

Technical Publication

Title: On-Line Analysis of Nitrate and Nitrite in Wastewater Without the Use of Reagents Through Multiple Wavelength Absorbance Spectrometry

ASA Publication Number: 63

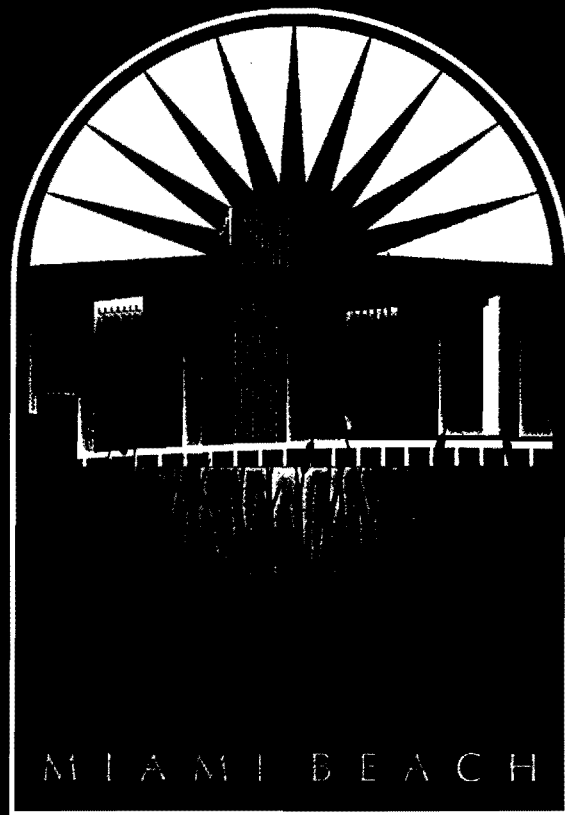
Presented at: WEF Specialty Conference
Automating to Improve Water Quality
Minneapolis, MN
June 25-28, 1995

Note: This document was originally published by Biotronics Technologies, Inc. in conjunction with the ChemScan Process Analyzer technology base, now owned by Applied Spectrometry Associates, Inc. Please direct all inquiries and correspondence to:

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ON-LINE ANALYSIS OF NITRATE AND NITRITE IN WASTEWATER WITHOUT THE USE OF REAGENTS THROUGH MULTIPLE WAVELENGTH ABSORBANCE SPECTROMETRY

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ON-LINE ANALYSIS OF NITRATE AND NITRITE IN WASTEWATER WITHOUT THE USE OF REAGENTS THROUGH MULTIPLE WAVELENGTH ABSORBANCE SPECTROMETRY

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ABSTRACT: Several years of field experience have been accumulated in the use of a multiple wavelength ultraviolet-visible absorbance spectrometer for on-line analysis of nitrate and/or nitrite in wastewater without the use of reagents. The on-line spectrometer transmits light through a process sample in a flow cell and then analyzes the absorbance signature of the process sample using special pattern recognition software.

Information presented includes the theory of analysis, application experience, calibration procedures, long term operating data and maintenance requirements. Comparisons between field results using the on-line spectrometer and laboratory analysis of grab samples using standard methods from several wastewater sites are presented.

INTRODUCTION

The analysis of chemicals to automatically monitor or control a treatment process is a type of analysis that can be performed using a probe located directly within the process (in-situ analysis) or using a fractional sample pumped from the process through a sample line to an analytical instrument (on-line analysis). This paper presents a review of recent experience obtained using a specific type of on-line analyzer. The analyzer detects light absorbance at numerous wavelengths in the ultraviolet-visible wavelength range to obtain an absorbance signature through a fixed path length of sample. The absorbance signature is analyzed using a special pattern recognition algorithm applied using an embedded computer within the instrument. The algorithm is specific for analysis of a single target chemical and is formed through the multivariate characterization of a set of site specific samples that contain known concentrations of the target chemical. These principles are presented in the work by Kahle and Beemster [KAH 95] at this conference and have also been presented to a number of industry and technical forums by Beemster, Schlager and others [SCH 90/3, SCH 91/1, SCH 91/2, SCH 91/3, BEE 91/1, BEE 91/2].

TECHNOLOGY ORIGINS

Analytical Photometry. The use of light absorbance intensity measurements to directly or indirectly measure the concentration of a target compound is a fundamental tool of analytical chemistry. The application of this tool includes procedures to develop a color change in a sample which can be detected by eye and subjectively interpreted by the observer. The use of light absorbance for chemical analysis also includes more sophisticated procedures which rely on a photodetector to measure a light intensity value at a specific wavelength through a sample so that the concentration of a target chemical in the sample can be calculated by comparison to standards of known concentration. These procedures typically rely on some form of sample preparation to suppress interferences and/or to add a reagent in order to form a new compound in the sample that includes the target chemical and possesses light absorbance spectra conforming to Beer's Law within a specific wavelength range. A single specific wavelength (usually the peak of the absorbance spectra) is used for analysis.

An example of a typical laboratory method using light absorbance measurements for chemical analysis is the cadmium reduction method for nitrate analysis [GRE 92]. This method uses a column of cadmium granules to reduce nitrate to nitrite in the sample, which must first be prepared by extracting any oil or grease present, removing any chlorine, color or turbidity in the sample and adjusting the pH if necessary. EDTA may also need to be added to maintain reduction column efficiency if metals are present in the sample. The cadmium reduced sample is then treated with a reagent to form an azo dye that is measured colorimetrically at 543 nm. The colorimetric intensity results are compared to a blank and to results from nitrate standards of known concentration that have been similarly reduced and treated with reagents. If nitrite is present in the sample, analytical results with and without cadmium column reduction need to be performed, with the results subtracted to obtain a nitrate value. Samples that contain both nitrate and nitrite must not be acid preserved if nitrate and nitrite are to be separately determined. This limits the time for sample storage prior to analysis to a 24 hour period.

Thus with the standard 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 colorimetric measurement. 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 1.

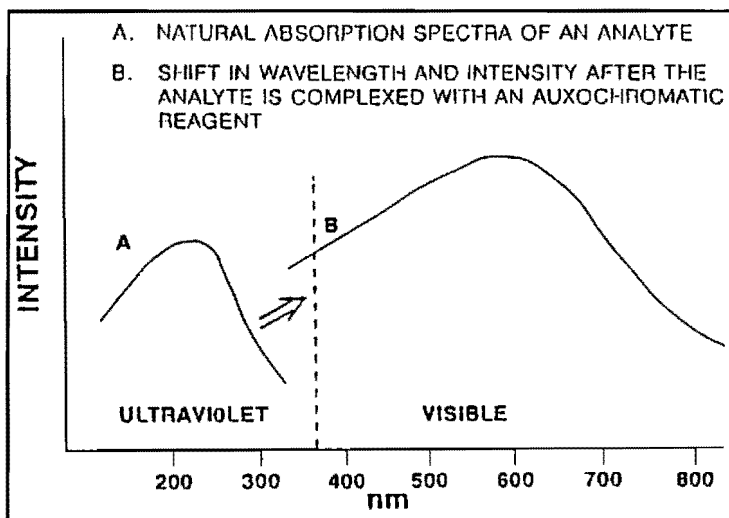


Figure 1. Spectral shift after reagent use.

On-Line Spectrometer Hypothesis. A spectrometer is capable of detecting light absorbance at numerous discrete wavelengths over a specific wavelength range. If multiple wavelength spectrometry is to be used for on-line chemical analysis, it must offer some improvement over automated versions of the standard one wavelength analytical methods. The hypothesis is that a more complex detection and analysis method can

reduce or eliminate the need for physical or chemical alteration of the sample prior to analysis. Otherwise, there would be no advantage in performing the same procedure with multiple wavelength detection that could otherwise be performed with single wavelength detection. This relationship between sample preparation and detection complexity is illustrated in Figure 2. The hypothesis was tested by the authors in a series of demonstration projects conducted starting in the fall of 1992 and continuing throughout 1993, 1994 and into 1995.

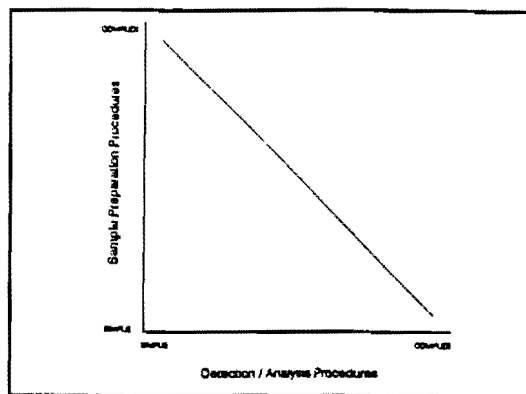


Figure 2. Procedure complexity.

ON-LINE NITROGEN ANALYSIS DEMONSTRATIONS

NASA and US Navy Applications. An initial application of multiple wavelength spectrometry was to perform on-line analysis of hydroponic nutrient solutions for NASA. A hybrid spectrometer designed to detect absorbance and emission spectra from 200 nm to 1100 nm was used to detect 15 different nutrient chemicals, including nitrate. The nutrient solutions provide a substantial background absorbance signature, with nitrate one of several components possessing absorbance spectra in the deep ultraviolet. The spectrometer for this project detects ultraviolet-visible absorbance at 1024 wavelengths thus providing a substantial amount of information for analysis. A pattern recognition algorithm was built from multivariate characterization of 40 nutrient solution samples with known nitrate concentrations. Correlation within the learning set for nitrate exceeded 0.998 with an average error of 0.8 % over the range. The analyzer has been used on-line at NASA Kennedy Space Center since May 1993. [SCH 93/1].

A similar hybrid spectrometer was developed for U.S. Navy use to monitor environmental parameters in Chesapeake Bay, including nitrate. This saltwater background did not inhibit the ability of the system to detect and analyze absorbance spectra from samples continuously pumped through the system, which is located on a research vessel stationed at the U.S. Naval Academy. Pattern recognition algorithms for nitrate and nitrite were constructed from multivariate characterization of several dozen laboratory and field samples. Learning set correlation for nitrate was also very high for this application, with an R^2 of .999 and an average error of 44.6 ppb over a range of 10 ppb to 5000 ppb as NO_3 . Nitrite correlation was also very good, with an R^2 of .924 and an average error of 41.6 ppb over a range of 10 to 500 ppb as NO_2 . [SCH 94].

Initial Commercial Applications. An initial commercial use of on-line ultraviolet spectrometry was in a special instrument designed to simultaneously detect two chemical components used for cooling water treatment. The two chemicals most frequently detected with this system are molybdate and tolytriazole. Approximately three dozen systems are currently in operation in North America and Europe.

Nitrate in Water and Wastewater. Initial on-line nitrate analysis experiments were performed at the Oconomowoc, WI Wastewater Treatment Plant starting in the fall of 1992 and continuing into the spring of 1993. This facility is a 10 MGD secondary treatment facility designed for BOD and ammonia reduction. Due

to industrial contributions and diurnal patterns the plant is subject to a considerable variation in ammonia loading and therefore has a considerable variation in nitrate concentration in the secondary effluent. A sample point following the secondary clarifier but prior to a polishing sand filter was selected. This site was used to field verify the use of multiple wavelength pattern recognition for analysis of nitrate in wastewater, with periodic grab samples compared to results from the on-line analyzer such as the result comparison shown in Figure 3. An algorithm was initially developed using laboratory standards, but several revised algorithms were developed and tested using a

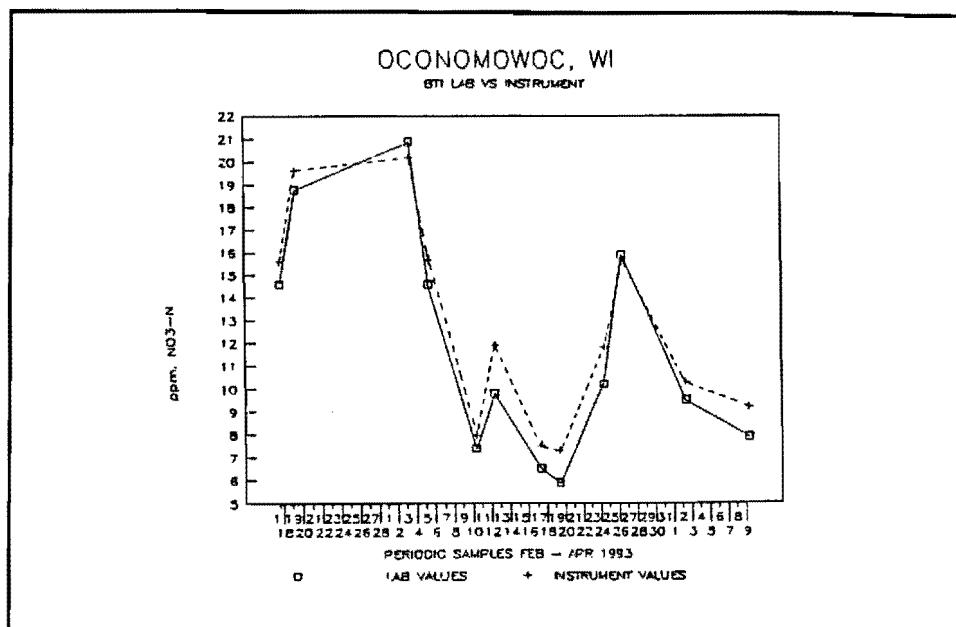


Figure 3. Initial nitrate analysis field test results.

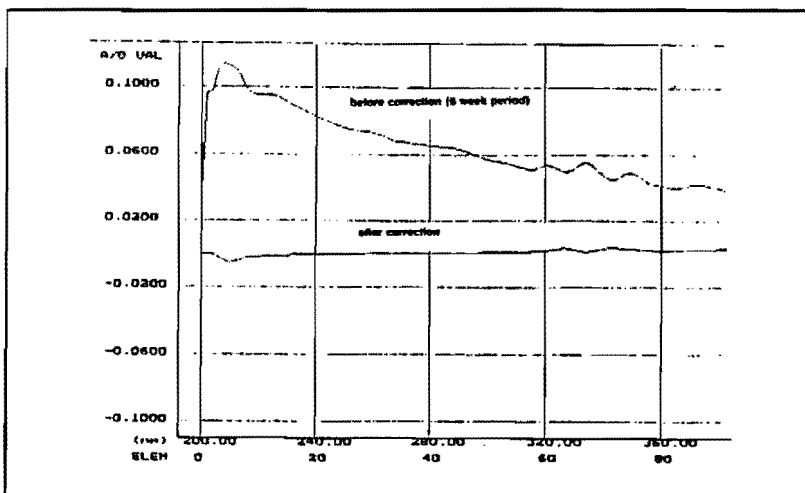


Figure 4. Effects of flow cell zeroing and cleaning.

developed and tested using a combination of laboratory standards and field samples. The final algorithm used during the test produced an average error of approximately 1.0 ppm over a 6 ppm to 21 ppm range as NO₃^{-N}. This site was also used to evaluate basic operating issues for the analyzer such as the effect of fouling and to develop and test fundamental operating procedures such as periodic zeroing using deionized water standards and chemical cleaning of flow cells using acid solutions as illustrated in Figure 4. These results were summarized for a meeting of wastewater operators in Wisconsin in 1993 [BEE 93/1, KAH 93/1].

A substantial long term on-line nitrate analysis demonstration was organized at the Hookers Point Advanced Waste Treatment Facility in Tampa, Florida. The demonstration was conducted over an 18 month period starting in early 1993. This facility is a 60 MGD plant including primary and secondary treatment plus denitrification using deep bed filters with methanol feed. The facility provided an opportunity to perform on-line nitrate analysis over a high concentration range (10 to 26 ppm NO₃^{-N}) in the influent to the denitrification process and over a low concentration range (0 to 5 ppm NO₃^{-N}) in the denitrification effluent. Influent analysis was further challenged by the presence of a substantial variable concentration of nitrite in the samples. Analyzer outputs were communicated over 4-20 mA lines to a central computer system, with a new

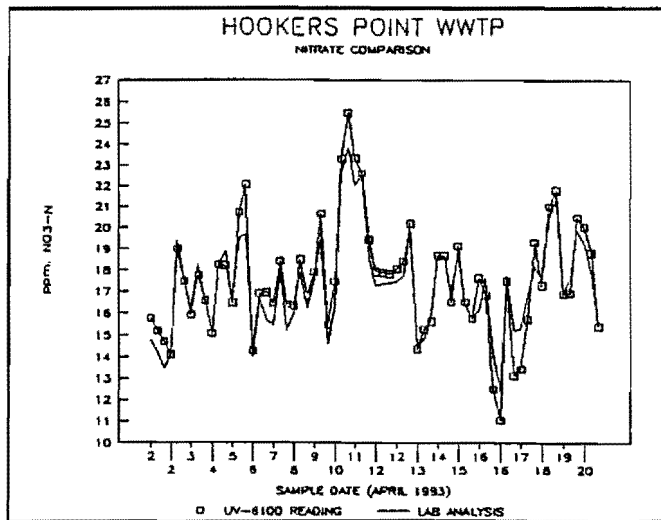


Figure 5. Tampa FL high range nitrate results.

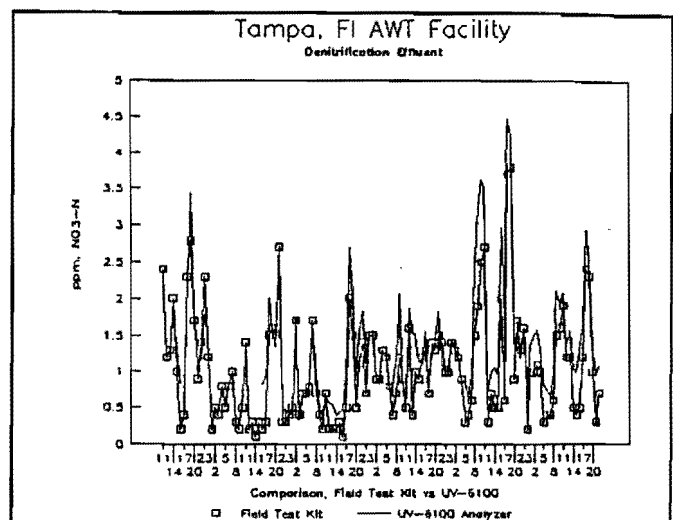


Figure 6. Tampa FL low range nitrate results.

value produced every five minutes. These results were compared to hourly grab samples analyzed using a field test kit and to periodic (once per shift) grab samples and daily 24 hour composite samples analyzed in an on-site certified laboratory using the cadmium reduction method of analysis.

Pattern recognition algorithms at Hookers Point were produced in early 1993 using a combination of standards and field samples. Denitrification influent results illustrated in Figure 5 show an average error of 0.50 ppm for $\text{NO}_3^- \text{N}$ over the 10.0 to 26.0 ppm range, an error rate of only 3.125% for this grab sample comparison. Denitrification effluent results illustrated in Figure 6 show an average error of 0.18 ppm for $\text{NO}_3^- \text{N}$ over a range of 0.01 to 2.70 ppm, an error rate of 6.69%. The effluent comparison is with field test kit results. [BTI 93/1, BEE 94/1].

Similar results for nitrate analysis were achieved at demonstration projects conducted at Whiting, WI on denitrified municipal well water and at Ft. Meyers, FL on clarified secondary wastewater prior to denitrification. The original results for Whiting show an average error of 0.69 ppm $\text{NO}_3^- \text{N}$, which is 12.55% of range. The off-site analytical laboratory used the ion selective electrode method for analysis. When results were questioned, tests using known laboratory standards indicated a consistent error in the laboratory results of 0.4 ppm. After correction of laboratory results, the grab sample comparison is consistent with results obtained at other sites. [BTI 93/2, BTI 93/3].

Results for nitrate analysis demonstration projects are summarized on Table I.

Table I. NO₃^{-N} Grab Sample Comparison

Site	Media	NO ₃ ^{-N} Range	Ave. Error	% Error	Ref. Method
Oconomowoc, WI	Wastewater	6.0-21.0	1.0	6.67	Hach Reagent
Tampa, FL	Wastewater	10.0-26.0	0.5	3.13	FIA Cd Reduction
Tampa, FL	Wastewater	0.1-2.7	0.18	6.69	Hach Test Kit
Whiting, WI	Well Water '93	6.0-11.5	0.69*	12.55*	ISE
Ft. Meyers, FL	Wastewater	6.0-11.0	0.30	6.00	IC
Whiting, WI	Well Water '94	5.5-11.0	0.07	1.33	ISE

*0.29 ppm average error and 5.27% error after 0.40 ppm correction to laboratory results.

Long Term Nitrate Analysis Results. A permanent system installed at Whiting and periodically tested during 1994 and early 1995 with grab samples sent to a new laboratory show excellent agreement with average error of 0.01 ppm NO₃^{-N}, which is 1.33% of range. These results were accumulated during a one year period using the site specific analytical algorithm constructed during initial installation of the instrument. This demonstrates the ability of multiple wavelength spectrometry to produce reliable on-line nitrate analysis results in a relatively stable media (well water) without the need to update the site specific algorithm. A similar study was conducted over a one year period at Tampa, FL in a more challenging and more variable media (municipal wastewater). During this test, conducted by plant personnel, a 24 hour composite sample was collected each day and analyzed in the on-site laboratory using the cadmium reduction method. This result was compared to a calculated composite of on-line analyzer results accumulated over the same 24 hour period and averaged. Results for the month of May 1994 are shown in Figure 7. These results show the general agreement for composite comparisons using the original site specific algorithm that had been developed in the spring 1993. The results clearly demonstrate the need for regular chemical cleaning of the analyzer to remove the effects of fouling. Although the analyzer can compensate mathematically for the effects of fouling if periodically zeroed using a deionized water standard, films can build up to the point where periodic zeroing is no longer effective. If not removed, film accumulation can diminish the accuracy of the analysis, as seen on Figure 7 for the periods before and after May 12. Once an effective program of zeroing and cleaning was resumed, composite results were nearly identical. (Current systems have automatic zeroing

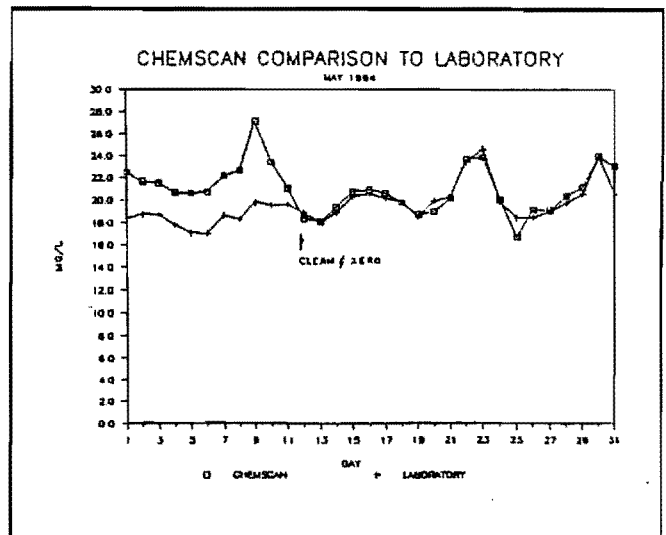


Figure 7. Tampa FL composite comparison.

and cleaning manifolds that can help avoid such lapses in maintenance, although some maintenance is still required to assure an adequate supply of DI water and cleaning solution.)

Total Oxidized Nitrogen Analysis. Total oxidized nitrogen is the sum of nitrate plus nitrite. Although multiple wavelength spectrometry is capable of performing an independent analysis of nitrate and nitrite, some applications do not require this separation. Also, sample handling or analysis techniques for learning set and comparison samples may prevent independent analysis of nitrate and nitrite. At Nye, MT an initial nitrate analysis algorithm was developed using standards. Initial comparison between on-line results and grab samples was poor (19.6% of range) until it was discovered that the samples contained significant nitrite and that the laboratory values being reported reflected combined nitrate and nitrite concentration. Once field samples were added into the multivariate characterization set and a site specific algorithm for total oxidized

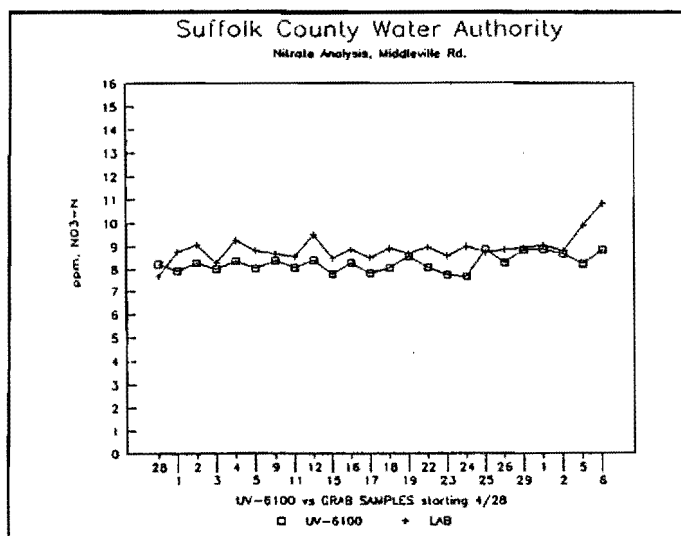


Figure 8. Nitrate only detection algorithm.

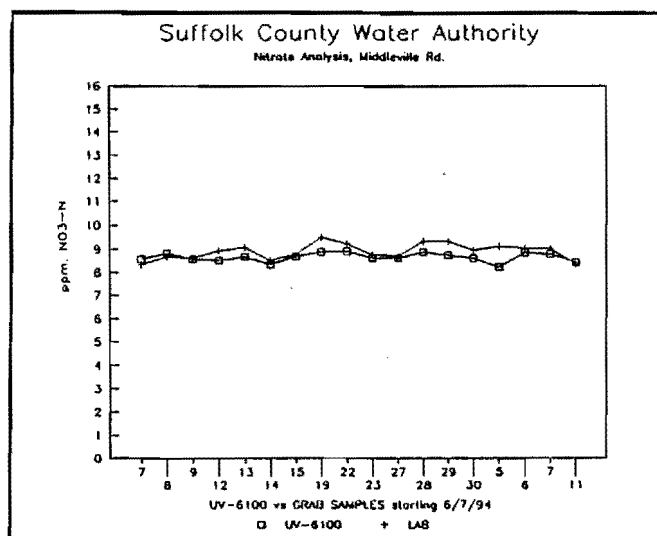


Figure 9. Nitrate plus nitrite detection algorithm.

nitrogen was developed, error was reduced to 7.1% of range for grab samples and 0.3% of range for composites. [BTI 94/1].

A similar result was obtained at a Long Island, NY well water site, where initial nitrate analysis results had reasonable comparison to laboratory results (Figure 8) but a revised algorithm for total oxidized nitrogen shows significant improvement (Figure 9). [BTI 95/1].

CONCLUSION

Based on results from general demonstration sites accumulated over individual test periods ranging from a few weeks to more than one year, on-line nitrate analysis using multiple wavelength spectrometry is producing reliable, accurate results when compared to standard laboratory analysis methods. These results are being achieved on-line from neat (unaltered) samples of well water, mine drainage water and treated wastewater.

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