EVALUATION OF AN ON-LINE ANALYZER SYSTEM FOR MONITORING ORTHOPHOSPHATE, AMMONIA, NITRATE AND TOTAL SUSPENDED SOLIDS AT CALGARY'S BONNYBROOK AWWTP

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ABSTRACT

The City of Calgary's advanced treatment plant currently treats an average daily flow of 350,000 m3/d and consists of 6 biological nutrient removal (BNR) reactors and 4 complete-mixed activated sludge (AS) aeration tanks. Four parameters were identified as important for process monitoring and control, namely orthophosphate, ammonia, nitrate and TSS. To evaluate the accuracy and reliability of currently available on-line analyzers, the sewer division invited price quotations from several suppliers. A total of four suppliers submitted their price quotations. A present worth analysis using the quoted capital costs and annual operation and maintenance costs determined that a multiple parameter analyzer system would be the most economical. As a result, the sewer division entered into a six-mouth lease contract with the supplier to verify the accuracy, reliability and economy of the analyzer system.

This paper will describe the process of selection, installation and complete evaluation of the analyzer system including installation, lab and analyzer data comparisons, operational and maintenance costs, plus post installation modifications and enhancements.

INTRODUCTION

The City of Calgary's Sewer Divisions intends to purchase several on-line analyzers that can accurately and reliably measure four important effluent parameters, orthophosphate, ammonia, nitrate and total suspended solids for the Bonnybrook Wastewater Treatment Plant.

A present worth analysis using the quoted capital costs plus annual operation and maintenance costs for a 20 year period determined that the ChemScan UV-6100 Analyzer System would be the most economical. Operation and maintenance costs include the cost of any reagents, standards and cleaning solutions for the system plus the cost of all labor for maintenance, repairs and calibration. As a result, the sewer division entered into a six-month lease contract with the manufacturer (Applied Spectrometry Associates (ASA) Inc., Waukesha, WI. USA) with the objective of verify the accuracy, reliability and operating cost of this instrument.

To evaluate the analyzer's accuracy and reliability while simultaneously measuring the four parameters a the single sample point was chosen in the Bonnybrook final effluent before its discharge to the receiving Bon River. All four parameters were measured once every 30 minutes.

ANALYZER SYSTEM DESCRIPTION

The UV-6100 analyzer system is an on-line ultraviolet spectrometer capable of measuring the concentration of multiple dissolved chemical constituents (parameters) of an aqueous sample with a single analyzer. The UV-6100 works by transmitting ultraviolet light through the sample. A portion of the light is absorbed by the chemical constituents and the analyzer splits the resulting light into 256 individual wavelengths from 200 to 450 nm. The spectral signature is analyzed using Chemometrics, a pattern recognition technique, to calculate the parameters concentrations. Parameters that absorb light naturally, such as nitrate, can be analyzed without the addition of reagents. Parameters that do not have adequate natural light absorbing

characteristics must be conditioned through the addition of chemical reagents (herein referred to as secondary chemical methods).

The analyzer system consists of a manifold with auto zeroing and cleaning, a sample pump, a sample conditioning unit and the UV-6100 analyzer (see figure 1).

ANALYTICAL METHODS

Nitrate method

The ChemScan UV-6100 measures nitrate concentration using the natural occurring absorbance signature of the nitrate ion in the ultra-violet wavelength region. Therefore, nitrate concentration is measured without the use of reagents. To determine the nitrate concentration, the sample is flushed through the flow cell and the analyzer detects the UV light absorbance spectrum. The previously derived chemometric calibration is applied to the spectrum to produce the concentration value. The Chemometric calibration was produced by the manufacturer during start-up using 10 - 12 site spectra added to a library of 50 - 70 spectrum with varying nitrate concentrations and background absorbance.

Ammonia method

Ammonia concentration is determined using a secondary chemical method. The ammonia is complexed with sodium Hypochlorite (bleach) at an elevated pH in the sample conditioning unit. The analyzer measures the resulting combined spectra and uses a Chemometric algorithm to determine the ammonia concentration. The chemical costs are very low and the resulting mixture is non-toxic and non-hazardous and can be drained to waste.

Orthophosphate method

Orthophosphate is determined using a secondary chemical method. The orthophosphate is complexed with ferric at a low pH in the sample conditioning unit. The analyzer measures the resulting combined spectra and uses the Chemometric algorithm to determine the orthophosphate concentration. Like the ammonia method, the chemical costs are very low and the resulting mixture is non-toxic and non-hazardous and can drained to waste.

Total suspended solids method

The TSS concentration is determined using the natural occurring absorbance signature of the solids in the ultra-violet wavelength region. The TSS has a high correlation to the light transmittance in the near visible wavelength range.

INSTALLATION AND CALIBRATION

The plant final effluent sample point was chosen for the analyzer evaluation. The analyzer system was installed in the disinfection building. The sample was drawn from the channel outside of the building in close proximity to a 24 hour composite sampler inlet. The analyzer peristaltic pump draws the sample up 2.5 - 3 meters to the analyzer for analysis. The pump

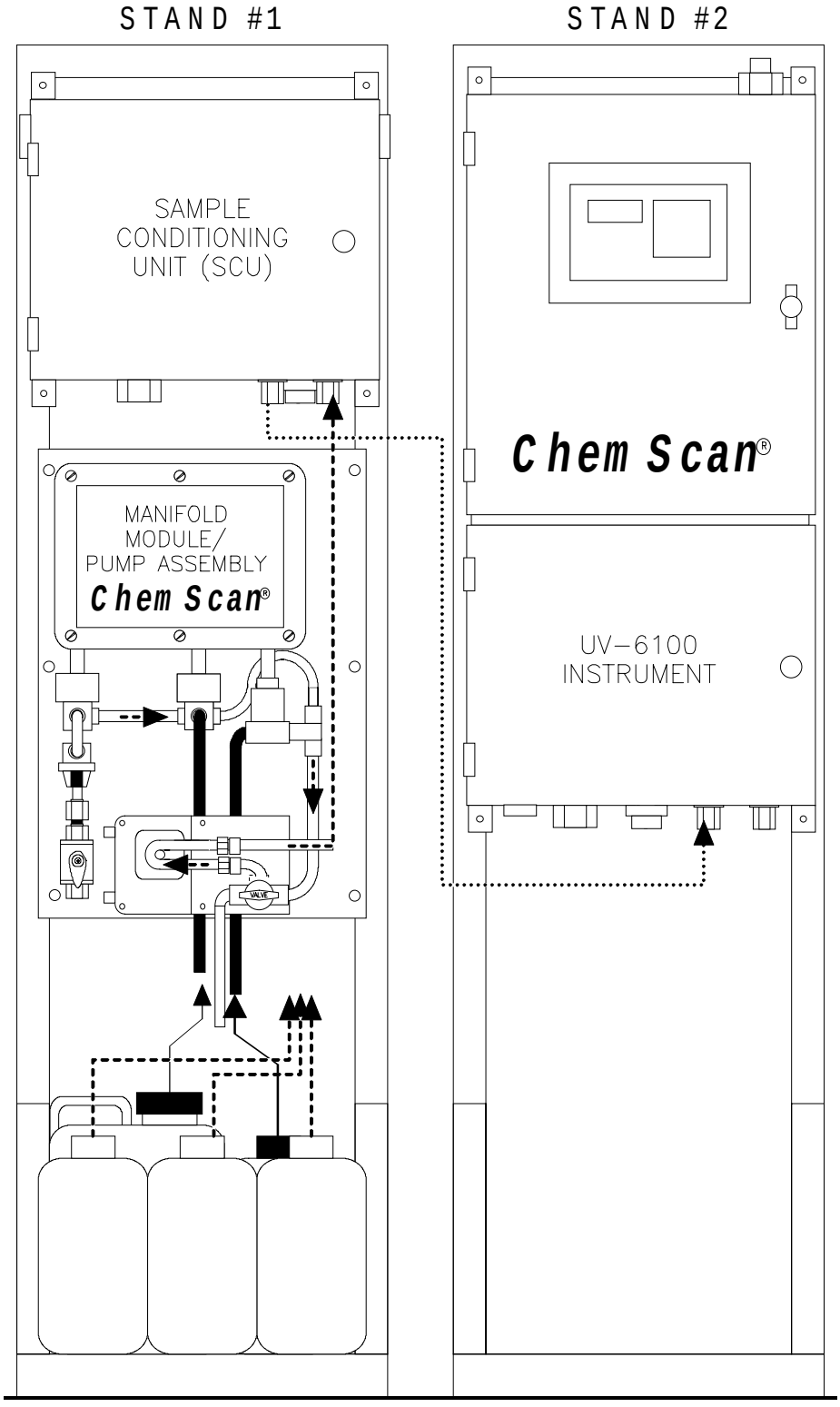


Figure 1: ChemScan Analyzer System

draws 3-4 liters for each analysis of the four parameters. The analyzer system is self standing on two mounting stands and is plugged into a 120 VAC wall outlet. The plant computer system receives the concentration data through the analyzer's 4-20 mA outputs. The analyzer was setup to perform an analysis on each of the four parameters every 30 minutes. Following the analysis, the 4-20 mA singles are updated to reflect the reading results. The results are data logged by the plant computer and the trend can be observed on the computer displays located though out the plant.

Before chemical monitoring can be accomplished, the analyzer must be calibrated for the subject parameter. The analyzer was calibrated for nitrate by analyzing split samples with the ChemScan system and the City of Calgary's laboratory. The samples are analyzed by the ChemScan system and the spectral absorbance signature is recorded in its internal memory. This spectral data is associated with the known concentration values from the laboratory. The site spectra was added to a library of spectra generated at other sites to produce a reliable and accurate site calibration to measure nitrate.

Ammonia and orthophosphate calibrations were performed using a similar sample analysis procedure as the that used for the nitrate calibration. Split samples were analyzed with both the ChemScan system and the laboratory. A comparison of ammonia and orthophosphate data predicted by the ChemScan, to the laboratory data proved that the factory installed calibration would provide accurate operation after only a slight slope and offset adjustment.

The TSS calibration was performed utilizing a linear regression that correlated the laboratory TSS values with the light transmittance at 400 nm.

Post installation modifications and enhancements

Following the initial installation, some modifications were required to optimize the operation of the analyzer system. A weighted 3/8" sample tube from the ChemScan analyzer was placed into the effluent channel. Over time the tubing became plugged with algae and a strainer was added to the end of the sample line to eliminate this problem. In late fall, as the temperature dropped, it was necessary to move the sample line indoors to eliminate the possibility of freezing. At that time a circulation pump was added to reduce the stress on the peristaltic pump caused by pulling the sample from an excessive distance. The circulation pump lifts the sample 2.5 - 3 meters and provided a continuous flow of sample at approximately 15-20 liters per minute. The sample flows into a small reservoir and the overflow returns to the effluent channel. The analyzer extracts the required 3-4 liters for each reading cycle from the reservoir.

During the demonstration it was determined that it was necessary to develop a different cleaning solution to keep the flow cell clean. This effort resulted in the use of a 10% phosphoric acid solution. This gave the best results when taking effectiveness, cost and chemical stability into account.

Operational and maintenance costs

As part of the quote, manufacturers were required to submit the analyzer's estimated operation and maintenance costs. During the evaluation period, records were kept for the operational and maintenance costs for comparison to the submitted estimates. For the ChemScan system the reagent and cleaning solution preparation averaged 2.3 hours per month. The analyzer calibration and cleaning averaged 3.4 hours per month. The repair averaged 1.4 hours per month (mainly due to peristaltic pump tube replacement). The total maintenance time averaged 7.1 hours per month to keep the analyzer system fully operational over the four month period. This was well below manufacture's estimated 8.3 hours per month.

The chemical costs to operate the analyzer system were also less than the estimated C$ 130.00 per month.

DATA COMPARISON

To evaluate the analytical performance, daily samples were collected and analyzed by the laboratory for each of the parameters. At the time of the sample collection, the ChemScan concentration values were recorded. The absolute error of range was calculated for the sample:

$$\% \text{ Absolute Error of Range} = \frac{|(\text{Lab value} - \text{Analyzer value})|}{\text{Range of Operation}} \times 100$$

The average error for each month has been calculated along with the average error over the 4 month evaluation period. The 4 month average error values were used to determine the accuracy of the analyzer's data.

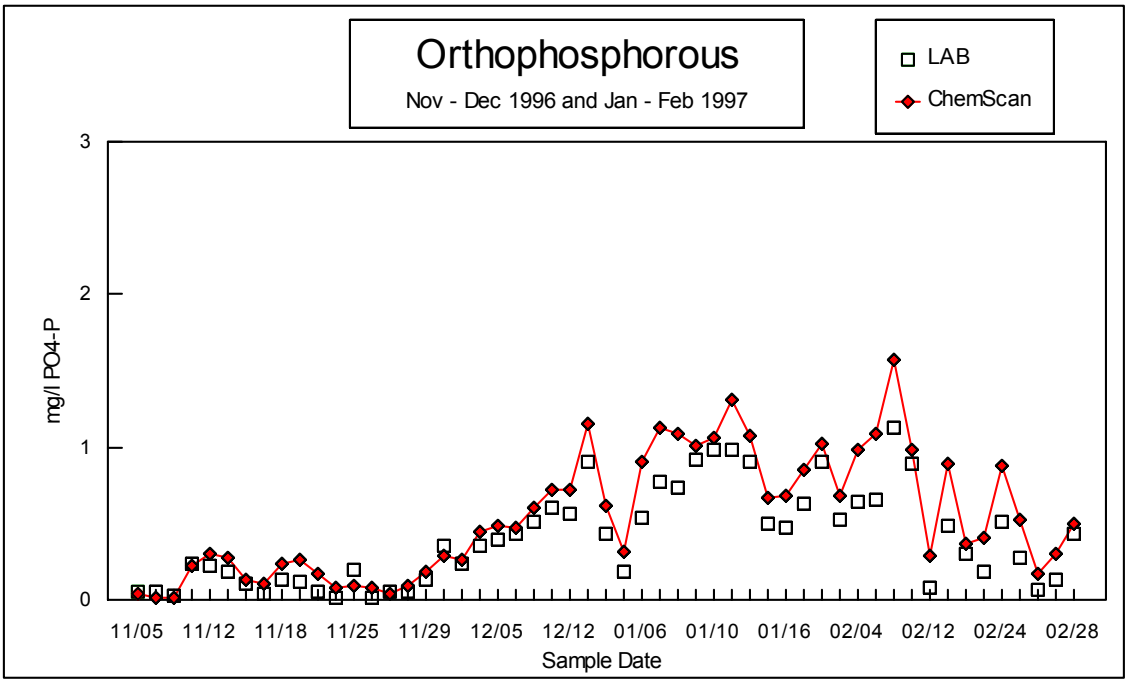
Phosphate, Ammonia, Nitrate and TSS results are displayed using three different plots of the Laboratory vs. ChemScan data. The first plot contains a two week period of operation where all the ChemScan data is plotted continuously and the lab points are added at the appropriate date and time. It shows daily patterns and occasional process upsets. The second plot contains the grab sample values for the Lab and the ChemScan vs. the day the sample was collected. This representation shows the analyzers ability to track the high and low concentration values. The third plot contains the Laboratory data plot vs. the ChemScan along with a line representing $\pm$ 5% of range. This representation shows the analyzer's ability to predict within the $\pm$ 5 % error range.

Orthophosphate data comparison

The phosphate operating range was set to 0.01 mg/l to 5.0 mg/l PO4-P. Over the 4 month evaluation period, the ChemScan and Laboratory results agreed with an average absolute error of 3.0 percent (see figure 2). The majority of the data points fall within the $\pm$ 5 percent error lines. The two week data plot (see figure 3) shows very stable reading to reading operation.

ChemScan Analyzer Orthophosphorous Data
Bonnybrook AWWTP Calgary Alberta

November Average Absolute Error	1.2%
December Average Absolute Error	2.0%
January Average Absolute Error	4.7%
February Average Absolute Error	4.3%
Four Month Average Absolute Error	3.0%



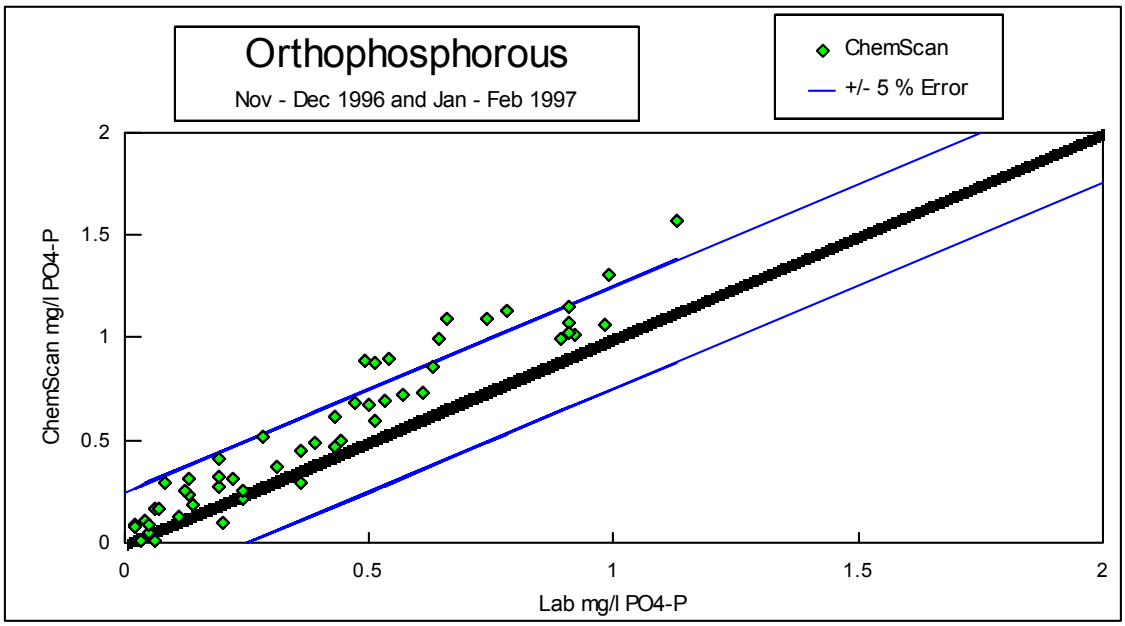


Figure 2: Orthophosphate Evaluation Data

During this period, there were no calibration adjustments performed. It appears that a slight slope adjustment would provide even more accurate results.

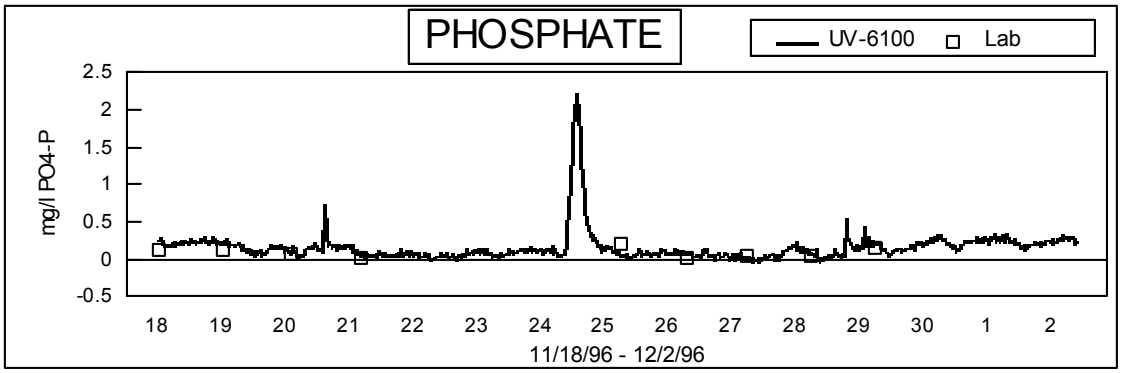


Figure 3: Phosphate Two Week Data Plot

Ammonia data comparison

The ammonia operating range was set to 0.5 mg/l to 30.0 mg/l NH3-N. The two week data plot (see figure 4) shows very stable reading to reading operation. Over the 4 month evaluation period, the ChemScan exhibited an average absolute error of 3.0 percent (see figure 5) with respect to the laboratory data. There was a slope and offset adjustment made to the ammonia calibration on November 27. At the start of the evaluation the ammonia concentrations were between 10 and 25 mg/l. In the first month of evaluation, the ammonia values dropped to between 0 and 7 mg/l. The calibration adjustment was performed to better predict the lower concentration range. The calibration adjustment consisted of collecting 5 samples at varying ammonia concentrations throughout the operating range. Each sample was measure by the analyzer and laboratory. The results were used to produce a slope and offset adjustment to the calibration. Once the calibration adjustment was entered into the analyzer, the ammonia predictions were very accurate (see figure 5).

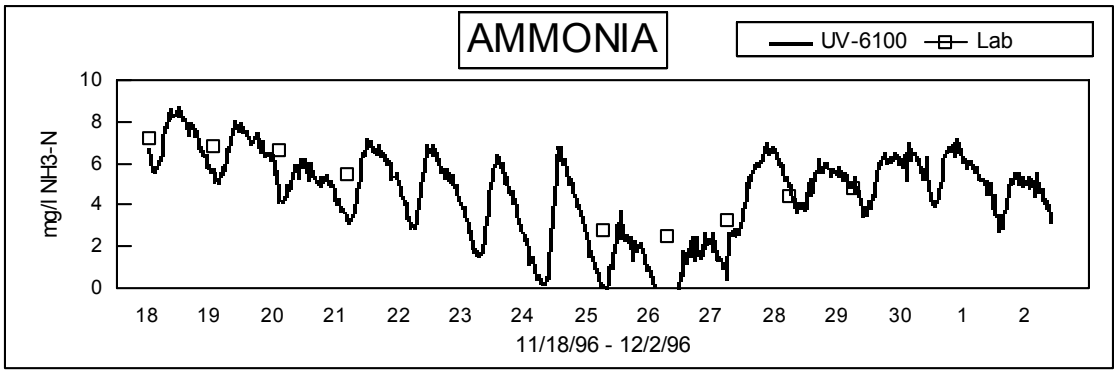


Figure 4: Ammonia Two Week Data Plot

ChemScan Analyzer Ammonia Data
Bonnybrook AWWTP Calgary Alberta

November Average Absolute Error	3.3%
December Average Absolute Error	2.5%
January Average Absolute Error	4.4%
February Average Absolute Error	2.5%
Four Month Average Absolute Error	3.0%

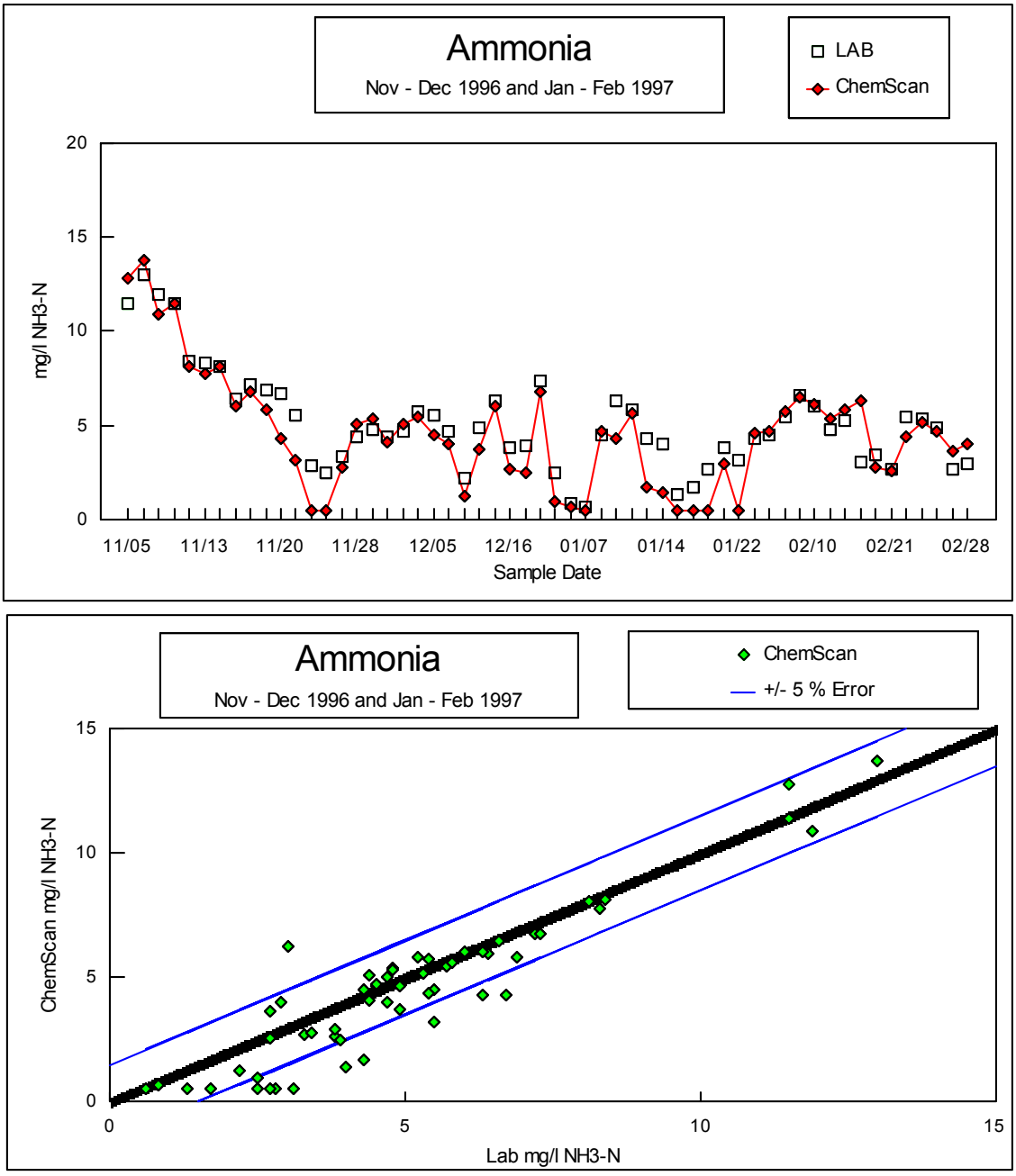


Figure 5: Ammonia Evaluation

Nitrate data comparison

The nitrate operating range was set to 0.5 mg/l to 20.0 mg/l NO3-N. The two week data plot (see figure 6) shows a small amount of reading to reading variation. Over the 4 month evaluation period, the ChemScan and Laboratory agree with an average absolute error of 1.7 percent (see figure 8). The majority of the data points fall within the $\pm$ 5 percent error lines. During this period, there were no calibration adjustments performed.

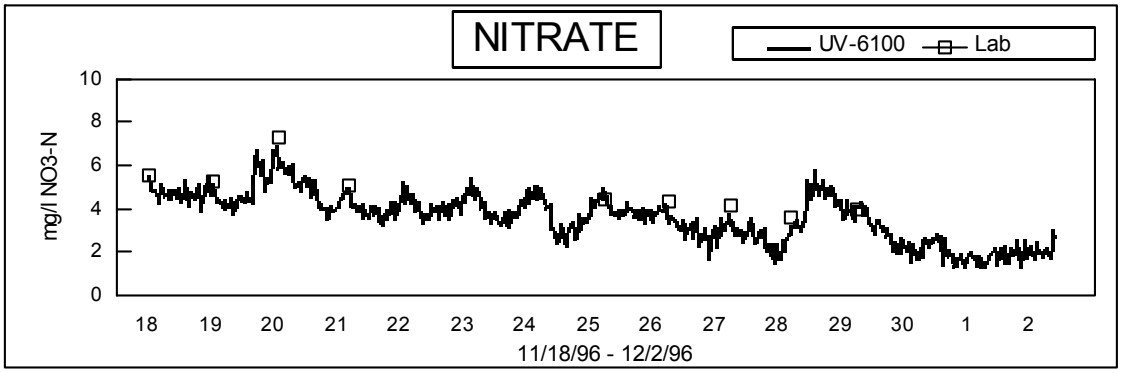


Figure 6: Nitrate Two Week Data Plot

Total suspended solids data comparison

A Total Suspended Solids calibration has been produced to provide TSS values using the percent transmittance value at 400 nanometers. There is a high correlation between TSS and 400 nanometer absorbance (see figure 7). The analyzer system provides a percent transmittance at 400 nm to the plant computer. The calibration is contained within the plant computer to provide TSS from the transmittance values. Over the four month period, the calculated regression provides an average absolute error of 3.3 percent (see figure 9). The majority of the data points fall within the $\pm$ 5 percent error lines.

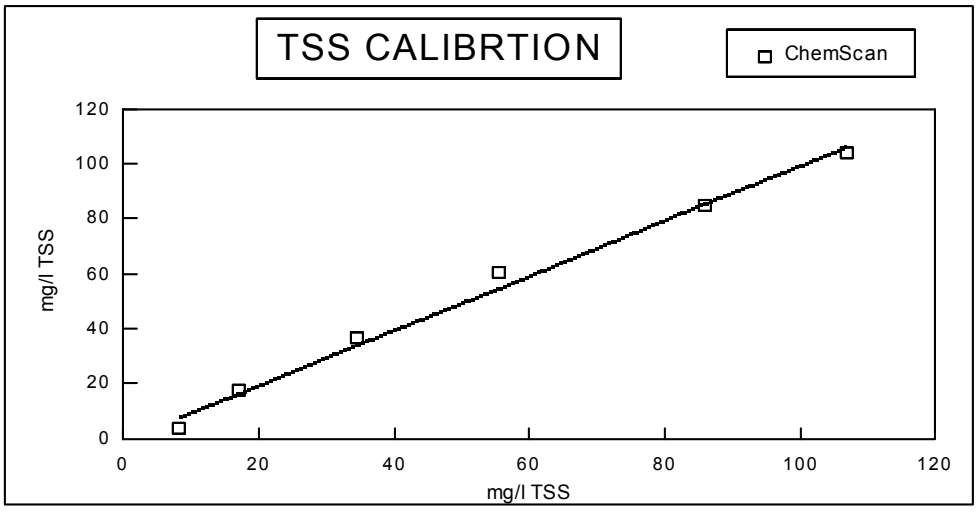


Figure 7: TSS Calibration Curve

ChemScan Analyzer Nitrate Data
Bonnybrook AWWTP Calgary, Alberta

November Average Absolute Error	2.0%
December Average Absolute Error	1.3%
January Average Absolute Error	1.8%
February Average Absolute Error	1.6%
Four Month Average Absolute Error	1.7%

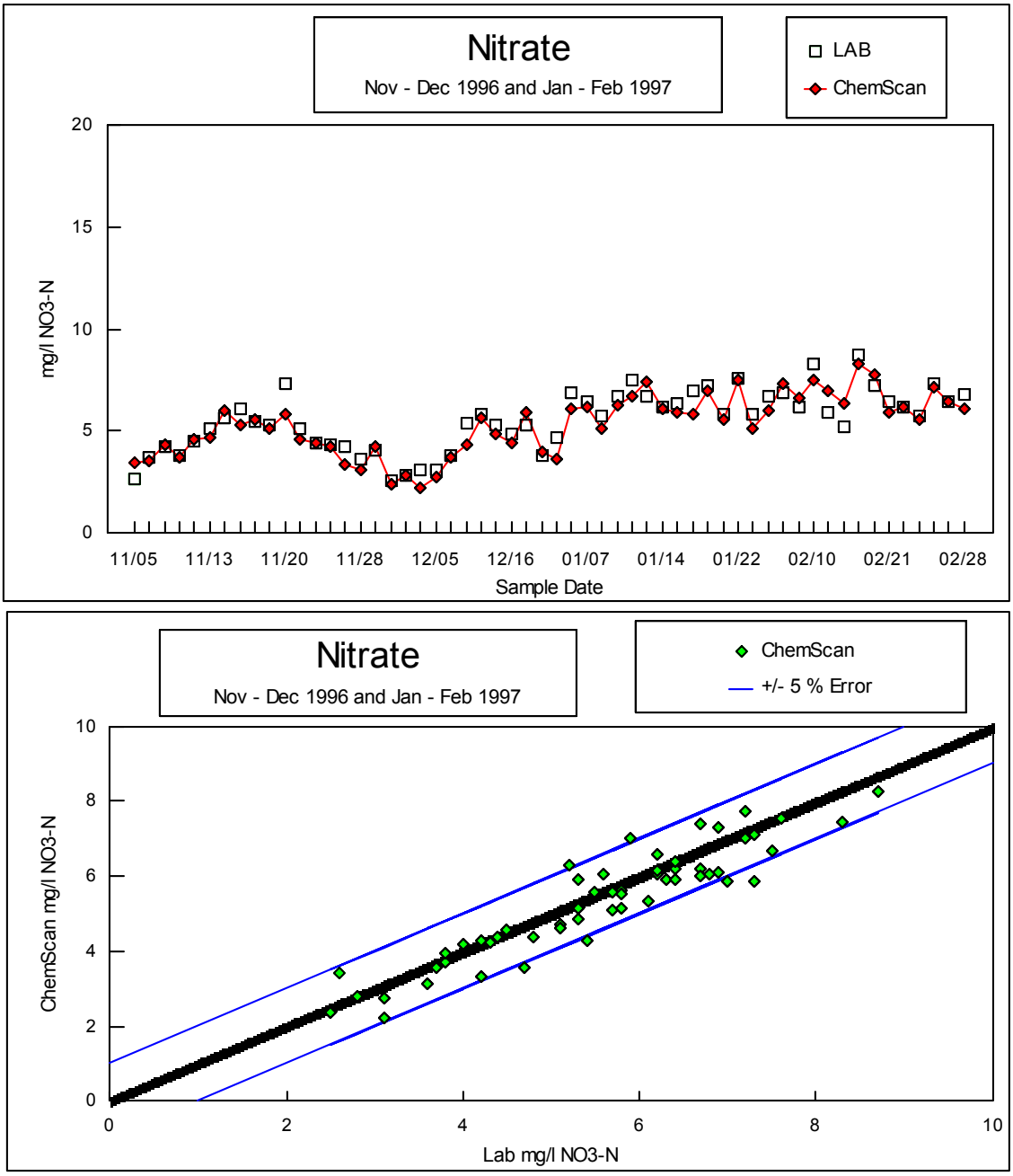
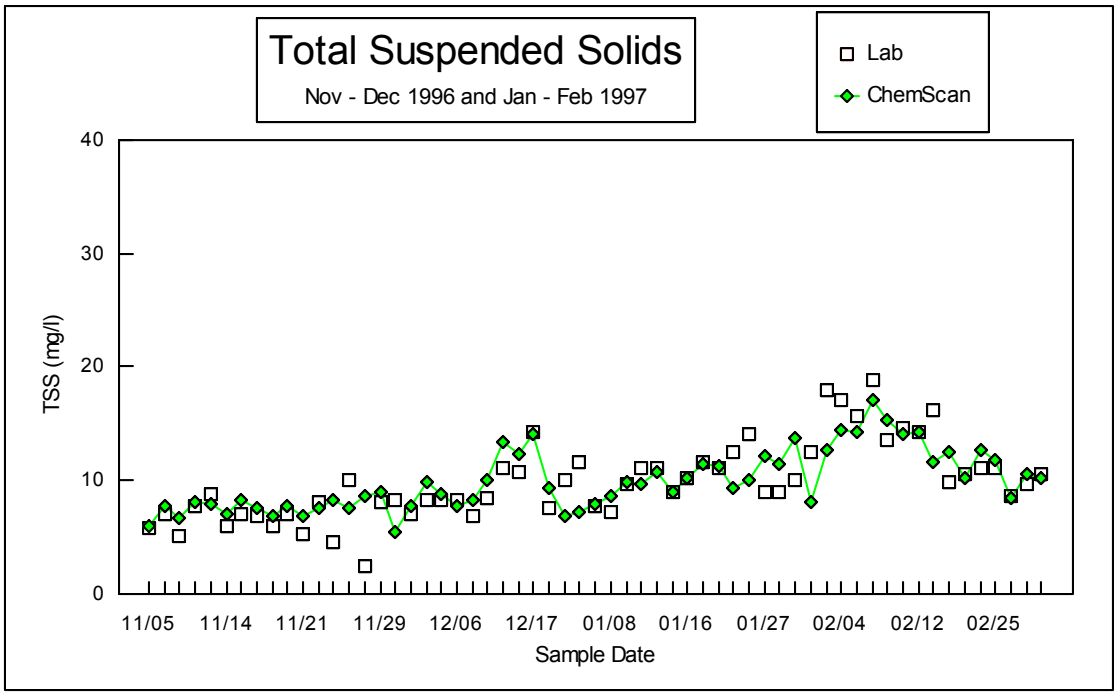


Figure 8: Nitrate Evaluation Data

ChemScan Analyzer Total Suspended Solids Data
Bonnybrook AWWTP Calgary, Alberta

November Average Absolute Error	3.0%
December Average Absolute Error	2.8%
January Average Absolute Error	2.5%
February Average Absolute Error	4.3%
Four Month Average Absolute Error	3.3%



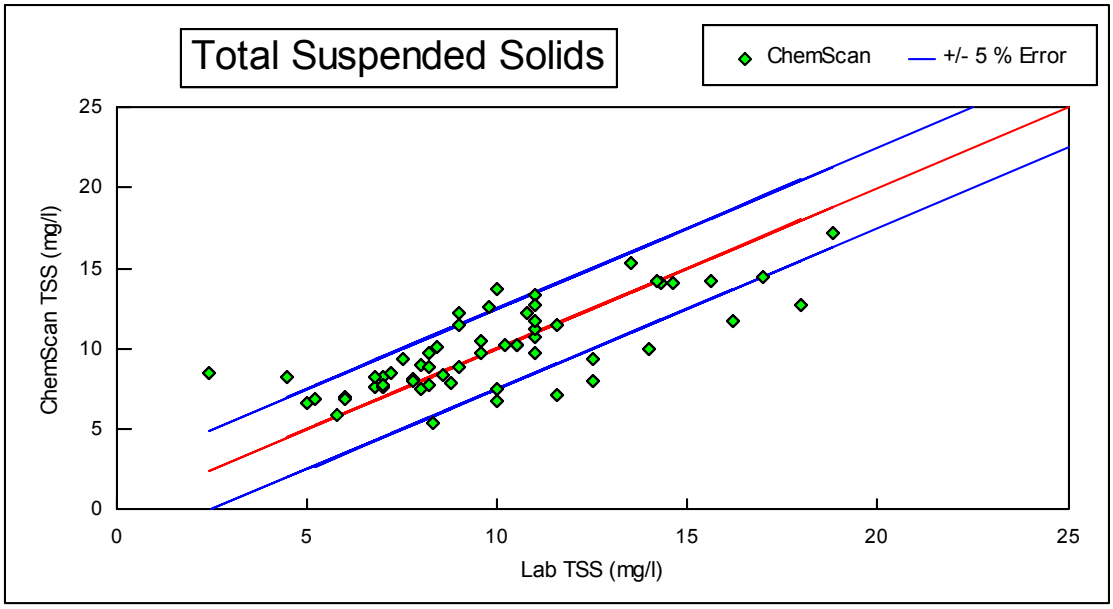


Figure 9: Total Suspended Solids Data Evaluation Data

CONCLUSION

The City of Calgary invited price quotations for capital costs and annual operation and maintenance costs for an on-line analyzer for the simultaneous measurement of nitrate, ammonia, phosphate and total suspended solids (TSS) at the Bonnybrook AWWTP. As a result the sewer division entered into a six-mouth lease contract with the ASA, Inc. to verify the accuracy, reliability and economy of the ChemScan UV-6100 analyzer system. The evaluation was carried out over a 4 month period form November 1996 through February 1997. During this period of time the average operational and maintenance time spent on the analyzer system was 7.1 hours per month and the average chemical costs were less than C$130 per month, both below the manufacturers quoted values. An average of 13 grab samples per month were collected to evaluate the performance of the analyzer with respect to the laboratory. Over the evaluation period the average absolute error of range were: orthophosphate 3.0%, ammonia 3.0%, nitrate 1.7% and TSS 3.3%. The analyzer measured all four parameters well below the maximum acceptable error of 5%. As a result of the analyzers performance, the City of Calgary purchased the leased analyzer along with 2 additional UV-6100 analyzer systems.