

ChemScan™ UV-6100 Process Analyzer

**PROJECT AND DATA SUMMARY
NITRATE MONITORING
DEMONSTRATION PROJECT**

**Stillwater Mining Company
Nye, Montana**

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STILLWATER MINING COMPANY

**CLARIFIED MINE DISCHARGE
NITRATE NITROGEN MONITORING DEMONSTRATION PROJECT**

Executive Summary

A demonstration project was initiated in October, 1993 for monitoring of nitrate-nitrogen levels in mine discharge water at the Stillwater Mining Company in Nye, Montana. This report covers information summarized from the October 1993 to February 1994 test period. The main objective of the demonstration project was to show that nitrate-nitrogen concentration of mine discharge could be reliably monitored on a continuous basis with minimum down-time, with reasonable accuracy and with low operation and maintenance costs. This objective was accomplished. The mine discharge water processing facility is currently operating at approximately 0.3 MGD.

Introduction

Stillwater Mining Company (SMC) in Southern Montana is located three miles south of Nye, Montana and three miles from the Absaroka Bear-tooth Wilderness Area.

The on-going mining and milling operation is recovering the only significant concentration of platinum and palladium in the United States to provide about seven percent of the U.S. annual requirements for these metals. The greatest use of platinum is in automobile catalytic converters. Other uses of platinum are as an industrial catalyst in the production of gasoline, fertilizer and various chemicals, as well as its role in the making of fine jewelry. Palladium is used in the electronics industry for micro-circuitry and is also used as a chemical industry catalyst and in catalytic converters and dental alloys. South Africa and Russia supply the dominant share of the U.S. demand.

Because these important metals are being mined in an environmentally sensitive setting, it is necessary to continuously monitor impacts of the mining operation on the environment, including water quality. Blasting operations, a normal mining procedure, use compounds such as ammonium nitrate. As a result of blasting residuals, the water that is discharged from the mine has a nitrate-nitrogen concentration that can range from 0 to 30 ppm. In addition, the water varies in hydraulic volume discharged daily and hydraulic volume discharged hourly resulting in an unpredictable nitrate-nitrogen concentration at any point in time. Suspended matter of a fine and colloidal nature is also an ingredient of the mine discharge.

To reduce the solids load of the variable flow mine discharge, the water is treated with an aqueous solution of ferric sulfate and a cationic polyamine polymer prior to conventional solids settling in a gravity solids concentrator (clarifier). However, the total oxidized nitrogen concentration (consisting primarily of nitrate-nitrogen) is not affected by the clarification step. With environmental protection in mind, Stillwater Mining Company sought means to continuously monitor the nitrate-nitrogen in the mine discharge, which was the basis for the demonstration project.

An objective of the demonstration was to show that the highly variable nitrate-nitrogen concentration of the clarified mine discharge water could be continuously and reliably monitored by the ChemScan™ UV-6100 process analyzer. Another objective was to

provide Stillwater Mining Company with an opportunity to evaluate operation and maintenance costs as compared to wet chemistry nitrate analyzers.

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 A 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.

Clarified Effluent Monitoring

The UV-6100 analyzer demonstration equipment was installed in September, 1993. A factory calibration was used while a series of site-specific samples were collected to eventually produce a site-specific calibration over the range of 0 - 30 mg/l NO₃-N.

A sample line was connected from the clarifier effluent flow to the UV-6100. At the start of the project, a sample pump was used to deliver clarified effluent to the UV-6100. However, later on gravity head pressure was used to deliver a fresh supply of sample through the flow cell. The sample line provided a continuous flow through the flow cell at all times. It was not necessary to stop the flow to produce a nitrate-N value. Information from the analyzer was recorded in several ways:

- A. The UV-6100 analyzer was programmed to scan the sample and calculate nitrate-nitrogen concentration at periodic (about 2.5 minute) intervals. This information could be converted to an RS-232 signal by the UV-6100 analyzer, with potential output to a plant data management network where the information could be available for recording or display by the computer system. A 4-20 in a signal is also available for recording or control of treatment processes. However, for this demonstration, data was not available to be directly utilized by SMC personnel. A manufacturer's representative with a portable computer made a site visit and provided the data by downloading the internal memory built into the instrument. About six weeks into the demonstration, a dot-matrix printer was integrated into the RS-232 output of the UV-6100 and recorded data continuously during the remainder of the demonstration project.

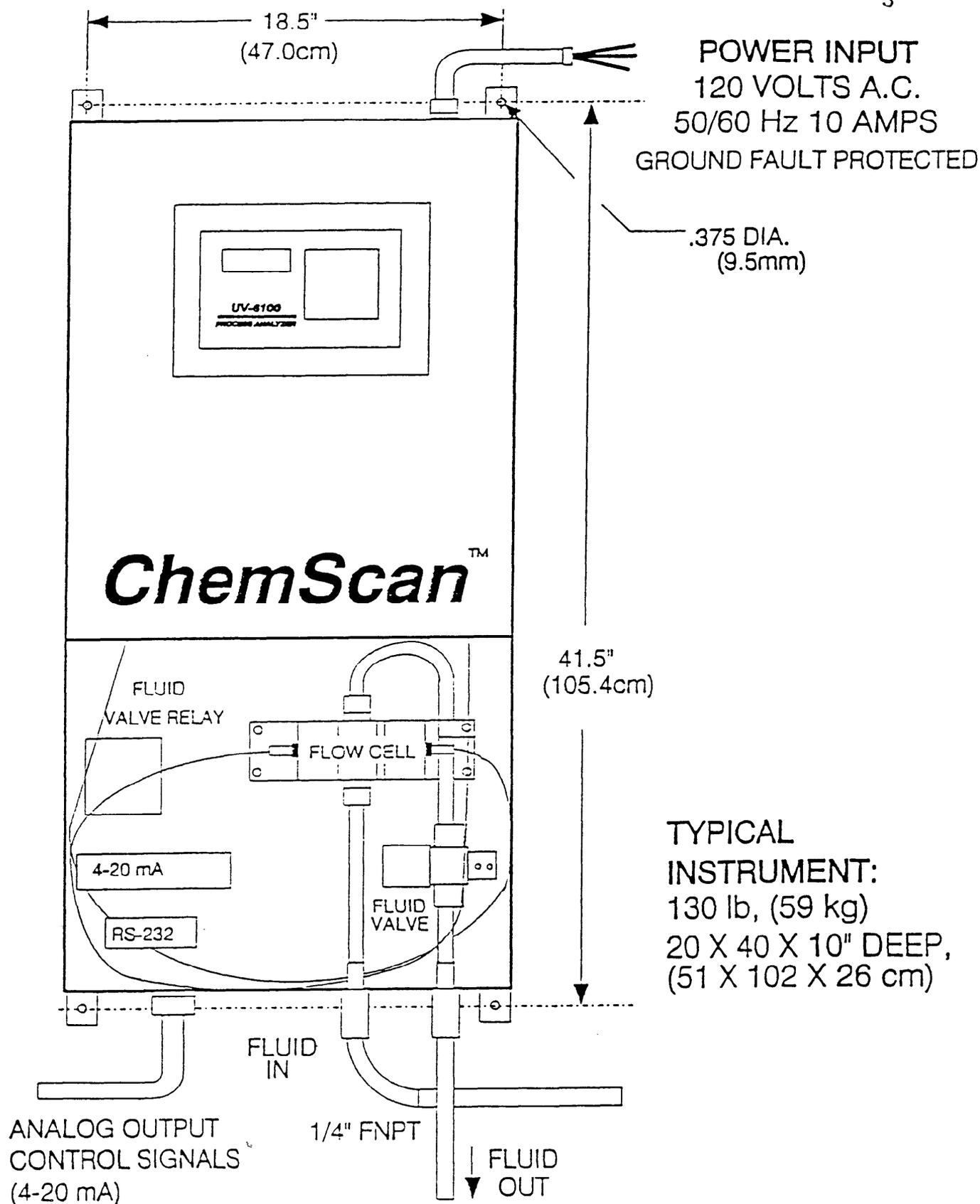


Figure A

- 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 each 8th reading (about every 20 minutes) during the demonstration period.
- C. Initially, operators were requested to extract grab samples from the sample line at least once per day during their maintenance rounds. 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 a third-party certified laboratory could be matched with the comparable values from the UV-6100 analyzer. These samples could also be used to further refine the calibration of the instrument.

Trending and Tracking Results

Early in the project, plant personnel compared UV-6100 results with results from periodic grab samples that were analyzed using EPA approved laboratory procedures. Instrument results were within a fraction of a ppm when compared to the certified laboratory values. Figure B shows the results of initial concentration monitoring using a calibration learning set of a range of nitrate-nitrogen standards.

Figure C shows comparisons between the UV-6100 and the certified laboratory with a DI water calibration (9/28 - 10/17) and with process water results added into the UV-6100 calibration learning sets (10/27 - 11/28).

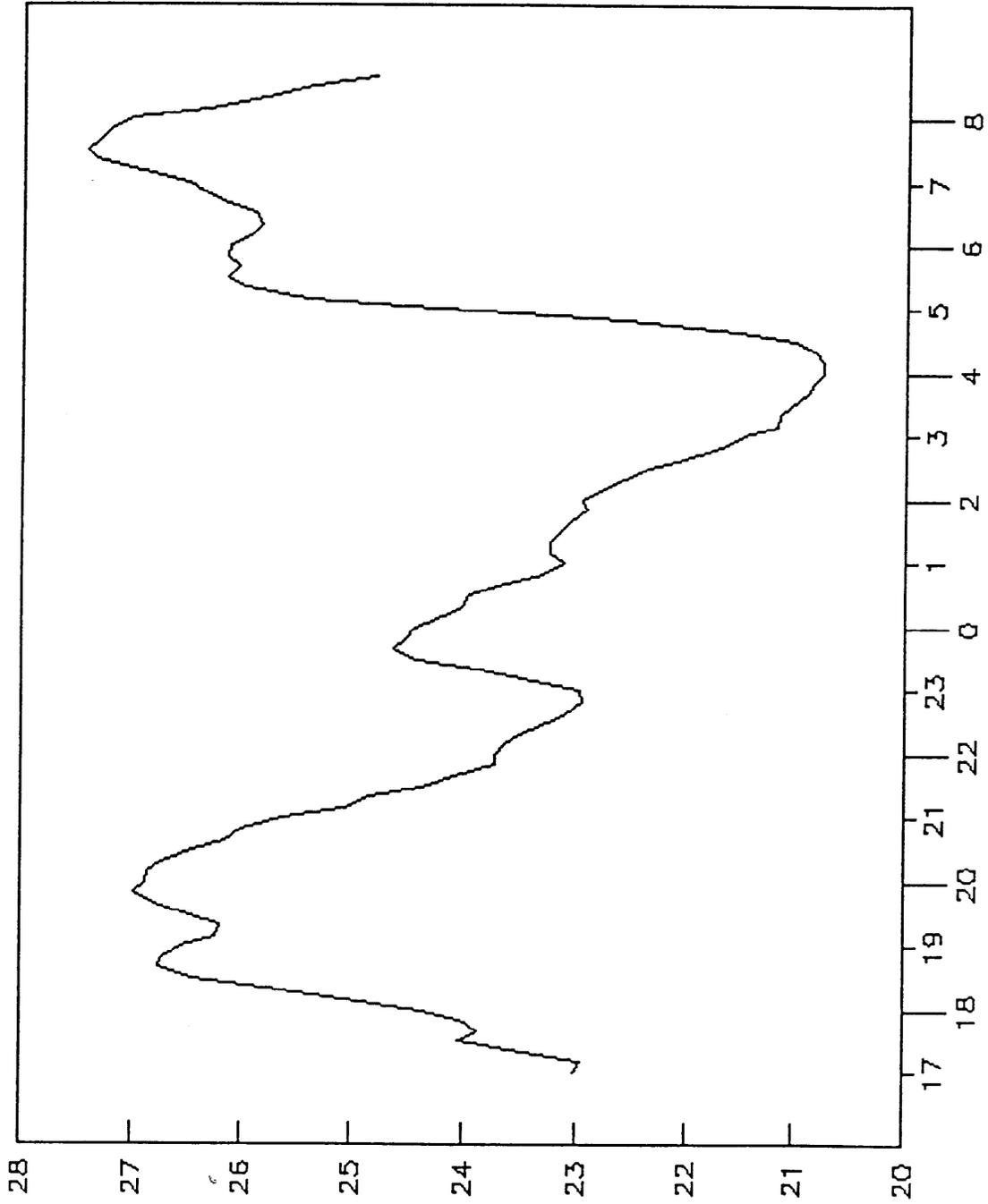
Figure D shows the close grouping of UV-6100 results around the laboratory values for the 10/27/93 - 11/28/93 period. The calibration of the instrument continued to be refined as additional data was accumulated. Figures 1 - 4 depict both continuous and reliably accurate results of variable nitrogen levels in the clarified mine discharge. The graphs indicate the variations in $\text{NO}_2 + \text{NO}_3\text{-N}$ concentration with time. Note that there are large variations in the concentration within the course of several minutes and hours which are being detected by the UV-6100 system.

The graphs also show several "zero" concentrations which are a result of an instrument standard (zeroing) done by SMC personnel. Figure 1 shows 11 days of operation at the end of 1993, while Figures 2, 3, and 4 show shorter time intervals in February, 1994. A more detailed trend can be noted as the x-axis (time) is shown in shorter intervals.

As a further method of comparison, SMC personnel attempted to use the UV-6100 $\text{NO}_3\text{-N}$ values logged over a 24-hour period to construct a calculated composite nitrate-nitrogen value to be compared with a 24 hour composite sample of the clarifier effluent sampled at approximately the same sampling intervals as the UV-6100 readings. The downloaded data files and later on the printer record were used to generate these calculated composites.

STILLWATER MINING

Thickener Overflow Nitrate Nitrogen

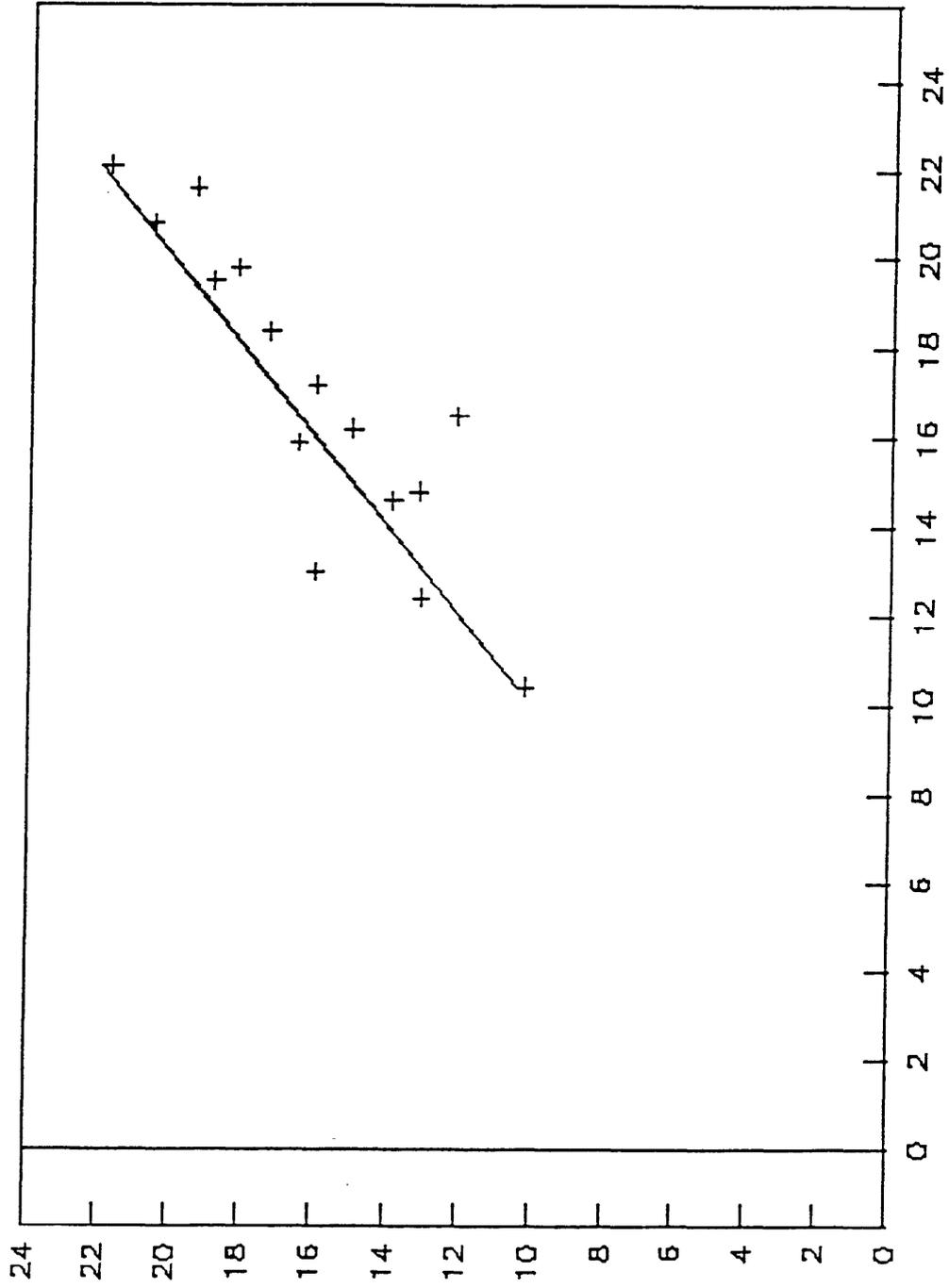


10 min interval, starting 5pm, 9-28-93

Figure B

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Mine Drainage Water



10/27 thru 11/28
— ENG Laboratory + UV-6100

Figure D

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MINE DISCHARGE CLARIFIED EFFLUENT

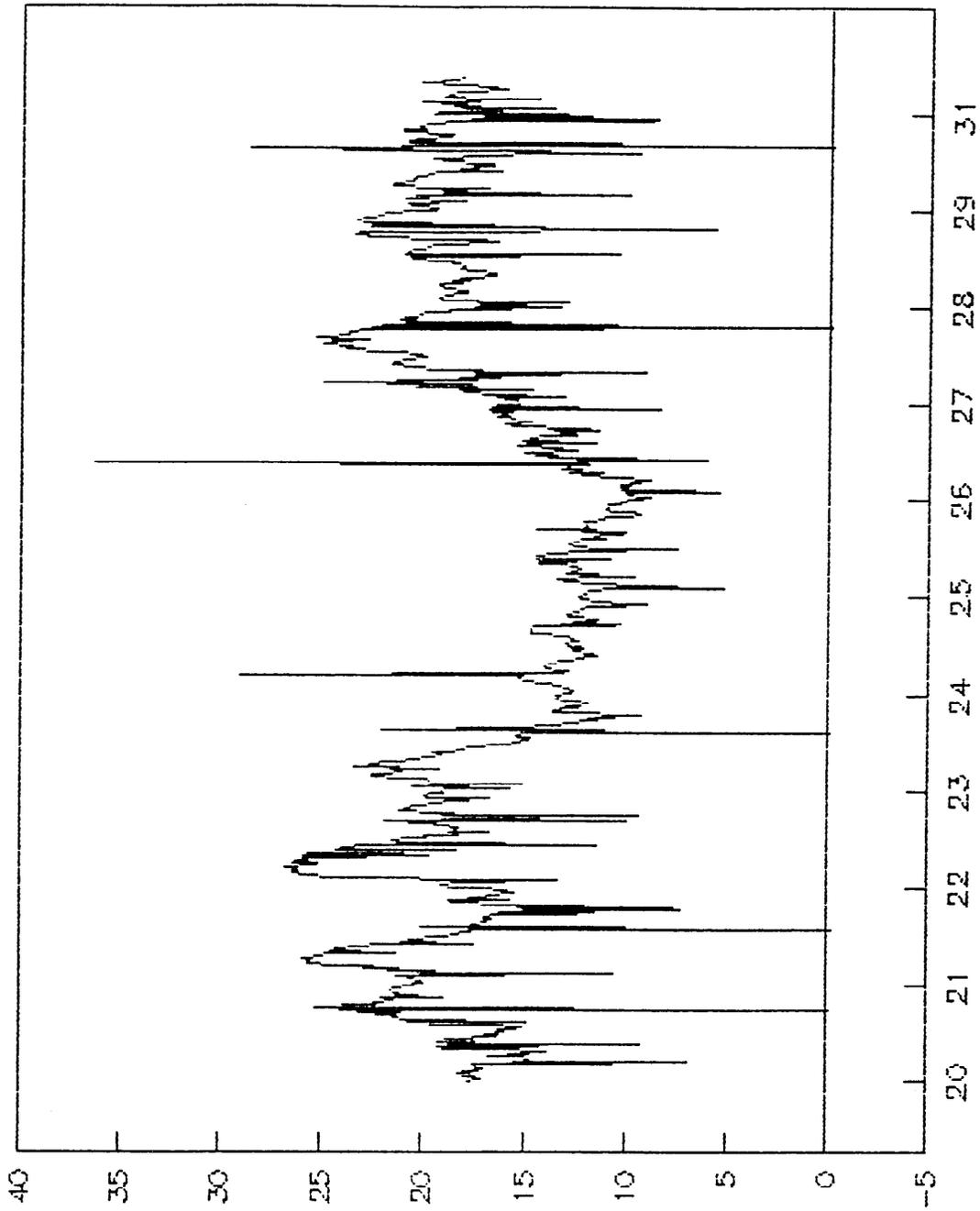


Figure 1.

PPM, NO₂+NO₃-N

20MIN INTERVAL, 12--20 TO 12-31-93

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MINE DISCHARGE CLARIFIED EFFLUENT

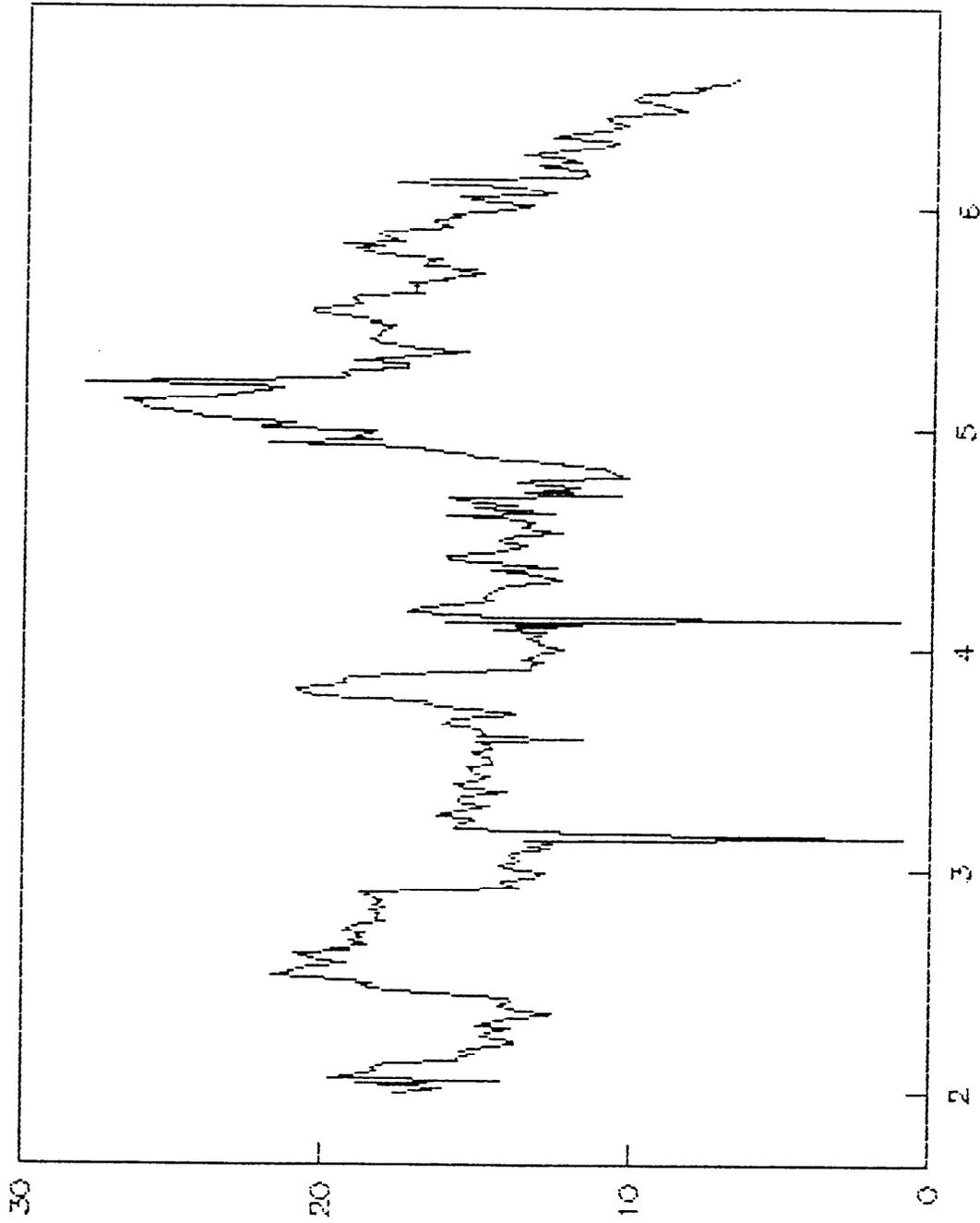


Figure 2.

PM, NO₂+NO₃-N

20 MIN INTERVAL, 2-2 TO 2-6-94

STILLWATER MINING COMPANY
MINE DISCHARGE CLARIFIED EFFLUENT

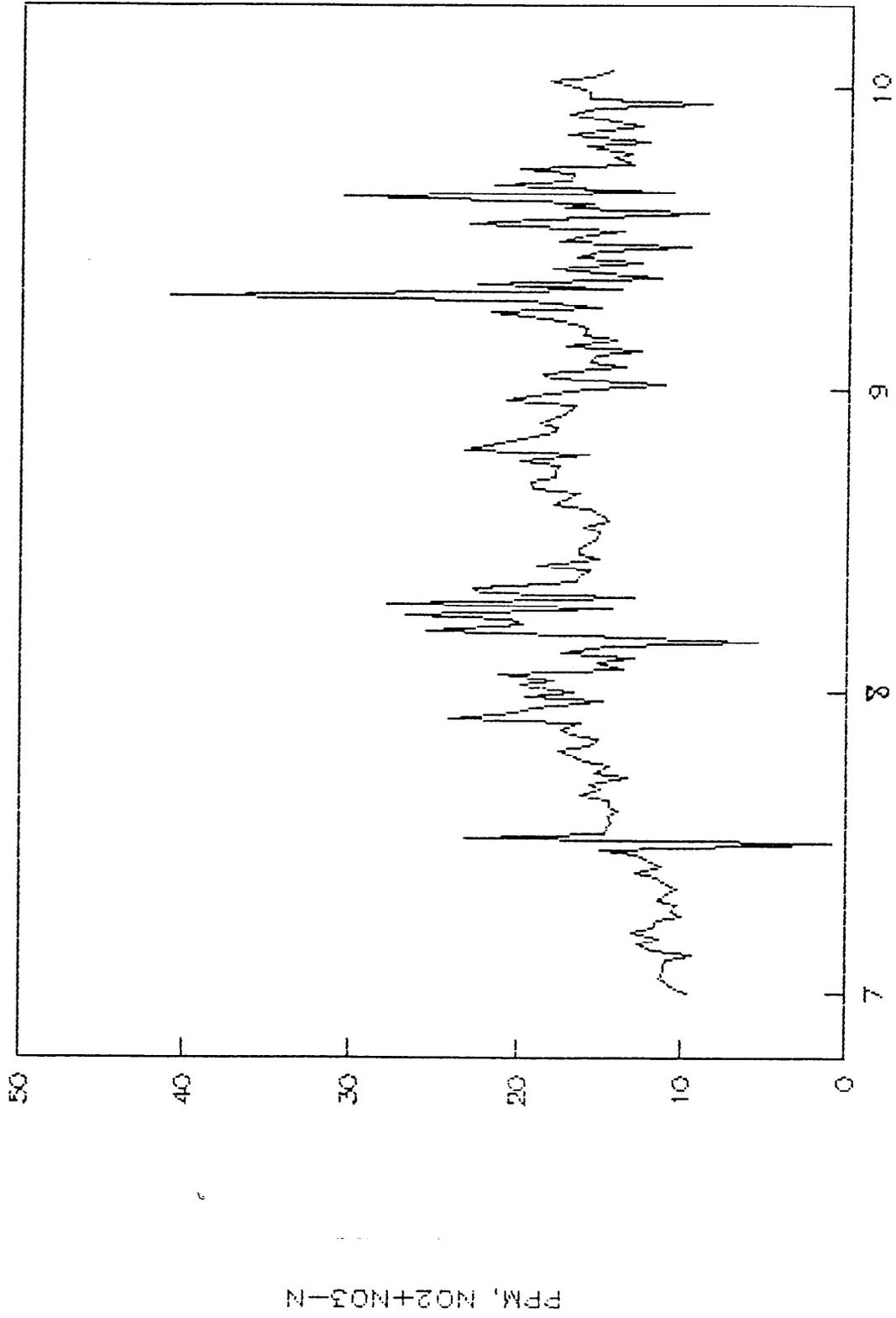


Figure 3.

STILLWATER MINING COMPANY
MINE DISCHARGE CLARIFIED EFFLUENT

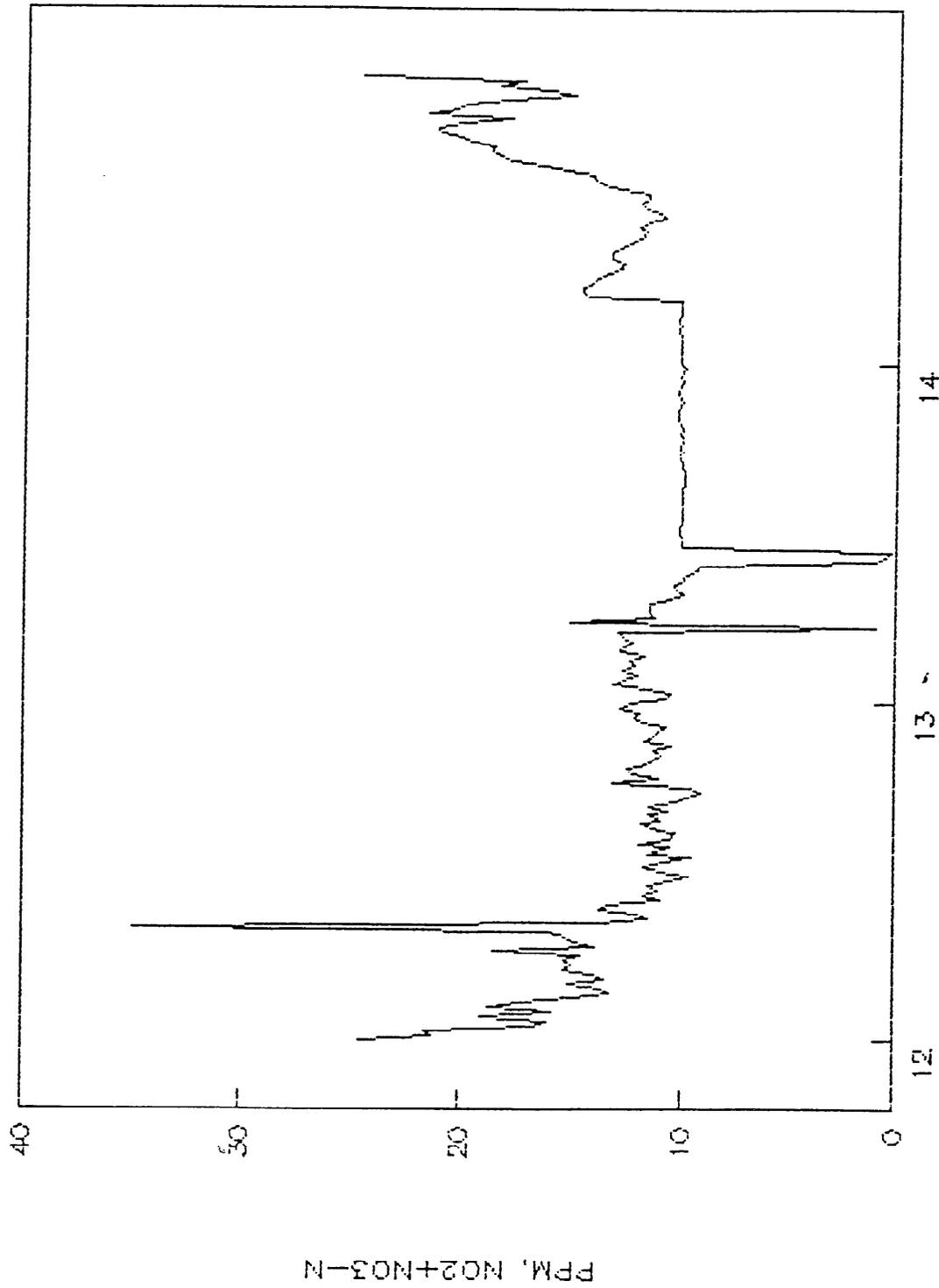


Figure 4.

20 MIN INTERVAL, 2-12 TO 2-14-94

In the early weeks of the demonstration, this method of comparison yielded data values that were not favorably comparable. There were sampling interval differences, sample line plugging and freezing problems, a troublesome printer that shut itself down occasionally and abnormally frequent electrical line voltage fluctuations that interfered with equipment operation. (Due to the remote “end-of-the-line” location of the Stillwater Mining Company, the electrical line aberrations are quite frequent.) The Holiday season backed up sample handling between mid-November and January 1, and sample reporting was not placed on priority status. This also lengthened the time to achieve a proper calibration.

Other circumstances that slowed the creation of a stable calibration was the distance to the nearest laboratory (90 miles), inconsistent delivery of samples to the laboratory, the laboratory procedure whereby preserved samples were run in batches once per week or so and the basis of comparison of UV-6100 results versus the certified laboratory results. At the beginning of the demonstration program, the blanks, standards, and spikes prepared for on-site DI water and/or process water calibration were analyzed for nitrate-nitrogen only on the UV-6100. These samples were run through the UV-6100 analyzer where $\text{NO}_3\text{-N}$ readings were recorded, then the remainder of the samples were acidified by SMC personnel, stored and delivered to the lab. The lab did batch analysis for $\text{NO}_2 + \text{NO}_3\text{-N}$ (NO_x , or total oxidized nitrogen [TON]). There was up to 1.4 mg/l $\text{NO}_2\text{-N}$ content in some samples. Therefore, while the UV-6100 was analyzing $\text{NO}_3\text{-N}$ only, the lab analysis produced a combined $\text{NO}_2+\text{NO}_3\text{-N}$ result.

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. To obtain a revised calibration file, starting about December 19 the sampling program was streamlined and sample handling and reporting were prioritized. An additional sampling procedure was organized to take a portion of the clarified 24 hour composite and pump it through the UV-6100 process analyzer. Three (3) separate UV-6100 readings were recorded, and the average of these readings were recorded to compare to the actual laboratory nitrate+nitrite nitrogen analysis on the remainder of the 24-hour composite. The remainder of the sample was preserved and transported to the laboratory in a cooler on ice. The lab conducted the analysis within 24 - 48 hours and reported the sample analysis ($\text{NO}_x + \text{NO}_3\text{-N}$) as soon as available, results immediately faxed to both Stillwater Mining Company and Biotronics. The $\text{NO}_x + \text{NO}_3\text{-N}$ data was then used to fine-tune the instrument calibration. As revisions to the calibration are made, new files were added, while others were removed. In this way, the “apples to oranges” comparison was rectified and the UV-6100 was recalibrated to reflect the $\text{NO}_2+\text{NO}_3\text{-N}$ combination. Results comparing the laboratory to both the 24 hour composite split sample (labeled OSA Composite Read-Back on Figures 5 and 7) and the SMC calculated composite derived from UV-6100 printer output (20 minute intervals) over a given 24 hour period (labeled OSA Daily Average on Figures 6 and 8) were much more comparable.

In summary, as a result of an additional sample procedure (24 composite through the analyzer) and the expedited and prioritized sample handling and reporting, the refined UV-6100 calibration yielded a favorable comparison between the laboratory cadmium reduction method and the on-line analysis method of nitrate + nitrite nitrogen analysis.

Statistical Analysis: ChemScan UV 6100 OS Nitrate Analyzer

December 21, 1993 thru January 20, 1994

Assay determination of: Nitrate + Nitrite as N

Number of paired Samples	20
Mean of OSA Composite Read-Back	18.97 mg/l
Mean of Energy Labs NO3+NO2	21.44 mg/l
Mean Difference (absolute)	-2.47 mg/l
Mean Difference (relative)	13.0%
Coefficient of Variation of Means	6.1%
Correlation Coefficient R ²	0.91957
t-Value	8.623 * significant

Degrees of Freedom	19
Tabulated t-values at:	
	90.0%
	95.0%
	99.0%
	1.729
	2.093
	2.861

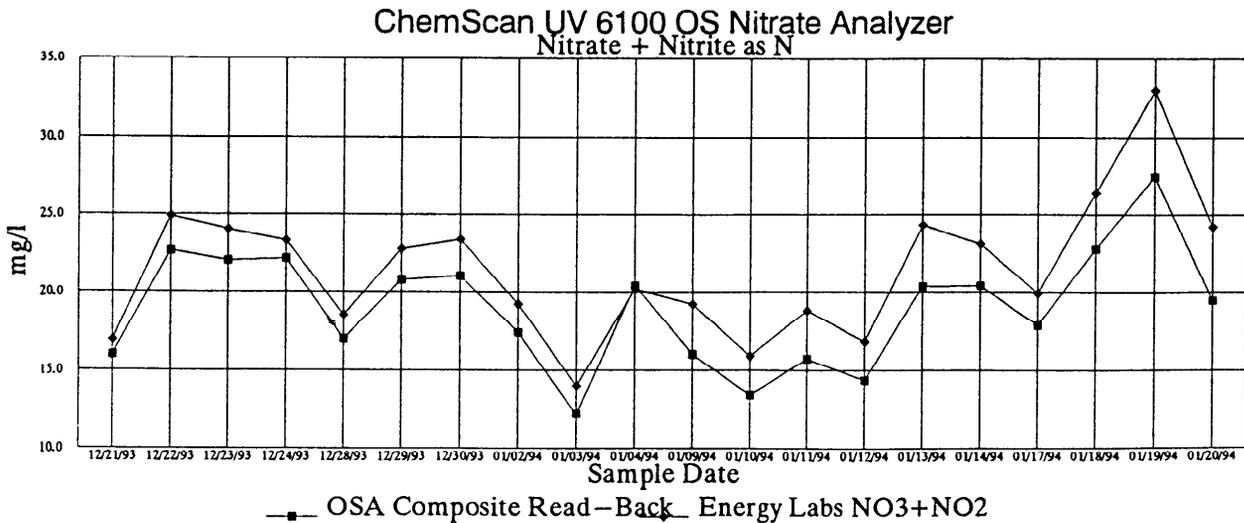
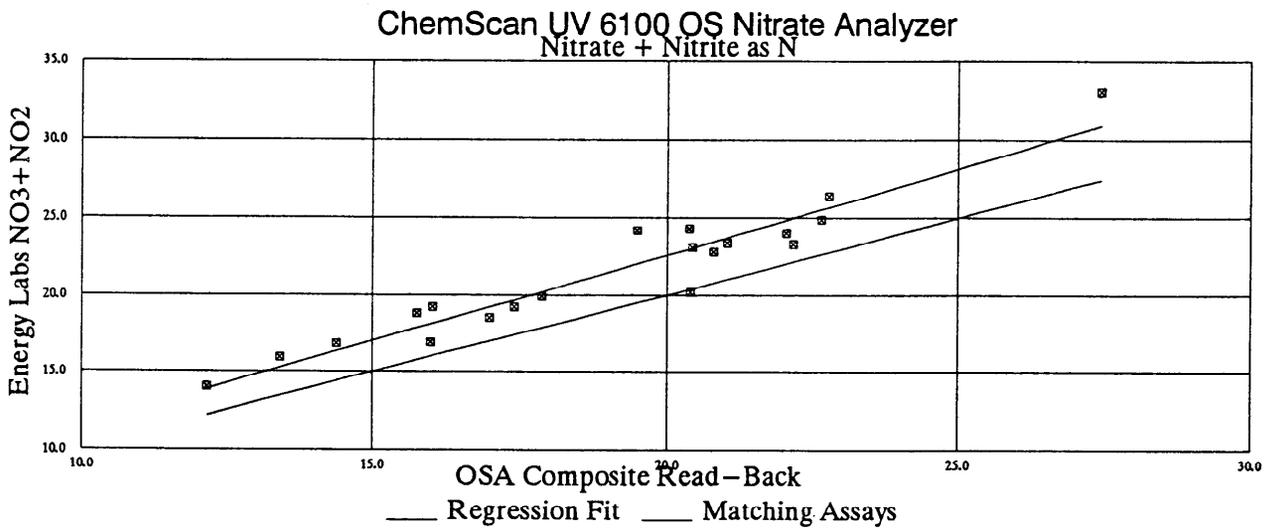


Figure 5

Statistical Analysis: ChemScan UV 6100 OS Nitrate Analyzer 14

December 21, 1993 thru January 20, 1994

Assay determination of: **Nitrate + Nitrite as N**

<u>Number of paired Samples</u>	<u>20</u>
<u>Mean of OSA Daily Average</u>	<u>17.92 mg/l</u>
<u>Mean of Energy Labs NO3+NO2</u>	<u>21.44 mg/l</u>
<u>Mean Difference (absolute)</u>	<u>-3.52 mg/l</u>
<u>Mean Difference (relative)</u>	<u>19.6%</u>
<u>Coefficient of Variation of Means</u>	<u>8.9%</u>
<u>Correlation Coefficient R²</u>	<u>0.89349</u>
<u>t-Value</u>	<u>9.508</u> * significant

<u>Degrees of Freedom</u>	<u>19</u>
<u>Tabulated t-values at:</u>	
	<u>90.0%</u> <u>1.729</u>
	<u>95.0%</u> <u>2.093</u>
	<u>99.0%</u> <u>2.861</u>

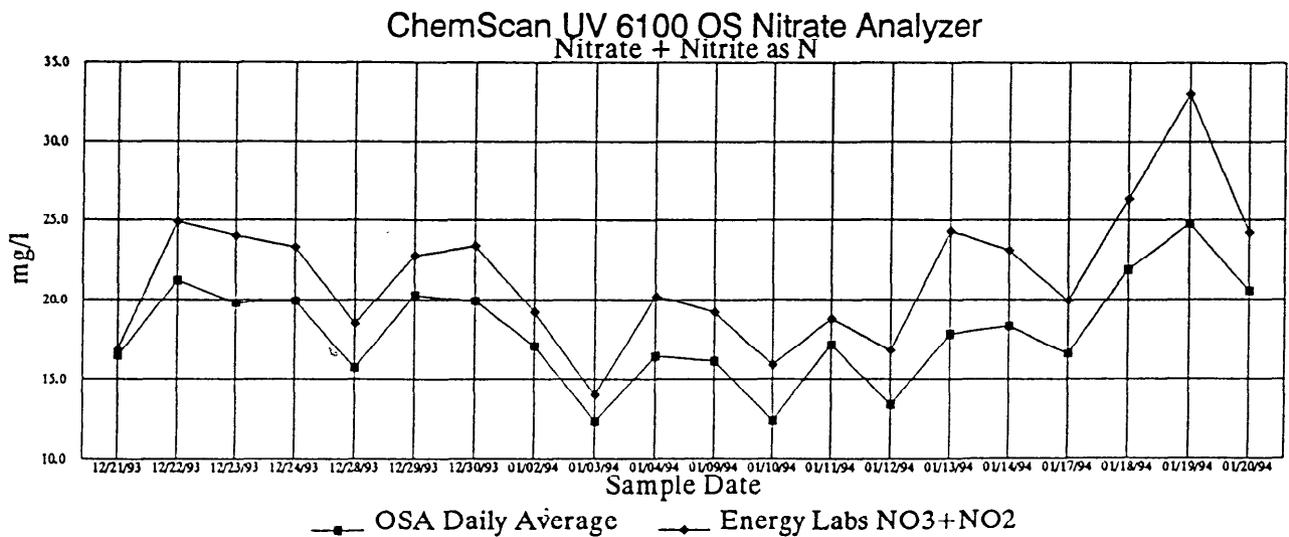
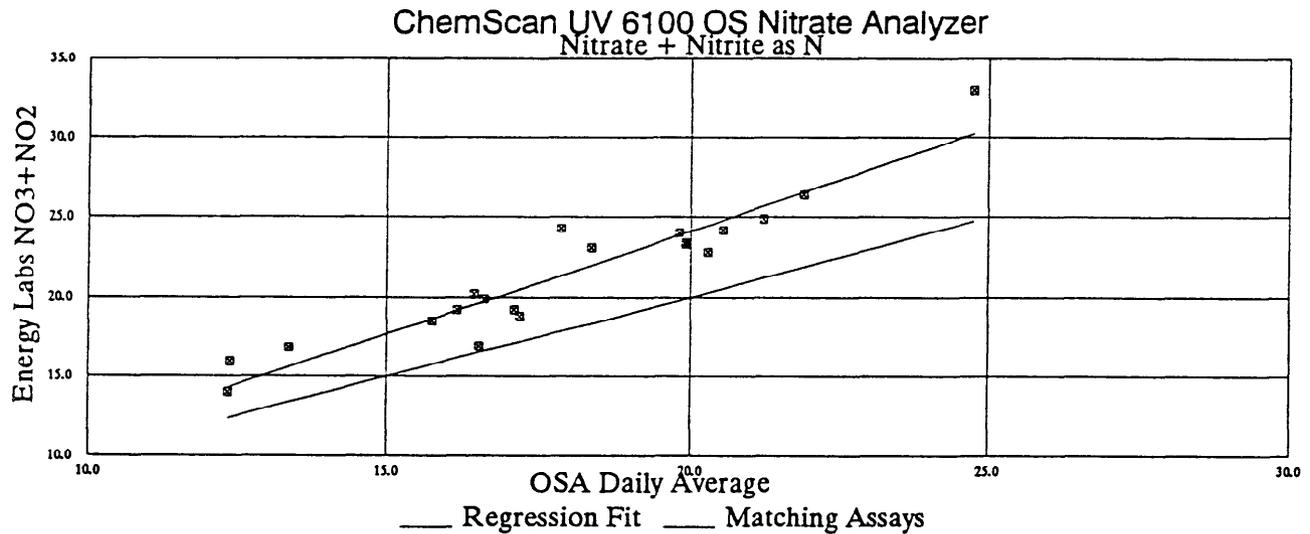


Figure 6

Statistical Analysis: ChemScan UV 6100 OS Nitrate Analyzer

February 1, 1994 thru February 11, 1994

Assay determination of: Nitrate + Nitrite as N

Number of paired Samples	7
Mean of OSA Composite Read-Back	17.19 mg/l
Mean of Energy Labs NO ₃ +NO ₂	17.14 mg/l
Mean Difference (absolute)	0.04 mg/l
Mean Difference (relative)	0.3%
Coefficient of Variation of Means	0.1%
Correlation Coefficient R ²	0.91381
t-Value	0.191

Degrees of Freedom	6
Tabulated t-values at:	
90.0%	1.943
95.0%	2.447
99.0%	3.707

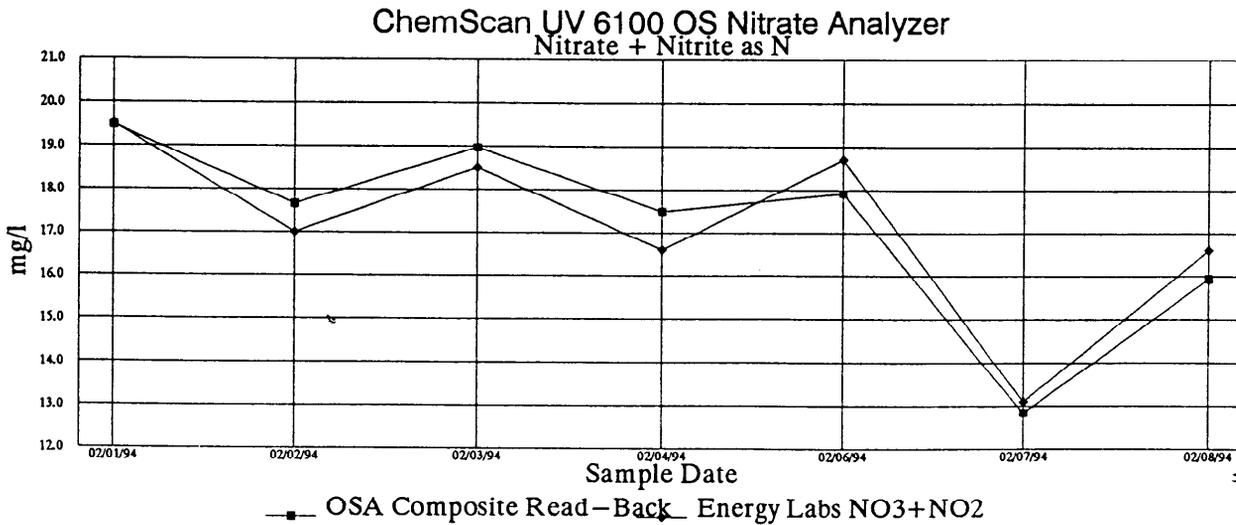
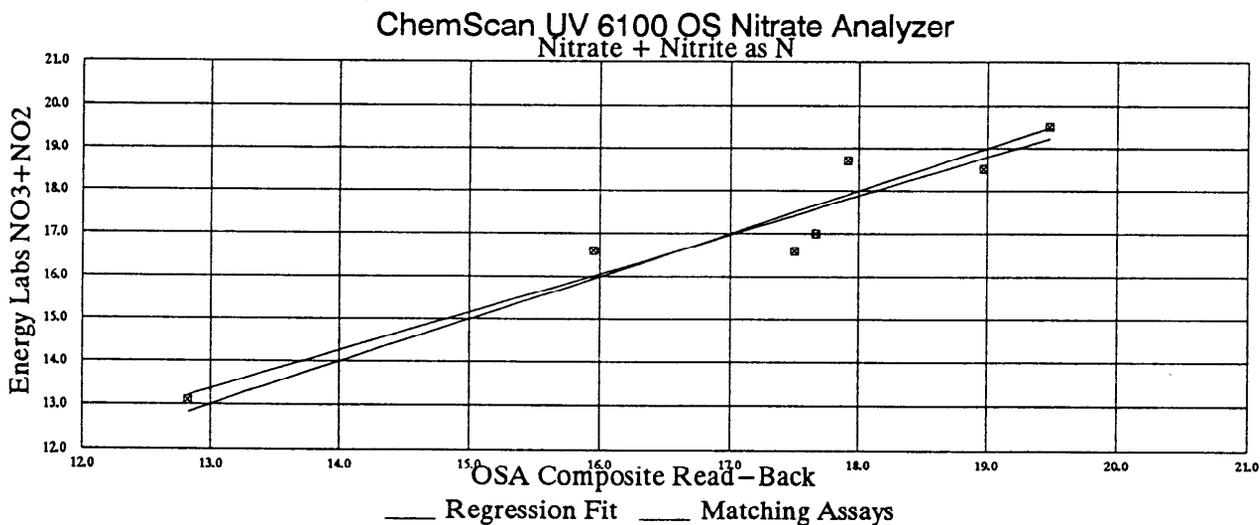


Figure 7

Statistical Analysis: ChemScan UV 6100 OS Nitrate Analyzer

February 1, 1994 thru February 11, 1994

Assay determination of: Nitrate + Nitrite as N

Number of paired Samples	8
Mean of OSA Daily Average	16.45 mg/l
Mean of Energy Labs NO ₃ +NO ₂	17.63 mg/l
Mean Difference (absolute)	-1.17 mg/l
Mean Difference (relative)	7.1%
Coefficient of Variation of Means	3.4%
Correlation Coefficient R ²	0.94577
t-Value	6.389 * significant

Degrees of Freedom	7
Tabulated t-values at:	
	90.0%
	95.0%
	99.0%
	1.895
	2.365
	3.499

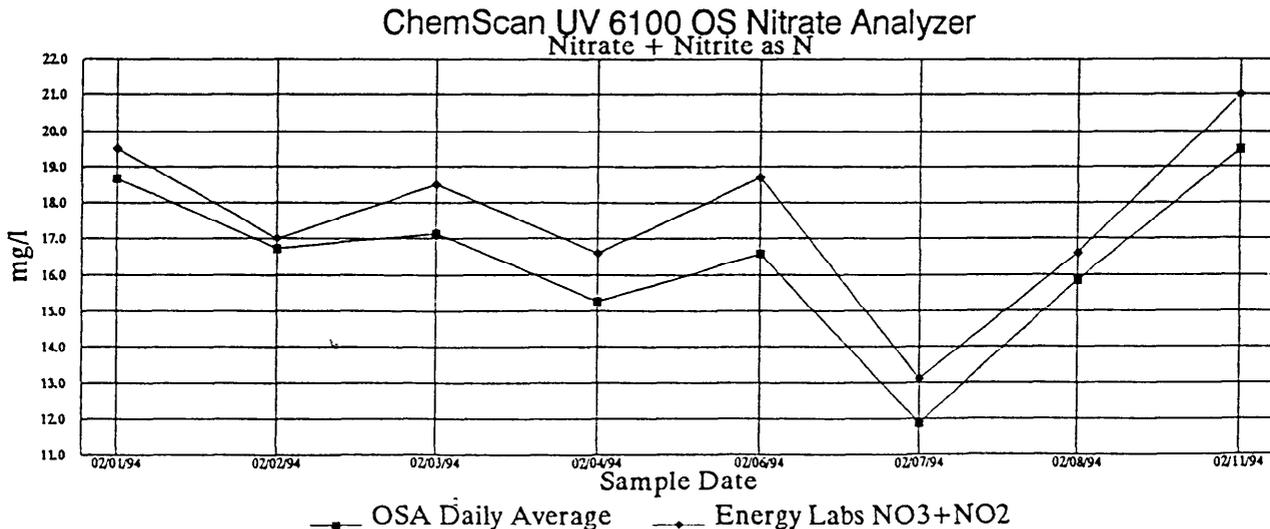
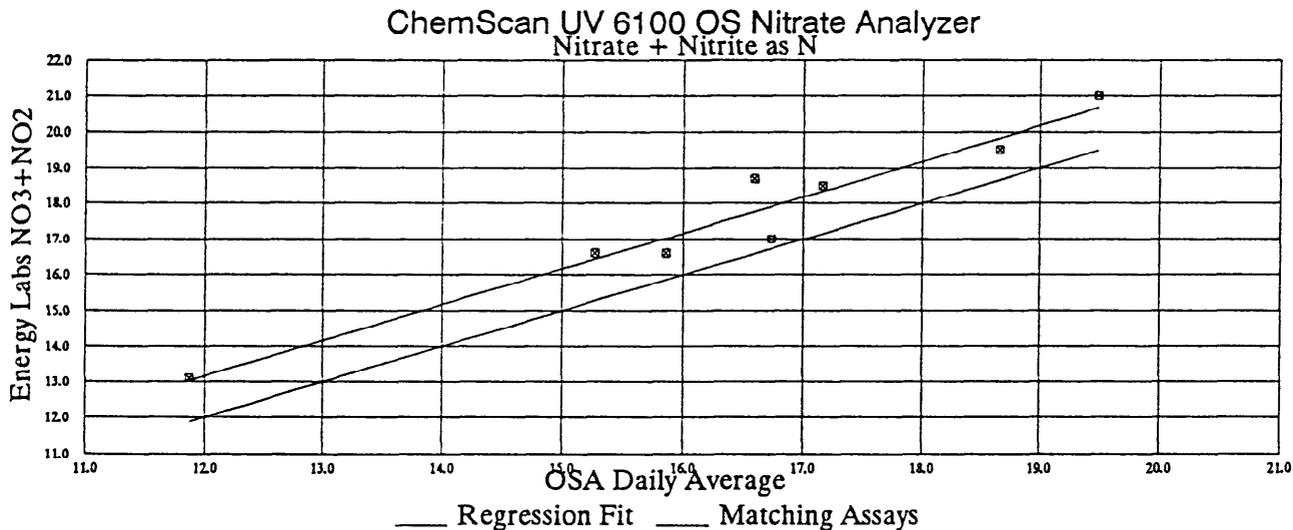


Figure 8

Composite Results

Just as Figures 1-4 showed consistent trending of variable TON for several periods, the data in Figures 5, 6, 7 and 8 show that the Chem-Scan UV-6100 process analyzer is consistent with regard to tracking independent laboratory tests. The UV-6100 data correlated quite well when compared to the 24-hour composite read-back results as shown in Figures 5 and 7 for December 21, 1993 to January 20, 1994 (correlation coefficient $R^2 = .91957$) and for February 1 - 11, 1994 (correlation coefficient $R^2 = .91381$).

The daily average calculated composites of the 20 minute interval UV-6100 printer output correlated fairly well during the December 21, 1993 to January 20, 1994 period shown in Figure 6 (correlation coefficient $R^2 = .89349$) but was the best after the new calibration in the February 1 - 11, 1994 period shown in Figure 8 (correlation coefficient $R^2 = .94577$).

These comparisons demonstrate the importance of a correct and accurate calibration learning set. The success of the demonstration project is shown by how well the Chem-Scan UV-6100 process analyzer matched grab samples, composite samples and calculated composite daily average laboratory values under adverse operating conditions.

Coagulant Feed to the Solids Concentrator

Due to the variable flow of mine discharge and the variability of solid and colloidal matter, there is a need to operate the chemical ferric coagulant in an overdose manner at times. Since there is no automated chemical feed system to optimize chemical feed, there is excess coagulant that has occasionally affected the UV-6100 optrodes ability to pass sufficient light through it in order to achieve an accurate TON reading.

This has increased maintenance of cleaning of the optrode as well as frequency of rezeroing. In order to achieve a better control of the ferric coagulant feed, the UV-6100 could be calibrated to monitor for excess ferric ion residual as an additional parameter. With the proper signal conditioning, a ferric delivery control system could be available. Turbidity changes could also be monitored, which should aid in the control of the automated ferric delivery system.

Summary

This project has demonstrated accurate monitoring of highly variable total oxidized nitrogen, TON or (NO_2+NO_3-N) under variable flow and ferric coagulant feed conditions. Also, operation and maintenance costs should be lower than a chemical reagent-based analyzer or a specific ion electrode analyzer, because there are no reagents to be purchased nor membranes or probes to replace.

A purchase order for a UV-6100 system to monitor TON and ferric was issued by Stillwater Mining Company on April 28, 1994.