

Technical Publication

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Demonstration Project

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Whiting, WI
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Applied Spectrometry Associates, Inc.
W226 N555G Eastmound Drive
Waukesha, WI 53186

Phone: (4 14) 650-2280
FAX: (4 14) 650-2285

ChemScan™ UV-6100 Process Analyzer

PROJECT AND DATA SUMMARY
DENITRIFICATION PROCESS MONITORING
DEMONSTRATION PROJECT

Whiting Utilities
Public Drinking Water Denitrification Facility
Whiting, Wisconsin

Published for

Biotronics Technologies, Inc.
W226 N555B Eastmound Drive
Waukesha, WI 53186
(414) 896-2650

December 2, 1993

WHITING UTILITIES

PUBLIC DRINKING WATER DENITRIFICATION
PROCESS MONITORING DEMONSTRATION

Executive Summary

A demonstration project was started on September 10, 1993 and is currently on-going regarding monitoring of nitrate-nitrogen levels at a public water supply treatment plant in Whiting, Wisconsin which is denitrifying its potable water supply. The time period of this report is from September 10 through November 19. Two main objectives of the demonstration project were to show that nitrate-nitrogen concentration of the treated and blended potable water supply could be reliably monitored on a continuous basis, and that the monitoring could be accomplished with minimum down-time, reasonably accurately and with low operation and maintenance costs.

Both of these objectives were accomplished:

- A) The Chem-Scan™ UV-6100 process analyzer was on line in continuous operation for the entire 70-day period, except for a three day period requested by the Utility. Upon re-connection, flawless operation continued.

The comparison between raw laboratory data and raw Chem-Scan™ data showed an average 0.69 ppm difference in nitrate-nitrogen values. The laboratory analysis method (ion selective electrode) is believed to produce values that may be 0.4 ppm lower than the true nitrate-nitrogen value. When this correction is made to the lab values in this study, this correction lowered the average difference to 0.29 ppm. The Chem-Scan™ readings could have also been improved by entering process water calibration data into the calibration curve to provide a more accurate measurement. However, at the request of plant operation staff, the UV-6100 was purposely operated to read 0.4 - 0.5 ppm higher than the true nitrate-nitrogen concentration.

Figure 1 shows a close correlation between the UV-6100 and laboratory data. Results shown in Figure 2 indicate that with the above corrections, the Chem-Scan™ values coincide almost exactly with lab values for the test period.

- B) As a result of the ability of the Chem-Scan™ UV-6100 process analyzer to give consistent, accurate results without the use of chemical reagents, the savings in chemical cost alone would be over \$30,000 within a 36-month period. Also, the Chem-Scan™ unit has very low maintenance requirements on the few mechanical parts it has.

Project Summary

The purpose of this project was to demonstrate the capability of the UV-6100 Process Analyzer to reliably perform on-line analysis of nitrate-nitrogen for a denitrification process at a public water utility treatment facility in Central Wisconsin. The information summarized in this report is from a demonstration project conducted in September, October and November 1993.

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ON-LINE ANALYZER VS COUNTY LAB

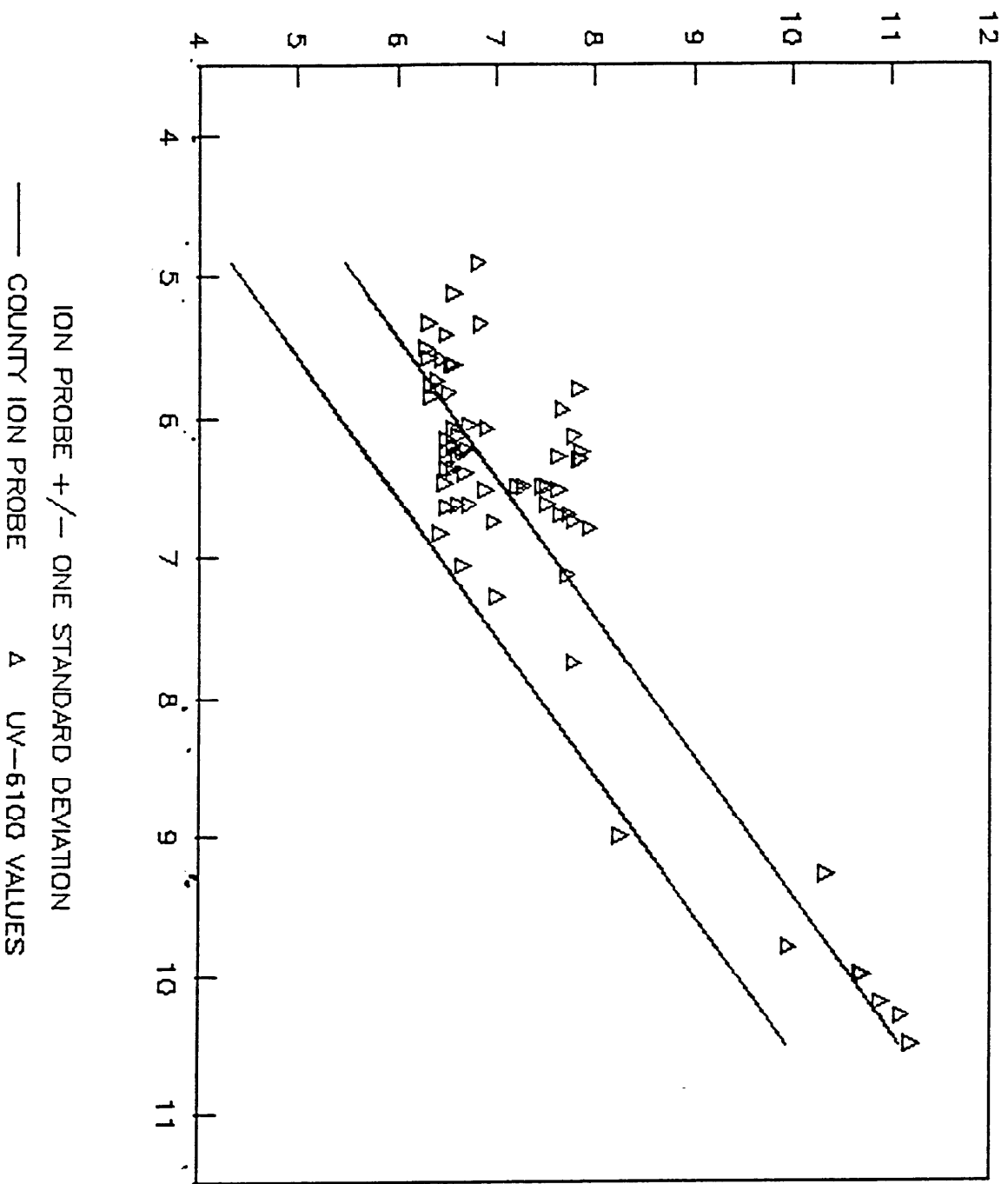
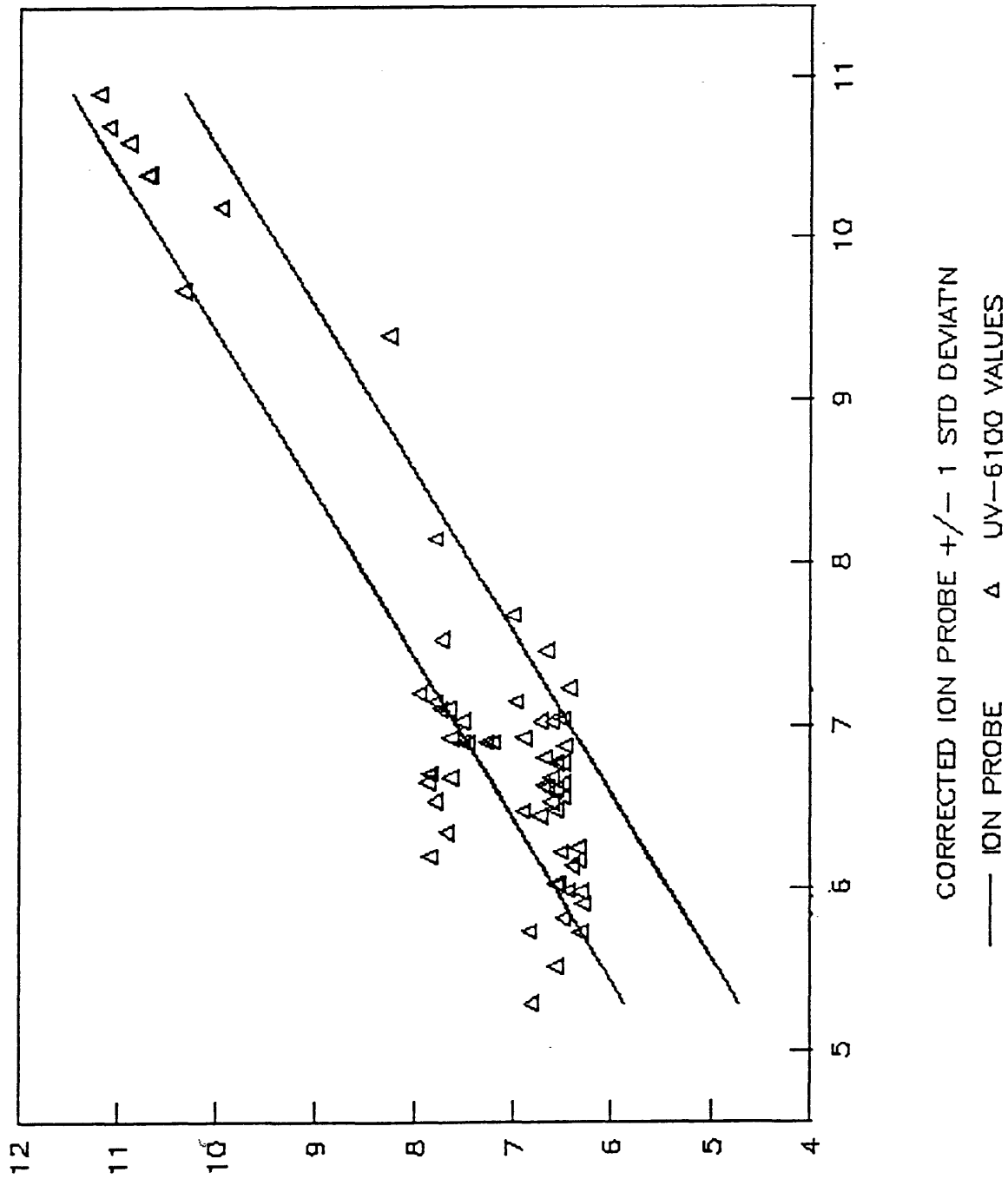


Figure 1.

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ON-LINE ANALYZER vs COUNTY LAB



ppm, NO₃-N

Figure 2.

The demonstration was conducted at the Whiting Utilities Public Water Supply Treatment facility in Whiting, Wisconsin. The facility is currently operating at approximately 0.3 MGD.

Introduction

The Village of Whiting is located in the Sand Plain of Central Wisconsin, an area of high ground water, porous sandy soil, and agricultural activity including irrigation from high capacity wells and chemical fertilization for the areas commercial potato crop.

The groundwater has been gradually polluted with levels of nitrate-nitrogen in excess of the 10 ppm State and National standards. Therefore, the village was required by the Wisconsin Dept. of Natural Resources to remove nitrate-nitrogen from the groundwater and achieve an acceptable concentration prior to distribution to the public.

Almost two years ago, an ion exchange denitrification system (manufactured by Hungerford and Terry, Inc.) went on line. About 70% of the daily water flow is denitrified to less than 1 ppm $\text{NO}_3\text{-N}$, then RAW well water is blended in to achieve a finished water of less than 10 ppm $\text{NO}_3\text{-N}$ for distribution after chlorination.

The Dept. of Natural Resources also required an on-line monitoring system to monitor primarily the finished product on a 24 hour basis so they could be assured that potable water of satisfactory quality was delivered to the residents of the village.

The denitrification treatment system functioned as intended since start-up with only a few minor incidents that may have led to nitrates above the national limit entering the distribution system. However, the equipment selected for monitoring the blended water quality had not functioned adequately since start-up. Therefore, the village, under pressure from the Wisconsin DNR, had searched for an alternate on-line monitoring device that would provide accurate results and be less costly to operate and maintain. The automated wet-chemistry analyzer in use initially cost \$800 - \$900/month in reagents alone. A reagentless analyzer using absorbance spectrometry would pay for itself within a reasonable period of time based on chemical savings alone.

On September 10, 1993, a demonstration project began that monitored the blended water quality using the Chem-Scan™ UV-6100 which was based on a new technology that was originally developed for NASA. This analyzer did not use chemical reagents.

An objective of the demonstration was to show that the nitrate-nitrogen concentration of the denitrified and blended potable water could be continuously and reliably monitored by the UV-6100. Another objective was to provide the village with an opportunity to evaluate operation and maintenance costs as compared to the wet chemistry analyzer in use at the treatment facility.

All objectives were accomplished. Data is presented that show that the nitrate-nitrogen concentration of the treated water "blend" was continuously and reliably monitored from

September 10 thru November 19 (and beyond) with only one interruption (requested by Whiting Utilities). Furthermore, when the UV-6100 was again put back into service, it took less than 10 minutes to re-attach the water line and restore power to the process analyzer, and it was back in operation, performing flawlessly, without the need for chemical reagents, re-programming or re-zeroing. Instrument results were within a fraction of a ppm when compared to the plant laboratory values. An RS-232 signal output from the UV-6100 was connected to a serial printer on day 10 of the demonstration and delivered a nitrate-nitrogen reading to the printer every 15 minutes for 60 days of the 70 day demonstration period.

Analyzer Description

The UV-6100 Process Analyzer is an on-line spectrometry system equipped with a multichannel array detector and an internal computer. This system is capable of simultaneously detecting numerous wavelengths of spectral information in the ultraviolet wave-range from process solutions in a flow cell or optical probe. The information is processed by the analyzer and compared to calibration files stored in memory in order to calculate the concentrations of chemical substances that cause absorbance of ultraviolet light in specific patterns. The UV-6100 analyzer detects and analyzes the natural light absorbance characteristics of the process solutions and does not use ion-selective electrodes or chemical reagents to perform the analysis.

Figure 3 is an illustration of the ChemScan™ analyzer. The upper enclosure contains the light source, power supplies, temperature controls, spectrograph, computer board, communications boards, control panel and associated electronics. The lower enclosure (shown without the front panel) contains a flow cell, control valve and connection points for analog or serial communications.

Denitrification Process Monitoring

The UV-6100 analyzer was originally calibrated using only laboratory constructed standards over a nitrate-nitrogen range of 0-15 ppm. No process samples were used to calibrate the demonstration system, although better accuracy can typically be achieved if field samples were used for calibration.

A sample line was connected from the blended water supply pipe just prior to the distribution system and connected to the UV-6100. The pressure in the distribution system was used to deliver a fresh supply of sample through the flow cell. Sample lines were automatically flushed for a minimum of one minute intervals prior to each reading. Information from the analyzer was recorded in several ways:

- A. The UV-6100 analyzer is programmed to halt the sample flow through the flow cell, scan the sample and calculate nitrate-nitrogen concentration at periodic (fifteen minute) intervals. This information is converted to an RS-232 signal by the UV-6100 analyzer, with output to the plant data management network where the information

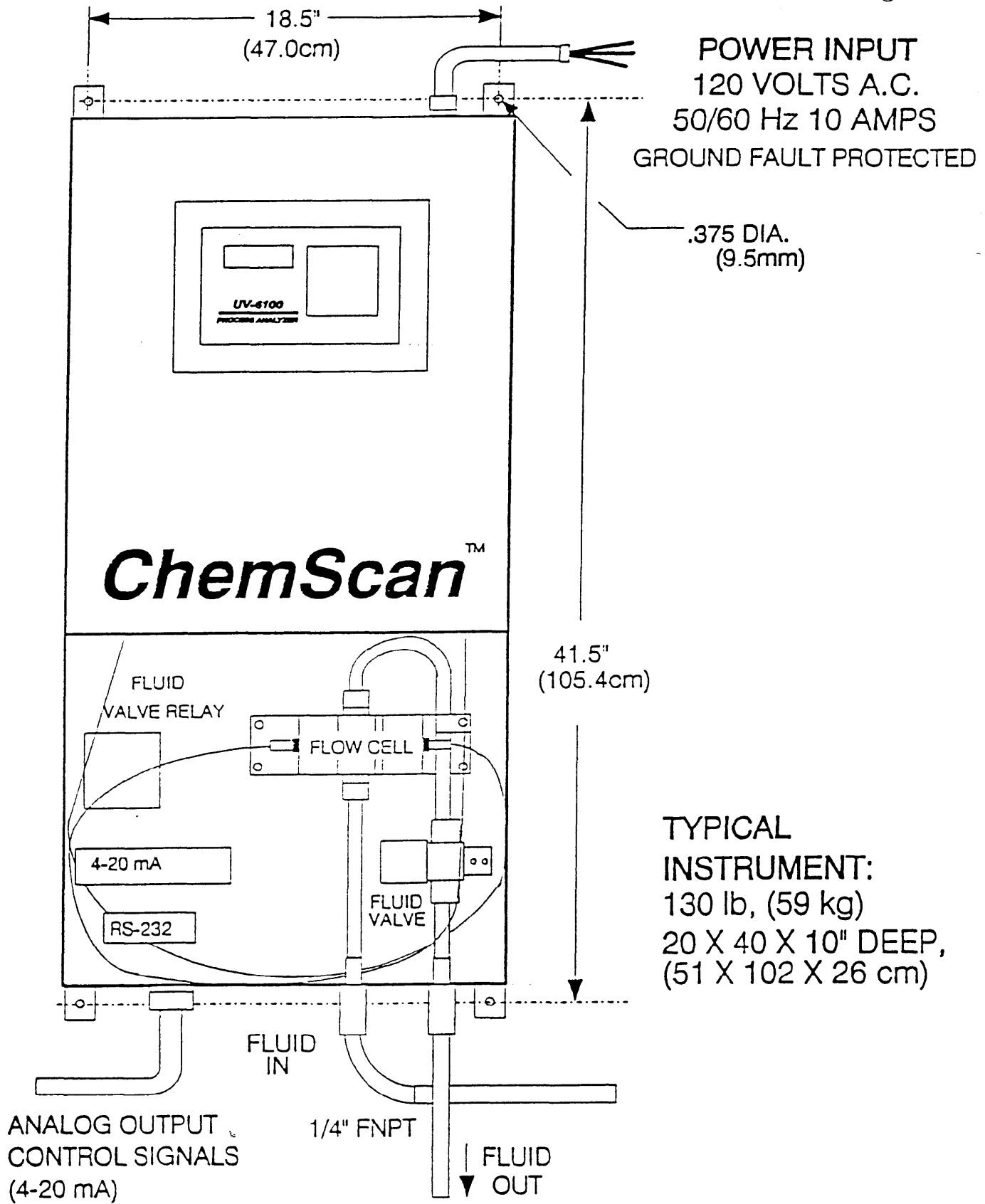


Figure 3 .

could be available for recording, display by the computer system and/or used to alarm operators of a high nitrate-nitrogen condition. A dot-matrix printer, supplied by Biotronics, was integrated into the RS-232 output of the UV-6100 and recorded data continuously starting 10 days after the beginning of the demonstration project.

- B. The UV-6100 analyzer contains an internal memory that accumulates the most recent 1,000 readings from the analyzer. This data logging capability was also used to accumulate a running record of nitrate-nitrogen concentrations as measured by the analyzer at 15 minute intervals during the demonstration period.
- C. For comparison, operators were requested to extract grab samples from the sample line at least once per day throughout the demonstration period. At the time the sample was extracted, the operator was also asked to record the most recent nitrate-nitrogen value as shown on the display panel of the UV-6100 analyzer. In this manner, nitrate-nitrogen values from the laboratory analysis of the samples conducted by the Portage County Public Health Laboratory could be matched with the comparable values from the UV-6100 analyzer.

Blended Water Nitrate-nitrogen Results

The ChemScan™ UV-6100 Process Analyzer was setup on September 10, 1993 to measure nitrate-nitrogen on the blended water supply line which contained about 70% treated and 30% RAW ground water. UV-6100 calibrations are constructed by building a set of files that contain the spectral characteristics of numerous samples and the corresponding concentrations of the analytes in each sample. The calibration files for the denitrification monitoring demonstration included only laboratory prepared samples with known analyte values. Process samples with analyte values based on process conditions have been collected and can be used to improve the calibration set at any time in the future. However, the accuracy of the initial calibration using laboratory constructed samples was thought to be satisfactory for demonstration purposes. After initial calibration, sample analysis comparisons were made between the UV-6100 and the results from the Portage County Public Health Laboratory.

There are at least two conditions to be pointed out with regard to any comparison of UV-6100 process analyzer data versus laboratory data.

- 1) The UV-6100 was calibrated in the 0-15 mg/l NO³-N range using DI-water prepared standards. Although a learning set of lab values using process stream water were collected, they were not installed into the calibration data bank during the demonstration period. The calibration could be made to be more robust and accurate with the addition of the accumulated data.

As a result of the calibration method, the UV-6100 provided nitrate-nitrogen values that were consistently about 0.5-0.8 ppm higher than the laboratory results. The operations staff requested that the process analyzer not be adjusted to more closely match the laboratory results. The operators felt that they would like to have a "0.5

ppm cushion” to give them adequate time to respond if the blended water was in danger of going over the 10 ppm nitrate-nitrogen limit.

- 2) The laboratory indicated that comparative results from known standards showed the ion selective electrode method to have results which are consistently 0.2 - 0.4 ppm under those known standards. Personnel at the lab were aware of the difference, and it is within the normal tolerances for the ion selective electrode method of nitrate-nitrogen analysis.

A comparison of the uncorrected values for the UV-6100 with the equivalent sample values as reported by the laboratory show an average error of only 0.69 ppm and a standard deviation of 0.57 ppm. Figure 1 illustrates these data, with the previously mentioned observation that the UV-6100 was showing nitrate-nitrogen results that were slightly higher than actual and higher than the equivalent laboratory value.

The data in Figure 2 shows that if corrected laboratory values are used, most of the UV-6100 data points fall within one standard deviation of the corrected laboratory ion probe data (the correction to the lab data was to add 0.4 ppm to each value prior to calculating the standard deviation). The standard deviation remains at 0.57 ppm, but the average error falls to 0.29 ppm.

Trending and Tracking Results

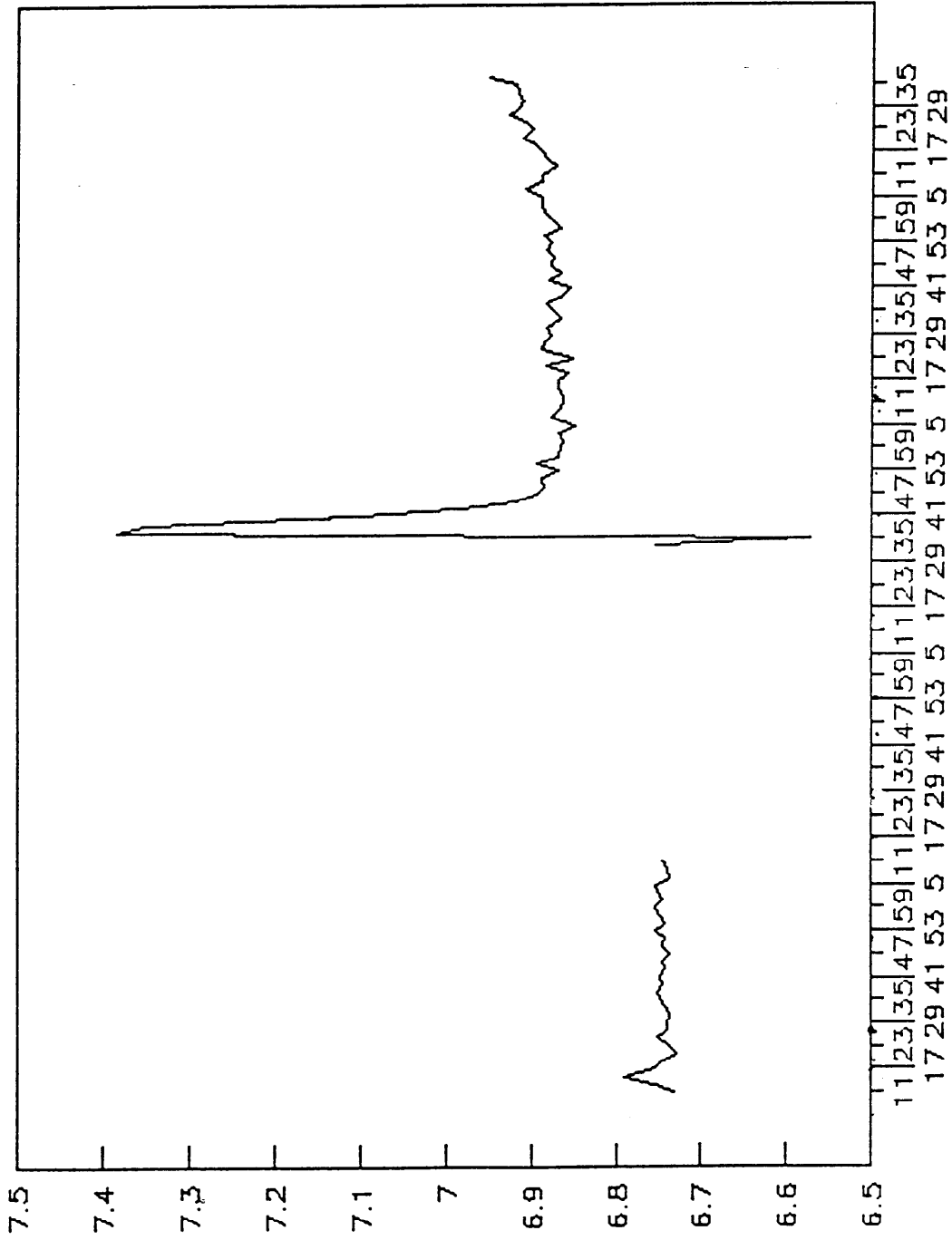
Comments and explanations can be made regarding several other Figures that show results for the demonstration period.

Figure 4 shows UV-6100 nitrate-nitrogen values plotted in two minute intervals for several hours after initial project start-up. Note that the nitrate-nitrogen values are steady during the time the pump is not delivering water to the distribution system, but that the instant the pump starts, a change in nitrate-nitrogen is noted and recorded by the UV-6100 process analyzer. The reason the nitrate-nitrogen values are so steady most of the time is that when the pump is not operating, the same portion of water in the distribution pipeline is analyzed repeatedly. However, when the pump starts, the Chem-Scan™ analyzer indicated the change in nitrate-nitrogen concentration immediately.

Figure 5 shows nitrate-nitrogen changes during the first 10 days of the demonstration project. During the demonstration project there were two incidents where blended water was momentarily in excess of the maximum allowable nitrate-nitrogen concentration. The first incident was recorded on the second day after the Chem-Scan™ was installed and can be seen on Figure 5. The Chem-Scan™ unit, set at 15 minute reading intervals, immediately documented a return to allowable nitrate-nitrogen values after process adjustments were made. Had there been an alarm system connected to the UV-6100, the period of high nitrate-nitrogen could have been substantially reduced.

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Blended Well Water Nitrate Analysis



2 Min Interval, From 12:11 pm 9-10-93

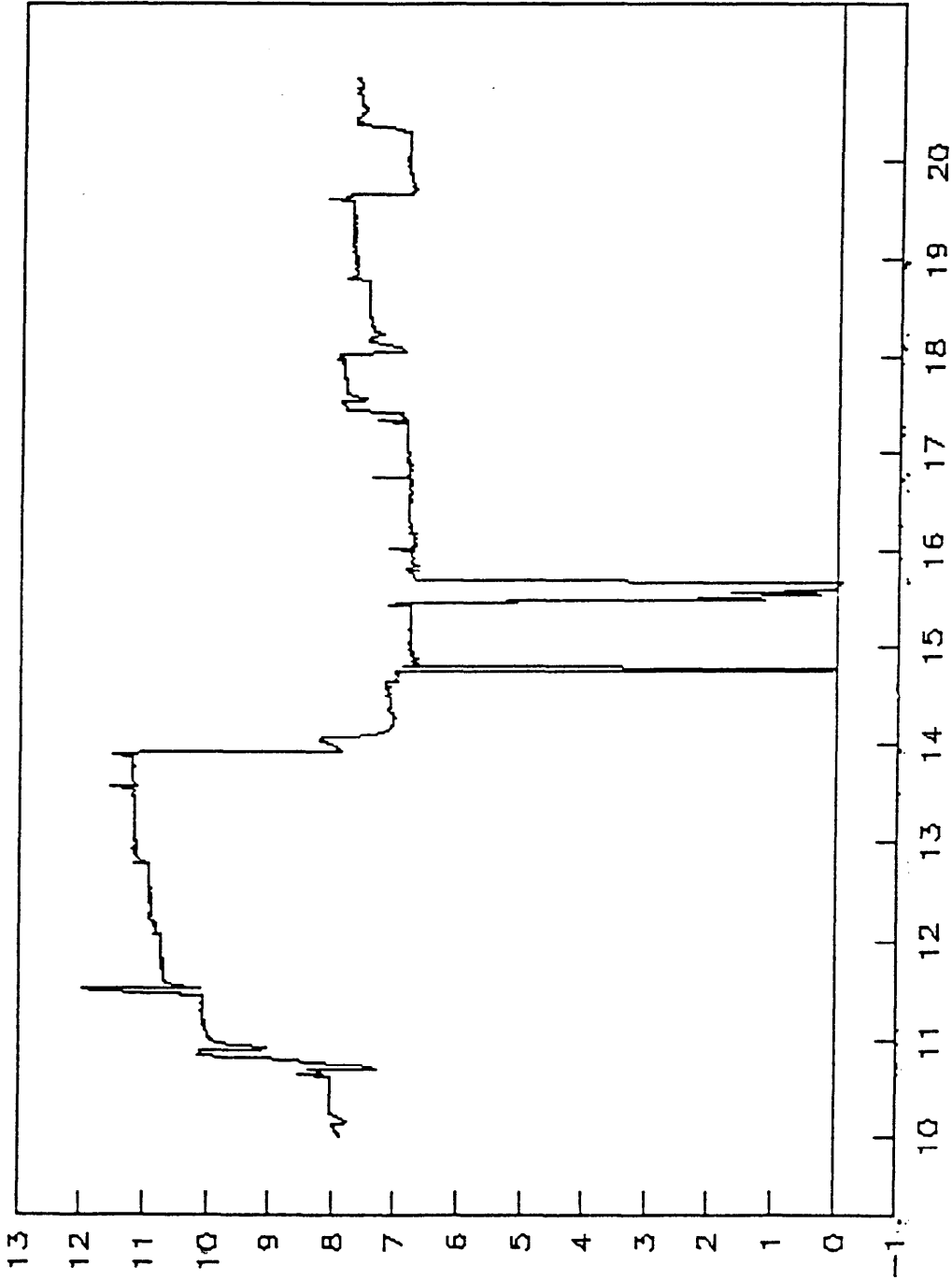
— UV-6100 Values

Figure 4.

PPM, NO₃-N

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Blended Well Water Nitrate Analysis



15 Min Interval, From 5:09 pm 9-10-93

— UV-6100 Values

ppm, NO3-N

Figure 5.

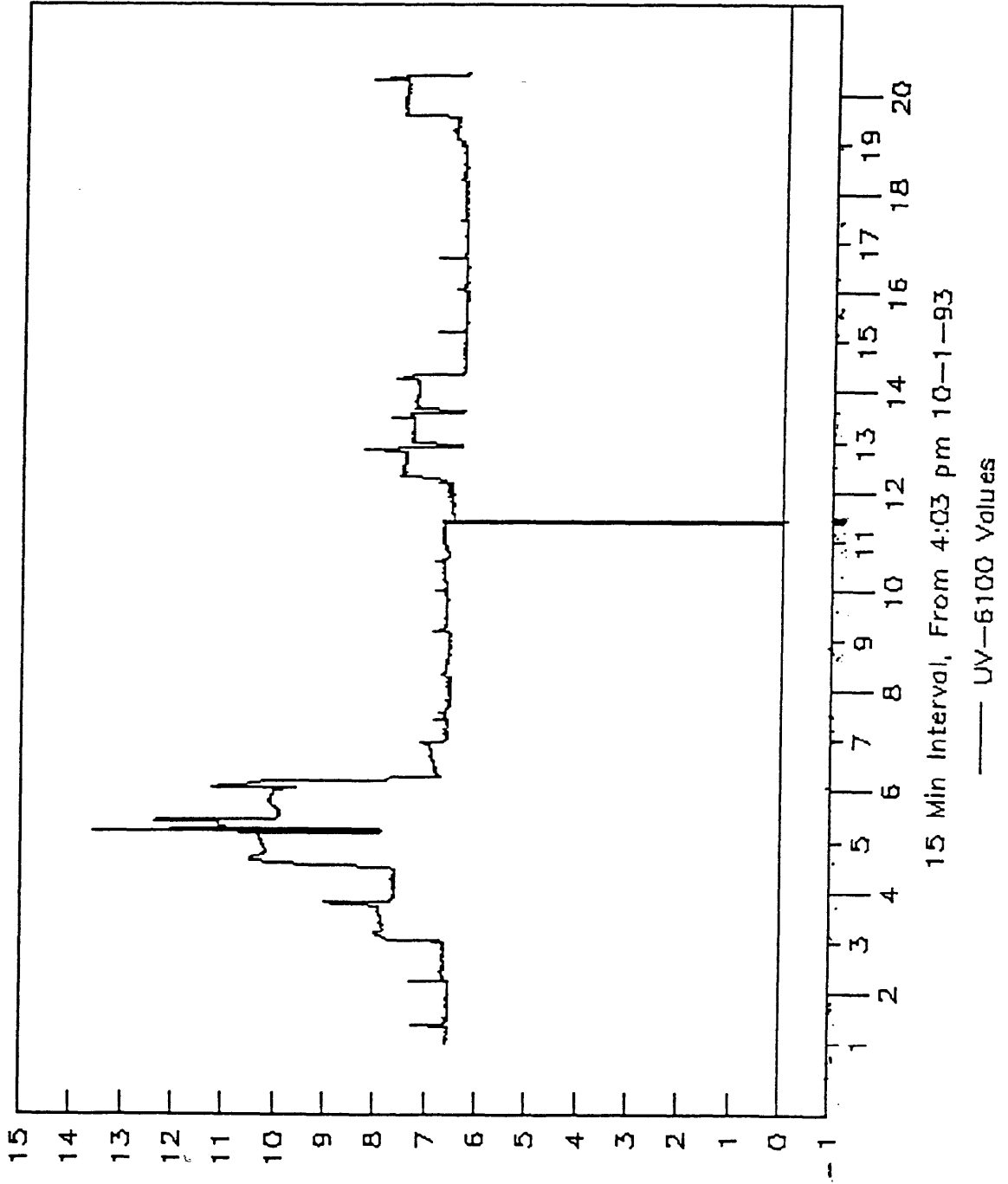
Figure 5 also shows the analyzer being “zeroed” using a deionized water standard on September 14, 1993 and a brief period where the sample line to the unit had been disconnected on September 15, 1993.

Figure 6 shows continuous nitrate-nitrogen monitoring results from October 1 thru October 20, 1993. Note the high nitrate-nitrogen value tracking from October 4 - 7. A high nitrate-nitrogen alarm could have signaled that corrective action needed to be taken on October 3. Continuous analysis can record instantaneous spikes of high nitrate-nitrogen that can easily be missed with a manual grab sampling program.

Figure 7 shows an expanded nitrate-nitrogen scale range (6.2 - 8.1 ppm) for the period from November 9 - 19, 1993. The regular pattern of changes in nitrate-nitrogen concentration versus time can be correlated to plant events such as pump intervals, ion exchange column switching, altered blend ratios, etc. Continuous analysis of process results, at regular intervals of a few minutes can be an important tool for troubleshooting and to optimize plant operations.

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Blended Well Water Nitrate Analysis

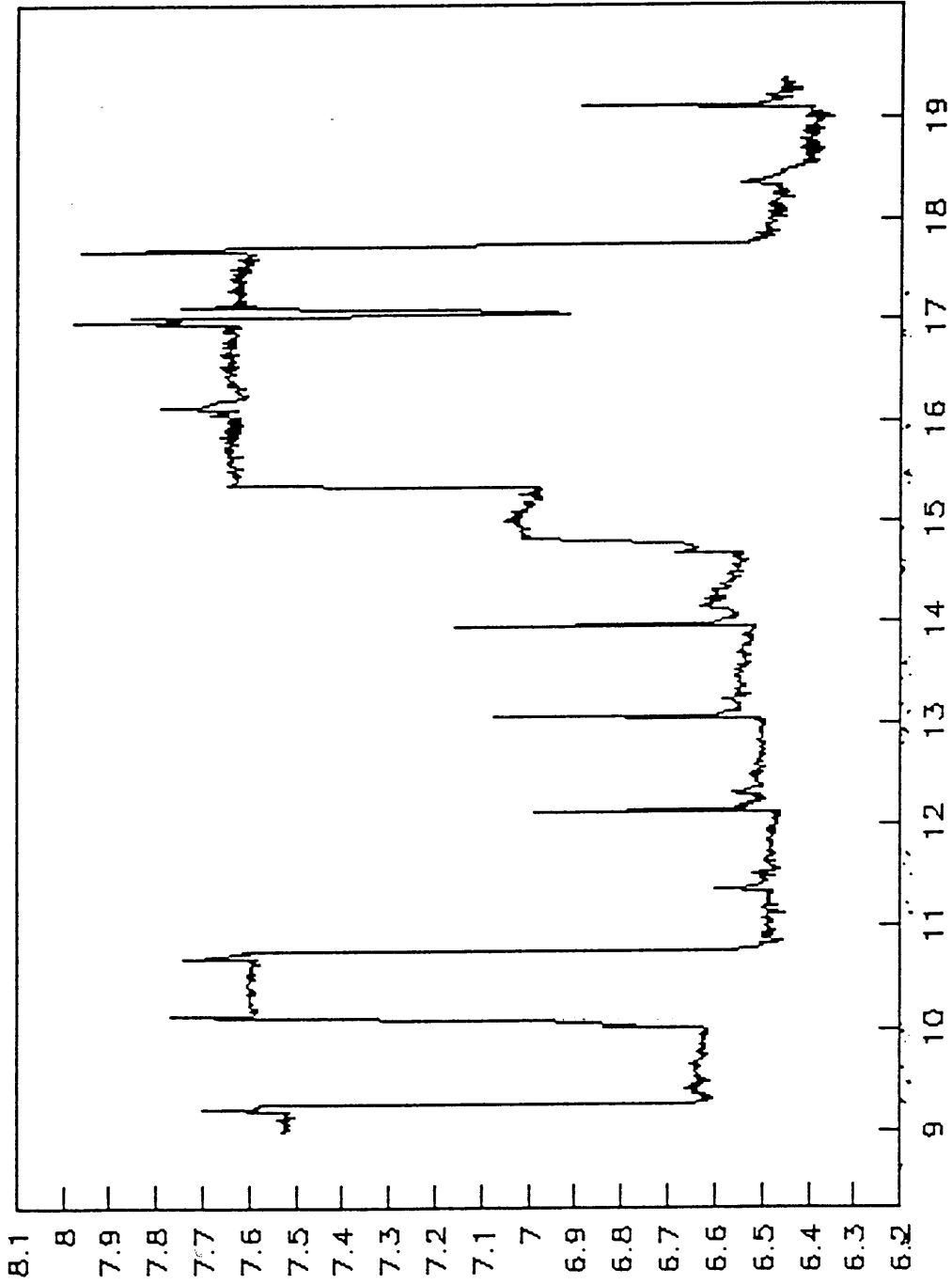


ppm, NO₃-N

Figure 6.

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Blended Well Water Nitrate Analysis



PPM, NO3-N

15 Min Interval, From 7:03 am 11-9-93
— UV-6100 Values

Addendum I
Project and Data Summary
Denitrification Monitoring Demonstration Project

ChemScan Process Analyzer Maintenance Report
Whiting, Wisconsin
February 16, 1995

Summary

After one year of operation the ChemScan Process Analyzer for nitrate-nitrogen on potable water performed very well with only minimal maintenance. The initial instrument standard (zeroing procedure) ranged from a one (1) week to an eight (8) week interval between instrument zeroing events. The nitrate concentration results started to drift over 0.5 mg/l versus lab results after 30 days of operation. A weekly DI water zeroing was instituted. This action restored instrument vs. laboratory differential to less than the target ± 0.5 mg/l variation. (A +0.75 mg/l offset used to compensate for lack of a routinely executed instrument standard was installed 4/12 then removed 7/11).

ChemScan Versus Laboratory Comparisons

During the year, on several occasions water processed by the ChemScan analyzer was sampled and split with a certified independent laboratory. The results are listed chronologically.

ChemScan Versus Laboratory Comparison
Whiting, Wisconsin
February 27, 1994 - February 16, 1995

Date	NO ₃ ^{-N} , mg/l		
	UV-6100	Certified Lab	Difference
2/27	6.60	6.63	-0.03
3/1	6.79	6.62	+0.17
3/2	10.72	11.00	-0.18
3/3	8.06	8.49	-0.43
3/6	7.08	6.60	+0.48
3/10	7.44	7.02	+0.42
3/11	6.47	5.99	-0.52
3/31	5.62	6.50	-0.88
4/1	7.21	8.00	-0.79
4/4	6.53	7.00	-0.47
4/5	5.59	6.20	-0.6

4/7*	6.66	6.06	+0.60
4/11*	7.78	7.11	+0.67
4/12*	6.52	6.50	+0.02
5/22*	6.22	6.16	+0.62
5/23*	6.75	6.13	
5/25*	6.27	6.12	+0.25
6/20*	7.27	6.53	+0.74
7/11*	8.80	8.00	+0.80
9/20	6.55	6.20	+0.22
12/1	5.11		
1/19/95	6.71	6.34	+0.37
2/16	6.55	6.65	+0.10
2/16	5.43	6.02	-0.59
$\bar{x} \pm s$	6.94 \pm 1.13	6.86 \pm 1.13	$\Delta = +0.052$

Finished water NO₃^{-N} Range: 5.01 mg/l
 Absolute error: 0.43 mg/l
 Abs. error as % of Range: 8.5%
 Ave. error as % of Range: 1.04%

Note: Four lab vs. ChemScan values that were greater than 1.0 mg/l difference were not used in this statistical averaging.

*+0.75 mg/l offset installed 4/7/94, removed 7/12/94. Zeroing had not been accomplished from start-up 2/27 through the end of March. The offset could accomplish matching of lab values with instrument values, but as soon as zeroing was done on a regular (weekly) basis, the offset was removed.

Maintenance Items Completed

(First of five (5) annual maintenance inspections)

- a visual inspection was made of all electronic connections.
- the flow cell was dismantled and physically cleaned and reassembled.
- the instrument was rezeroed using deionized water.
- the light intensity level was checked.
- all hydraulic connections were checked and secured.
- digital display screen was checked for proper illumination.
- software commands were checked for proper responsiveness.
- printer output was verified.

Overall, the operators estimate < 5 hours per month devoted to ChemScan analyzer maintenance. Maintenance cost for the year was limited to less than \$30.00 for DI water and muriatic acid purchases. (Versus cost of approximately \$10,000 per year in previous years when an on-line water chemistry analyzer with proprietary chemicals was used.) Maintenance time was also drastically reduced. A 5 year service agreement is in place for this instrument.

There were a few occasions during the year when the analyzer did indicate values higher than the 8.5 mg/l alarm setpoint. However, because of the continuous 15 minute interval sample monitoring, the finished water quality was brought under control quickly and without incident.

The overall attitude of the operators regarding the instrument performance and maintenance is very positive after one year of operation. The operators appreciate an accurate, reagentless low maintenance analyzer at their work site. It also assists them in maintaining a higher quality standard on a more consistent basis for their finished product, potable water for public consumption which is below the national standard of 10 mg/l NO₃^N.

Jeff Schlegel (715) 344-4545 Superintendent of the Whiting Utilities, is available for questions or to arrange a plant site visit.