

# ChemScan® Process Analyzer

Title: Project Report and Data Summary Evaluation of On-Line Ammonia, Nitrate  
and Nitrite Analysis for Process Control and Energy Management

Budd Inlet Wastewater Treatment Plant (BITP) in Olympia, Washington

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PROJECT REPORT AND DATA SUMMARY  
EVALUATION OF ON-LINE AMMONIA, NITRITE AND NITRATE  
ANALYSIS FOR PROCESS CONTROL AND ENERGY MANAGEMENT

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**ABSTRACT**

Results are provided from an evaluation of on-line nitrate and nitrite monitoring systems, utilizing quantification of ultraviolet absorption, tested directly in mixed liquor at the Budd Inlet Wastewater Treatment Plant (BITP) in Olympia, Washington. Included are a discussion of alternatives for on-line measurement, technical background regarding nitrate/nitrite monitoring systems, descriptions of several nitrate/nitrite monitoring systems tested, results from the in-plant testing, and evaluation of results. Additionally, the rationale and role for the on-line monitoring system in the BITP process control scheme is discussed. Recommendation for system modifications to implement automation of methanol feed are provided to optimize denitrification, based on the results of a process evaluation.

For this study, three systems that use ultraviolet spectrophotometry for nitrate/nitrite quantification were evaluated at the BITP. These systems each use a different approach to quantify nitrate/nitrite, as well as to compensate for interference from other nitrogen species, organics, and suspended particles. Results from the on-line nitrate/nitrite testing were compared against laboratory analysis conducted with methods from *Standard Methods* (APHA, WEF, AWWA). The analytical precision and bias of the three on-line systems were quantified relative to the laboratory methods. Also, results from recent operation of the selected system are provided. The results and accompanying discussion illustrate the potential for, and challenges of, on-line nitrate/nitrite analysis in high solids streams such as mixed liquor.

**KEYWORDS**

Nitrate, nitrite, on-line, ultraviolet, monitoring, analyzer, denitrification, methanol

## INTRODUCTION

The Budd Inlet Treatment Plant (BITP) is an advanced secondary wastewater treatment facility located in downtown Olympia, WA at the southern end of Puget Sound, as shown in Figure 1. This facility serves the cities of Lacey, Olympia, and Tumwater, and Thurston County (“LOTT Alliance”). The plant was originally constructed in 1948 and subsequently has undergone major

upgrades in 1979, 1994 and 2004 to arrive at its present configuration. The plant is currently permitted for maximum month dry weather, maximum month wet weather and peak hour flows of 15, 22 and 55 MGD, respectively. The 1994 upgrade to the facility was driven by new effluent limitations for total inorganic nitrogen. Nitrogen was identified as the limiting nutrient for algae growth in Budd Inlet and Capital Lake, and the wastewater treatment plant was

identified as a major contributor of nitrogen to the basin. As a result, seasonal total inorganic nitrogen limits of 3.0 mg/L were placed in the LOTT NPDES permit (Permit # WA-003706-1). These nitrogen limitations are in effect from April 1 to October 31 each year. In addition to the existing seasonal limits, the treatment plant also has a nitrate limit of 10 mg/L the remainder of the year for any portion of secondary effluent treated to Class A reuse quality by the newly constructed reclaimed water treatment facility, and used for beneficial reuse.

In order for the plant to effectively meet this effluent inorganic nitrogen limit, it must efficiently remove the nitrate nitrogen that is produced during the nitrification of the influent ammonia and hydrolyzed influent organic nitrogen. To achieve the level of nitrate reduction required, the influent wastewater must contain adequate organic carbon to satisfy the needs of the denitrifying bacteria. Until 2003, the wastewater discharged to the plant by the Miller Brewery provided a more than ample supply of readily biodegradable substrate to meet these needs. The closure of the brewery in 2003, however, altered the influent wastewater characteristics to the extent that the influent wastewater no longer contains sufficient readily

**Figure 1: Location of Budd Inlet Treatment Plant**



biodegradable substrate to consistently achieve the level of nitrate reduction required. Consequently, the plant began continuously adding methanol to the treatment process to replace the readily biodegradable substrate that was lost with the closure of the brewery. The continuous dosing of methanol increased chemical operating costs by as much as \$14,000 per month (in 2004), and led to additional monitoring and maintenance requirements.

The impact of the additional operating expense prompted LOTT personnel to investigate alternatives for reducing the use of methanol through automation and other process modifications. Reduced operating costs and increased system reliability through the automation of the methanol feed system and process optimization were the primary goals of this effort. To this end, the scope of this project included the following goals regarding the methanol feed system:

1. Evaluating the existing treatment process and provide recommendations for optimizing the process to reduce methanol consumption
2. Providing recommendations for mechanical and electrical modifications to the methanol feed system
3. Reducing attended operation through automation of the methanol feed system.
4. Assisting LOTT personnel in testing, evaluating and selecting an on-line nitrate/nitrite analyzer to be used in automating the methanol feed system. This paper focuses primarily on the evaluation of nitrate/nitrite analyzers, and the results of implementation of full-scale use of the analyzers and process control system.

#### NITRIFICATION –DENITRIFICATION

The BITP relies on nitrification and denitrification for removal of inorganic nitrogen from the influent wastewater. Nitrification is a microbial process by which ammonia is sequentially oxidized to nitrate. The nitrification process is primarily accomplished by two groups of chemolithoautotrophic nitrifying bacteria that can build organic molecules using energy obtained from inorganic sources, in this case ammonia or nitrite and cellular carbon obtained from dissolved carbon dioxide. In the first step of nitrification, ammonia-oxidizing bacteria (AOB) oxidize ammonia to nitrite according to the following equation.



In the second step of the process, nitrite-oxidizing bacteria (NOB) oxidize nitrite to nitrate according to the following equation.



Nitrospira-like bacteria have been observed to be the dominant NOBs in most full-scale treatment plants.

Denitrification is a microbially facilitated process of dissimilatory nitrate reduction that ultimately produces molecular nitrogen  $\text{N}_2$  through a series of intermediate gaseous nitrogen oxide products.

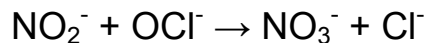


Denitrification occurs when nitrate acts as an electron acceptor, and thus only occurs under anoxic conditions. Denitrification also requires an electron donor, typically organic carbon.

### Nitrite Lock

Under certain process conditions, including inhibition by toxic compounds, alkalinity deficiency (<70 mg/L), low pH, low temperature or low dissolved oxygen, the second step of nitrification can be significantly slower than the first, leading to an accumulation of nitrite ions. Such a situation is called “Nitrite lock”. Nitrite lock is a common occurrence in plants that seasonally nitrify. AOB must grow and produce nitrites before NOB *can* grow. Consequently, there is a build-up of nitrites due to the lag in NOB growth. (Muirhead and Appleton, 2007)

Oxidation of nitrite to nitrate is a thermodynamically favored reaction, and in absence of an enzymatic pathway, nitrite ions seek an alternate route to convert to nitrate. When chlorine is added for disinfection to a treated wastewater containing large amounts of nitrite ions, it oxidizes nitrite and gets partially consumed by the nitrite oxidation reaction:



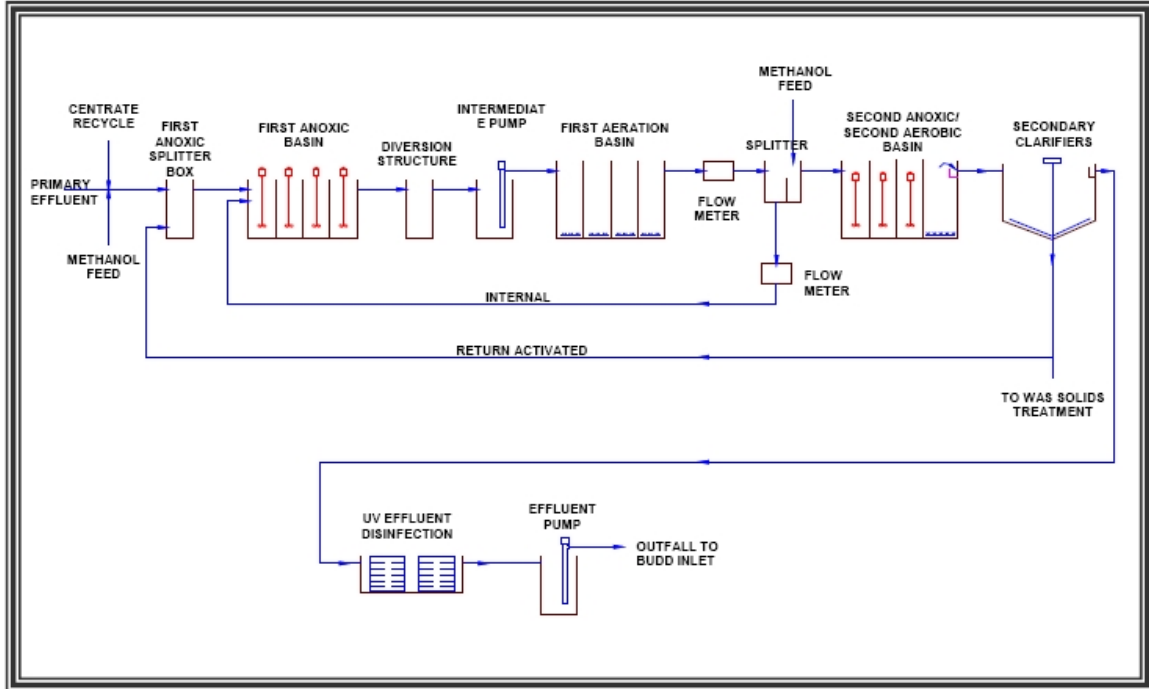
Stoichiometrically, one nitrite ion consumes one hypochlorite ion to complete the oxidation reaction. When ammonia-N is partially nitrified to nitrite, it creates a chlorine demand of 5 mg/l of chlorine for the oxidation of 1 mg/l of nitrite-N to nitrate-N (Basu, 2008). At BITP, reclaimed water is chlorinated with hypochlorite prior to distribution. If the biological treatment system were to go into nitrite lock, the system may not be able to maintain a chlorine residual. Thus, accurate quantification of nitrite a nutrient monitoring system could allow it to serve as an “early warning” system to alert operations staff of a nitrite lock condition.

## BUDD INLET TREATMENT PLANT

The BITP employs a four stage biological nitrogen removal process in which a series of anoxic and aerobic compartments are utilized to create the environmental conditions necessary to allow both nitrification and denitrification to occur within the same activated sludge treatment process. In this treatment process, primary effluent enters the first anoxic basin, where it is combined with the return activated sludge from the secondary clarifiers and the nitrified mixed liquor recycle from the first aerobic basin. In the first anoxic basin, a portion of the heterotrophic bacteria utilize nitrate in lieu of oxygen to oxidize the organic carbon present in the influent wastewater. After undergoing nitrification in the first aerobic basin, mixed liquor from this basin is not only recycled back to the first anoxic basin, but also flows to the second anoxic basin where additional nitrate is removed through endogenous respiration prior to entering the final aerobic basin for re-aeration and effluent polishing. A process flow diagram of the treatment facility is shown in Figure 2.

Because of the low effluent nitrogen limits for the BITP, the availability of organic carbon in the influent is critical to the overall performance of the treatment process. Sufficient organic carbon must be present to allow the denitrifying organisms to remove nitrate in the mixed liquor recycle to the first anoxic basin. If sufficient substrate is not available, the remaining nitrate will have to be removed in the second anoxic basins either through the addition of a supplemental carbon source, such as methanol, or through endogenous respiration. Since relying on endogenous respiration to significantly reduce effluent nitrate concentrations requires much longer anoxic hydraulic and solids retention times, the addition of an external carbon source to supplement the carbon in the influent is one of the typical process solutions. The challenge is to maximize the use of the influent carbon and endogenous respiration within the operational constraints of the treatment system, thereby minimizing the use of external carbon and, consequently, operating costs.

**Figure 2: Budd Inlet Treatment Plant Process Flow Diagram**



Historically, the WWTP has benefited from the high organic carbon load contributed by wastewater from the Miller Brewery. Plant records indicate that during the brewery's operation this industry contributed approximately 40 percent of the plant's organic load while only producing 12 percent of its flow. In addition, a large part of the organic load discharged by the brewery was in the form of readily biodegradable substrate, which does not require the bacteria to enzymatically break down long chain molecules into shorter chain molecules prior to utilization for cell growth. Therefore, while the brewery was in operation, an adequate source of organic carbon for nitrate reduction was available. Following the brewery's closure in 2003, the plant was forced to rely on methanol to replace a portion of the readily biodegradable substrate previously discharged by the brewery, to meet the effluent total inorganic nitrogen limits. In the period from July through October 2003, the plant injected between 7,000 and 12,000 gallons of methanol per month into the treatment process, at a cost of up to \$14,000 per month.

### PROCESS EVALUATION

A process evaluation led to recommendations to minimize supplemental carbon addition through process optimization and automation of the existing treatment process and by providing additional process monitoring and automation. This process evaluation consisted of preliminary activated sludge modeling and simple mass balances using historical operating data. This effort confirmed that given the current influent wastewater characteristics and process configuration, the effluent

inorganic nitrogen limit of 3 mg/L could not be met without supplemental carbon addition.

Methanol has been the most commonly used supplemental carbon source to enhance nitrate reduction in biological nutrient removal processes, as it has been found to be the most cost-effective carbon source per unit of nitrate removal. The reason for the more favorable cost effectiveness is that methanol degradation results in a very low biomass yield. Consequently a larger portion of the methanol is oxidized and thus used for nitrate reduction in the absence of oxygen.

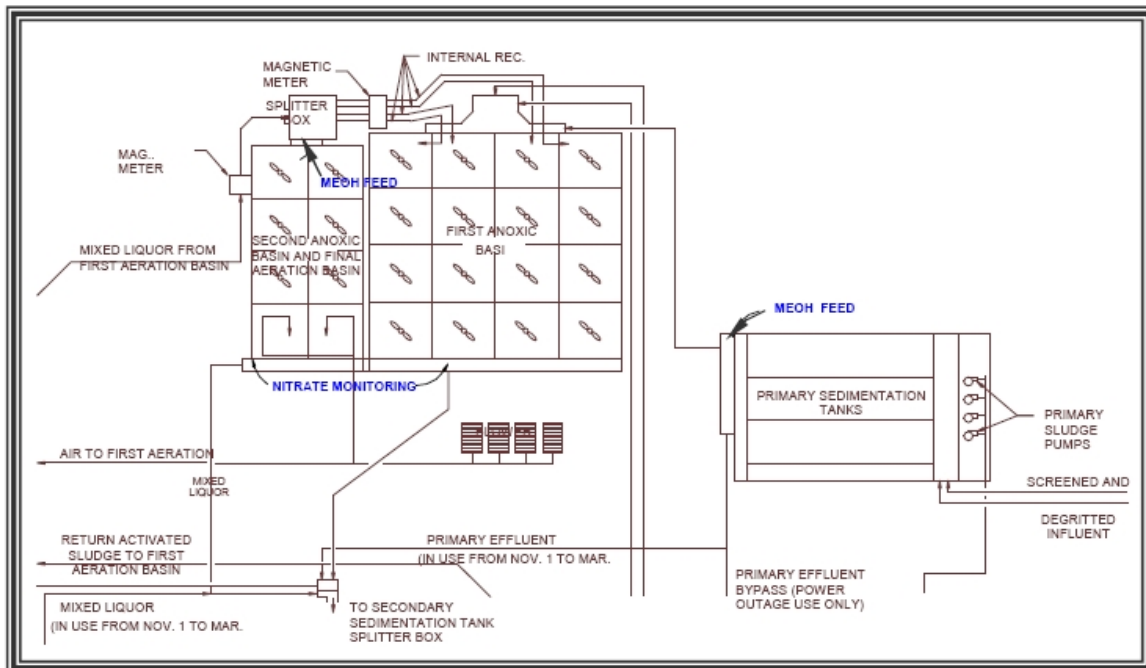
In applying methanol to the mixed liquor of an activated sludge process, one must keep in mind that the heterotrophic bacteria developed from degrading the municipal wastewater carbon source are not methanol utilizers. In fact, the original application of methanol for nitrate removal was in separate reactors that supported a biological population developed primarily from methanol utilization. Methanol is a single carbon compound and is only metabolized by a unique set of bacteria, termed the methylotrophs. Thus, an effective population of these bacteria can only be established in the system after some period of methanol feeding. As a result, intermittent use of methanol is inefficient because the necessary population may not be present for methanol utilization and nitrate reduction when dosing begins.

Based on the modeling effort and an evaluation of the process monitoring and control system, the following recommendations were made:

- To minimize methanol addition, suspend the current practice of adding methanol upstream of the first anoxic zone and add it to the second anoxic zone only, as methanol is more efficiently utilized in post-denitrification (See Figure 3.)
- On-line process monitoring of nitrate, and potentially, other nitrogen species should be initiated. (The then current procedure of manual measurements with a Hach kit proved to be time consuming, inaccurate and created lag time between measurement and dose response, leading to overdosing of methanol.
- Develop a PLC based control system capable of modulating the methanol dose based on feedback from the process instrumentation to optimize the treatment process and reduce methanol utilization.
- Monitor the nitrate concentration at the outlet of the anoxic basins and utilize feed backward control. As the nitrate concentration increases above an upper set point dead band, the control algorithm will increase the supplemental carbon dose to drive the nitrate concentration toward the lower set point dead band. The control algorithm will be a simple proportional-integral (PI) control loop in which the methanol dose will vary based on the effluent nitrate concentration measured by the analyzer and influent flow to the treatment plant.

- Additionally, monitor nitrite/nitrate in the effluent from the first anoxic basin to provide additional redundancy, and benefit plant operations by providing additional process information that can be used to enhance process control.

**Figure 3: Methanol Addition Points and Nitrate Monitoring Locations**



## NITRATE MONITORING ALTERNATIVES

Technologies for on-line systems for nitrate monitoring include colorimetry (i.e., the cadmium reduction method), specific ion electrodes, and ultraviolet spectrophotometry. Like all process analytical chemistry analyzers, these systems adapt laboratory methods to the more difficult task of automatic, relatively unattended monitoring directly in process streams (in-situ) or pumped to external analyzers (ex-situ). As described in the 20th edition of *Standard Methods for the Examination of Water and Wastewater*, (*Standard Methods*) “determination of nitrate is difficult because of the relatively complex procedures required, the high probability that interfering constituents will be present, and the limited concentration ranges of the various techniques.” When adapted to the rigors of on-line wastewater analysis, nitrate analysis has even more challenges. Difficulties exist with all of the methods listed above when applied to on-line nitrate measurement. The specific ion electrode method has been applied to on-line nitrate monitoring, but is affected by interference from chloride and bicarbonate and significant calibration drift. The cadmium reduction method, in which nitrate is converted to nitrite on a cadmium catalyst, is used in many laboratories, but, when

applied to on-line wastewater monitoring, is affected by interference from organics (oil and grease) and requires frequent replacement of reagents.

The advantages of the ultraviolet method include relatively rapid response, low maintenance requirements, lack of required reagents other than cleaning solutions, and only moderate interference that, in typical domestic wastewater, can be successfully compensated for. Interferences with the ultraviolet method include other substances that absorb UV light at 210-220 nm: nitrite, thiosulfate, chlorate and chlorite (which are not expected in high concentrations in wastewater treatment plants) and organic compounds, particularly aromatic compounds (including NOM, natural organic matter). Additionally, suspended matter will block (absorb, reflect, refract) ultraviolet light – a problem that often occurs when measurements are taken in mixed liquor. Per discussion with LOTT staff, use of monitoring systems requiring replenishment of toxic reagents and the generation of hazardous laboratory waste should be minimized. Therefore, use of ultraviolet monitors was recommended for consideration for LOTT for monitoring of denitrification and control of methanol feed.

Various strategies are employed by different manufacturers of ultraviolet monitors to reduce interference from organics and suspended particles, including filters, semipermeable membranes, and analytical correction at alternate wavelengths. Each method of compensating for interference has its advantages and disadvantages. Filters and membranes can foul, requiring maintenance (cleaning and replacement). When analytical correction at an alternate wavelength is utilized, as the magnitude of the correction wavelength approaches that of the determinative wavelength, the relative uncertainty in the reported concentration increases.

Based on a review of available nitrate monitoring systems, four monitors (manufactured by Danfoss, Hach, AWA and ChemScan) were selected for evaluation in 2005. All four used ultraviolet techniques for monitoring nitrate that are fundamentally based on an established screening method published in *Standard Methods*, 4500-NO<sub>3</sub>-B. Ultraviolet Spectrophotometric Screening Method . In the method, a calibration curve is established relating corrected ultraviolet absorbance to nitrate-nitrogen concentration in the range of 0 to 11 mg/L. Corrected absorbance is calculated by subtracting the product of sample absorbance at 275 nm and a factor, f, from the absorbance at 220 nm.

$$\text{Corrected Absorbance} = \text{Absorbance}_{220\text{nm}} - f \times \text{Absorbance}_{275\text{nm}}$$

Historically, the default factor, f, for correction in laboratory use of this method has been 2.0, but the current method now states that the factor should be determined within each site wastewater matrix. Additionally, Method 4500-NO<sub>3</sub><sup>-</sup>, states that it is suitable for screening uncontaminated water (low in organic matter), and recommends that it not be used if the correction value (absorbance at 275 nm) is more than 10% of the absorbance at 220 nm.

## Beer-Lambert Law

The relationship between absorbance and the concentration of dissolved UV-absorbing compounds is shown in the equation below. Absorbance is a linear function of concentration (Beer's Law) and of the path length (Lambert's Law). Combined, these relations form the Beer-Lambert Law.

$$\text{Absorbance} = \epsilon \text{ C L (Beer-Lambert Law)}$$

where  $\epsilon$  is the molar absorptivity of the compound, **C** is the *dissolved* (not total) concentration (molarity) of the compound, and **L** is the path length.

Deviations from Beer's Law are situations in which the absorbance is not linearly related to concentration with constant path length and absorptivity. Such deviations typically occur at high concentrations and are due to interactions between constituents in the solution, as well as the significant influence of stray light in high absorbance (low transmittance) solutions. There exists a linear region, or concentration range, where the Beer-Lambert Law is obeyed (typically up to 10 mg/L).

Nitrate and nitrite ions have different reported values for molar absorptivity ( $\epsilon$ ) as well as different wavelengths of peak absorption. Nitrite has a log molar absorptivity of 3.5 with a peak absorption at 210 nm, while nitrate has a log molar absorptivity of 4.0 with a peak absorption at 195 nm. Thus, the amount of interference of nitrite in the determination of nitrate concentration will be a function of the wavelength used for that determination by the various analyzers. When, as is typical, the concentration of nitrite is much lower than that of nitrate, nitrite levels will usually have a relatively insignificant effect on the results.

## DESCRIPTION OF ULTRAVIOLET MONITORING SYSTEMS

Ultraviolet Monitoring Systems from four manufacturers were evaluated for the BITP: Danfoss, Hach, AWA and ChemScan. Photos of all four systems are provided in Figure 5 in the Evaluation section below. All of the systems have a 4-20 mA output to allow direct signal communication with PLC or supervisory control and data acquisition (SCADA) system. Since nitrite is an interferent (is quantified as nitrate), the Danfoss, Hach, and AWA systems report combined nitrate and nitrite (also known as NO<sub>x</sub>). The ChemScan system uses a mathematical approach to automatically evaluate the ultraviolet spectrum to quantify nitrate and nitrite separately. Technical specifications provided by the manufacturers are listed in Table 1.

### Danfoss

The EVITA INSITU 5100 meter uses an antibacterial ion membrane to reduce

interference from suspended matter. The meter with the membrane is immersed directly in the process water (e.g., aeration basin). A separate transmitter is mounted outside the basin and has a cable connection to the floating meter. The INSITU 5100 uses the Danfoss “orange ball” float, which the manufacturer claims is self-cleaning.

TABLE 1. Analyzer Specifications

Parameter	Danfoss EVITA INSITU	Hach OptiQuant	AWA UV pcx	Chemscan
Analysis	Combined Nitrate and Nitrite, NO <sub>x</sub> -N, No differentiation between Nitrate and Nitrite			Differentiation Between Nitrate and Nitrite
Measuring range (mg/l)	0-50	0-50	0-100	0.1 to 10.0 mg/l or 10.0 to 100.0 mg/l
Measuring principle	UV absorption	UV absorption at 2 wavelengths (210 nm and 350nm)	UV absorption at 3 wavelengths (214 nm, 254 nm and 350nm)	256 wavelengths between 200 and 450 nm.
Reported Limit of Detection (LOD)	0.2 ppm	--	0.1 ppm	0.1 ppm
Reported Limit of quantification (LOQ)	0.6 ppm	2 ppm	--	--
Measuring uncertainty	2-50 ppm: ± 10% of actual concentration <2 ppm: +/- 0.2 ppm	0-160 mg/L NO <sub>3</sub> <sup>-</sup> : ±2 mg/L or ± 5% of the reading, whichever is greater.	+/- 0.1 ppm	Typ. 2% to 5% of Range
Other Parameters	None	None	COD, Turbidity	Nitrite, Ammonia
Notes				Optional ultrafilter available for high solids or turbidity (required for mixed liquor)

## Hach

The Hach OptiQuant UV Nitrate Analyzer uses a stainless-steel probe, containing two pairs of UV emitters and photometers, which is positioned in the wastewater stream for continuous measurement. The ultraviolet beams are projected across a 2 mm gap. The Hach OptiQuant UV Nitrate Analyzer relies on a built-in photometer that directly measures the primary UV 210 nm beam, while a second beam of UV light at 350 nm provides a reference standard and corrects for interference caused by turbidity and organic matter.

## AWA

The AWA UV pcx system is a modular system capable of monitoring several parameters at once. The nitrate monitoring system evaluated uses a peristaltic pump to convey sample to the analyzer, which is located outside the basin. The system automatically compensates for the non-linearity of the Beer-Lambert law at high concentrations. Turbidity, organic matter, suspended solids or debris on the flow cell is compensated by a differential measurement with a second detector at a reference wavelength. The multiparameter system also uses UV for other

parameters: ammonia, COD, and hydrocarbons. The ammonia module uses a unique approach – a Fast Fourier Transform Infrared system that measures ammonia in the gaseous phase that is proportional to that in the wastewater. This reduces interference with turbidity or suspended solids. The manufacturer claims that, due to the large bore tubing and an inlet electric valve with pivoting armature, unfiltered water can be admitted into the series 300 and UVpcx analyzer with low risk of clogging. The analyzer measures nitrate/nitrite at 214 nm, with correction for interference at 254 nm (primarily organics) and 310 nm (primarily turbidity).

## **ChemScan**

ChemScan applies pattern recognition techniques to the full absorbance signature of a sample in order to detect multiple chemical parameters using a single analyzer. The ChemScan system uses chemometrics - a cross-disciplinary approach of using mathematical and statistical methods to extract information from chemical (in this case, spectroscopic) data. A manifold system is used to monitor multiple sample points in a process. The analyzer is mounted outside the basin. The system detects absorbance at 256 wavelengths from a sample in the ultraviolet and visible wavelength ranges and uses chemometric analysis techniques to process this information. The manufacturer claims that an advantage for the detection of a 256-wavelength absorbance signature is the amount of information contained in the signature, which is typically contributed from multiple constituents in the sample. This information can be used to compensate for interference when determining the concentration of a single constituent.

The nitrate analyzer has two alternate calibration ranges, “Nitrate, Low Range” at 0.1 to 10 mg/l as NO<sub>3</sub>, and Nitrate, High Range at 10 to 100 mg/l as NO<sub>3</sub>. Site-specific calibration by the manufacturer is required. Per the manufacturer, filtration of mixed liquor samples is required prior to analysis. A single pump and filter system can be used for up to eight sample points, controlled using valves connected to the external controller.

## **EVALUATION OF NITRATE / NITRITE MONITORING SYSTEMS**

An evaluation of UV nitrate monitoring systems was conducted in 2004 through on-line testing at the BITP, laboratory UV spectral analysis, and review of references and data from other plants provided by the manufacturers. A similar, but substantially more comprehensive evaluation was conducted by WERF and published in 2007 (Palmer, 2007). The evaluations conducted at the BITP in 2004 and later in 2008 provides supplemental information to the WERF study, including topics that were not the focus of the WERF study, including the performance of ex-situ analyzers, multi-wavelength analysis, and nitrite quantification.

## On-Line Testing At The Budd Inlet Treatment Plant

On-line nitrate analyzers manufactured by Hach, AWA, and ChemScan were tested at the BITP in 2004. The Hach analyzer was tested in the Mixed Liquor Channel, while the AWA and ChemScan analyzers were tested in Cell 1 of the First Aeration Basin. Since the testing was not conducted during the six months that the BITP must remove nitrogen, the plant was not in its denitrification mode and thus the concentrations of nitrate were higher than the 1- 3 mg/L expected during the periods that the plant denitrifies. Figure 4 shows the results of the on-line nitrate analyzers plotted with the results of laboratory analysis conducted with the cadmium reduction method in the LOTT laboratory. Table 2 summarizes the results of the testing. Photos of the nitrate monitors and data transmitters tested at LOTT are presented in Figure 5. (Danfoss was asked to supply an analyzer for this testing but did not do so.)

**Table 2. Summary of On-line Nitrate Analyzer Testing at the LOTT BITP**

MANUFACTURER	Hach	AWA	ChemScan
System	A	B	C
Model Evaluated	Optiquant	UVpex	UV-4100
Nitrate Concentration Range (mg/L, as N)	9.2 – 11.4	3.0 - 16.9	4.4 - 7.7
Nitrite Concentration Range (mg/L, as N)	0.006 - 0.096	0.43 - 1.1	0.28 - 0.45
Number of Samples <sup>2</sup>	16 (0)	17 (6)	15 (5)
Average RPD (Relative Percent Difference <sup>1</sup> ) versus Cadmium Reduction Method <sup>2</sup>	12.8% (N/A)	14.5% (13.5%)	13.0% (9.8%)
Maximum RPD versus Cadmium Reduction Method	23.9%	56.6%	34.3%
95th percentile RPD versus Cd Reduction Method	19.9%	33.2%	20.2%
Average Bias versus Cadmium Reduction Method	+12.8%	+0.6%	+13.0%
Std. Deviation of RPD versus Cadmium Reduction Method	6%	14%	9%

1. Averages Of Absolute Values Of RPD Reported

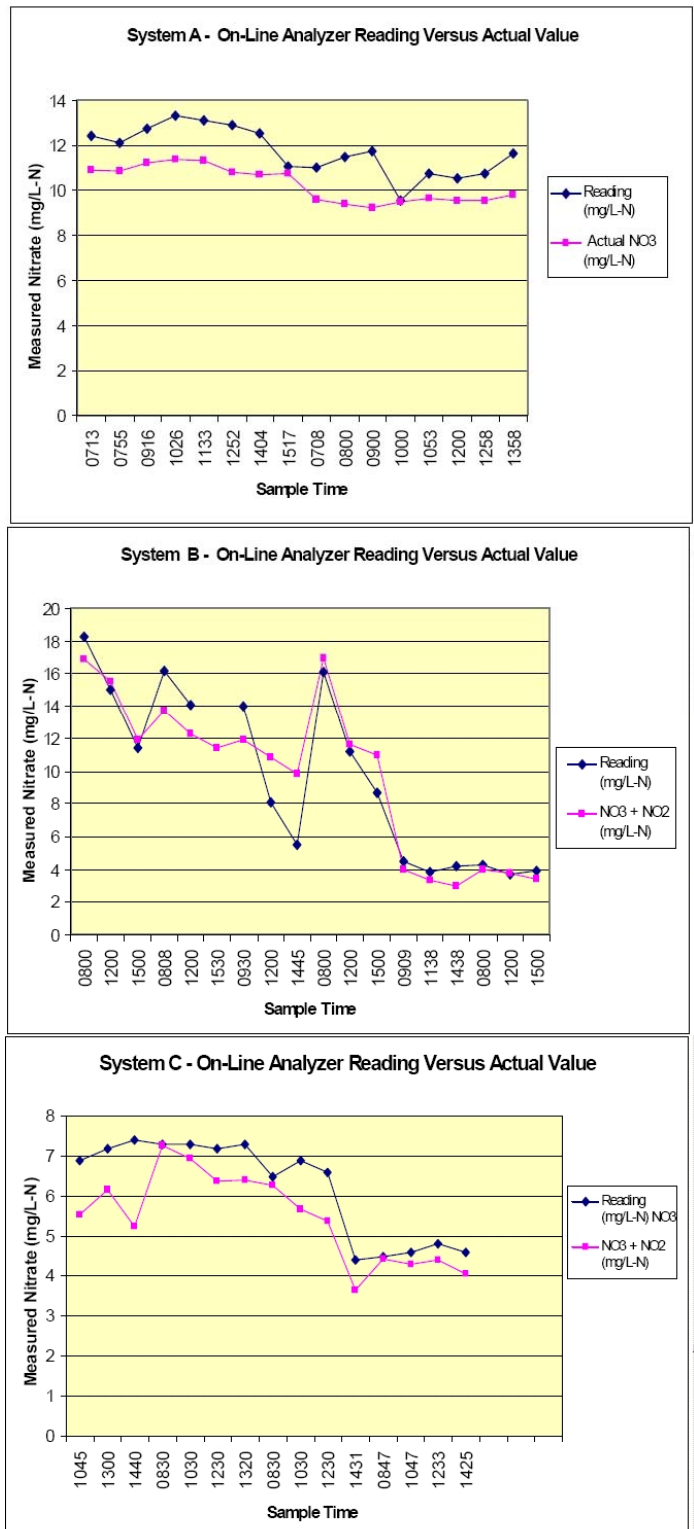
2. Values for nitrate/nitrite-N concentrations < 5mg/L are shown in parentheses

Results are reported for the BITP study for relative percent difference versus the cadmium reduction method for nitrate plus nitrate nitrogen (NO<sub>x</sub>-N) for Hach and AWA and for nitrate nitrogen for ChemScan. (Nitrite concentrations ranged from <1% of nitrate concentrations during testing of the Hach system to as much as 10% of the nitrate concentrations when testing the other two systems.) All three of the analyzers had similar accuracy (12.8 – 14.5% RPD) when measured against the laboratory cadmium reduction method. In comparison to the AWA system, the ChemScan system showed the best accuracy (9.8% RPD) when nitrate concentrations were below 5 mg/L; the Hach system was not tested in this lower range. The AWA system showed the poorest worst-case accuracy (56.6% maximum, 33.2 % 95<sup>th</sup> percentile). The Hach system had the lowest maximum RPD of the three, but was tested at a considerably higher concentration than the ChemScan system. Both the ChemScan and Hach systems showed a 95<sup>th</sup> percentile RPD of about 20% RPD. Results for the ChemScan and Hach systems showed a positive (high) bias (apparent systematic error) - about 13 % relative to the cadmium reduction method. The AWA system showed essentially no apparent bias (<1% on average), but high apparent random error.

### UV Spectral Analysis

UV spectral analysis was conducted on a series of samples including BITP Aeration Basin Mixed Liquor (LOTT ML), laboratory water, nitrate standards, nitrite standards, and LOTT ML with spikes of nitrate and nitrite. Samples with varying levels of solids, ranging from 0.2-micron filtered to completely mixed, were tested. Ultraviolet

Figure 4: On-Line Analyzer Reading Versus Lab Concentrations (System A (Hach), System B (AWA), System C (Chemscan))



**Figure 5: Nitrate Monitoring Systems Evaluated**

Hach-Test  
Installation at  
BITP



**Hach Nitrate Probe**



**Hach Data Panel**

AWA – Test  
Installation at  
BITP



**AWA Sampling Tube and Strainer**



**AWA Nitrate Monitoring System**

Danfoss-  
Permanent  
Installation at  
Aberdeen,  
WA



**Danfoss Nitrate Monitors in  
Anaerobic and Anoxic Zones**



**Danfoss Nitrate Monitors in  
Aerobic Zone**

ChemScan-  
Test  
Installation at  
BITP



**ChemScan System Internals**



**ChemScan System in Enclosure**

spectra from 190-310 nm were acquired at the Ionics Bellevue laboratory in Bellevue, Washington, using a Beckman DU-6 UV/Vis. Spectrophotometer. The goals of the testing were:

- Evaluation of the accuracy of the UV monitoring system through analysis of spiked LOTT ML
- Impact of nitrite on the determination of nitrate concentration in LOTT ML
- Quantification of UV absorbance background contributing to absorbance and determinative wavelength and evaluation of methodology to correct for background
- Impact of variable amount of suspended solids on background correction and nitrate quantification.

Results of the testing are included in Table 3.

**Table 3. Summary of Spectral Analysis**

Sample No.	Sample	Preparation	Spike	Absorbance	Absorbance	Calculated NO3-N mg/L		
				220 nm	275 nm	using Conc. = k (Abs. @220nm - f x Abs. @275nm)	with f = 1	with f = 2
1	Distilled Water			0	0	0	0	0
2	10 mg/L NO3-N			2.1	0	10	10	10
3	10 mg/L NO2-N			2.55	0	12.1	12.1	12.1
4	LOTT AB 1/21/04	0.2 um filt.		0.7	0.12	2.8	2.2	3.0
5	LOTT AB 1/21/04	0.2 um filt.	5 mg/L NO3-N	1.7	0.15	7.4	6.7	7.7
6	LOTT AB 1/21/04	0.2 um filt.	5 mg/L NO2-N	1.95	0.15	8.6	7.9	8.9
7	LOTT AB 1/21/04	40 um filt.		0.7	0.2	2.4	1.4	2.9
8	Distilled Water			0	0	0	0	0
9	LOTT AB 1/21/04	Unfiltered		>3	>3	Unknown	Unknown	Unknown
10	LOTT AB 1/21/04	Unfiltered		>3	>3	Unknown	Unknown	Unknown
11	LOTT AB 1/21/04	Gravity -settled		1.85	0.9	4.5	0.2	6.7
12	LOTT AB 1/21/04	Gravity -settled		1.9	0.95	4.5	0.0	6.8

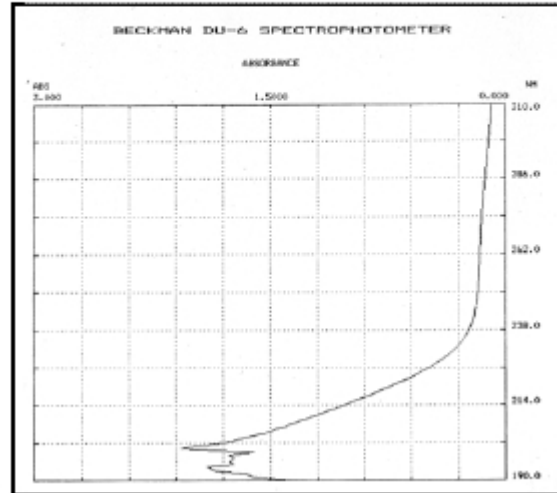
Conclusions of the testing are summarized below.

- Each mg/L of nitrite-nitrogen was quantified as approximately 1.2 mg/L nitrate nitrogen.
- Good spike recovery (92%) indicated good accuracy of the UV method when used with low particulate samples. (See Figure 6 for an example of spike sample spectra.)
- Comparison of results with variable amounts of particulate indicated poor reproducibility. No single correction factor allowed accurate, consistent compensation for particulate with variable solids removal method. (This suggests that filtration and/or a more complex, non-linear background correction technique, such as that employed by ChemScan system, may be required for accurate results with the on-line analyzers).

## Discussion

Based on the testing conducted in 2004, the Hach system tested at the BITP showed relatively good accuracy (average 12.8% RPD, 23.9% maximum RPD), based on comparison of NO<sub>x</sub>-N values with the NO<sub>x</sub>-N values obtained with the laboratory cadmium reduction method. The Hach system provided results consistently high relative to the cadmium reduction method, i.e., showed relatively consistent high bias (12.8% average bias, 6% standard deviation), that might allow use of a compensating factor to normalize the concentration. (This bias may be due to the use of a wavelength, 350 nm, for interference compensation that is higher than the range that NOM absorbs. Thus, NOM may cause a positive interference in these measurements.) The Hach system was not tested at nitrate concentrations < 5 mg/L. However, the system specifications state that the accuracy is “±2 mg/L or ±5% of the reading, whichever is greater”. The “±2 mg/L” accuracy criterion was unacceptable for this application at LOTT, where the system must be accurate in the 0.5 – 3.0 mg/L nitrate-nitrogen range.

**FIGURE 6**  
**BITP AB 1/21/04 (0.2 micron filtered)**  
**spiked with 5 mg/L NO<sub>3</sub><sup>-</sup>-N**



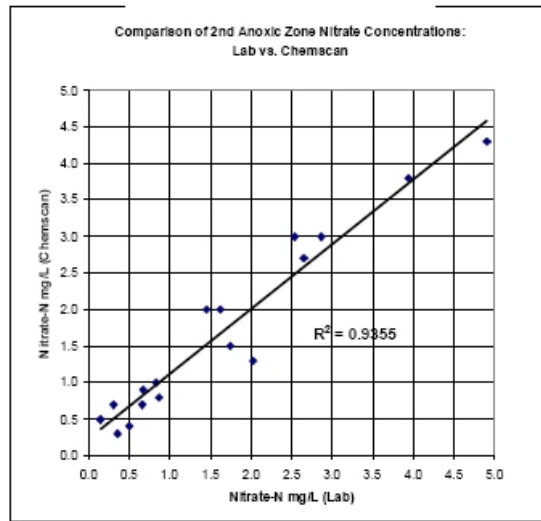
The AWA system tested at the BITP had several samples with poor accuracy (29-57% RPD), and had a relatively high overall standard deviation (14%), when compared with the laboratory cadmium reduction results. Based on these results, and the lack of good references and /or similar tracking data from other plants, this analyzer was not further evaluated.

The ChemScan system showed reasonable results even at nitrate concentrations < 5 mg/L (9.8% average RPD versus the cadmium reduction method). Performance at low concentrations is significant since:

- ~2 - 2.5 mg/L NO<sub>x</sub>-N is the range expected in the aeration basin effluent during the summer season.
- At these lower concentrations, it is more challenging to have low RPDs relative to the reference method, because, the closer to the detection limit, the higher the expected RPD due to a decrease in the analytical signal-to-noise ratio (ratio of the absorption associated with nitrate to random absorption, e.g., stray light).

The ChemScan system showed a consistently high bias (average bias 13.0%, standard deviation 9.1%), that may improve as the system is tuned and nitrite is properly calibrated. The ChemScan system was favored by LOTT operational staff as a more robust unit, requiring much less operator attention than the AWA, partially due to the successful use of the reusable filter on the suction line. The ChemScan system had considerably more experience (9 years) than the other systems, thus making its purchase less risky than a system with a shorter track record. Additionally, as previously mentioned, the Chemscan system offers the possibility of quantification of nitrite separately from nitrate, potentially allowing identification of nitrite lock conditions.

**Figure 7 - Comparison of Laboratory Versus On-line Results for Nitrate (2005)**

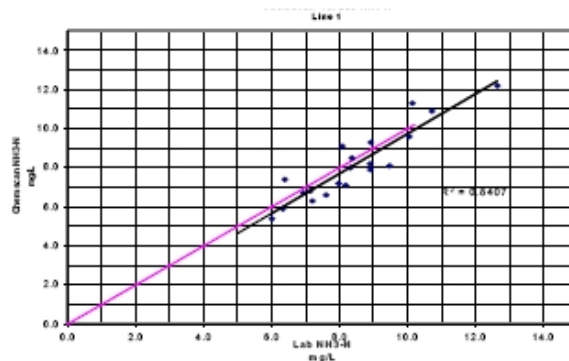


Since accuracy at low concentrations is critical for this application, based on the available information, the recommended system was ChemScan. Since ChemScan is the most expensive system under consideration, another manufacturer's system would have been strongly considered had they provided definitive data that its analyzer could accurately measure nitrate in mixed liquor at <5 mg/L NO<sub>x</sub>-N; however, such data was not received. LOTT ultimately purchased the Chemscan UV-4100, which can detect nitrate, nitrite, ammonia and phosphate at two sample locations.

**PERFORMANCE OF THE CHEMSCAN SYSTEM**

Since the Chemscan system was installed in 2005, performance has generally been good. Figure 7 shows the results of nitrate monitoring conducted with the Chemscan in 2005, compared to results with the cadmium reduction method. Initial nitrite quantification, however, was poor, with false positives (positive bias) commonly reported by the Chemscan. In 2008, additional calibration and programming was performed by LOTT and Chemscan

**Figure 8. Comparison of Lab and Chemscan Ammonia Nitrogen Results**

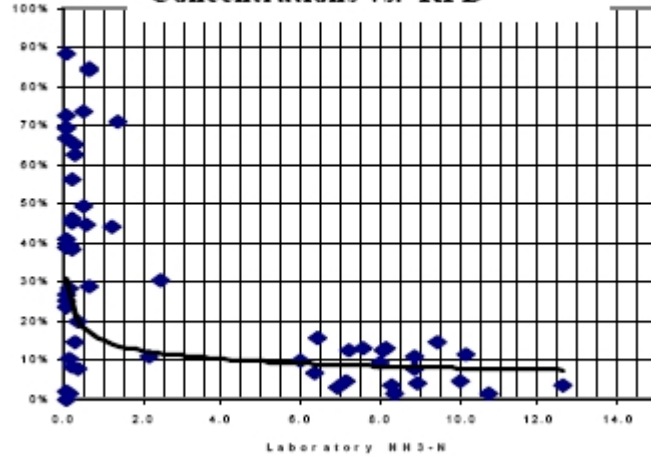


personnel to improve the accuracy of nitrite quantification. Nitrite quantification is of increased benefit to the BITP now because LOTT has recently constructed water reclamation facilities to treat a portion of BITP effluent. The reclaimed water

is chlorinated with hypochlorite prior to distribution. If the biological treatment system were to go into nitrite lock, as discussed earlier, the system may not be able to maintain a chlorine residual. Thus, accurate quantification of nitrite by the Chemsan system could allow it to serve as an “early warning” system to alert operations staff of a nitrite lock condition. Following the completion of new calibration

programming, BITP staff conducted extensive testing in April – June 2008 to (1.) characterize the overall accuracy of the system for quantification of nitrate, nitrite and ammonia in mixed liquor in both the first and second anoxic zones, (2.) determine practical method reporting limits (MRLs) based on the results, particularly the relationship between concentration and relative percent difference (RPD). (Typically, as concentrations decrease in an analyzer, RPDs increase as the signal-to-noise ratio decreases.) The effective MRL takes into account the impact of the sample matrix, mixed liquor, which as discussed earlier, with high concentrations of solids and organics, is challenging for accurate quantification. The following section summarizes the results of this testing.

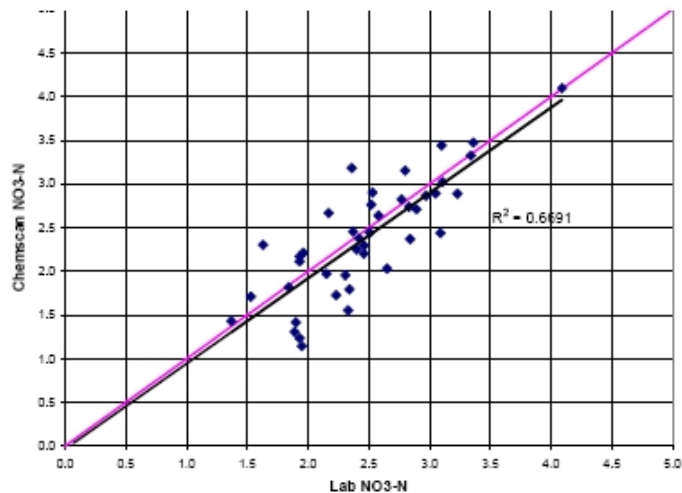
**Figure 9. Ammonia Concentrations vs. RPD**



### Ammonia Nitrogen

Ammonia nitrogen concentrations varied from 5 to 13 mg/L in Anoxic Zone No. 1 and 0 to 2 mg/L in Anoxic Zone No. 2. Figure 8 shows the results of comparisons of lab versus Chemsan concentrations for ammonia nitrogen in Anoxic Zone No. 1. Accuracy was good, with a correlation coefficient of 0.8407. Accuracy, as indicated by RPDs and correlation coefficient, was poorer in Anoxic Zone No. 2, simply because the concentrations were lower (closer to the MRL). This is demonstrated in Figure 9, which shows a graph of the RPDs for NH<sub>3</sub>-N in both anoxic zones as a function of concentrations. It appears an

**Figure 10. Lab vs. Chemsan NO<sub>3</sub>-N Concentrations**

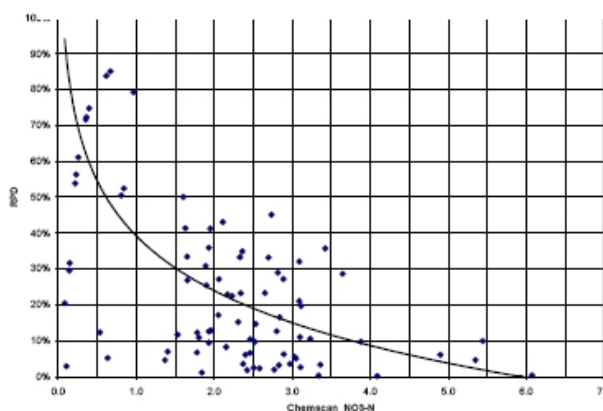


effective MRL for ammonia for these matrices is approximately 1 mg/L; below this level, the average RPD rises steeply.

## Nitrate Nitrogen

Nitrate nitrogen concentrations varied from 0 to 2 mg/L in Anoxic Zone No. 1 and generally 2 to 5 mg/L in Anoxic Zone No. 2. Figure 10 shows the results of comparisons of lab versus Chemsan concentrations for nitrate nitrogen in Anoxic Zone No. 2. Accuracy was acceptable, with a correlation coefficient of 0.6691. Accuracy, as indicated by RPDs and correlation coefficient, was poorer in Anoxic Zone No. 1, again because the concentrations were lower. As for ammonia, this is demonstrated for nitrate in Figure 11, which shows a graph of the RPDs for NO<sub>3</sub>-N in both anoxic zones as a function of concentrations. It again appears an effective MRL for nitrate in these matrices is approximately 1 mg/L; below this level, the average RPD rises steeply.

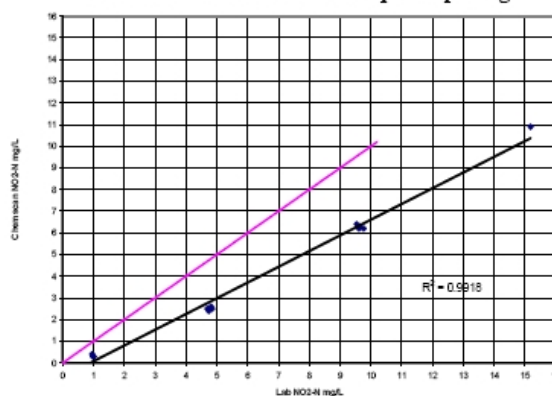
Figure 11. Nitrate Concentrations vs. RPD



## Nitrite Nitrogen

As previously discussed, a major goal of the 2008 testing was to determine if the Chemsan system could accurately quantify nitrite and thus alert BITP personnel of nitrite lock conditions. Prior to the 2008 calibration and programming, the Chemsan would report false positives and negatives, likely due to interference from nitrate, which has a similar spectral signature. Under normal operating conditions, nitrite concentrations are quite low – below the effective MRL – so accurate quantification was difficult. After the 2008 calibration and programming, the Chemsan was able to correctly indicate that concentrations were below 0.1 mg/L, even in the presence of up to 5 mg/L nitrate. This suggested adequate resolution of the spectral signatures of nitrate vs. nitrite. However, because nitrite concentrations in the anoxic zones were so low, the accuracy of quantification of significant concentrations could not be verified. Because of this, spiking experiments were conducted in which nitrite was added to buckets of mixed liquor from Anoxic Zone No. 2 at known concentrations, and tested with the Chemsan and lab methods. The

Figure 12. Lab vs. Chemsan Nitrite Concentrations for Mixed Liquor Spiking



results are summarized in Figure 12. The results show an excellent correlation coefficient,  $R^2 = 0.9918$ . The linear trend line is well below the 1:1 line of lab vs. Chemsan concentrations. However, with minor calibration adjustments, it appears that the Chemsan can quantify nitrite accurately, and effectively warn BITP staff of nitrite lock conditions. It is recommended that additional testing be completed after the calibration modifications are completed; however, early indications suggest an MRL of ~1 – 2 mg/L may be reasonable. Overall, the results of the testing indicate that Chemsan quantification of nitrate, nitrite and ammonia nitrogen concentrations is sufficiently accurate for control of the methanol feed process and warning of nitrite lock conditions.

## CONCLUSIONS

1. Accurate measurement of nitrate and nitrite in mixed liquor is challenging, but aided by filtration, non-linear calibration and multi-variate (multi-wavelength) analysis. Based on an evaluation of nitrate analyzers in 2004, the Chemsan system was chosen for this application because of these features, and its ability to quantify nitrite.
2. The system is currently monitoring nitrate, ammonia and nitrite with acceptable accuracy. The system can be used to control the methanol feed system and as an indication of possible nitrite lock conditions.
3. Since implementation of process automation and optimization, monthly consumption of methanol has decreased from 7,000 – 12,000 gallons to 3,500 gallons.

## REFERENCES

1. *Operational Keys to Nitrite Lock*, W.M. Muirhead and R. Appleton, Hawaii Water Environment Association, 2007.
2. Somnath Basu, CDM, personal communication, 2008.
3. *On-line Nitrogen Monitoring and Control Strategies*, Palmer, Ross, Nutt, Kharkar,