

## Technical Publication

**Title: Demonstration of On-Line Nitrate Analysis at Several Florida Wastewater Treatment Facilities**

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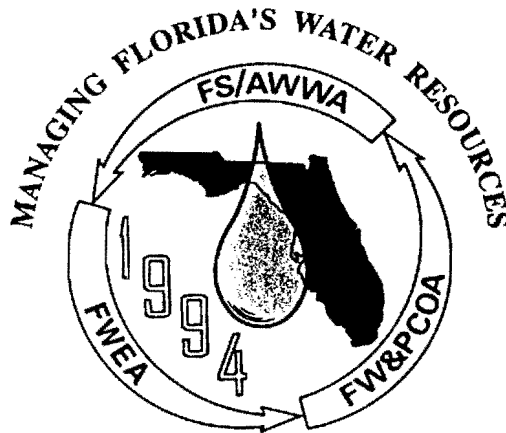
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# DEMONSTRATION OF ON-LINE NITRATE ANALYSIS AT SEVERAL FLORIDA WASTEWATER TREATMENT FACILITIES

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## ABSTRACT

A new technology to reliably detect nitrate in wastewater has been demonstrated at several wastewater treatment facilities in the State of Florida, including a period of use in excess of one year at the Hookers Point Advanced Wastewater Treatment (AWT) facility in Tampa. The technology does not require the use of reagents or ion-specific electrodes. Instead, multiple wavelengths of ultraviolet light are used for the analysis.

Demonstration project results are presented, including comparisons between the on-line results from the nitrate analyzer and results from grab samples that were analyzed using standard laboratory methods. The ability of the analyzer to withstand background chemistry variations and compensate for turbidity variations is discussed. A discussion of routine maintenance requirements is also presented.

Applications for the technology include monitoring and control of nitrification and denitrification processes, well blending and water reuse.

## INTRODUCTION: TECHNOLOGY DESCRIPTION

The recent introduction of on-line spectrometry systems has added a new alternative for automatic monitoring of a number of chemical parameters in wastewater, including nitrate. Previously available technologies for on-line nitrate analysis included ion-specific electrodes and automated wet chemistry analyzers. Some facilities found these technologies to be unreliable or maintenance intensive for wastewater applications.

An on-line spectrometry analyzer is similar to a laboratory spectrometer. A light source is used to generate a known intensity of light over a range of wavelengths and transmit this light through a sample. Unlike laboratory instruments, the sample is introduced through a flow cell and the light absorbance information is collected at multiple wavelengths, resulting in the

detection of a light absorbance signature for the sample. The on-line spectrometer used for nitrate analysis operates in the ultraviolet wavelength range.

Because numerous chemical substances contribute to light absorbance in the ultraviolet range, accurate on-line analysis requires the use of multiple wavelengths of information. This complicates the initial calibration of the analyzer, due to the need for a sufficient number of samples with variation in the concentration of the chemical to be detected and the concentration of the background chemistry. Unlike single wavelength instruments that can be calibrated using two or three data points, multiple-wavelength instruments require 30 or more randomly varied samples for "calibration."

Calibration for a multiple-wavelength analyzer is actually a data gathering process to supply information for a pattern recognition software program. The algorithm is used by an embedded computer within the analyzer to process the absorbance signature information from the sample and calculate the contribution to that signature resulting from a given concentration of a specific chemical substance. Although this initial data collection effort may be more elaborate than the effort required to calibrate other types of instruments, the end result should be an on-line analysis that will not require frequent recalibration yet can tolerate substantial variation in background chemistry without the use of reagents to suppress these interferences.

## COMPARATIVE RESULTS

Demonstration projects have been conducted at several facilities in Florida including the Hookers Point AWT Facility in Tampa and the Fiesta Village AWT Facility in Ft. Meyers. The Hookers Point demonstration has been in operation for a period in excess of one year. Both demonstration projects featured extensive comparisons of nitrate data from the on-line analyzer with results from laboratory analysis of periodic grab samples. The Hookers Point demonstration also compared analyzer results over a 24-hour period with results from the analysis of a 24-hour composite sample.

### Laboratory Analysis Comparison

The Hookers Point facility operates a deep bed denitrification filter following secondary clarification. The on-line analyzer was used for the separate detection of both nitrate and nitrite in the influent to the denitrification process (the "on" side) and also in the effluent from the process (the "off" side). Initially, a denitrification influent demonstration was conducted during the month of April 1993. At the beginning of May 1993, the analyzer sample line was switched to the "off" side, where it operated until April 1994. In April 1994 the analyzer was returned to the "on" side sample line, where it has been operating until the present time.

Figure 1 shows the results from April 1993. The analyzer was calibrated during March 1993 using a combination of laboratory prepared samples and

process samples that had variation in the concentrations of nitrate, nitrite and background chemistry. Following calibration, the analyzer was set-up to perform an analysis every five minutes. Operators were requested to extract a sample for laboratory analysis once per shift and to record the nitrate reading from the analyzer at the time the sample was taken. Samples were preserved and analyzed in the plant laboratory using the cadmium reduction method on a flow injection analyzer. The comparison of these values in Figure 1 shows close agreement (less than 0.5 ppm error over the 10.0 to 26.0 ppm range). More importantly, the tracking (agreement with respect to the ups and downs of nitrate in the process influent) was excellent, which is an important consideration if an on-line analyzer is to be used for process control.

Figure 2 shows results from a similar demonstration at Fiesta Village during July 1993. Although the nitrate range at this facility was much lower (6.0 to 11.0 ppm), the average error between laboratory values and on-line analyzer values for nitrate was less than 0.3 ppm, also with very good tracking.

#### Field Test Kit Comparison

At Hookers Point, a long-term test was conducted with the analyzer for nitrate analysis at low (0.1 to 3.0 ppm) concentrations in the effluent from the denitrification process. Normal procedure at this plant is for an operator to obtain a grab sample once each hour that is immediately analyzed for nitrate using a field test kit. The analyzer was initially calibrated for effluent nitrate analysis using test kit values. Hourly grab samples produced an enormous data base for comparison between the analyzer values and analytical values from the same method as was used for calibration. Figure 3 shows results from a 48-hour period in early May 1993. These data were extracted from a larger set of data used to evaluate analyzer performance and show error rates of under 0.18 ppm.

Figure 4 shows results from the same location during February 1994. The analyzer is using the **original calibration from May 1993**. After more than 10 months, there continues to be excellent agreement between the analyzer results and the field test kit.

#### Composite Sample Comparison

During April and May of 1994 a comparison was made between the results from the on-line analyzer over a 24-hour period and the results from laboratory analysis of a 24-hour composite sample. This test was conducted on the influent to the denitrification process. A 4-20 mA output from the analyzer was being continuously recorded in the plant computer system, with new nitrate values produced every 5 minutes. Figure 5 shows a comparison of daily on-line analyzer averages compared to laboratory analysis of the daily composite for the May 1994 period.

## MAINTENANCE REQUIREMENTS

Following initial calibration, periodic maintenance of the on-line analyzer is limited to zeroing and chemical cleaning.

Zeroing is required every other day in wastewater to eliminate errors that can result from the buildup of films or deposits on optical surfaces within the flow cell. The sample flow to the analyzer is interrupted and a deionized water flow is introduced to flush out the cell. After the cell is flushed, a command is initiated to "zero" the instrument against the deionized water standard. The effects of film or deposits on the windows are measured and subtracted from any subsequent analysis.

The analyzer can also make an absolute measurement of film or deposits that will indicate the need for cleaning. If cleaning is required, an acid solution is used to remove a substantial portion of the fouling. Chemical cleaning is generally performed on a weekly basis in wastewater. The cleaning is followed by a deionized water flush and a zeroing.

At Hookers Point, these procedures have been performed manually for a period of over one year. Average maintenance is estimated at 30 to 45 minutes per week.

The manufacturer has recently introduced a system that can automatically perform periodic zeroing and chemical cleaning. With this system, maintenance is reduced to periodic checking to assure that an adequate volume of deionized water and acid solution is in place and that sample pumps are in good working order.

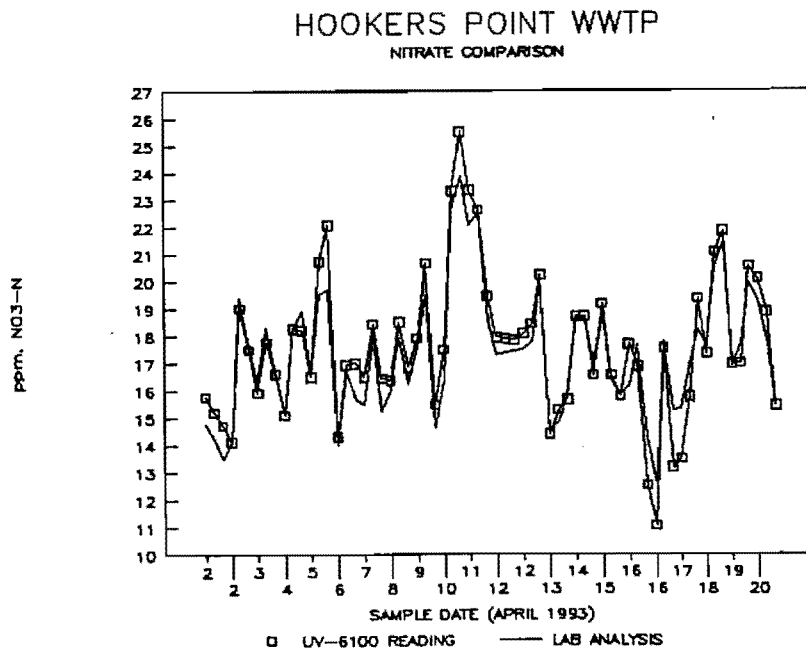


Figure 1.

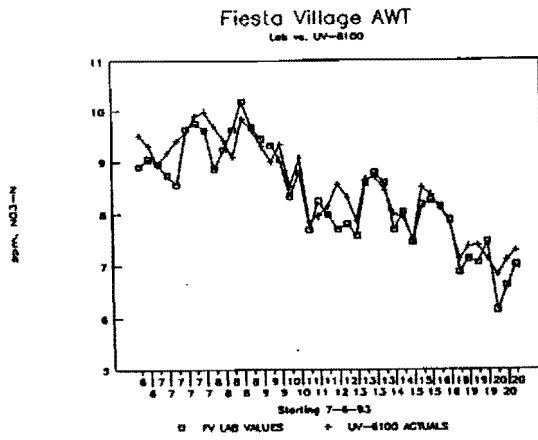


Figure 2.

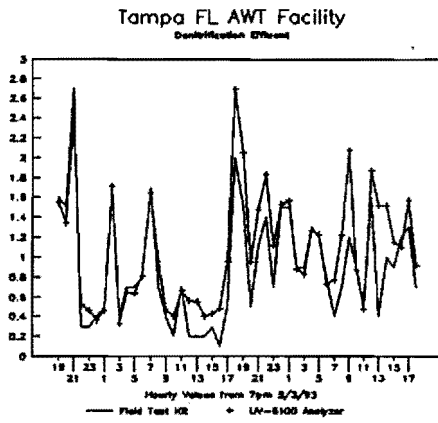


Figure 3.

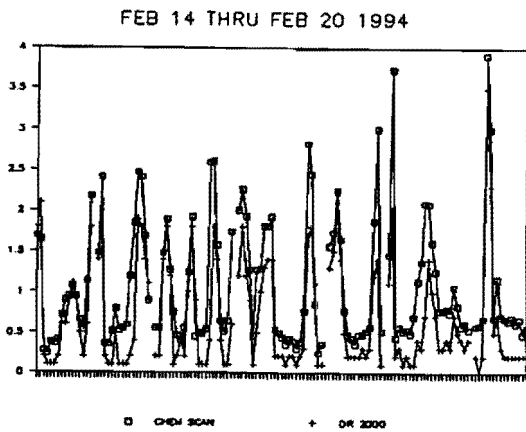


Figure 4.

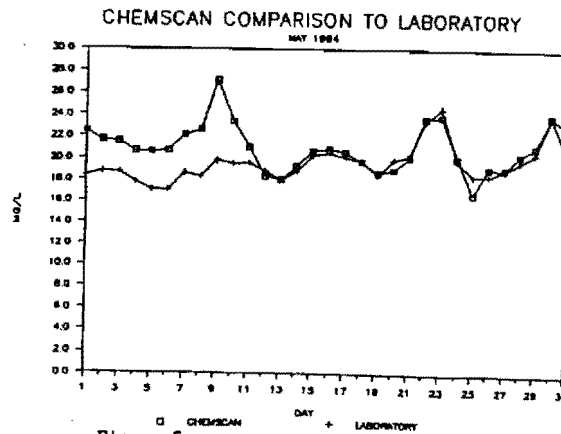


Figure 5.