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# ON-LINE MONITORING OF NITRIFICATION PROCESSES USING MULTIPLE WAVELENGTH ULTRAVIOLET ABSORBANCE PROCESS ANALYZERS

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**CHEMSCAN PROCESS ANALYZER PRODUCTS**
**and**
**TECHNICAL PRODUCT REPRESENTATIVES**
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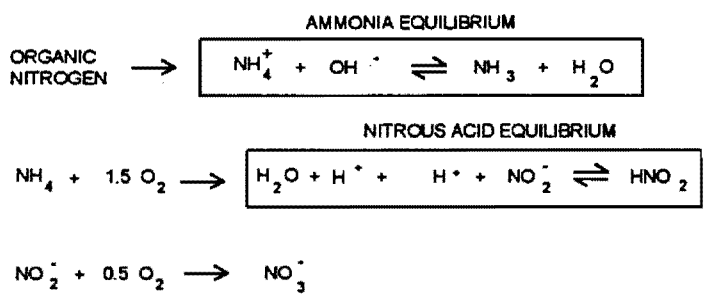
## I. SUMMARY OF NITRIFICATION/DENITRIFICATION PROCESSES

The nitrification reaction that takes place at wastewater treatment plants (WWTPs) is a two-step process carried out by two separate microorganisms. The first step, conversion of ammonium to nitrite, is mediated by Nitrosomonas. The second step, conversion of nitrite to nitrate, is mediated by Nitrobacter microorganisms. Oxygen is essential to both steps. The equations below demonstrate this two-step conversion of ammonia to nitrate (U.S. EPA, 1993):

$$NH_4^+ + 3/2\ O_2 \longrightarrow 2H^+ + H_2O + NO_2^-$$

$$NO_2^- + 1/2\ O_2 \longrightarrow NO_3^+$$




In a plant that usually nitrifies fully (< 1.0 ppm ammonia-nitrogen [$NH_3$-N ] remaining in the effluent), one of the first signs of a decrease in nitrification rate is usually a decrease in the $NO_3$-N concentration and an increase in the $NH_3$-N and $NO_2$-N concentrations. If the process is incorrectly monitored, nitrite (and possibly free $NH_3$, free nitrous acid or other substances) may build up to toxic concentrations or dissolved oxygen could drop to inhibition levels, all of which could create ammonia bleed-through. Some researchers (Alleman, J.E., 1984; Anthonisen, et al., 1976; Suthersan and Ganczarczyk, 1986) estimate that excess nitrite, could be up to 100 times more inhibitory to the metabolism of the microbes than the equivalent concentration of nitrate.

The need for on-line nutrient monitoring is great because these biological processes are effected by biological mechanisms rather than simple chemical reactions. Therefore the rate of the various stages of the reaction can be affected by the non-optimization of any one of several parameters, rapidly putting the process into non-compliance. Some of the factors that affect nitrification and denitrification are listed in Table I.

Table I
Factors Affecting Nitrification

- Temperature
- pH and alkalinity relationships
- MCRT/WAS rate, RAS rate
- Bulk dissolved oxygen concentration
- Heterotroph/nitrifier competition
- Nitrosomonas to Nitrobacter ratio
- Substrate composition variation, electron donor substrate concentration
- Half saturation coefficient in relationship to mass transport limitations and diffusional resistances
- Multi-substrate limiting kinetics that may affect the relative oxygen uptake rate under transient conditions and varying floc sizes
- Toxic substance concentrations, including free ammonia, or free nitrous acid or nitrite buildup.

Non-inhibited and inhibited nitrification transformations are shown in Figures 1 and 2.

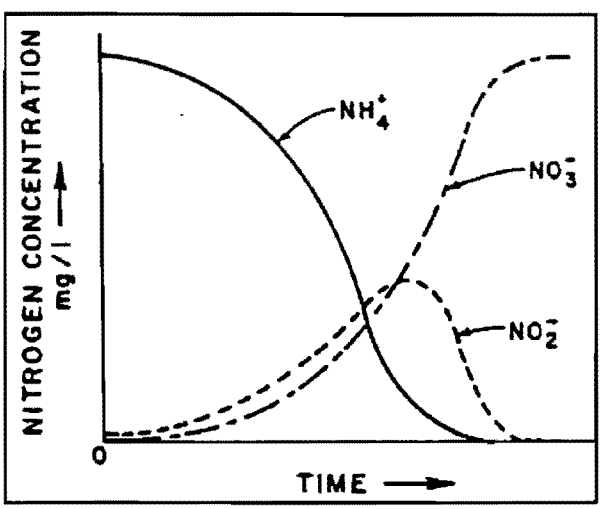



**Figure 1. Schematic of nitrogen transformations during noninhibited nitrification, batch experiment.**

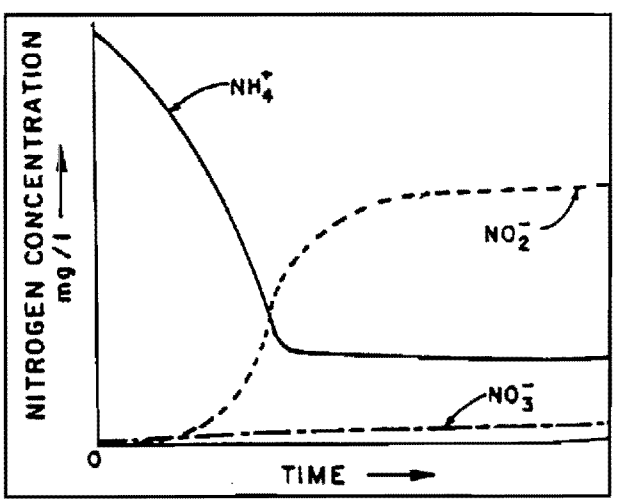



**Figure 2. Schematic of nitrification with inhibition of nitrite oxidation, batch experiment.**

It may be seen that instantaneous nutrient balances can be estimated within the process tank itself, and certain chemical forms of nutrients will become important in optimizing treatment, especially when engineers and operators are being asked to produce cleaner water without increased expenditure. For example, Comeau and his associates (1987) found that nitrate, but not nitrite, could replace oxygen for phosphate uptake and PHA (PHB and PHV) consumption. This could mean that partial nitrification/denitrification in the low DO zone where phosphorus release is stimulated is acceptable and even desirable to improve process efficiency. In other words, nitrite-nitrogen will not adversely affect the biological phosphorus removal process, whereas nitrate-nitrogen could affect this process.

If a plant is intended to denitrify, on-line nitrite concentration monitoring become especially important. A widely accepted progression of nitrification/denitrification is shown:

$$NH_3\text{-}N \rightarrow NO_2\text{-}N \rightarrow NO_3\text{-}N \rightarrow NO_2\text{-}N \rightarrow N_2\uparrow$$

Many plants are modified or retrofitted to incorporate low DO zones to promote nutrient reduction. Nitrite, but not nitrate, could be created in a high-rate activated sludge system with a low D.O. concentration ( $<$ 1.0 mg/l). Nitrite-nitrogen denitrification could proceed directly to nitrogen gas as shown here:

$$NH_3\text{-}N \rightarrow NO_2\text{-}N \rightarrow N_2\uparrow$$

Figures 3 and 4 show the Biological Phosphorus Uptake and Removal Mechanisms.

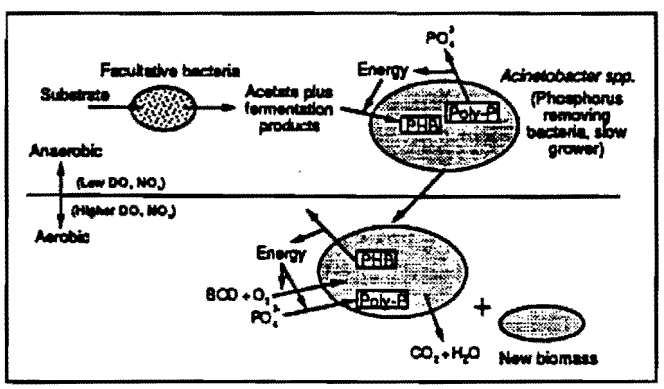



**Figure 3. Biological Phosphorus Uptake Mechanism**

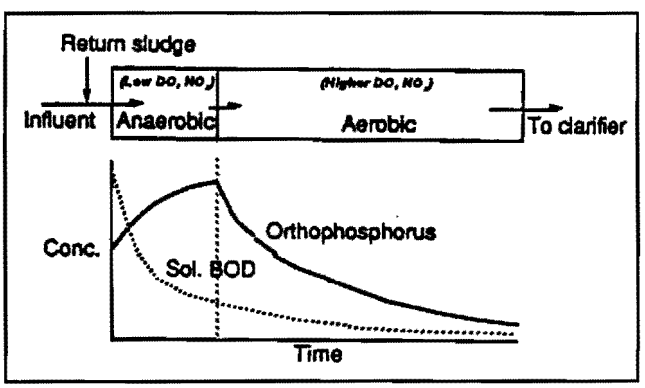



**Figure 4. Biological Phosphorus Removal**

The new, on-line $NO_2$-N/$NO_3$-N monitoring system could be useful to monitor and optimize denitrification in a WWTP, as well as phosphorus release and uptake once basic parameter concentration range set points have been defined. Suthersan and Ganczarczyk (1986) suggest that denitrification could proceed directly from nitrite and be more economical because reduced oxygen and energy requirements would result. This would coincide directly with the fact that nitrite is less likely to affect the phosphorus release/uptake mechanism than nitrate.

## II. THE CHEMSCAN PROCESS ANALYSER

Traditional Concepts - Analytical Photometer

With the conventional standard laboratory analysis method, a fairly demanding sample handling, pre-processing and color development procedure is required in order to measure concentration using a comparatively simple single wavelength colormetric measurement (Figure 5). Following suppression of interferences, the absorbance spectra for the target chemical is shifted and amplified through the creation of a new complex as illustrated in Figure 6.

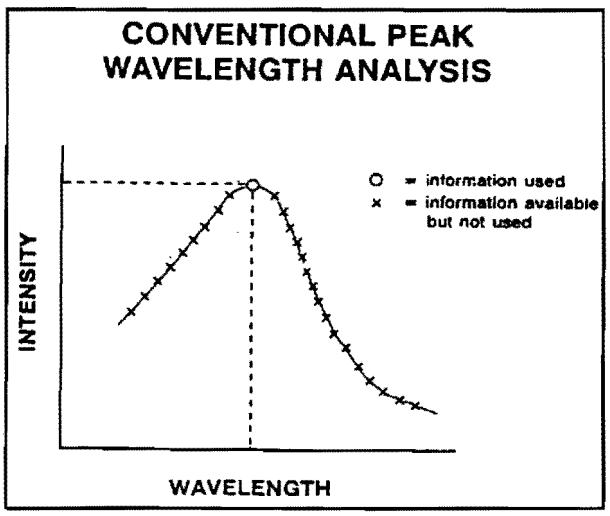



**Figure 5.**

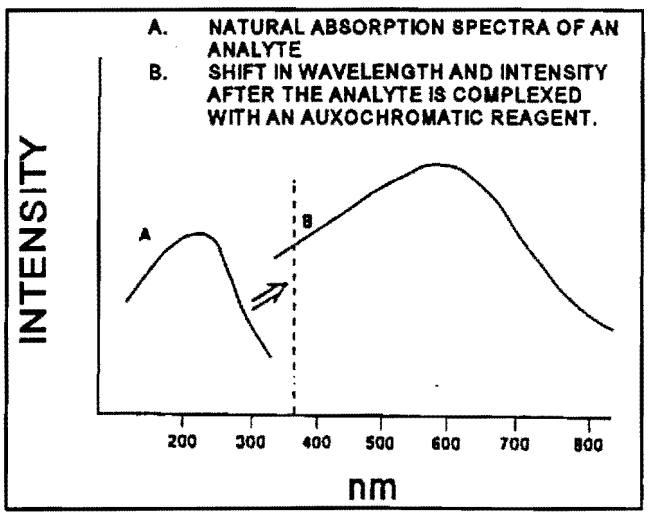



**Figure 6. Spectral shift after reagent use.**

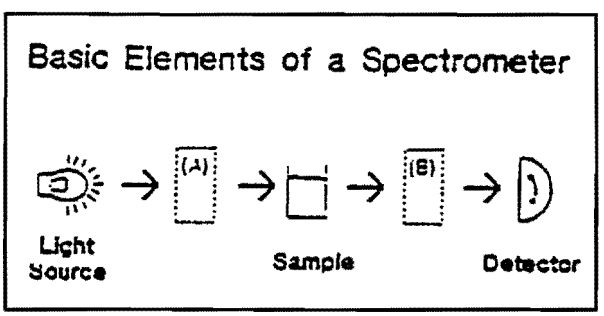



**Figure 7. Spectrometer Elements.**

There are several laboratory instruments in wide use whose purpose is to detect and record absorbance spectra within a specific region of the spectrum. These instruments are limited tothe analysis of static (non-moving) samples and require a controlled environment for the analyzer due to the sensitivity of the optical components. Detection is performed in a stepwise manner from one wavelength to the next with adjustments performed immediately before or immediately after transmission of light through the sample (see Figure 7). Such instruments are relatively slow and can be very sensitive to temperature variation and vibration, making them unsuitable for use in many factory or field environments, especially where rapid or on-line analysis is required.

Real-Time Analysis

To be successful in the marketplace and accepted by end users such as treatment plant operators and process control and design engineers, on-line monitoring and automated process control instruments must be reliable, easy to operate and low in maintenance.

An on-line, real-time, reagentless multiple wavelength ultraviolet (UV) absorbance monitoring device has been developed, partly funded by NASA research, that is capable of accurately differentiating between and measuring nitrate-nitrogen ($NO_1$-N) and nitrite-nitrogen ($NO_2$-N) in water and wastewater streams.

The Chem Scan™ multi-wavelength, multi-analyte ultraviolet absorbance process analyzer is a "smart analyzer" that provides the above qualifications. It is the result of years of development work based on the physical absorbance spectra of ultraviolet light on atoms, molecules, and biological cells in liquid, gas or solid media. This technology uses fiber optics, electro-optical spectrometers and advanced signal processing/pattern recognition analysis (software). In essence, this technique is able to identify elements and compounds by comparing a known wavelength absorbance pattern over a range of wavelengths (calibration analyte) with absorbance patterns over a range of wavelengths (the absorpnce band) in an unknown mixture (water samples).

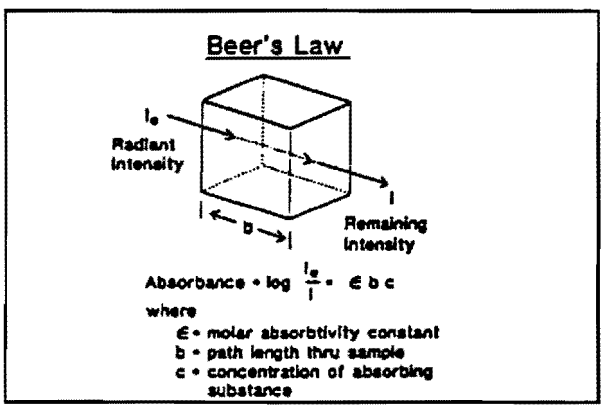


Figure 8. Beer's Law.

An exact match of patterns identifies the analyte of interest as being present in the unknown mixture. The intensity of absorbance across a specific wavelength range corresponds to the concentration of the specific analyte, in most cases following Beer's Law (Figure 8).

The absorbance signature for a sample is a function of all chemicals in the sample that absorb UV light. A sophisticated pattern recognition algorithm is utilized to calculate the contribution to the overall absorbance signature from each chemical component of interest.

Multicomponent Chemical Analysis

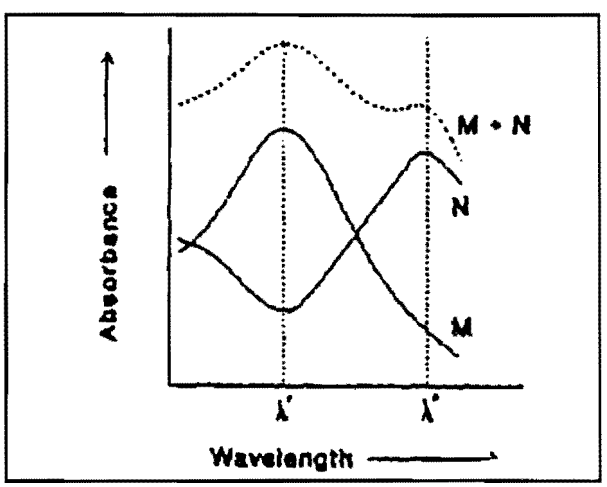


Figure 9. Two component absorbance signatures.

If a solution to be analyzed contains more than one absorbing component, the absorption spectra detected will be a function of all absorbing components. In liquid media, the overlap of absorption spectra for the individual components will result in smooth combined spectra as illustrated in Figure 9.

Each component of interest that absorbs UV light has its own unique, one-of-a-kind absorbtion pattern, similar to the differentiation available with human fingerprint analysis.

The analyzer first recognizes the absorbance signature, then processes that information with complex mathematical software to identify and quantify each component of the mixture.

On-Line Analysis Steps

There are three basic steps involved in the process of using multiple wavelength absorbance spectra for on-line chemical analysis. These steps are illustrated in Figure 10.

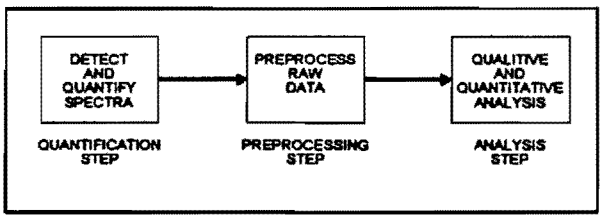



**Figure 10. Spectral Analysis Steps.**

Quantification involves converting detected spectra for multivariate characterization solutions and unknowns into numerical values that can be processed using mathematical and statistical procedures. Preprocessing of raw data reduces the effects of instrument noise and transforms absorption information into forms that permit more efficient analysis. Analysis of absorbance values uses pattern recognition techniques to identify individual components and calculate their concentrations in a sample.

Thus, multiple analytes can be identified and quantified simultaneously, each having its own unique absorbtion pattern. Concentration calculations are consistently accurate even while background concentrations vary, because there is ONE and only ONE absorbance pattern for each of the analytes of interest. The capability of multiple chemical analyte detection with a single analyzer reduces overall instrumentation cost per analysis for most applications where multiple analyte analysis capability is needed.

Ammonia and phosphorus do not have strong natural UV absorbance patterns. Methods have been developed which use inexpensive, non-toxic chemicals for sample conditioning. A sample conditioning module creates compounds with the ammonia or orthophosphate that are able to be accurately detected using the same analyzer unit for which non-conditioned samples are analyzed.

Calibration Unlike Conventional Instruments

Calibration is a "one-time" event and involves an accurate set of known absorbance patterns for the analytes of interest across the concentration range of interest. The instrument compensates for changes in sample backgrounds. Results are not biased by the presence of chemicals that would normally be considered interferences for single wavelength or ion electrode methods because this instrument uses multiple wavelength pattern recognition methods.

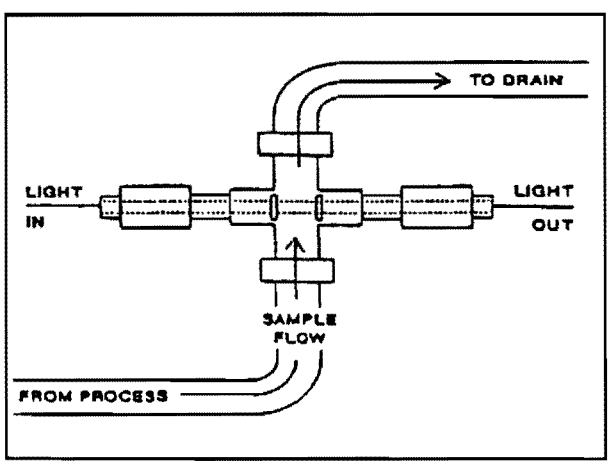



**Figure 11. Flow Through Optical Cell.**

Flow Cell

An example of a flow-through optical probe is illustrated in Figure 11. This design allows an either continuous or intermittent flow of a sample through the cell. Light can be transmitted through the sample continuously or at intervals governed by the instrument design.

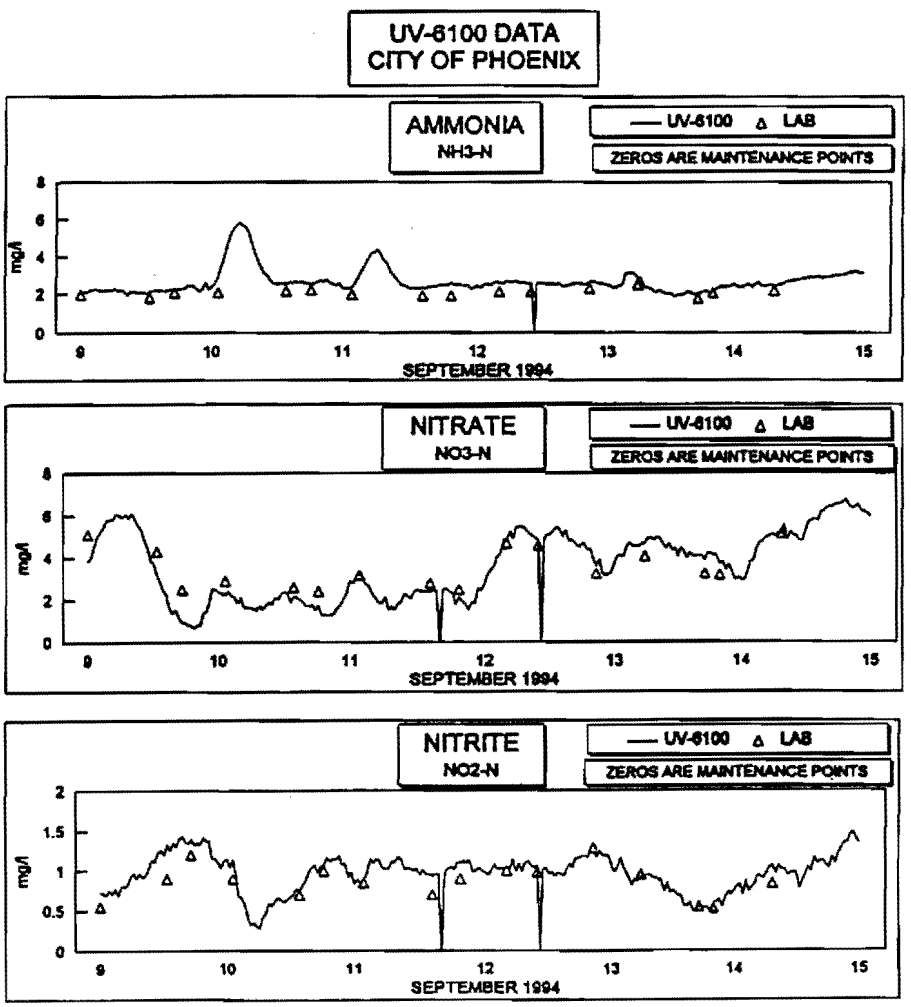
The flow cell is perhaps the most important maintenance item. Only periodic zeroing using deionized water is needed. The pattern recognition software compensates up to a certain level for light loss due to chemical or biological fouling of the glass surfaces of the flow cell. When the light level

becomes too low, periodic chemical cleaning of the flow cell restores the light level. Cleaning and zeroing can be performed by maintenance level personnel, or the cleaning and zeroing function can be automated with maintenance reduced to keeping the cleaning and zeroing solution in the bottles sufficiently filled.

Other maintenance items include the sample pump(s) (if applicable), screen/filter maintenance (if applicable) and recommended two-year back-up battery and flash lamp replacement.

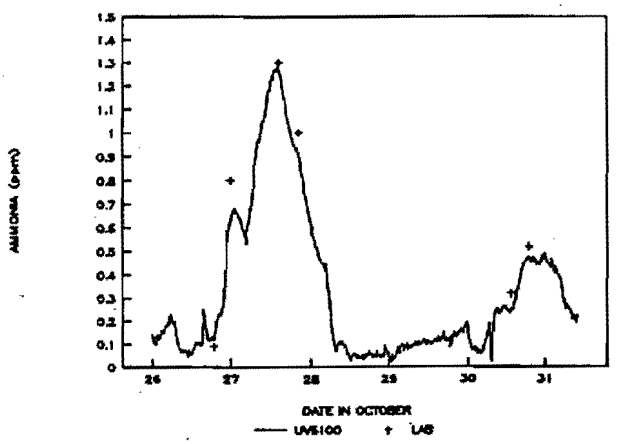
## III. SUMMARY AND INSTALLATION/PROJECT DEMONSTRATION DATA

The advent of the ChemScan™ on-line process analyzer, a device sensitive enough to accurately differentiate $NO_2$-N from $NO_3$-N instantaneously and repeatedly in an on-line wastewater treatment environment, could provide a dimension of nitrification process control not previously available. This tool could reduce potential permit violations and improve effluent quality and process efficiency. It would improve plant personnel awareness of the treatment process and process control strategies. In summary, on-line process monitoring with a multiple analyte process analyzer would save energy and lower operation and maintenance costs due to overall energy, chemical and manpower cost reductions.



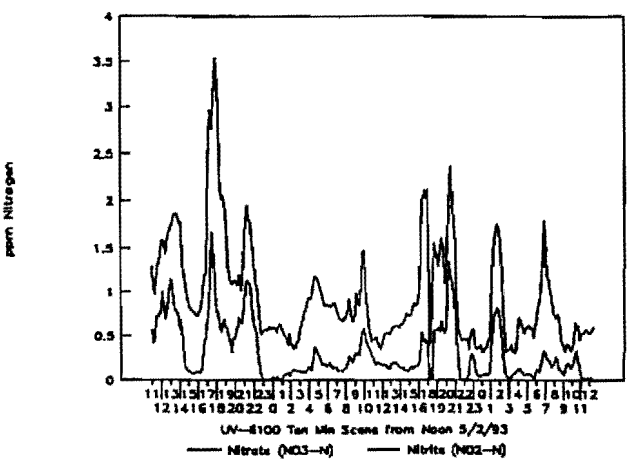
UV6100/SCU ONLINE AT WISCONSIN ELECTRIC

AMMONIA IN BOILER FEEDWATER




Tampa Florida AWT Facility

Denitrification Effluent




UV6100/SCU ONLINE AT WISCONSIN ELECTRIC

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