. Each chemical that is present on the Authorisation List has a Latest Application Date that users of the chemicals must apply by in order to use the chemical in the future. Recently, potassium dichromate, which is used in the dichromate method of estimating COD, has been placed on the ECHA authorisation list. The Latest Application Date for potassium dichromate is March 21st, 2016, while the Sunset Date for this chemical is September 21st, 2017. If a user of a certain chemical has not submitted their application before the Sunset Date, then they will not be permitted to use the substance in question. If an application for authorisation is submitted between the Latest Application Date and the Sunset Date, then the application will be reviewed in time, however the applicant will not have the ability to use the substance until a final decision has been made by the European Commission. The inclusion of potassium dichromate on this authorisation list indicates how severe the hazards are when performing the dichromate method of measuring COD, and its use in Europe will decrease dramatically in the coming years.

Michael Esler, Kumiko Chinen, Heather Higginbotham and Priyanka Reddy tested Aqua Diagnostic's peCOD technology in 2010[3], regarding its proficiency at testing the oxygen demand

of laboratory-prepared standard solutions of 34 organic species. The study compared peCOD to the standard dichromate method. The peCOD and dichromate COD methods used in this study follow the same procedures and materials as those same methods used in the remainder of this report. The peCOD was calibrated using a sorbitol solution, while the dichromate methodology involved calibration with KHP. After each organic species was tested via both the dichromate and peCOD COD methods at various concentrations, the data was plotted against ThOD. The gradient of these graphs, m=d(COD)/d(ThOD), was then calculated. Ideal results for this study would have produced a gradient close to m=1.0 for each organic species, therefore the gradient values were sorted into categories. It was found that the majority of organic species had a gradient of $0.8<m<1.2$ for both methods. The dichromate COD method measured 5 organics outside this range, while the peCOD COD method measured only 2 organics that fell outside this range. In addition, the results obtained via the dichromate COD method exhibited approximately twice as much uncertainty compared to the peCOD COD method when correlating the experimental standard solution data with the ThOD.

Dr. Vasile Furdi, from the Ontario Ministry of the Environment described the MOE's findings when analyzing surface water samples using peCOD technology[4]. The peCOD COD results for surface water and wastewater samples were compared to ThOD and dichromate COD. When the peCOD results were plotted against ThOD, the R^2 value of the line of best fit was 0.990, a strong correlation. The plot of the peCOD COD results against the dichromate results produced an R^2 value of 0.974. It was also found that the precision of the results for water samples when run in duplicate using peCOD was good, with a 4.3% average relative difference calculated. In addition to the water samples, a reference material with an expected COD of 103mg/L was tested by both the peCOD and dichromate COD methods. The percentage relative standard deviation was identical for both methods. The conclusions of this presentation stated that the peCOD is fast and reliable when analysing individual water samples, as well as highlighting the fact that it does not use any toxic or hazardous reagents. This validation study has led to the publication of a new method by the MOE which has replaced the standard dichromate COD method, thus eliminating environmentally hazardous waste and the use of toxic reagents[5].

MANTECH INC worked with Environment Canada's National Laboratory of Environmental Testing (NLET) to analyze the peCOD Multi System and compare it to traditional laboratory techniques[6]. The fully automated system included a peCOD for the analysis of COD, although conductivity, pH and alkalinity were also measured. The project involved the regular collection and analysis of surface water samples from the Athabasca watershed. Results indicated that peCOD COD correlated well with dichromate COD, although the peCOD can provide crucial information on contamination faster than the dichromate COD method. This means that the peCOD technology could be a useful monitoring device so that if a spill occurs that contaminates nearby surface waters, action can be taken to clean the spill before it infiltrates into the ground water.

Amina Stoddart and Graham Gagnon from Dalhousie University performed a study that investigated the potential of using the peCOD to measure model organic compounds (carboxylic acids and amino acids) commonly found in surface drinking water sources and water from four drinking water treatment plants in Nova Scotia, Canada[7]. COD measured by the peCOD was compared to ThOD, as well as traditional natural organic matter (NOM) parameters such as TOC and dissolved organic carbon (DOC), as well as specific ultraviolet absorbance at 254nm (SUVA).

Results showed that reasonable correlations were observed between peCOD COD and ThOD for most organic compounds tested and the peCOD correlated well with TOC, DOC and SUVA for these compounds. Furthermore, compared to these other NOM parameters, peCOD had superior resolution which highlighted its ability to provide information even when organic removal during treatment is small. The results from this study therefore demonstrated the potential for the use of peCOD in the drinking water industry.

PROCEDURE AND SOFTWARE

1. Plug in the peCOD L100 and ensure it has booted up correctly. The light on the display should turn green. (See Figure 2.1)
2. Ensure that the peCOD device is set to the correct range. Menu→ Set Up→ Analysis Method→ COD range. Use arrows to select range (Blue, Green, Yellow, Red) then press enter.
3. Ensure that the Baseline is at the desired setting. Menu→ Set Up→ Sensor Operation→ Set Baseline. Use arrow keys to select baseline in units of μA. Typically, this value is 15.0 or 20.0. Press enter or exit to save your baseline.
4. Place the tube connected to the waste port (labelled with a W) into a waste container.
5. Prepare a blank solution by mixing a ratio of deionized water (DI) with electrolyte solution. The required ratio of DI:electrolyte for each range is listed in Table 2.1.
6. Prepare a calibrant solution by mixing the appropriate ratio of calibrant with electrolyte. Ensure the calibrant used is in the same range as the electrolyte solution (i.e. Yellow calibrant and Yellow electrolyte).
7. Prepare samples to be tested. Mix the appropriate ratio of sample with electrolyte solution, using the same ratio used for calibrant and blank solutions.
8. Place the line from port B into the blank solution that was prepared in step 5.
9. Prime line A until the stream coming out of the waste line is strong and free from bubbles. Menu→Operation→Prime Lines. Select “Prime Line A”
10. Place the line from port A into the calibrant solution prepared in step 6. Menu→ Operation→ Prime Lines. Select “Prime Line B”
11. Prime line B until the stream coming out of the waste line is strong and free from bubbles.
12. Calibrate the device using either the computer software or the peCOD interface. Menu→ Operation→ Run Calibration
13. Once the light on the display is green again, check the calibration data to see if another calibration is required. Menu→ Data→ Result Log. The peCOD will display M and C values with each calibration. Iterm values can be readily accessed using the computer software (discussed below). If another calibration is required, repeat step 12.
14. Repeat step 13 until the calibration results are acceptable.
15. Keep the port A line in the calibrant solution, and run as a sample. Menu→ Operation→ Run sample.
16. If the result obtained from step 15 is appropriate, the device is now ready to run your samples.
17. Place line A in DI and prime the line.
18. Place line A into your desired sample and prime the line. Run the sample.
19. Place line A in DI and prime the line.

20. Repeat steps 18 and 19 until all samples have been run.
21. Place line A in the blank solution, keeping line B in the blank solution as well. Prime line A.
22. Run the blank solution as a sample. The COD result should be ~0mg/L.
23. To check the results from each sample press: Menu→ Data→ Result Log.

Figure 2.1: PeCOD L100 device with labels

As noted above, there are different mixing ratios for blank and calibrant solutions, as well as samples, in each range. The ratios are as follows:

Table 2.1: Mixing ratios for various peCOD ranges

Blue: 4 parts DI/Sample/Calibrant with 3 parts blue electrolyte
Green: 1 part DI/Sample/Calibrant with 1 part green electrolyte
Yellow: 1 part DI/Sample/Calibrant with 9 parts yellow electrolyte
Red: 1 part DI/Sample/Calibrant with 49 parts red electrolyte

When running the calibrant solution as a sample, the theoretical COD (ThOD) values are as follows:

Table 2.2: Theoretical COD values of peCOD calibrant solutions

Blue Calibrant: 20mg/L	Green Calibrant: 120mg/L
Yellow Calibrant: 1200mg/L	Red Calibrant: 12000mg/L

Also noted in the procedure were M values (expressed as COD/μC), C values (expressed in μC) and Iterm values (expressed in μA). The following are acceptable values of M, C and Iterm, as defined by MANTECH.

Table 2.3: Acceptable calibration values (M, C and Iterm)

$0.02 < M < 0.06$	
Blue: $300 < C < 500$	Green: $350 < C < 700$
Yellow: $450 < C < 750$	Red: $500 < C < 800$
Iterm >= 0.75*Baseline	

If the procedure is followed correctly, and M, C, or Iterm values are not within the acceptable range, then the sensor or electrode block may need to be replaced.

Each peCOD L100 device can be synced with a laptop, which contains software that is compatible with the peCOD device. There are two software programs available, PC-Titrate and Labterm.

PC-Titrate allows a schedule to be developed to perform testing of many samples, and in the case of a stand-alone model as was used for this project, it also provides prompts in the form of "OK messages", so the user knows exactly how to use the peCOD device. When the last sample in the schedule has been run, the software prompts the user to run Blank solution, which is deionized water (DI) mixed with electrolyte solution, in order to ensure the system has been fully flushed for overnight storage. The PC-Titrate software then gives a report summary sheet, which displays results for each sample. In the case of calibration reports, the acceptable values of M and C for each sampling range are also displayed.

The Labterm software requires the user to be more familiar with the peCOD device as it requires full manual operation, including rinsing and priming steps. This software plots a graph in real-time that displays the oxidation profiles of the solution being analyzed as well as other key parameters, the most significant value being the Iterm. The oxidation curves provide more visual information about what is happening during analysis which can be useful for troubleshooting when issues arise. Furthermore, monitoring the current generated over time can be helpful in determining if the sensor or electrode block needs to be replaced. This software is not typically used for daily operation; it is meant more as a diagnostic tool.

WASTEWATER SAMPLES

There are many stages in a typical waste water treatment plant, in which the wastewater gets treated using various methods at each stage. The influent to the Guelph Wastewater Treatment Plant (WWTP) is municipal sewage. The initial process, known as primary treatment, is where large solids separation occurs. The liquid that comes out of solid separation is known as the Primary Influent, which is split into four streams, into Plants 1, 2, 3 and 4. Not all of the primary influents are the same, however they are all treated using very similar methods. See Figure 3.1 for numbered sampling locations.

For this experiment, samples were collected from Plants 1 and 2, as well as Tertiary Effluent and Final Effluent. The Initial Effluent from Plants 1 and 2 is collected after the wastewater travels through the primary clarifiers, which allow solids to settle to the bottom of the tanks to be sent to various digesters for treatment. The effluent water is then introduced into aeration basins, where microorganisms are recycled to the wastewater in order for treatment to take place. This process is known as Activated Sludge. The wastewater undergoing Activated Sludge treatment is known as mixed liquor, which was collected from Plant 1. After the Activated Sludge treatment, the wastewater travels to the final clarifiers where more settling of solids occurs. The final clarifiers are the last step in the secondary treatment process, which makes the water from the final clarifiers Secondary Effluent. Secondary Effluent was collected from Plants 1 and 2. The wastewater completes secondary treatment and is fed into Rotating Biological Contactors (RBCs) for tertiary treatment. Tertiary effluent is the wastewater that flows from the RBCs, and is collected before the filtration process. The next treatment process is known as Sand Filtration, which removes particles and some impurities in the wastewater. Following filtration, the water is chlorinated and then dechlorinated. The Final Effluent that was collected is obtained after disinfection, and is the discharge into the Speed River.

These waste water samples were collected for analysis by two peCOD devices as well as by the dichromate method. A large variety of samples were collected to ensure a wide range of COD values, as well as to most accurately compare the two different COD technologies. The first round of sampling occurred on March 31st, 2014, where 10 different samples were collected from 9 different sampling locations. The second and final round of sampling occurred on April 8th, where 9 samples were collected from the same sampling locations as before (no duplicate Primary Influent). The sample legend for both sampling dates is presented in Table 3.1.

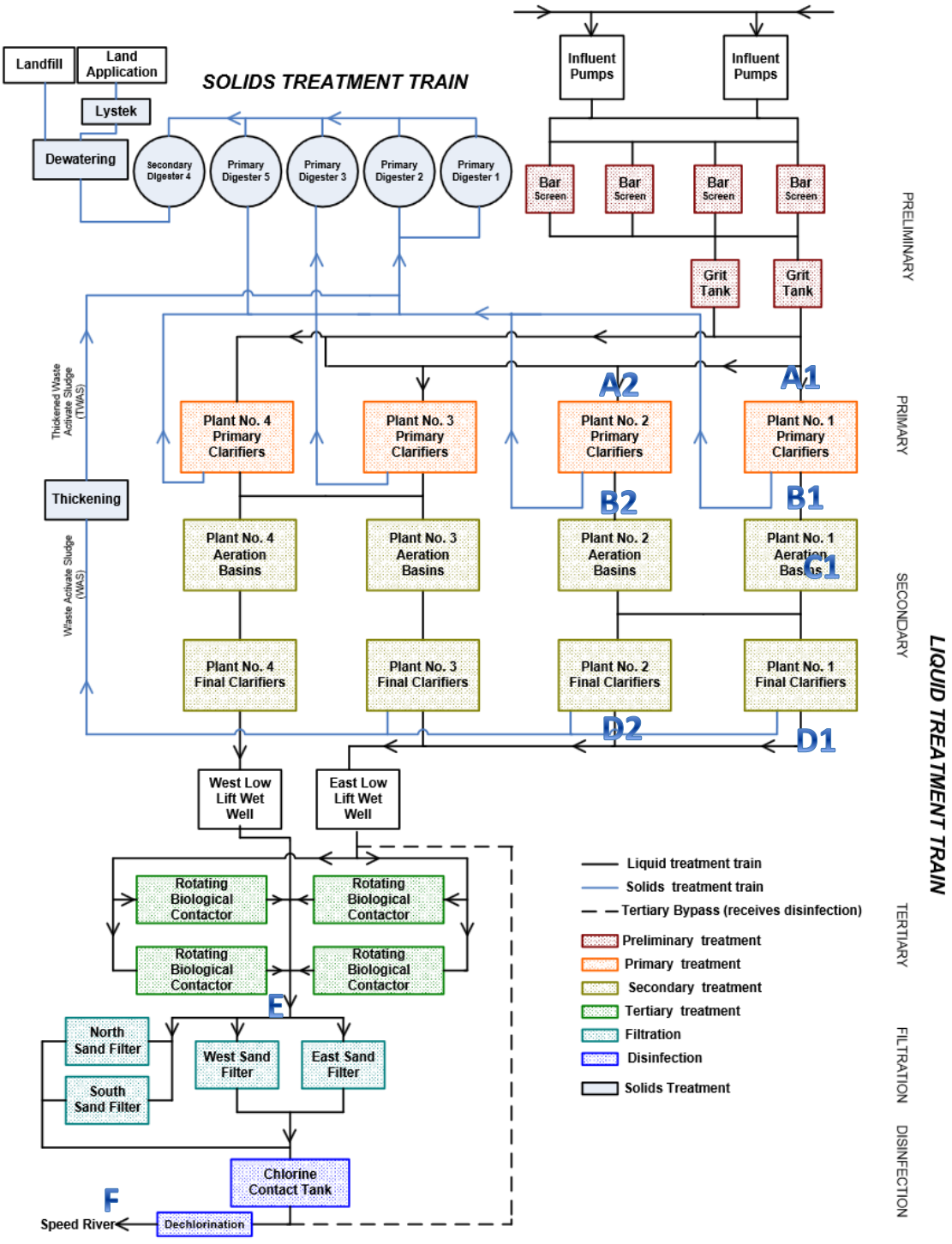

Figure 3.1: Guelph Wastewater Treatment Plant Process Diagram with Labels Indicating Sampling Locations

Table 3.1: Wastewater Treatment Plant Sample Legend

A1. Primary Influent Plant 1 (a)	A1. Primary Influent Plant 1 (b)
A2. Primary Influent Plant 2	B1. Primary Effluent Plant 1
B2. Primary Effluent Plant 2	C1. Mixed Liquor (from Plant 1)
D1. Secondary Effluent Plant 1	D2. Secondary Effluent Plant 2
E. Tertiary Effluent	F. Final Effluent

In the remainder of the report, these samples will be referred to using their corresponding letters in the table above. The following four figures display results obtained from samples that were filtered prior to being tested. The wastewater samples were filtered using a 0.45µm filter and a syringe prior to testing.

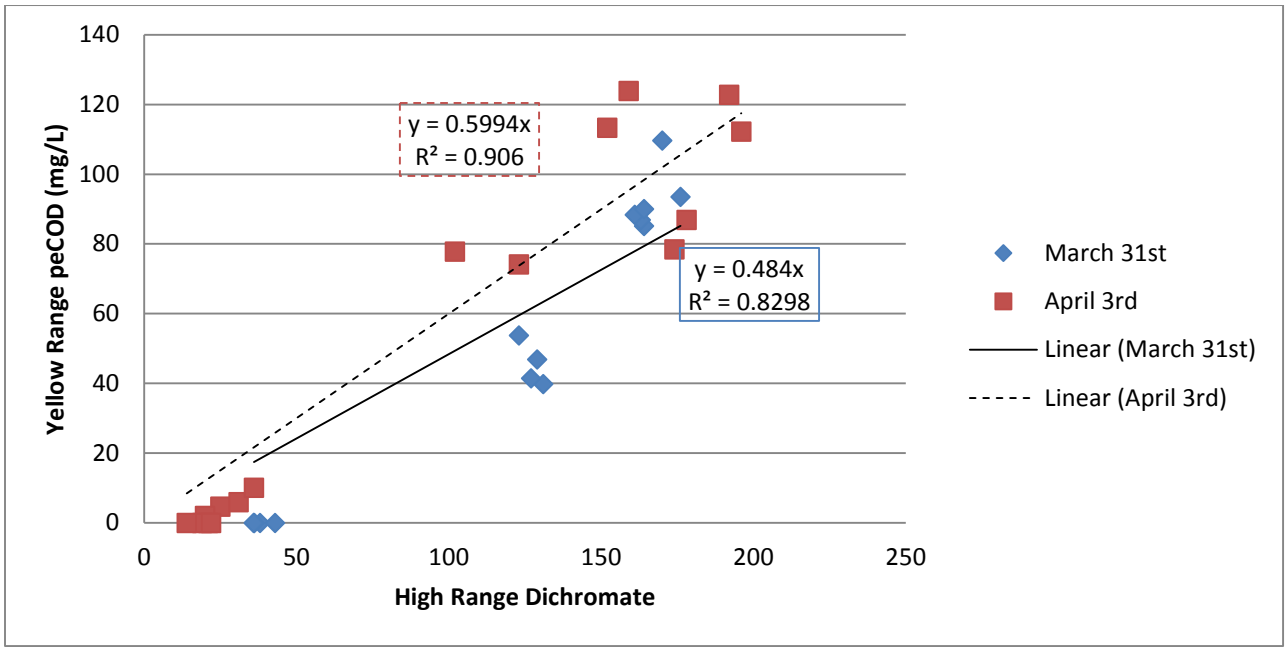

Figure 3.2: Yellow Range peCOD vs High Range Dichromate of Filtered Wastewater Samples

Figure 3.2 displays the relationship between the COD results obtained when analyzed by the peCOD COD method using the yellow range and the dichromate method using high range vials. There are two data series plotted on the graph, representing the COD results obtained for wastewater samples that were analyzed on two different dates: March 31st, 2014 and April 3rd, 2014. Lines of best-fit were plotted for both sampling dates, and R^2 values are displayed on the plot. These R^2 values are both above 0.80, indicating that there is a strong correlation observed between the COD methods.

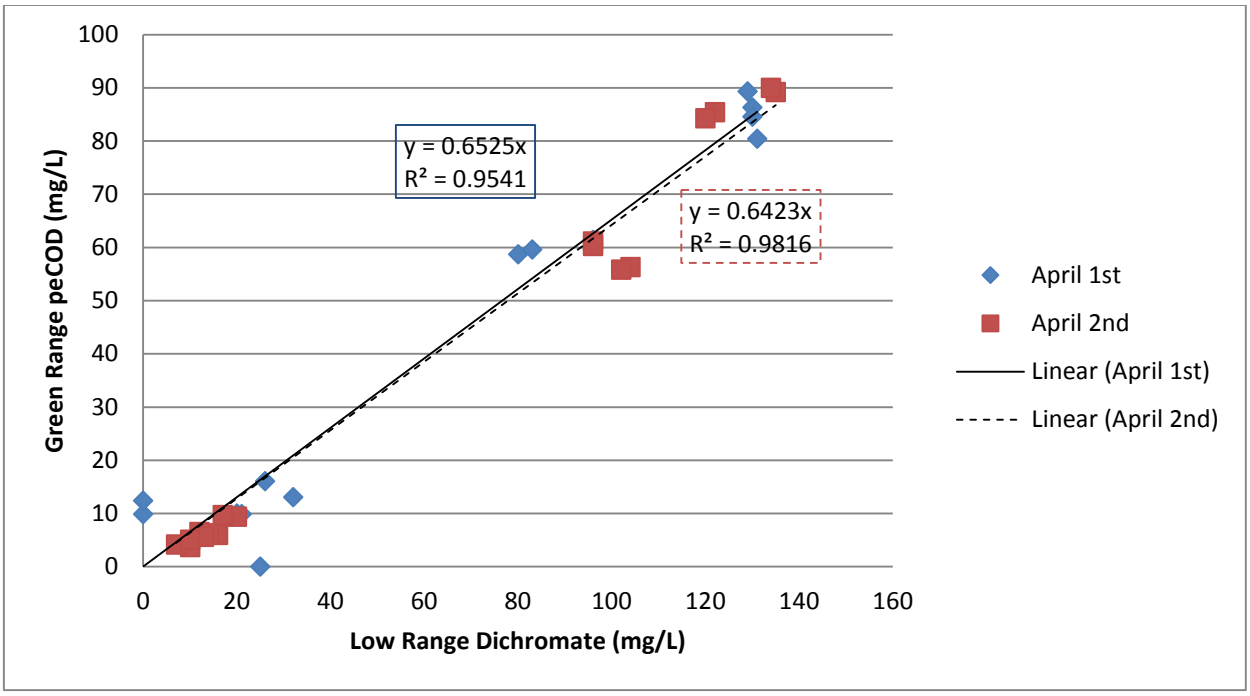

Figure 3.3: Green Range peCOD vs Low Range Dichromate of Filtered Wastewater Samples

Figure 3.3 displays the relationship between the COD results obtained when analyzed by the peCOD COD method using the green range and the dichromate method using low range vials. Once again, two data series are presented on the plot; however this time the COD results were obtained from wastewater samples that were tested on April 1st and April 2nd, 2014. Values of R^2 were once again calculated using lines of best-fit, to relate the peCOD COD results to dichromate results. These R^2 values are both quite close to 1, meaning there is a strong correlation between COD methods. It is apparent when comparing the R^2 values presented in Figure 3.2 to those in Figure 3.3 that the lower ranges of COD analysis have a stronger correlation than the higher ranges.

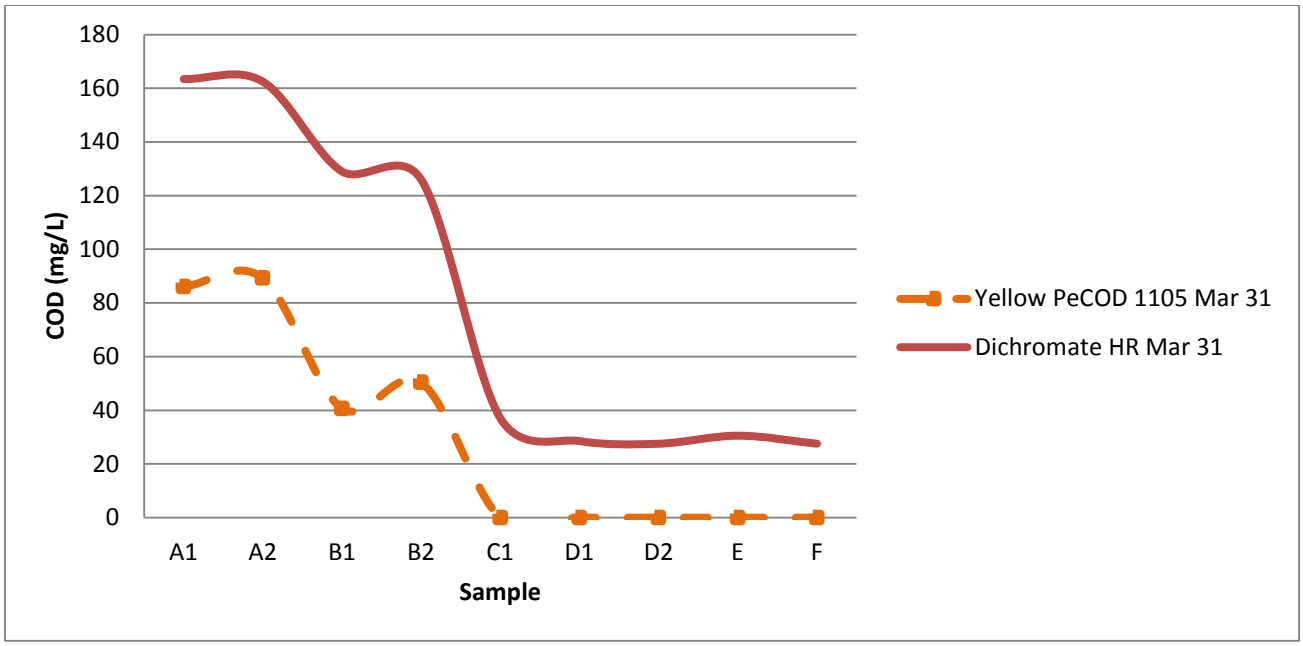

Figure 3.4: Yellow Range peCOD 1105 and High Range Dichromate Results from March 31

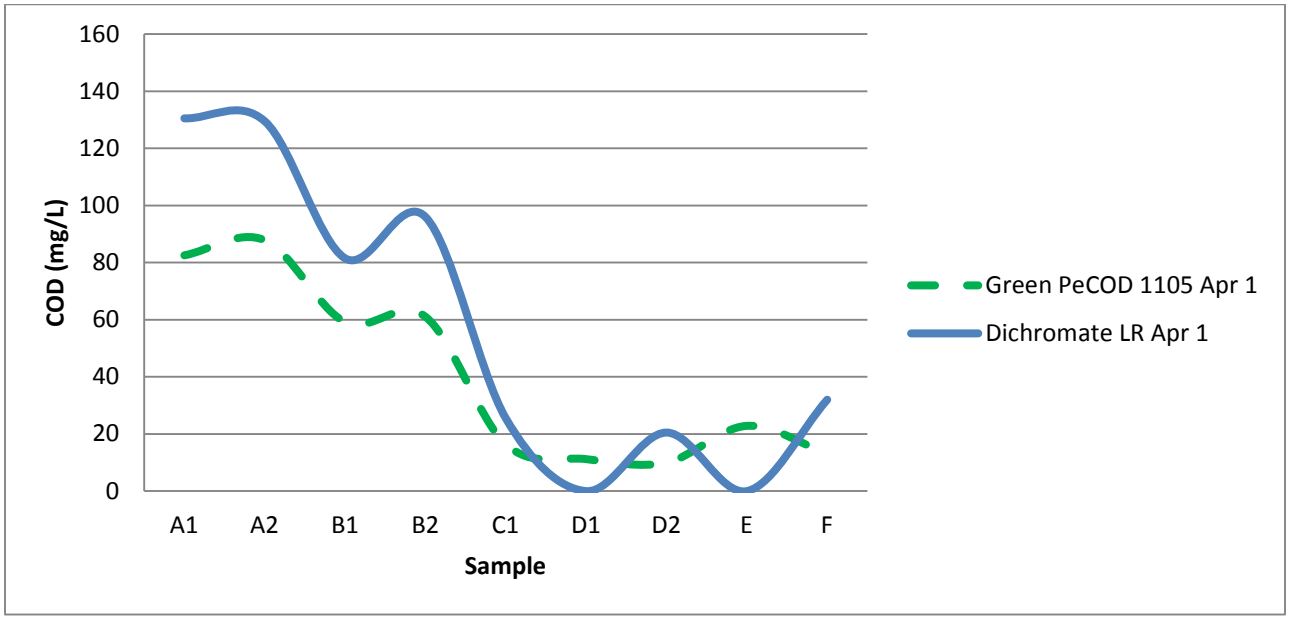

Figure 3.5: Green Range peCOD 1105 and Low Range Dichromate Results from April 1

Figures 3.4 and 3.5 above (more in Appendix) provide estimates of COD obtained using the dichromate and peCOD COD methods for each wastewater sample collected on March 31st, 2014. The wastewater samples ran smoothly via the peCOD COD method and the calibrations never presented any issues. The peCOD COD results analyzed in the green range were compared with dichromate COD results analyzed with low range vials since they cover the same scope of COD values (up to 150mg/L), while the yellow range was compared to high range dichromate since they cover COD values up to 1500mg/L. As expected, the higher ranges both demonstrated more

uncertainty when faced with lower COD values, and the low ranges were able to detect lower values than their respective high ranges**.**

When examining Figures 3.4 and 3.5, it is apparent that the dichromate and peCOD COD results follow a very similar trend, however the dichromate method produces higher COD results than the peCOD. When comparing the peCOD COD results to dichromate results for sampling locations C1 through F, it can be said that the two methods do not follow the same trend as closely as the results from sampling locations A1 through B2. The reason for this is that the COD results from sampling locations further along in the treatment process are much lower than the COD values of the primary influents and primary effluents. Although not represented on the graph, each sample that was tested had a duplicate run, which rarely deviated more than 10% from the original readings (see Appendix for raw data). The results in these figures were all obtained from filtered samples.

Samples were also run unfiltered by both the peCOD and dichromate COD methods to examine the differences in COD values between unfiltered and filtered samples. The peCOD system measures only soluble COD while the dichromate method has the ability to measure the COD of both the soluble portion and the solids component of a sample, providing a value for total COD. The total COD is expected to be higher than the soluble COD. The following three graphs display the relationship between unfiltered and filtered samples for both high and low range dichromate.

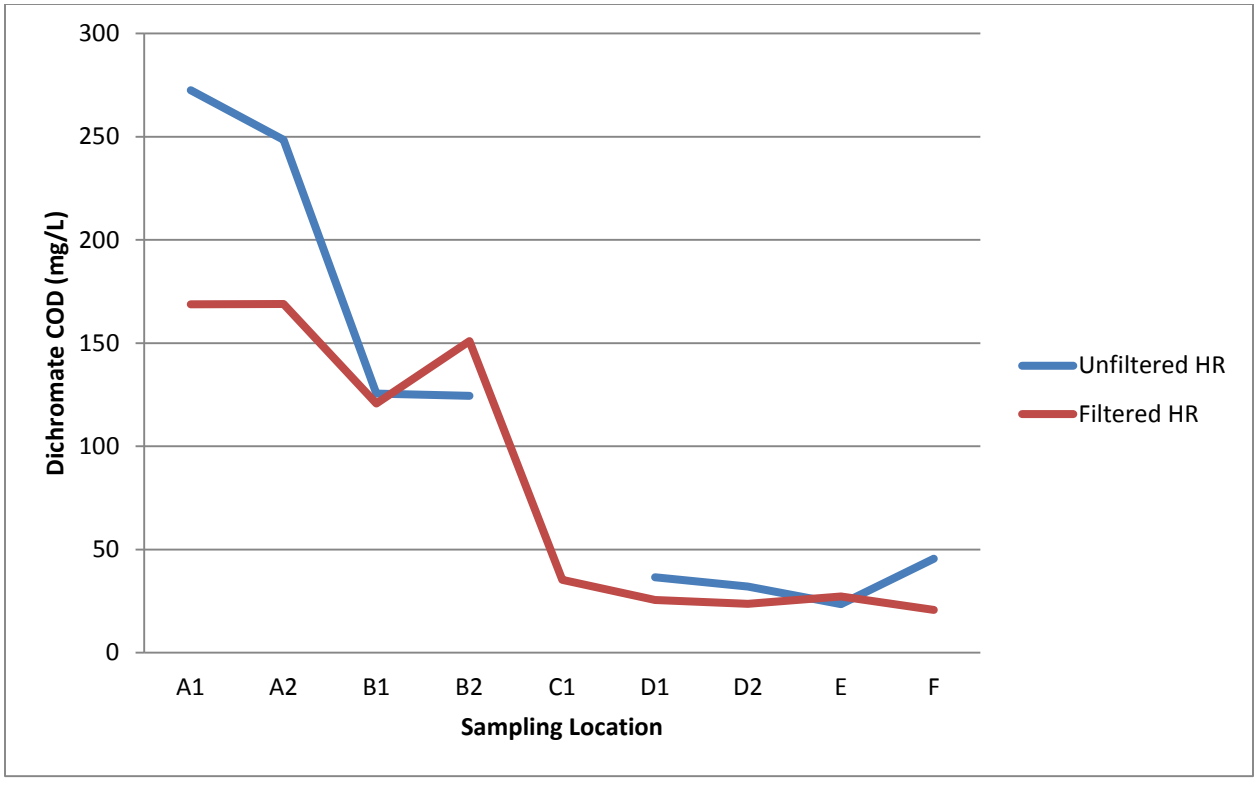

Figure 3.6: Unfiltered and Filtered High Range Dichromate Results of WWTP Samples

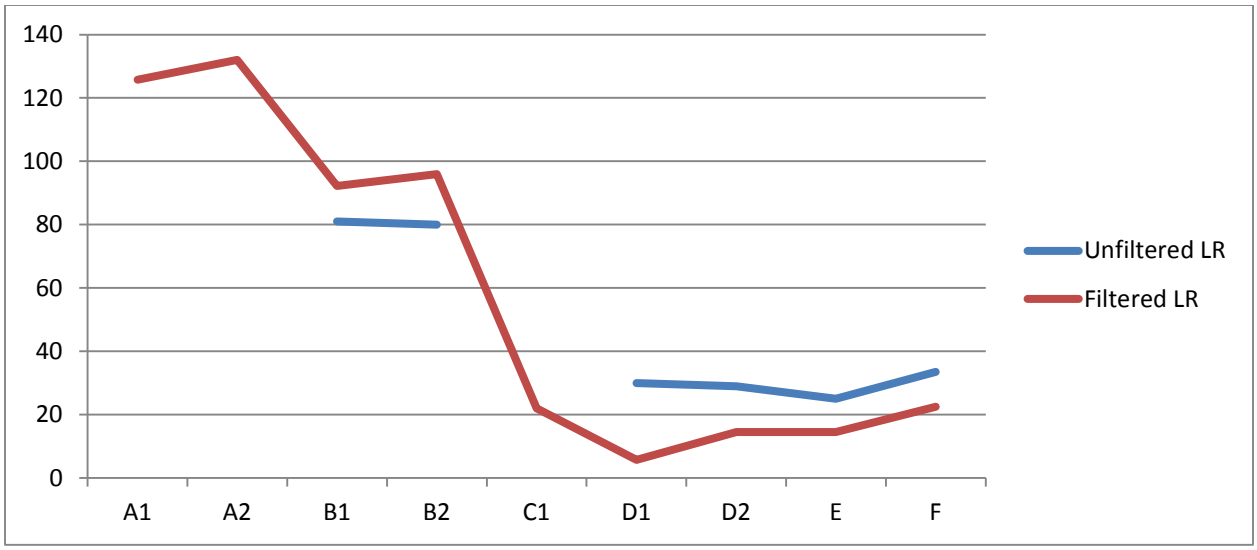

Figure 3.7: Unfiltered and Filtered Low Range Dichromate Results of WWTP Samples

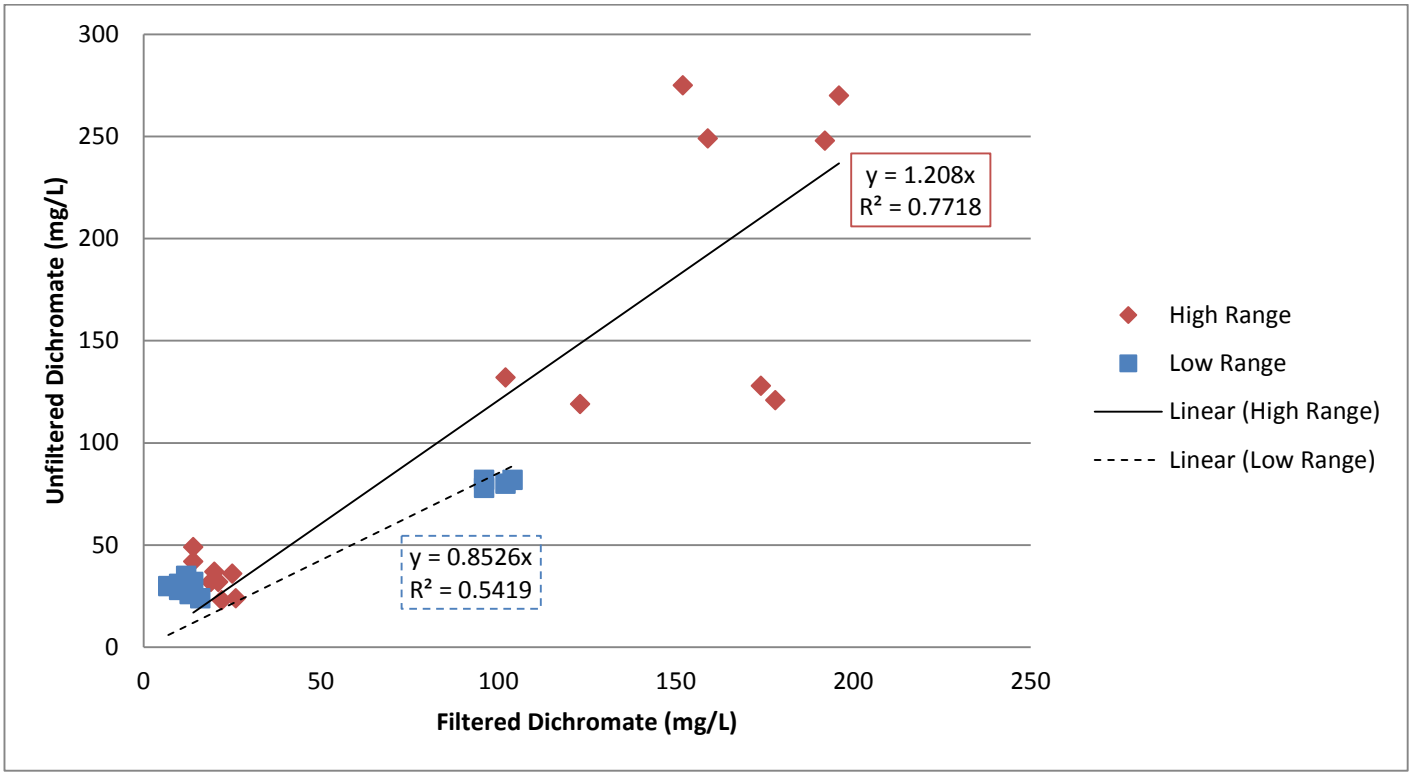

Figure 3.8: COD Results for Unfiltered Samples vs Filtered Samples using Dichromate COD Analyses

Figures 3.6, 3.7 and 3.8 above demonstrate that in most cases, the unfiltered samples provided a higher value of COD than the filtered samples, which was expected. This was more apparent in the high range, since the samples with the most solids, A1 and A2, had a COD>150mg/L, which was outside the measuring range of the low range methods. The Mixed Liquor sample (sample C1) was very turbid and had a brown colour which proved to interfere with the spectrophotometer,

therefore sample C1 could not be analyzed by the dichromate method. The R^2 values, derived from the lines of best fit in Figure 3.8, indicate that while there is a fairly good correlation between filtered and unfiltered samples in the high range dichromate, there is not a good correlation between the low range dichromate results. It can be noted, however, that many of the filtered samples provided an estimate of COD which was greater than the COD of the unfiltered samples, which was not expected.

Samples A1(a), A1(b), and 2 could not be run via the peCOD COD method since the solids content was too large, causing immediate clogging of the peCOD fluidics. Furthermore, the samples that were run unfiltered provided results much lower than the filtered samples, or in some cases a value of 0mg/L. This also indicates that the fluidics were clogging, meaning that samples containing solids should not be analyzed via the peCOD COD method without prior filtration or settling of solids.

On April 8, 2014, 9 more samples were collected from the wastewater treatment plant. The sampling locations are identical to the first round of sampling, except only one primary influent sample was collected from Plant 1, which is referred to as sample 1. These samples were once again tested following filtration by dichromate (low and high ranges) and peCOD (Green and Yellow ranges). This time, however, the samples were only run on the SOWC peCOD and not the peCOD in 1105. COD results for each sample were plotted and lines of best-fit drawn comparing the Green range peCOD COD results to the low range dichromate results and the Yellow range peCOD COD results to the high range dichromate results. See Figure A.5 in Appendix. Similar to figures 3.2 and 3.3 above, R^2 values were calculated for both low and high ranges, both of which were above 0.90, meaning there is a strong correlation between peCOD and dichromate COD for this round of wastewater samples. The following figures display the peCOD and dichromate COD results for all filtered samples.

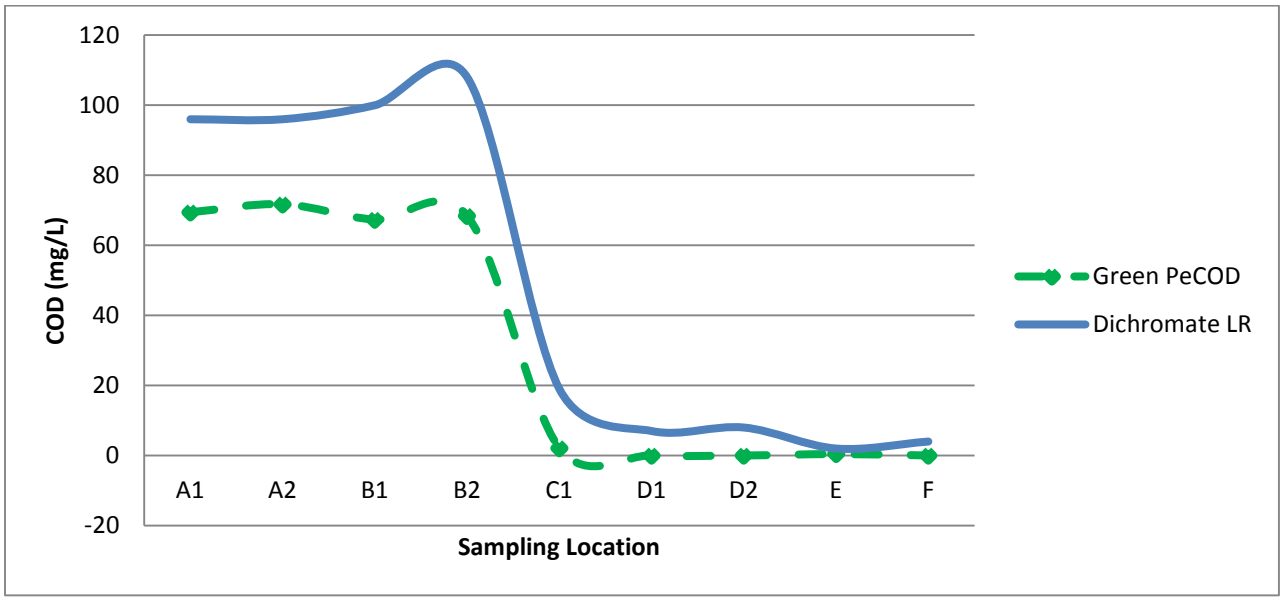

Figure 3.9: Green Range peCOD and Low Range Dichromate Results of Second Round WWTP Samples

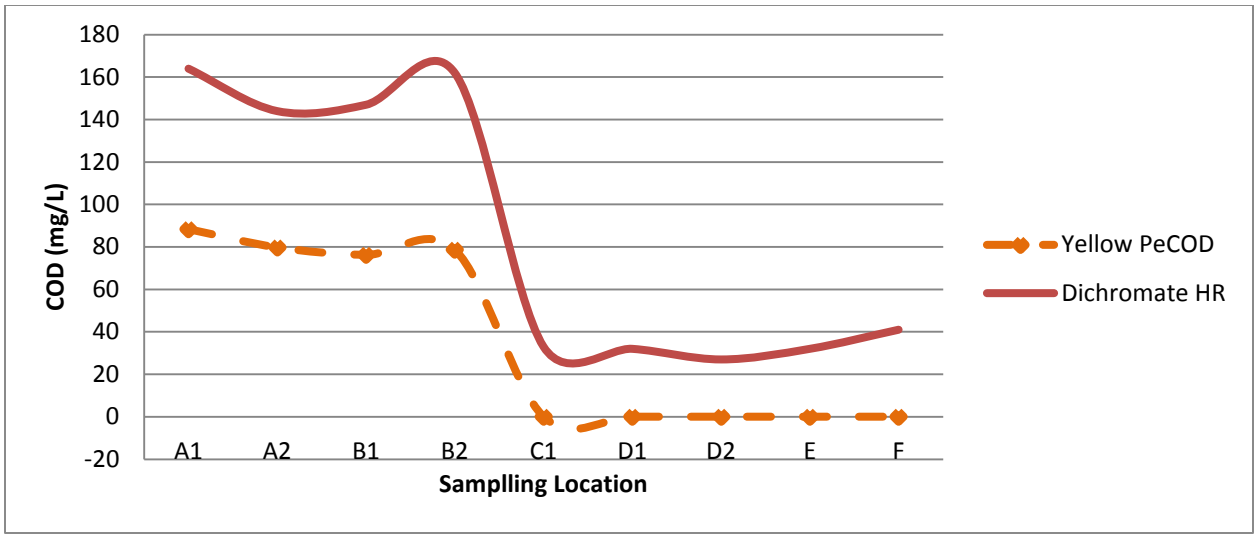

Figure 3.10: Yellow Range peCOD and High Range Dichromate Results of Second Round WWTP Samples

Figures 3.9 and 3.10 plot the peCOD and dichromate results of each wastewater sample for both low and high ranges of COD estimation. Similar to figures 3.4 and 3.5 above, the dichromate results follow a very similar trend to the peCOD COD results for the first 4 sampling locations; however, for the last 5 sampling locations, the peCOD output values of 0mg/L

TESTING OF COD STANDARDS

In order to assure the validity of the calibrations being performed on the peCOD devices, as well as the accuracy of the dichromate method, standard solutions were tested using both the peCOD and dichromate COD methods. A 1000mg/L COD standard was prepared from glucose and deionized water. This 1000mg/L standard was diluted to obtain values of 500mg/L, 100mg/L, 50mg/L and 10mg/L. These glucose standards were tested via the peCOD and dichromate COD methods in both the high and low ranges.

The figures below illustrate the results obtained from each COD method plotted against the theoretical Oxygen Demand (ThOD) of the Glucose Standard Solution. The equation of the line of best fit is shown on the graph, as well as the R^2 values. An R^2 value of 1.0 would represent experimental COD values that were identical to the ThOD, therefore the closer the proximity to 1.0 the more accurate the method of determination. From Figures 4.1, 4.2, 4.3 and 4.4 below, it is apparent that the peCOD device was more accurate than the dichromate method. It is also interesting to note that the Yellow range was very accurate even at the low end, as the peCOD was able to measure the 10mg/L and 50mg/L standards while the dichromate method could not. When attempting to measure these standards, the spectrophotometer output an “underrange” error. The standards that the dichromate COD method could measure however were quite accurate, they simply were not as accurate as the peCOD COD results.

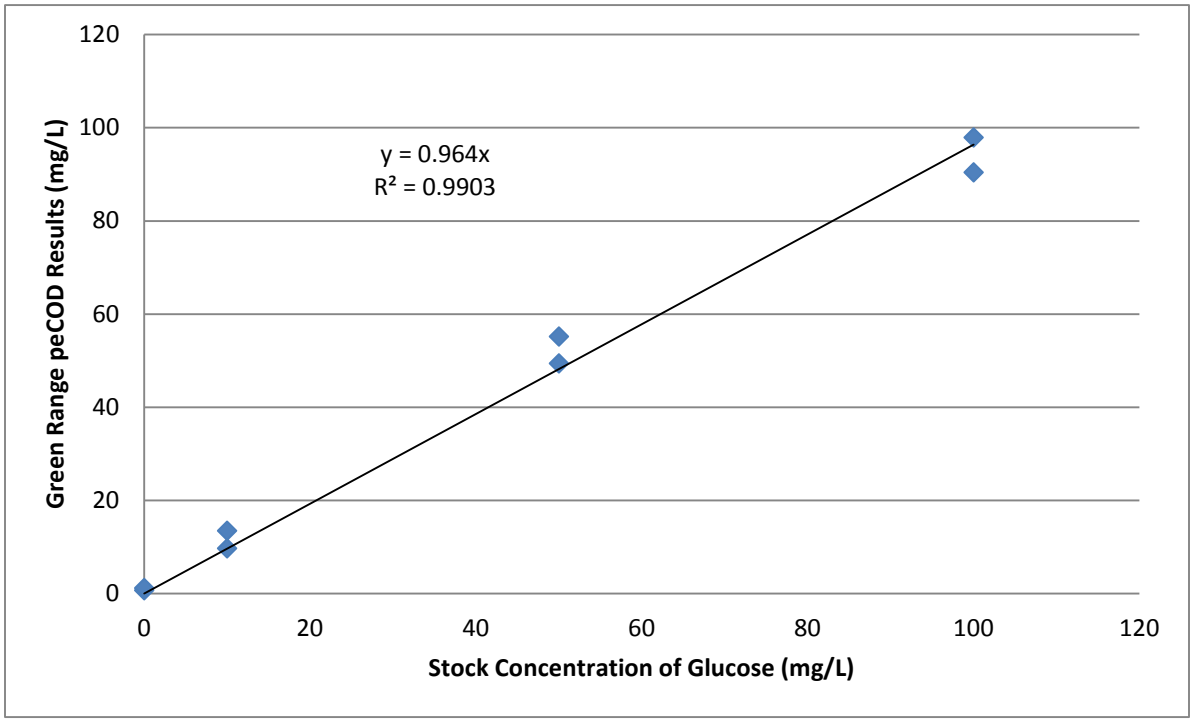

Figure 4.1: Green Range PeCOD vs ThOD of Glucose Samples

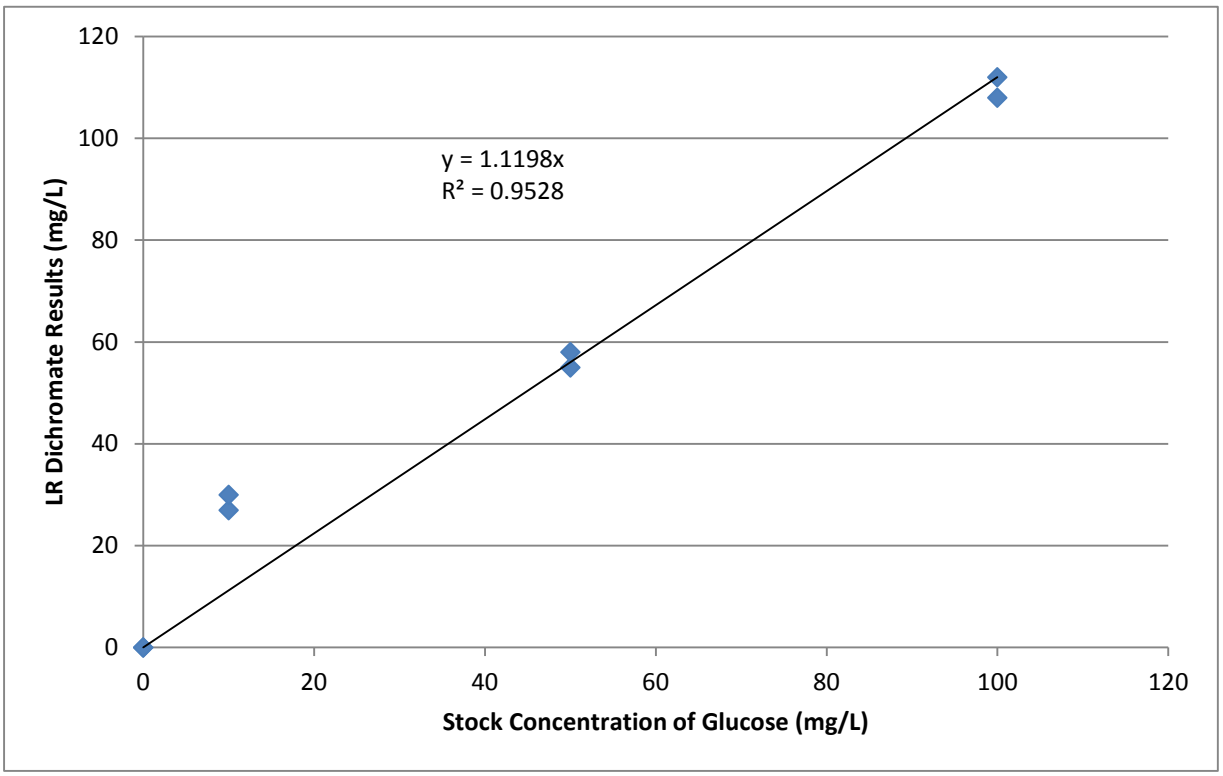

Figure 4.2: Low Range Dichromate vs ThOD of Glucose Samples

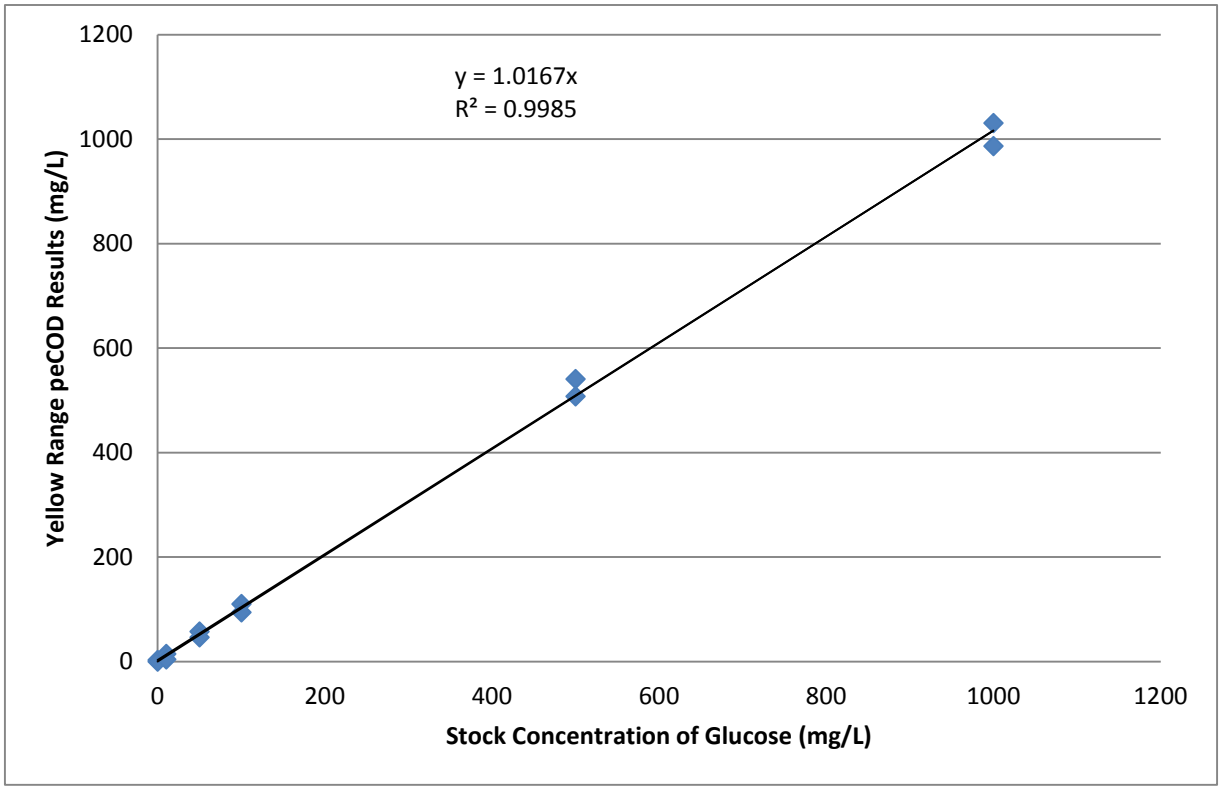

Figure 4.3: Yellow Range PeCOD vs ThOD of Glucose Samples

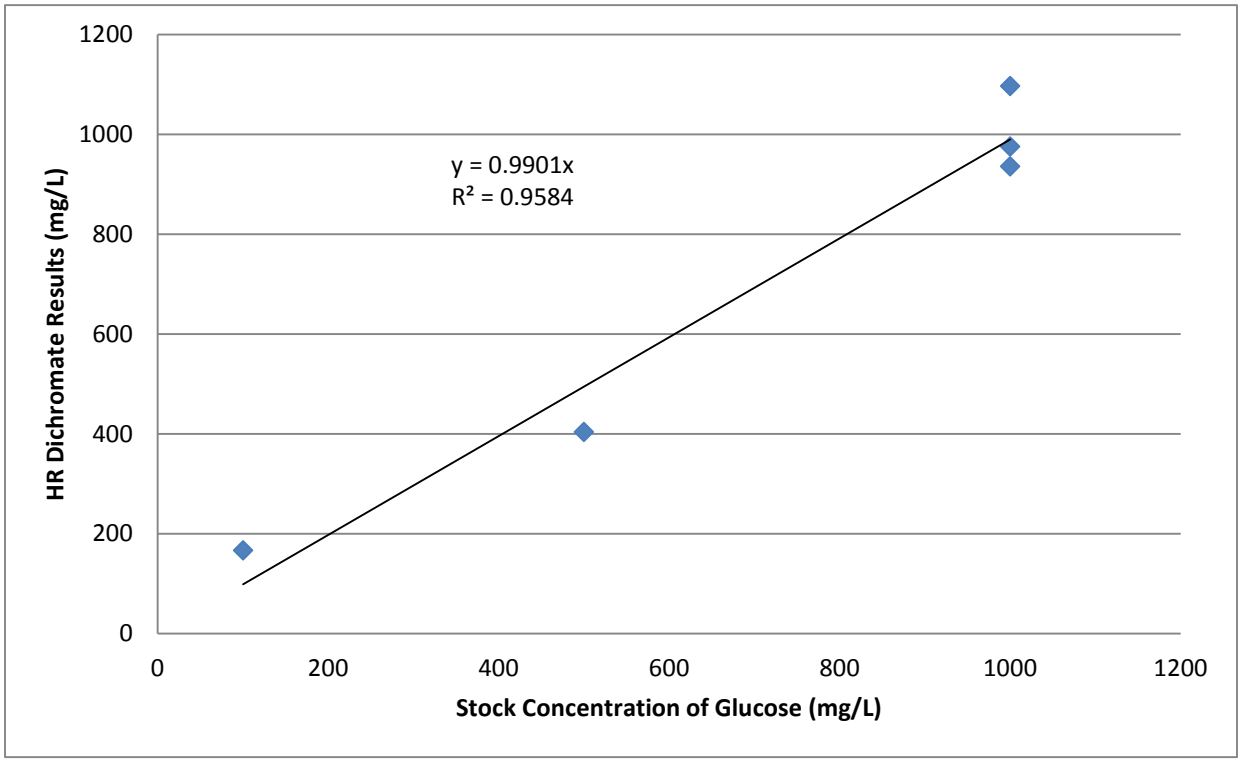

Figure 4.4: High Range Dichromate vs ThOD of Glucose Samples

In addition to the Glucose standards that were prepared and sampled, two bottles of COD Standard prepared with Potassium Hydrogen Phthalate (KHP) were ordered from Hach® Company. Two different values of COD were ordered, 300mg/L and 1000mg/L. In order to provide a larger sample set, the 1000mg/L solution was diluted to 600mg/L, while the 300mg/L solution was diluted to make a 100mg/L COD solution. KHP is used as the standard reference solution for the dichromate method of COD, while the peCOD COD method uses sorbitol. The peCOD device therefore output high results for these standards, therefore in order to test these solutions the peCOD devices were calibrated using the KHP standards.

The KHP COD standards were analyzed on March 11th and 12th, 2014, with the 100mg/L standard being run using both the low and high range dichromate vials, while the 300mg/L, 600mg/L and 1000mg/L standards were run using only the high range. The KHP COD standards were also analyzed via the peCOD COD method using both the peCOD in 1105 and the SOWC peCOD. All four standards were tested in the yellow range while the device was calibrated with the 1000mg/L standard. The 300mg/L and 100mg/L standards were also tested in the yellow range, however the device was calibrated with the 300mg/L standard.

In order for these samples to produce accurate results, the peCOD settings had to be modified due to the fact that the reference solution being used was not the default concentration. To do this the user must press: Menu→ Set Up→ Analysis Method → Reference Solution. The value was changed from 1200mg/L, the value of the standard yellow calibrant, to 1000mg/L and then to 300mg/L.

Figure 4.5 below is a plot of all data obtained via the peCOD and dichromate COD methods plotted against the ThOD of the KHP standard solutions. A line of y=x is also plotted on the graph, which would be the line of best fit of ideal results. It is evident that the majority of the data points are very close to y=x, however the peCOD data points are closer than the dichromate data points, especially for the higher standards. As was found when analyzing the glucose standards, although both methods obtained good results, the peCOD device provided better accuracy and precision in both the high and low ranges when compared to the results obtained by the dichromate COD method when analyzing standards made from KHP. The full raw data from this experiment can be found in the Appendix.

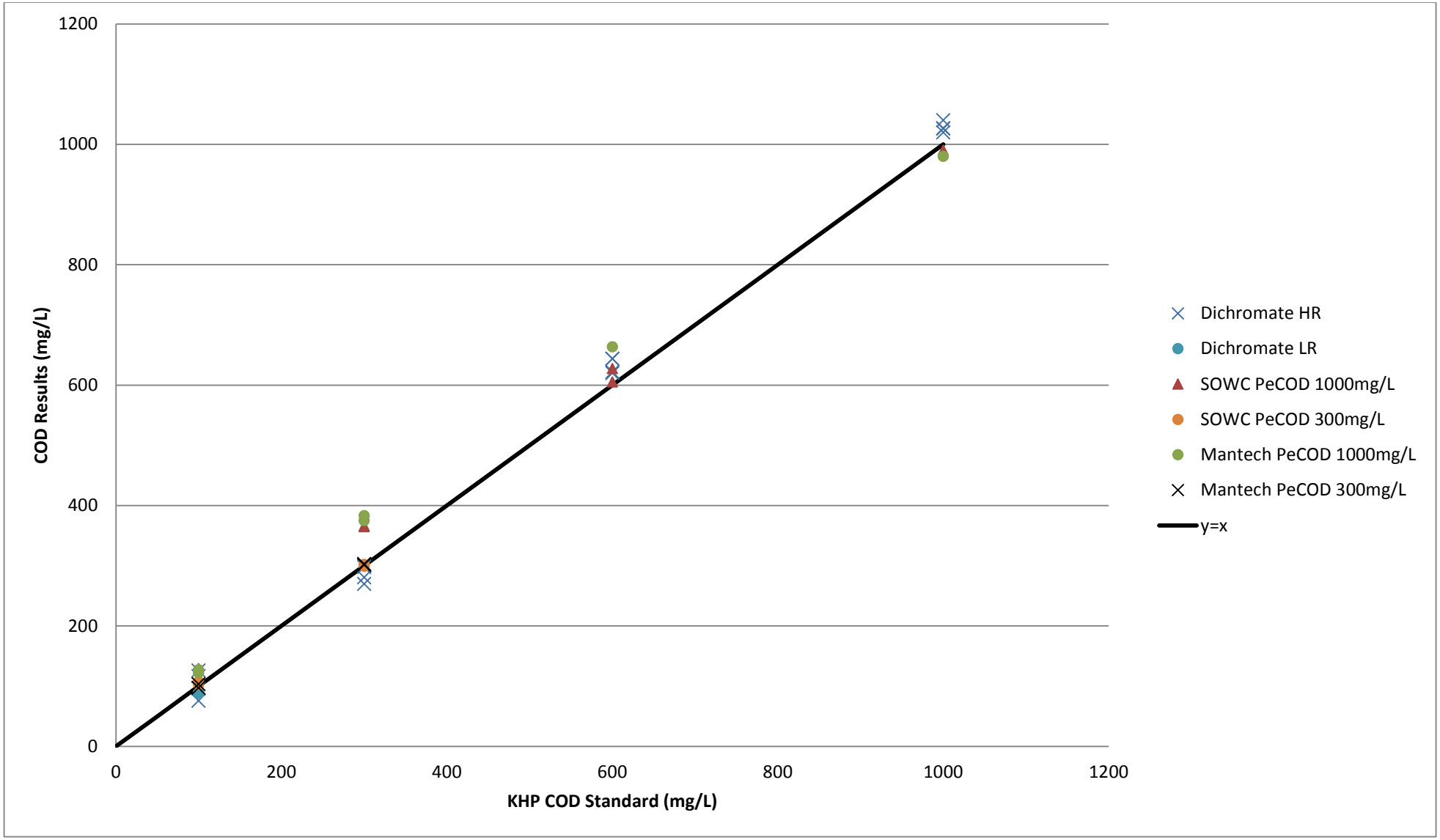

Figure 4.5: Dichromate and peCOD COD Results vs ThOD of KHP COD Standards

CONCLUSIONS AND RECOMMENDATIONS

- peCOD produces more accurate and precise results than the dichromate method when testing COD standard solutions.
- peCOD provides precise results when testing wastewater samples, and displays a good correlation with the dichromate method.
- peCOD is a safer technology with easier and less expensive cleanup and disposal methods than dichromate.
- peCOD takes longer to run samples compared to the dichromate method when there are more than 12 or 15 samples, since each sample takes 10 or more minutes depending on the range. Dichromate analyses can run up to 24 samples in approximately 3 hours. The peCOD is faster for smaller batches of samples however, since the dichromate method still requires the same amount of time whether running 1 or 24 samples.
- The peCOD measures soluble COD only. If solids are present in the samples, filtration is required.
- MANTECH offers automated solutions that simplify operation and automate sample preparation.
- The peCOD could be used to displace dichromate as the standard for measuring the COD of wastewater samples.

References

[1]Aqua Diagnostic, (2008), Application Note 001 v2: Real-time Biological Oxygen Demand (BOD_5) Measurements by Correlation with Rapid PeCOD™ Chemical Oxygen Demand (COD) Measurements, Australia.

[2]European Chemicals Agency, (n.d.), Addressing Chemicals of Concern, Retrieved from http://echa.europa.eu/addressing-chemicals-of-concern

[3]Esler, M., Chinen, K., Higginbotham, H., Reddy, P, (2010), Application Note 005 v2: Systematic Comparison of PeCOD® and Dichromate Methods of COD Measurement for a Suite of 34 Organic Species, Aqua Diagnostic, Australia.

[4]Furdui, V.I., Palmer, D., Menegotto, R.V., Peddle, L.D, (2013), Rapid Measurement of Chemical Oxygen Demand in Surface Water Samples Utilizing a New Green Technology. [PowerPoint slides], Canada.

[5]Furdui, V.I. & Palmer, D, (2014), The Determination of Chemical Oxygen Demand (COD) in Water by Photo-Electrochemical Measurement, Method E3515, Ontario Ministry of the Environment, Canada.

[6] MANTECH INC, (2013), Analysis of Surface Water Samples for Conductivity, pH, Alkalinity and Chemical Oxygen Demand via the PeCOD® Multi System as Compared to Traditional Laboratory Techniques, Canada.

[7] Stoddart, A.K., & Gagnon, G.A. (2014). Application of Photoelectrochemical Chemical Oxygen Demand to Drinking Water. American Water Works Association, 106(9), Canada, (E383-E390).

About the Author:

Please write one paragraph summary about the author and his/her professional experience.

APPENDIX

Wastewater Samples

Table A.1: PeCOD and Dichromate Raw Data for Wastewater Samples Collected on March 31st

PeCOD 1105

March 31st

Sample	Trial	COD (mg/L)	Range
Yellow Cal	1	1230.7	Yellow
A1	1	109.7	Yellow
A1	2	93.5	Yellow
A1	1	85.2	Yellow
A1	2	86.9	Yellow
A2	1	88.4	Yellow
A2	2	90.0	Yellow
B1	1	39.8	Yellow
B1	2	41.5	Yellow
B2	1	46.9	Yellow
B2	2	53.8	Yellow
D1	1	0	Yellow
D2	1	0	Yellow
E	1	0	Yellow
F	1	0	Yellow
C1	1	0	Yellow
Blank	1	N/A	Yellow

Dichromate

March 31st

Sample	COD (mg/L)	Range
z Blank	0	High
A1	170	High
A1	164	High
A2	161	High
B1	131	High
B2	129	High
Blank	UR	High
z Blank	-1	High
D1	38	High
D2	36	High
E	36	High
F	36	High
C1	43	High
Blank	15	High
z Blank	-1	High
C1	31	High
F	19	High

April 3rd

Sample	COD (mg/L)	Range
z Blank	0	High
A1	123	High
A1	152	High
A2	159	High
B1	102	High
B2	174	High
Blank	UR	High
z Blank	2	High
D1	25	High
D2	21	High
E	22	High
F	14	High
C1	31	High
Blank	-3	High
z Blank	0	High
C1	36	High
F	14	High

SOWC PeCOD

April 3rd — Iterm=13.18 (3rd cal) — C is a bit low (~350)

Sample	Trial	COD (mg/L)	Range	Iterm
Yellow Cal	1	1190.8	Yellow	12.76
A1	1	50.4	Yellow	12.61
A1	2	39.4	Yellow	12.37
A1	1	113.4	Yellow	12.3
A1	2	112.3	Yellow	12.15
A2	1	123.9	Yellow	12.22
A2	2	122.8	Yellow	12.5
B1	1	77.8	Yellow	N/A
B1	2	74.2	Yellow	11.88
B2	1	78.5	Yellow	11.74
B2	2	86.9	Yellow	12.48
D1	1	4.6	Yellow	12.41
D1	2	2.0	Yellow	12.17
D2	1	0	Yellow	12
D2	2	0	Yellow	11.91
E	1	0	Yellow	N/A
F	1	0	Yellow	11.73

April 1st

Sample	Trial	COD (mg/L)	Range
Green Calibrant	1	115.4	Green
A1	1	67.3	Green
A1	2	65.9	Green
A1	1	80.4	Green
A1	2	84.6	Green
A2	1	86.3	Green
A2	2	89.3	Green
B1	1	58.7	Green
B1	2	59.6	Green
B2	1	60.6	Green
B2	2	61.4	Green
D1	1	9.9	Green
D1	2	12.4	Green
D2	1	9.9	Green
D2	2	10.0	Green
E	25	High	
D2	19	High	
D1	19	High	
Blank	2	High	
B2	123	High	
B1	127	High	
A2	164	High	
A1	163	High	
A1	176	High	
Blank	1	High	

April 1st

Sample	COD(mg/L)	Range
z Blank	0	Low
A1	132	Low
A1	131	Low
A2	130	Low
B1	80	Low

E	26	High
D2	19	High
D1	20	High
Blank	UR	High
z Blank	1	High
B2	178	High
B1	123	High
A2	192	High
A1	196	High
A1	142	High
Blank	8	High

April 2nd

Sample	COD(mg/L)	Range
z Blank	0	Low
A1	116	Low
A1	122	Low
A2	135	Low

C1	1	5.9	Yellow	11.57
C1	2	10.1	Yellow	11.52
Blank	1	0	Yellow	11.3

April 2nd Iterm=12.76 (4th cal)

Sample	Trial	COD (mg/L)	Range	Iterm
Green Calibrant	1	119.0	Green	N/A
A1	1	44.0	Green	11.9
A1	2	45.4	Green	11.93
A1	1	85.4	Green	12.19
A1	2	84.3	Green	11.95
A2	1	89.2	Green	12.03
A2	2	90.0	Green	11.91
B1	1	56.3	Green	11.76
B1	2	55.8	Green	12
B2	1	61.1	Green	13.09

E	1	22.4	Green
E	2	23.2	Green
F	1	COD<blank	Green
F	2	13.1	Green
C1	1	16.1	Green
C1	2	16.6	Green
Blank	1	N/A	Green

B2	96	Low
Blank	0	Low
z Blank	N/A	Low
D1	0	Low
D2	21	Low
E	UR	Low
F	32	Low
C1	26	Low
Blank	1	Low
z Blank	0	Low
C1	25	Low
F	32	Low
E	UR	Low
D2	20	Low
D1	0	Low
Blank	1	Low
B2	96	Low
B1	83	Low
A2	129	Low
A1	130	Low
A1	131	Low
Blank	-2	Low

B1	104	Low
B2	96	Low
Blank	1	Low
z Blank	0	Low
D1	13	Low
D2	10	Low
E	16	Low
F	14	Low
C1	20	Low
Blank	2	Low
z Blank	0	Low
C1	17	Low
F	12	Low
E	13	Low
D2	7	Low
D1	10	Low
Blank	-4	Low
z Blank	0	Low
B2	96	Low
B1	102	Low
A2	134	Low
A1	120	Low
A1	115	Low
Blank	2	Low

B2	2	60.3	Green	12.72
D1	1	5.9	Green	12.48
D1	2	5.1	Green	12.28
D2	1	3.7	Green	12.6
D2	2	4.2	Green	12.45
E	1	6.0	Green	12.31
E	2	5.6	Green	12.13
F	1	6.3	Green	11.98
F	2	6.5	Green	11.84
C1	1	9.4	Green	11.76
C1	2	9.7	Green	11.67
Blank	1	0	Green	12.07

Table A.2: peCOD and Dichromate Raw Data of Unfiltered Samples Collected on March 31

UNFILTERED SAMPLES (all ran on Apr 7th)

peCOD 1103 Iterm=13.15(2nd cal)

Sample	Trial	COD (mg/L)	Range	Iterm
Green Calibrant	1	119.5	Green	13.18
A1	1	32.5	Green	14.17
A1	2	Incomplete ox	Green	15?
A1	1	N/A	Green	N/A
A1	2	N/A	Green	N/A
A2	1	Incomplete ox	Green	17.88?
A2	2	N/A	Green	N/A
B1	1	0	Green	?
B1	2	12.0	Green	14.57
B2	1	16.6	Green	14.49
B2	2	18.4	Green	14.2
D1	1	0	Green	14.59
D1	2	0	Green	14.41
D2	1	0	Green	14.18
D2	2	0	Green	13.93
E	1	0	Green	13.99
E	2	0	Green	13.88
F	1	0	Green	14.31
F	2	0	Green	14.11
C1	1	N/A	Green	N/A
C1	2	N/A	Green	N/A
Blank	1	COD<blank	Green	14.22

Sample	COD (mg/L)	Range
z Blank	0	Low
A1	OR	Low
A1	OR	Low
A2	OR	Low
B1	82	Low
B2	82	Low
Blank	2	Low
z Blank	0	Low
D1	29	Low
D2	28	Low
E	24	Low
F	32	Low
C1	UR	Low
Blank	-2	Low
z Blank	0	Low
C1	UR	Low
F	35	Low
E	26	Low
D2	30	Low
D1	31	Low
Blank	3	Low
z Blank	0	Low
B2	78	Low
B1	80	Low

Sample	COD (mg/L)	Range
z Blank	-1	High
A1	324	High
A1	275	High
A2	249	High
B1	132	High
B2	128	High
Blank	-1	High
z Blank	-2	High
D1	36	High
D2	32	High
E	23	High
F	49	High
C1	OVERRANGE	High
Blank	-2	High
z Blank	-1	High
C1	OR	High
F	42	High
E	24	High
D2	32	High
D1	37	High
Blank	-4	High
z Blank	-1	High
B2	121	High
B1	119	High

A2	OR	Low	A2	248	High
A1	OR	Low	A1	270	High
A1	OR	Low	A1	294	High
Blank	-1	Low	Blank	6	High

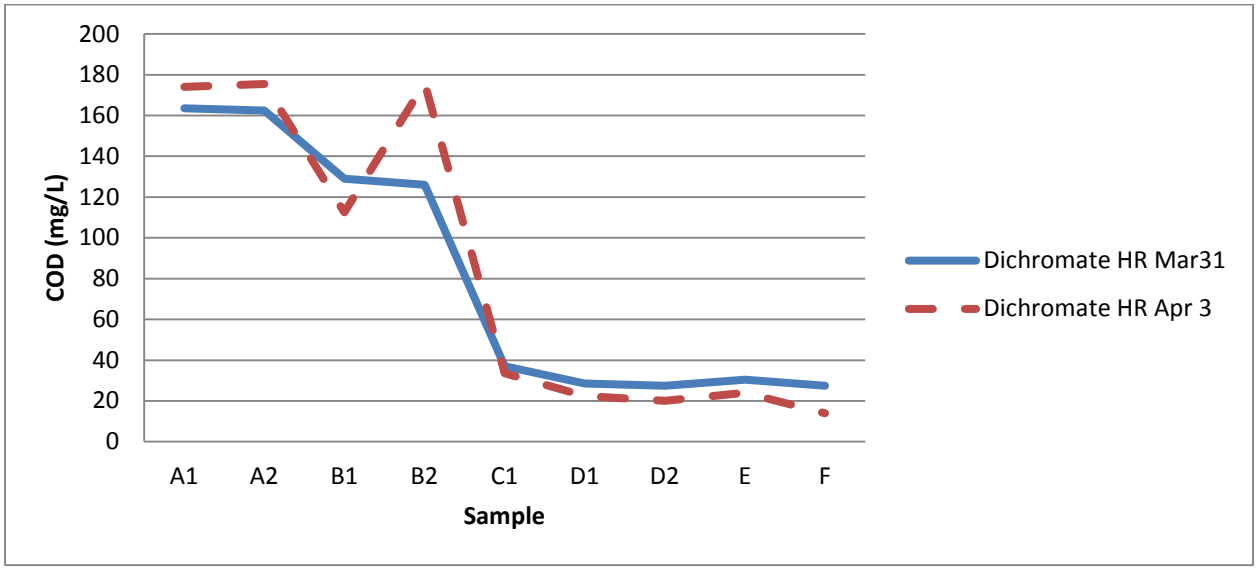

Figure A.1: High Range Dichromate Results of WWTP Samples Collected on March 31. March 31 vs April 3

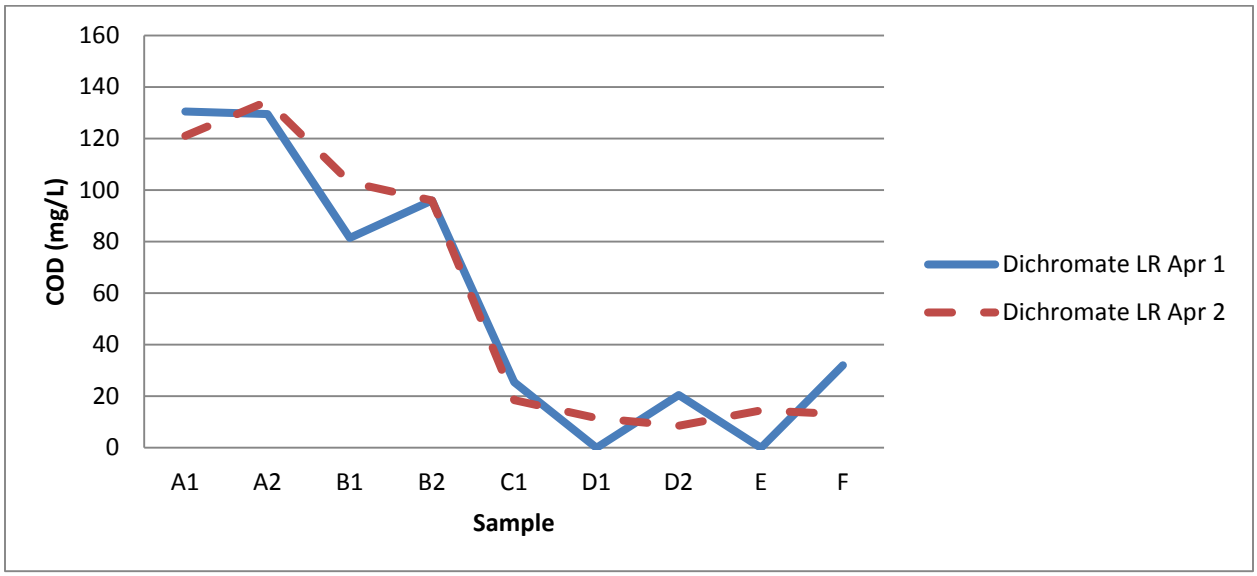

Figure A.2: Low Range Dichromate Results of WWTP Samples Collected on March 31. April 1 vs April 2

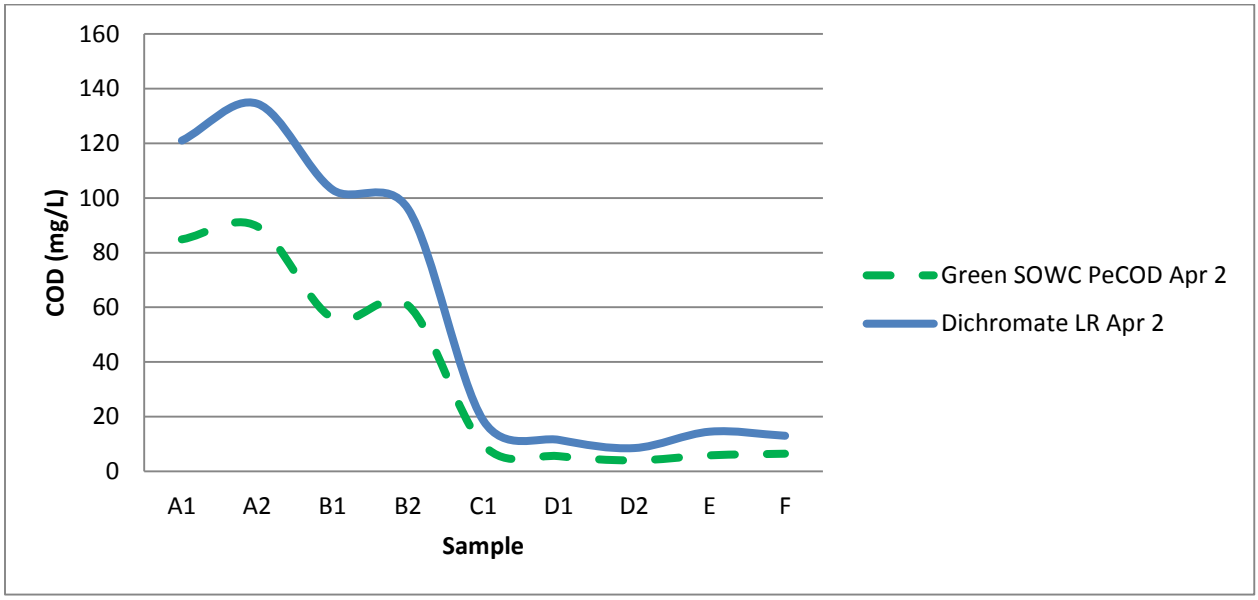

Figure A.3: Low Range Dichromate and Green Range peCOD Results of First Round WWTP Samples Tested on April 2

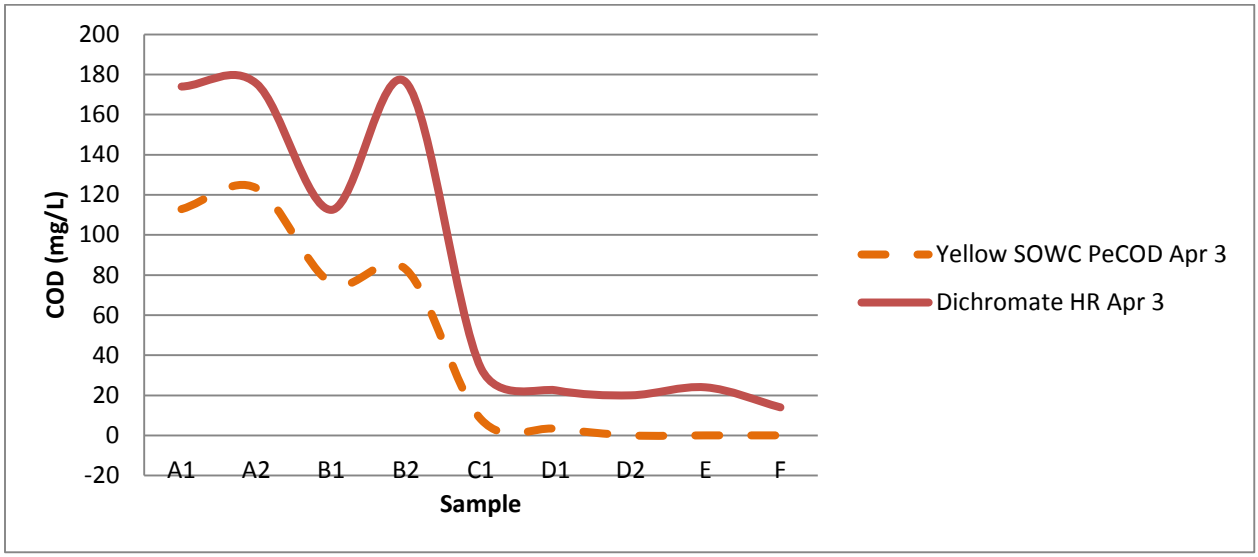

Figure A.4: High Range Dichromate and Yellow Range peCOD Results of First Round WWTP Samples Tested on April 3

Table A.3: peCOD and Dichromate Raw Data of Wastewater Samples Collected on April 8

SOWC peCOD

Apr 8th

Changed sensor since it looked discoloured. **Baseline=12**. For the first few calibrations the Iterm was quite low and C was quite high. 4th cal with new sensor, **Iterm=9.2** (>75% of 12), so I ran green cal as sample

Sample	COD (mg/L)	Range	Iterm
Green Cal	119.0	Green	9.33
A1	69.4	Green	10.69
A2	71.7	Green	11.1
B1	67.3	Green	11.58
B2	68.4	Green	12.01
D1	0	Green	12.26
D2	cod<Blank	Green	12.72
D1	0	Green	13.34
D2	0	Green	13.17
E	0.4	Green	13.3
F	0	Green	13.36
C1	2.1	Green	13.27
Blank	0.3	Green	N/A

Dichromate

Apr 8th

Sample	COD (mg/L)	Range
z Blank	1	High
A1	164	High
A2	144	High
B1	147	High
B2	162	High
D1	32	High
Blank	-2	High
z Blank	1	High
D2	27	High
E	32	High
F	41	High
C1	33	High
Blank	UR	High

Sample	COD (mg/L)	Range
z Blank	0	Low
A1	96	Low
A2	96	Low
B1	100	Low
B2	108	Low
D1	7	Low
Blank	-1	Low
z Blank	0	Low
D2	8	Low
E	2	Low
F	4	Low
C1	19	Low
Blank	-1	Low

UNFILTERED

Apr 9th

Sample	COD (mg/L)	Range
z Blank	-1	High
A1	363	High
A2	190	High
B1	188	High

Sample	COD (mg/L)	Range
z Blank	0	Low
A1	OR	Low
A2	162	Low
B1	OR	Low

recalibrated after sample 6, at baseline=15, since I values were above 12. Reran 5&6

Apr 9th CAL 2: I=12.87

Sample	COD (mg/L)	Range	Iterm
Yellow Cal	1189.4	Yellow	13.27
A1	88.4	Yellow	13.87
A2	79.8	Yellow	13.52
B1	76.3	Yellow	12.96
B2	78.7	Yellow	12.9
C1	0	Yellow	12.58
Blank	0	Yellow	11.5

UNFILTERED

Apr 9th

Sample	COD (mg/L)	Range	Iterm
A1	64.5	Yellow	15.21
B1	53.4	Yellow	13.71
B2	42.5	Yellow	14.01
D1	0	Yellow	13.24
D2	0	Yellow	13.57
E	0	Yellow	13.45
F	0	Yellow	13.31
Blank		Yellow	

B2	275	High
D1	37	High
Blank	0	High
D2	57	High
E	32	High
F	27	High
C1	OR	High
Blank	3	High
z Blank	0	High
C1	OR	High
F	28	High
E	30	High
D2	60	High
Blank	1	High
D1	34	High
B2	278	High
B1	193	High
A2	204	High
A1	364	High
Blank	2	High

B2	OR	Low
D1	29	Low
Blank	0	Low
D2	21	Low
E	31	Low
F	24	Low
Blank	0	Low
F	23	Low
E	30	Low
D2	22	Low
D1	28	Low
Blank	-1	Low
B2	OR	Low
B1	OR	Low
A2	162	Low
A1	OR	Low
Blank	0	Low

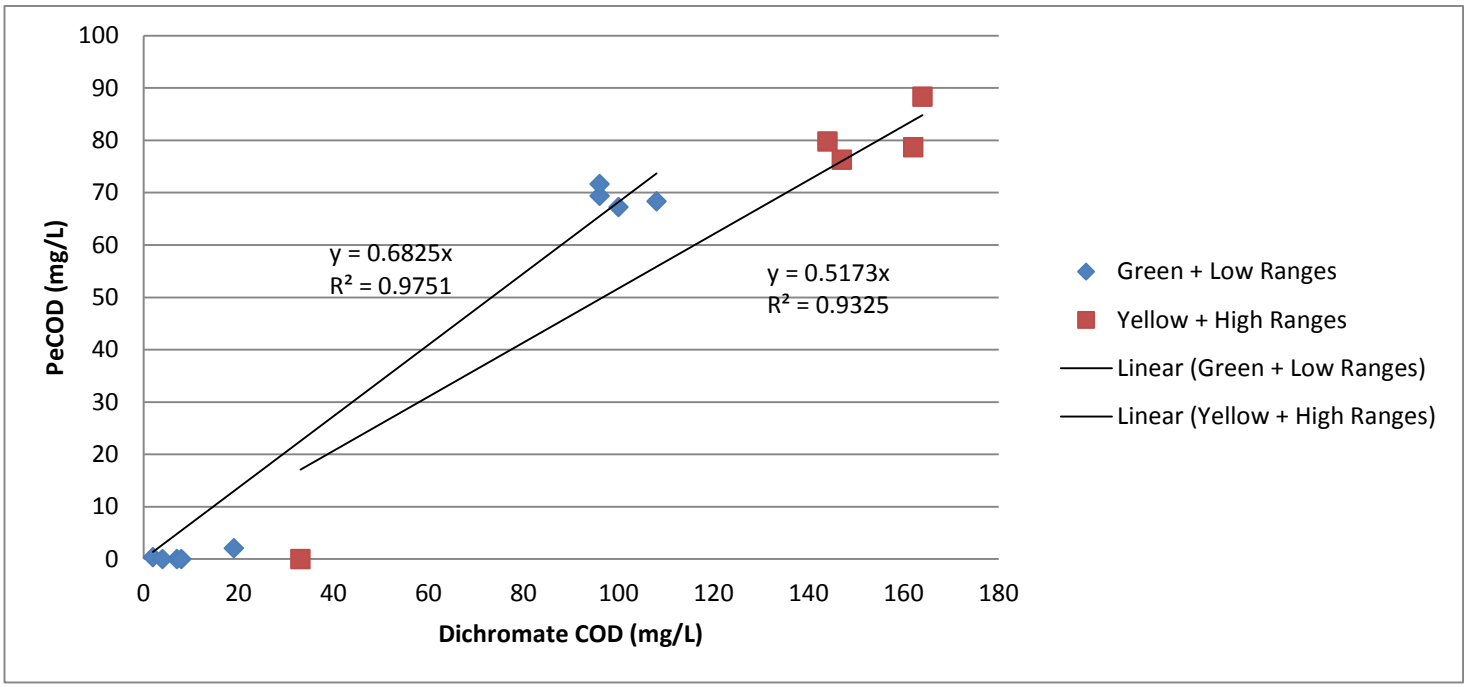

Figure A.5: Estimates of COD Obtained using peCOD vs Dichromate for Low and High Ranges of Wastewater Samples

Testing of COD Standards

Table A.4: Raw Dichromate Data of Glucose Stock Solutions

Date Sampled	Stock Concentration	COD (mg/L)	Trial	Shake(S) / Noshake(NS)/ Settle(Se)	Range (H/L)
Z Blank	0	UR		NS	H
30/01/2014	10	UR	1	NS	H
30/01/2014	50	UR	1	NS	H
30/01/2014	100	167	1	NS	H
30/01/2014	500	681, 419	1	S,Se	H
30/01/2014	1000	1097	1	NS	H
Blank	0	71, 46, 12		S,Se,Se	H
Z Blank	0	UR		NS	H
30/01/2014	10	UR,UR	2	NS,S	H
30/01/2014	50	UR,UR	2	NS,S	H
30/01/2014	100	UR, 309, 128, 56, 20	2	NS,S,Se,Se,Se	H
30/01/2014	500	404, 877, 642, 523	2	NS,S,Se,Se	H
Blank	0	UR, 621		NS,S	H
Z Blank	0	-3		NS	H
30/01/2014	10	UR	3	NS	H
30/01/2014	50	UR	3	NS	H
30/01/2014	100	189, UR	3	S, Se	H
30/01/2014	500	757, 543, 462, 454	3	S, Se, Se, Se	H
30/01/2014	1000	936, 1065	3	NS, S	H
Blank	0	UR, 651, 181		NS, S, Se	H
Z Blank	0	0		NS	L
30/01/2014	10	27	1	NS	L
30/01/2014	50	55	1	NS	L
30/01/2014	100	108	1	NS	L
Blank	0	-2		NS	L
Z Blank	0	0		NS	L
30/01/2014	10	30	2	NS	L
30/01/2014	50	58	2	NS	L
30/01/2014	100	112	2	NS	L
Blank	0	2		NS	L

Table A.5: Raw peCOD Data of Glucose Stock Solutions

Date Sampled	Stock Concentration	peCOD (mg/L)	Range (B/G/Y)
21/01/2014	0	3.2	Y
22/01/2014	0	0	Y
21/01/2014	10	14.9	Y
22/01/2014	10	4.4	Y
21/01/2014	50	57.3	Y
22/01/2014	50	46.3	Y
21/01/2014	100	110.1	Y
22/01/2014	100	94.5	Y
21/01/2014	500	540.8	Y
22/01/2014	500	507.9	Y
21/01/2014	1000	1030.8	Y
22/01/2014	1000	986.3	Y
06/02/2014	0	0.7	G
06/02/2014	0	1.2	G
06/02/2014	10	9.7	G
06/02/2014	10	13.5	G
06/02/2014	50	49.4	G
06/02/2014	50	55.2	G
06/02/2014	100	90.4	G
06/02/2014	100	97.9	G

Table A.6: High and Low Range Dichromate Results of KHP COD Standards

Dichromate

Mar 11th

Sample	COD(mg/L)	Range	Std Dev
z Blank	0	Low	N/A
100a	90	Low	7.071068
100b	89	Low	7.778175
Blank	-1	Low	N/A
z Blank	0	Low	N/A
100b	88	Low	8.485281
100a	90	Low	7.071068
Blank	-1	Low	N/A
z Blank	0	High	N/A
100a	126	High	18.38478
100b	96	High	2.828427
300a	300	High	0
300b	298	High	1.414214
Blank	3	High	N/A
z Blank	0	High	N/A
300b	281	High	13.43503
300a	270	High	21.2132
100b	76	High	16.97056
100a	117	High	12.02082
Blank	9	High	N/A
z Blank	-1	High	N/A

Mar 12th

Sample	COD (mg/L)	Range	Std Dev
z Blank	1	High	N/A
600a	620	High	14.142136
600b	644	High	31.112698
1000a	1027	High	19.091883
1000b	1040	High	28.284271
Blank	7	High	N/A
z Blank	0	High	N/A
1000b	1026	High	18.384776
1000a	1020	High	14.142136
600b	644	High	31.112698
600a	622	High	15.556349
Blank	3	High	N/A

Table A.7: SOWC peCOD and peCOD 1105 Results of KHP COD Standards, Including Calibration Data

peCOD in SOWC Lab

Mar 13th

Calibrated with 1000mg/L KHP Std. Seven calibrations required at baseline=15. Iterm=9.52, which stayed low throughout testing

Sample	COD (mg/L)	Trial	Std Dev
1000	990.2	1	6.930
600	627.6	1	19.52
600	605.2	2	3.677
300	366.0	1	46.67
300	365.1	2	46.03
100	129.4	1	20.79
100	COD<blank	2	N/A

Mar 14th

Calibrated with 300mg/L KHP Std.
2 calibrations, good Iterm (12.28)

Sample	COD (mg/L)	Trial	Std Dev
300	302.2	1	1.556
300	299.2	2	0.5657
100	107.8	1	5.515
100	102.3	2	1.626
Blank	0	1	N/A

peCOD from MANTECH Lab

Mar 17th

Calibrated with 1000mg/L KHP Std
3 calibrations, Iterm=12.84

Sample	COD (mg/L)	Trial	Std Dev
1000	984.3	1	11.10
1000	980.2	2	14.00
600	682.4	1	29.98
600	663.6	2	44.97
300	375.1	1	53.10
300	383.2	2	58.83
100	122.7	1	16.05
100	127.3	2	19.30
Blank	0	1	N/A

Mar 18th

Calibrated with 300mg/L KHP Std
2 calibrations, Iterm over 12

Sample	COD (mg/L)	Trial	Std Dev
300	301.3	1	0.9192
300	303.2	2	2.263
100	97.3	1	1.909
100	103.6	2	2.546
Blank	0	1	N/A