

**ON-LINE ANALYSIS OF NITRATE WITH
ULTRAVIOLET ABSORBANCE SPECTROMETRY**

**Bernard J. Beemster and Scott J. Kahle
Biotronics Technologies, Inc.
W226 N555B Eastmound Dr.
Waukesha, WI 53186
(414) 896-2650**

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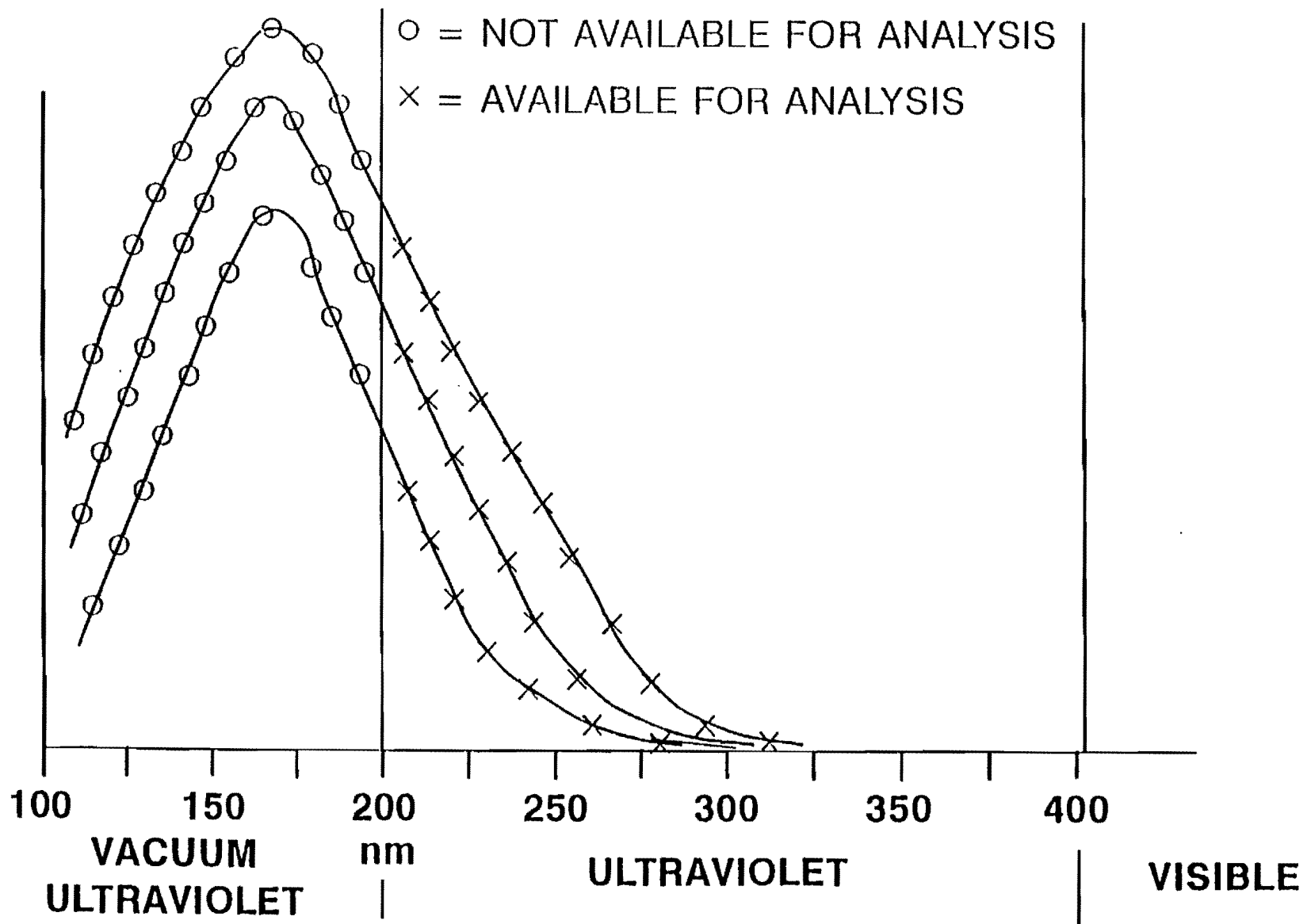
**Wisconsin Wastewater Operators Conference
Southeast Region Meeting
Oconomowoc, WI**

April 14, 1993

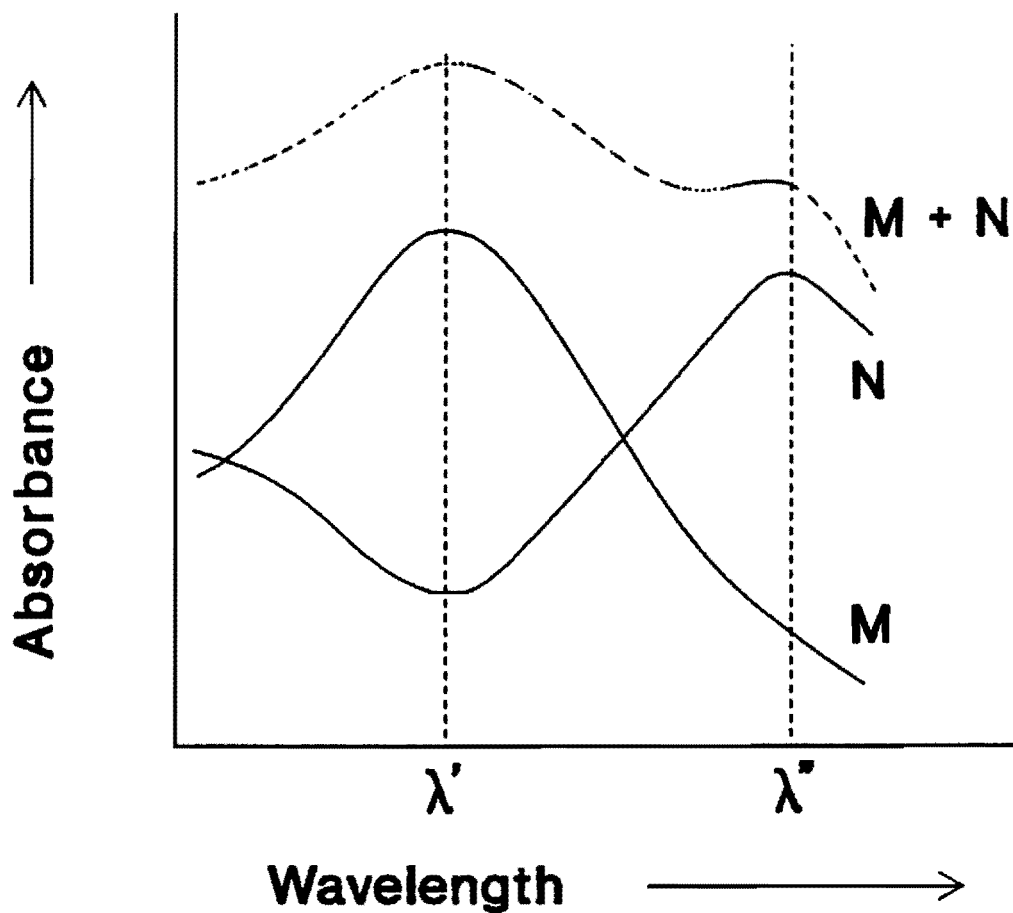
ON-LINE NITRATE ANALYSIS BACKGROUND

A. BASIC CONCEPTS

- 1. CHARACTERISTICS OF NITRATE ABSORBANCE SPECTRA**
- 2. MULTIVARIATE ANALYSIS TECHNIQUES**
- 3. UV-6100 SYSTEM DEVELOPMENT**
- 4. IS NOT**
 - a. AUTOMATED WET CHEMISTRY**
 - b. ION SELECTIVE ELECTRODE**



THE PEAK AND A SUBSTANTIAL PORTION OF THE SPECTRUM IS IN THE VACUUM ULTRAVIOLET AND NOT ABLE TO BE DETECTED USING CONVENTIONAL INSTRUMENTS. THE PORTION OF THE SPECTRUM ABOVE 200nm IS AVAILABLE FOR DETECTION AND ANALYSIS.



Absorption Spectrum of a Two Component Mixture

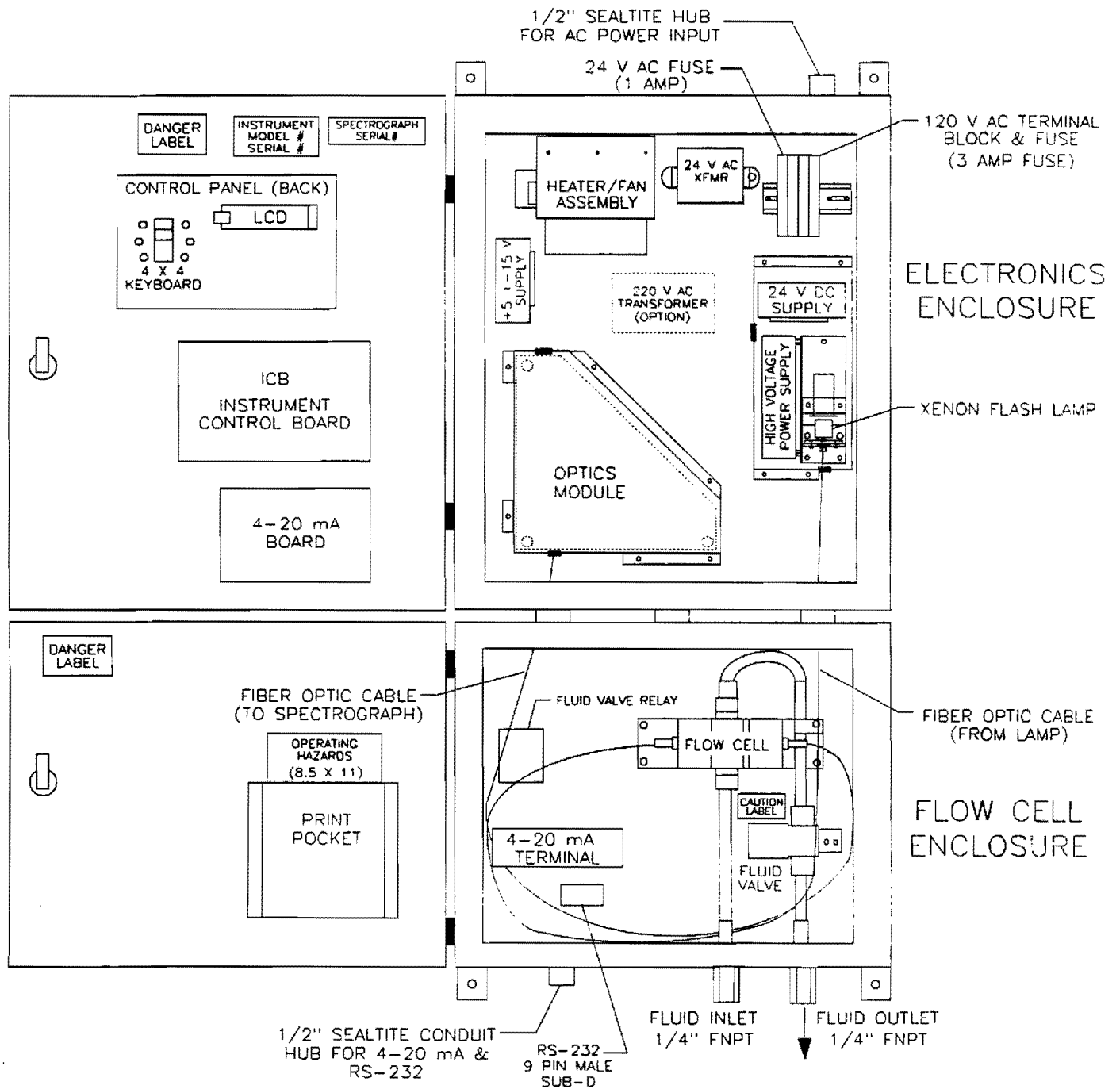


Figure 2. UV-6100 Analyzer Layout

ON-LINE NITRATE ANALYSIS BACKGROUND

B. OCONOMOWOC TEST SITE OBJECTIVES

- 1. EVALUATE THE ABILITY OF ULTRAVIOLET ABSORBANCE SPECTROMETRY TO ANALYZE NITRATE IN WASTEWATER SECONDARY EFFLUENT WITHOUT THE USE OF REAGENTS.**
- 2. EVALUATE LONG TERM OPERATION OF THE UV-6100 PROCESS ANALYZER IN A WASTEWATER TREATMENT FACILITY.**
- 3. EVALUATE TECHNIQUES TO MINIMIZE THE USE OF LARGE, SITE SPECIFIC CALIBRATION SETS.**
- 4. EVALUATE O&M REQUIREMENTS FOR THE ANALYZER SYSTEM.**

OCONOMOWOC TEST SITE HISTORY

A. INITIAL PERIOD STARTING 9-29-92

- 1. INITIAL FOCUS ON MECHANICAL AND O&M ISSUES**
 - a. SAMPLE LINE AND PUMP**
 - b. INTEGRITY OF ELECTRONICS ENCLOSURE**
 - c. SAMPLE INTERVALS**
 - d. DATA COLLECTION MECHANICS**
 - 1) LOG FORMAT AND PROCEDURES**
 - 2) INTERNAL MEMORY MANAGEMENT**

OCONOMOWOC TEST SITE HISTORY

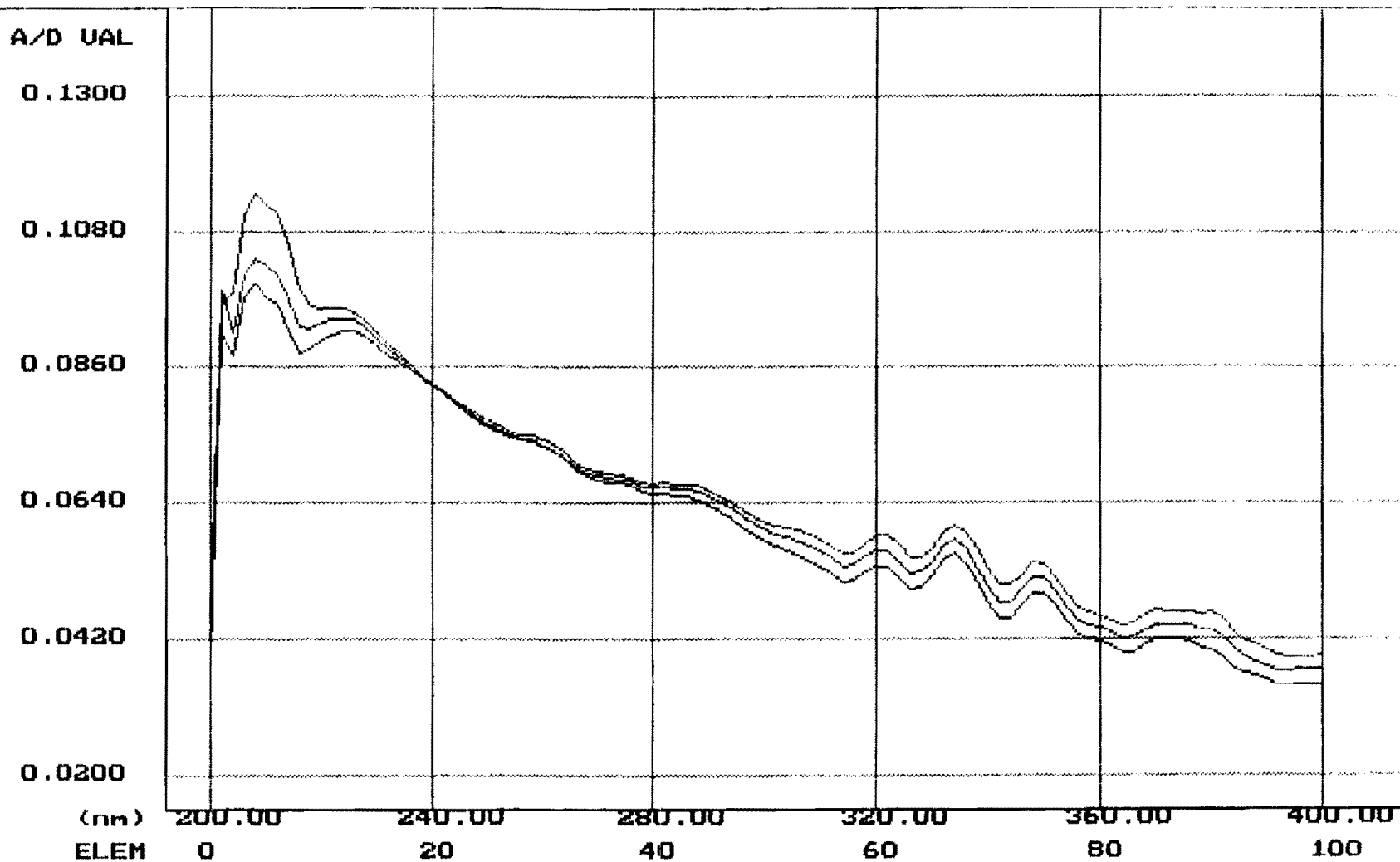
2. FACTORY CALIBRATION (30 POINT) PRIOR TO INSTALLATION
 - a. 0 TO 30 ppm NO₃ (6.77 ppm NO₃-N UPPER LIMIT)
 - b. 0 TO 5 ppm Fe RANDOM VARIATION IN NO₃ SOLUTION
 - c. EVALUATE DYNAMIC RANGE ISSUES
 - d. EVALUATE IMPACT OF BACKGROUND VARIATIONS

OCONOMOWOC TEST SITE HISTORY

3. DEVELOP AND TEST O&M TECHNIQUES
 - a. MEASUREMENT OF INSTRUMENT STABILITY
 - b. MEASUREMENT OF WINDOW FOULING
 - c. VERIFICATION OF BASELINE CORRECTION (INSTRUMENT STANDARD)
 - d. PROBE CLEANING PROCEDURES
 - 1) MECHANICAL
 - 2) CHEMICAL
 - e. MEASUREMENT OF CLEANING EFFECTIVENESS
 - f. DEVELOPMENT OF TEST PROTOCOL
 - 1) GRAB SAMPLE HANDLING AND PRESERVATION
 - 2) LABORATORY ANALYSIS PROCEDURES

FILE 1: UCDCI291.CST
FILE 2: UCDCI292.CST
FILE 3: UCDCI293.CST
FILE 4:
FILE 5:

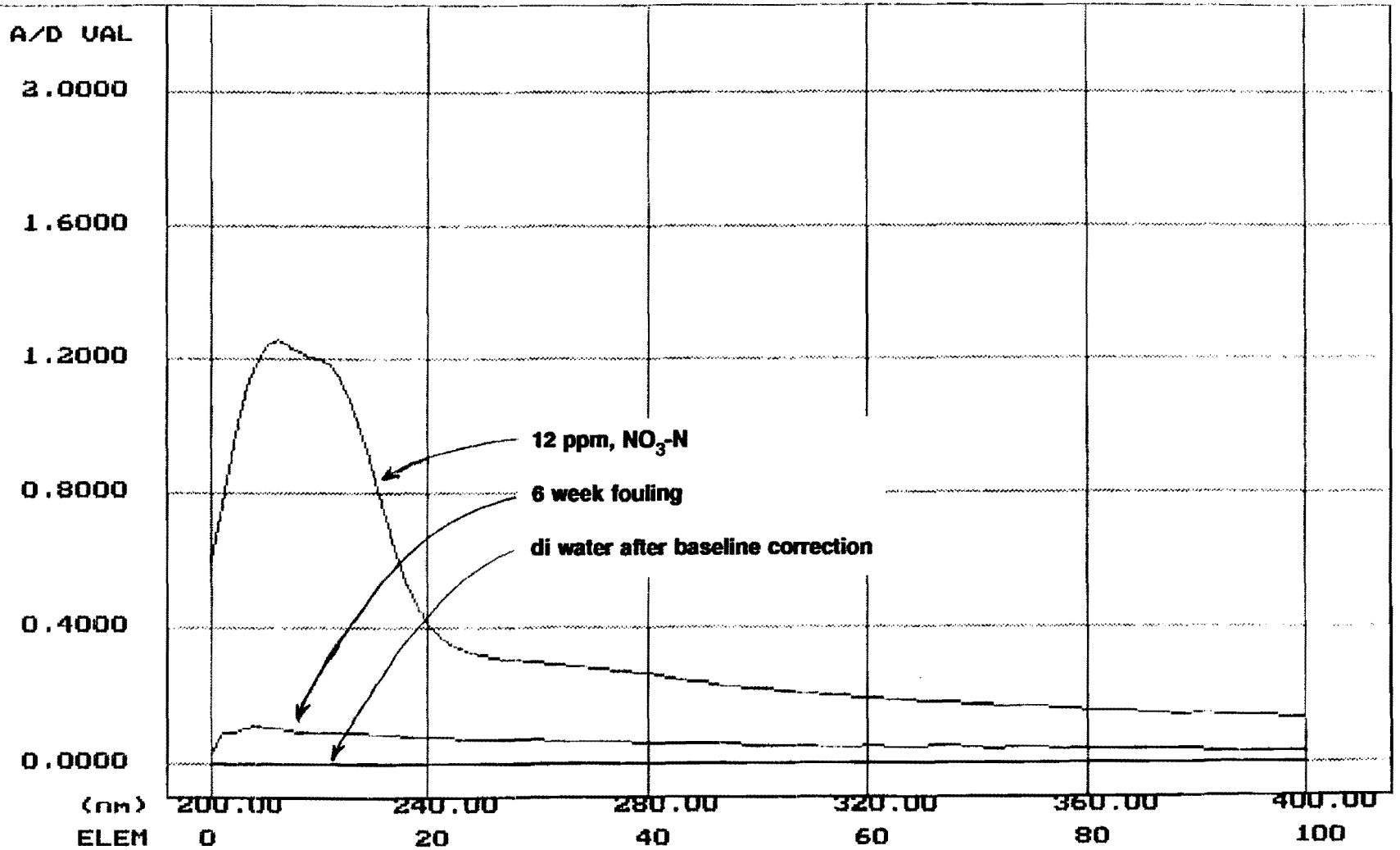
FILE 6:
FILE 7:
FILE 8:
FILE 9:
FILE 10:



OCONOMOWOC, WI
RELATIVE STABILITY, DI WATER WITH FOULING

FILE 1: OCWN290.CST
FILE 2: OCDI291.CST
FILE 3: OCDI295.CST
FILE 4:
FILE 5:

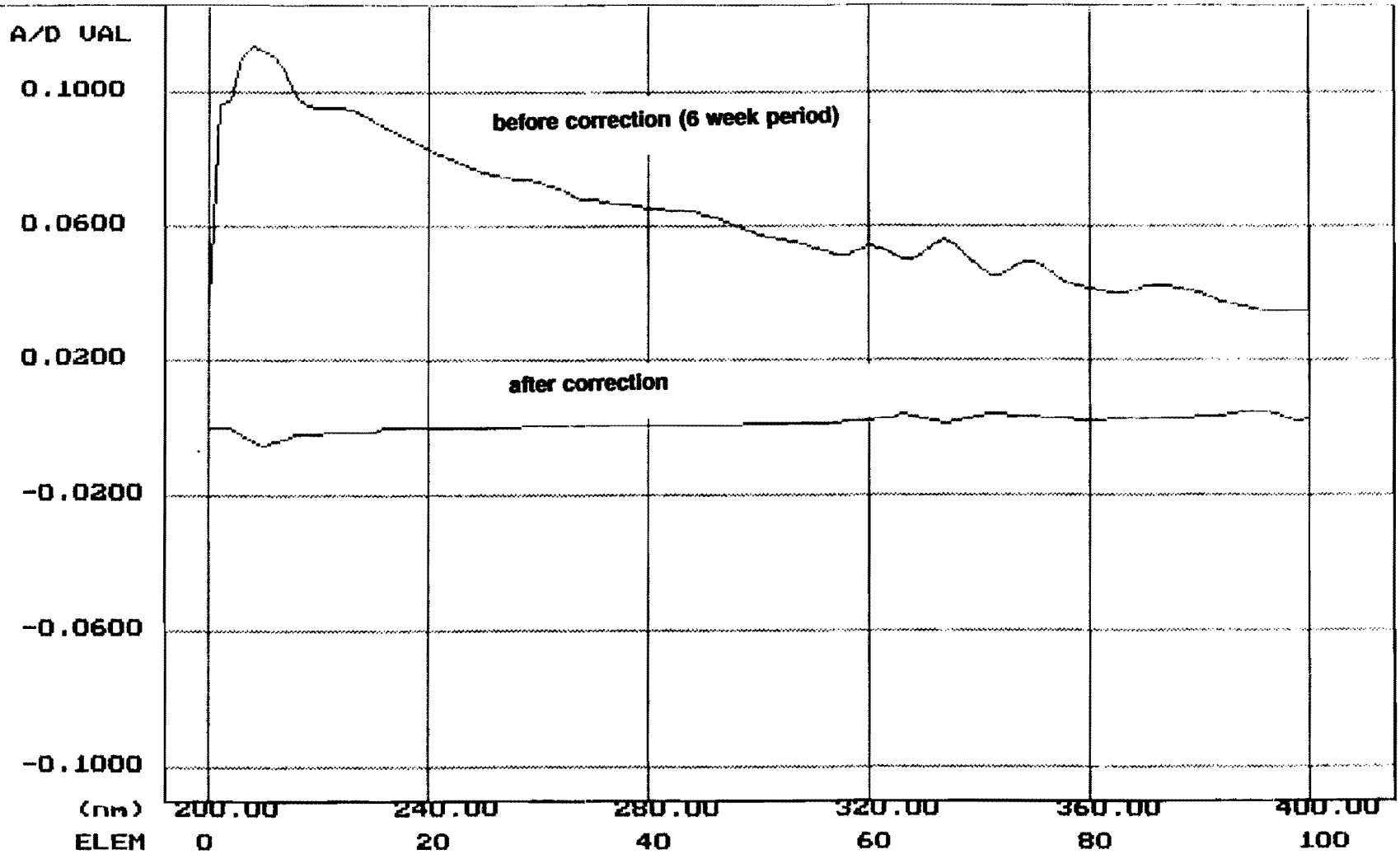
FILE 6:
FILE 7:
FILE 8:
FILE 9:
FILE 10:



OCONOMOWOC, WI
RELATIVE SCALE, SPECTRA vs MAJOR FOULING

FILE 1: OC DI 291.CST
FILE 2: OC DI 295.CST
FILE 3:
FILE 4:
FILE 5:

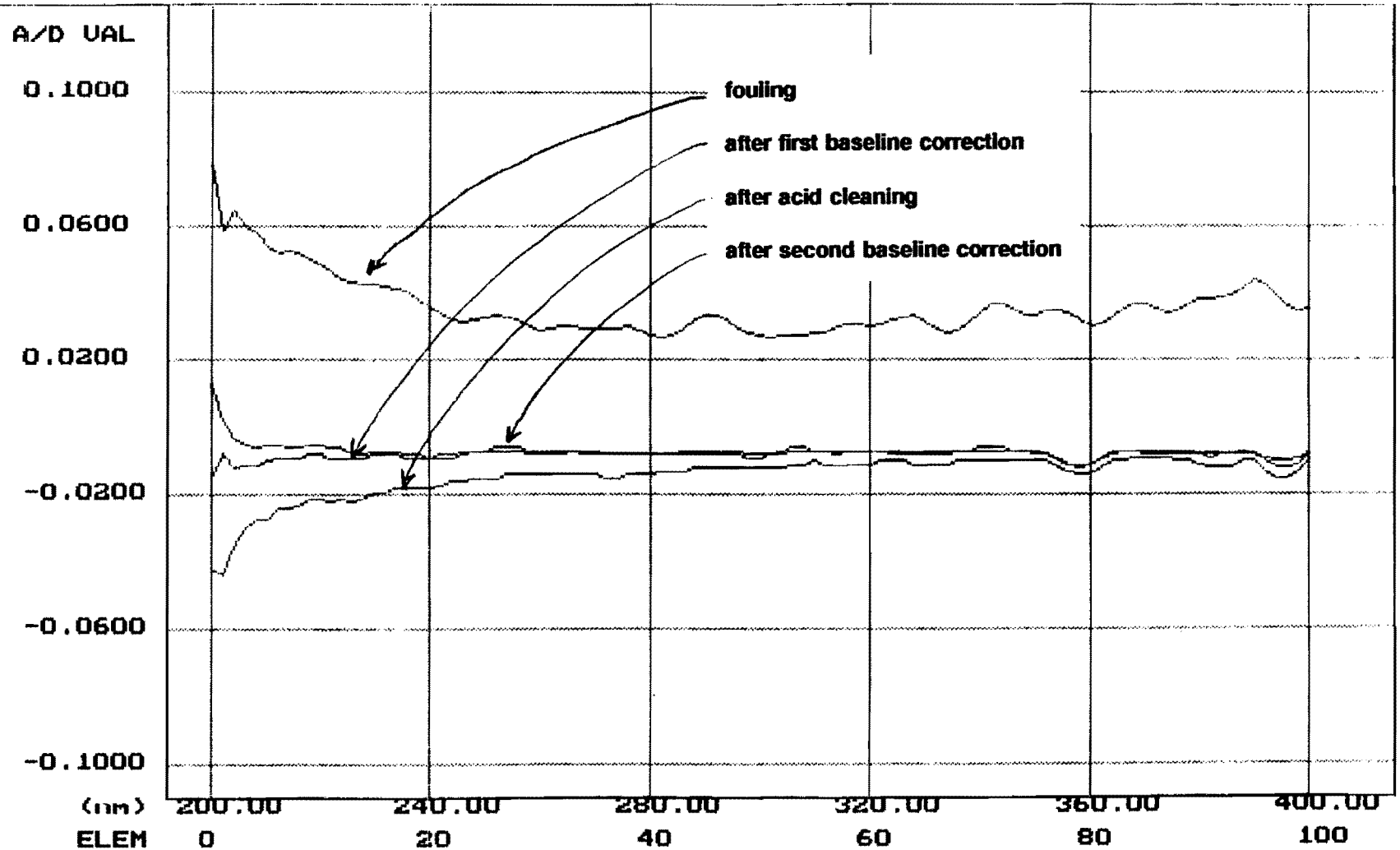
FILE 6:
FILE 7:
FILE 8:
FILE 9:
FILE 10:



OCONOMOWOC, WI
BASELINE CORRECTION FOR FOULING

FILE 1: OC DI 340.CST
FILE 2: OC DI 341.CST
FILE 3: OC DI 342.CST
FILE 4: OC DI 343.CST
FILE 5:

FILE 6:
FILE 7:
FILE 8:
FILE 9:
FILE 10:



OCONOMOWOC, WI
AFTER SECOND BASELINE CORRECTION

OCONOMOWOC TEST SITE HISTORY

4. DESIGN VERIFICATION
 - a. OPERATIONAL SOFTWARE
 - b. ANALYTICAL SOFTWARE
 - c. OPTICAL "FOCUS"

OCONOMOWOC TEST SITE HISTORY

B. NEW OPTICS MODULE (SPECTROGRAPH) INSTALLED

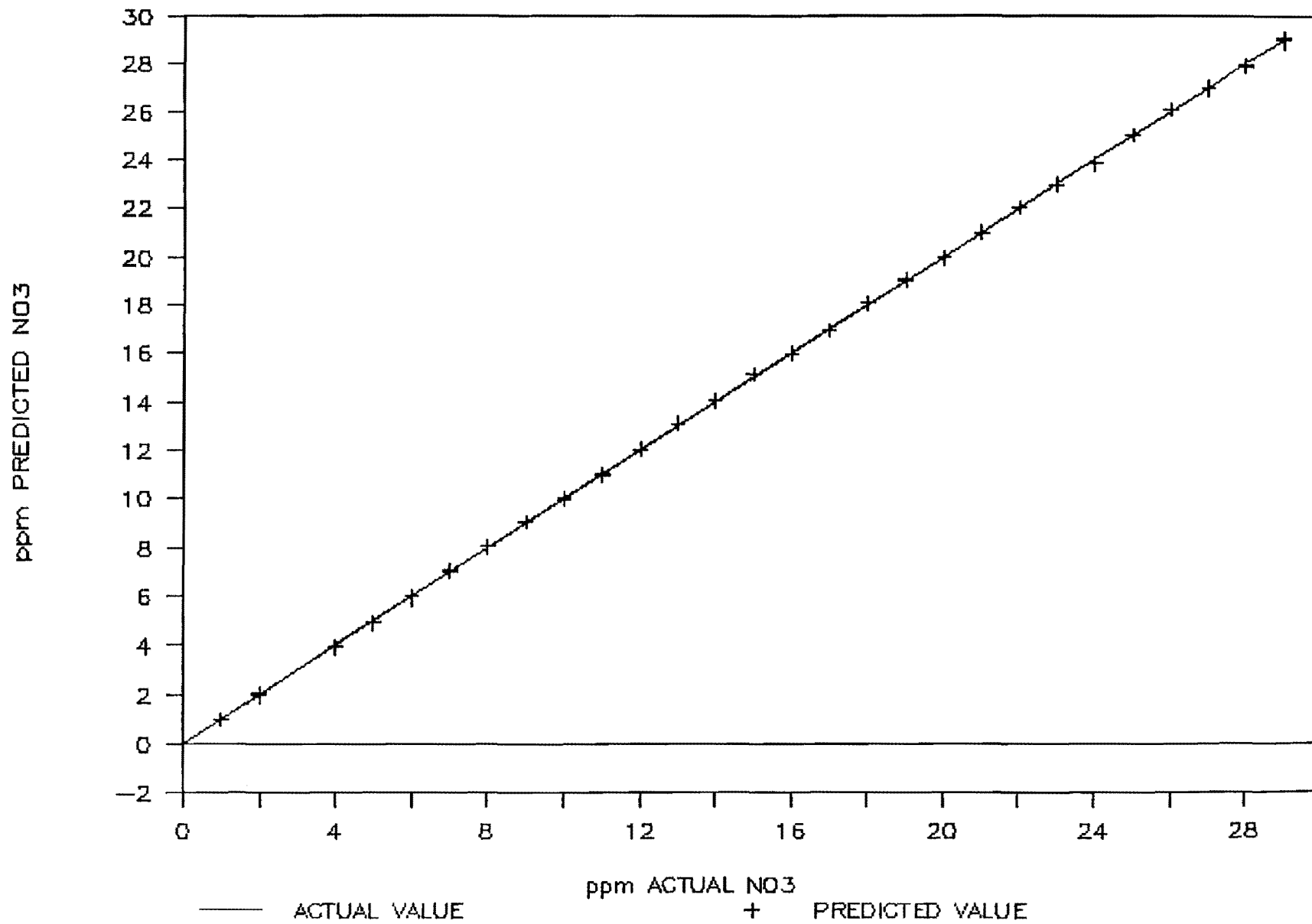
- 1. NEW 30 POINT CALIBRATION USING LABORATORY PREPARED DI STANDARDS**
 - a. EVALUATE SENSITIVITY TO BACKGROUND VARIATIONS**
 - b. EVALUATE ABILITY TO ANALYZE SAMPLES THAT HAVE VALUES OUTSIDE OF THE ORIGINAL CALIBRATION RANGE**
- 2. RUNNING RECORD MAINTAINED THROUGH USE OF INSTRUMENT INTERNAL DATA LOG FEATURE**
 - a. OBSERVATION OF TRENDS AND LOAD VARIATIONS**
- 3. REGULAR SAMPLING AND LAB ANALYSIS PROGRAM**

COMPARISON WITH INSTRUMENT READINGS

BUILD A SITE SPECIFIC FILE WITH SPECTRA AND LAB VALUES TO ADD TO CALIBRATION FILE

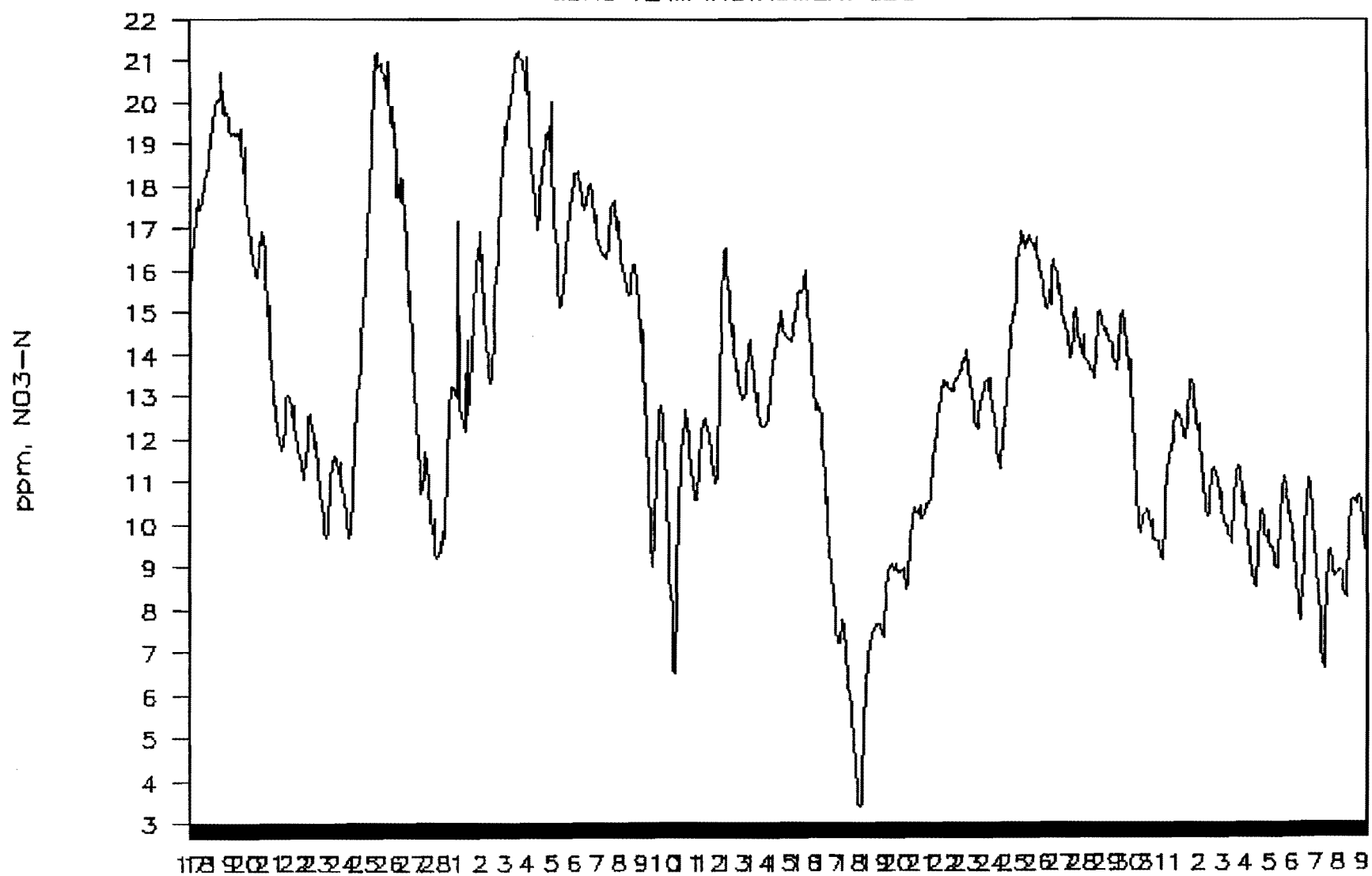
OCONOMOWOC, WI

30 POINT CALIBRATION



OCONOMOWOC, WI

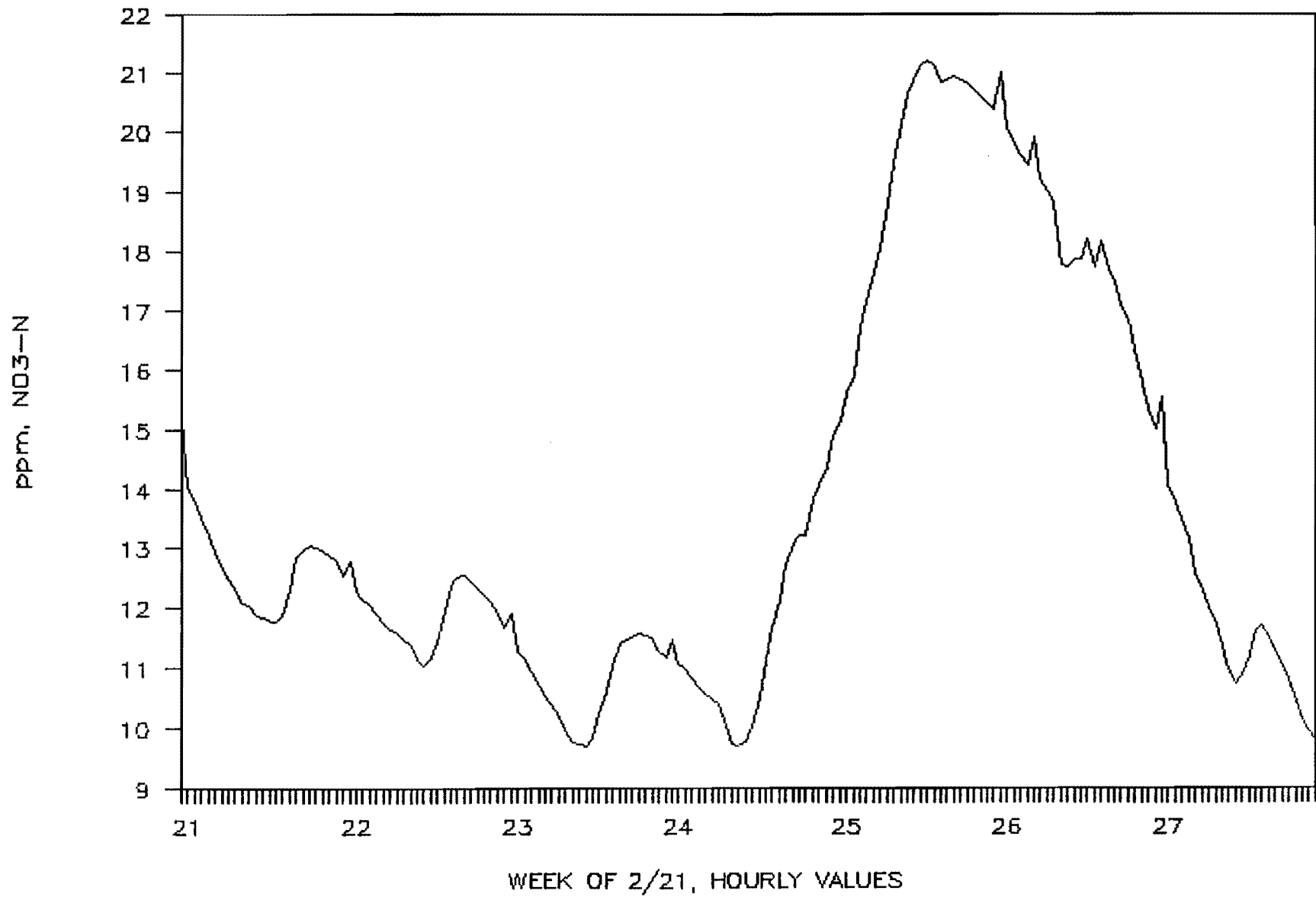
LONG TERM INSTRUMENT LOG



HOURLY LOG, STARTING 2-17-93

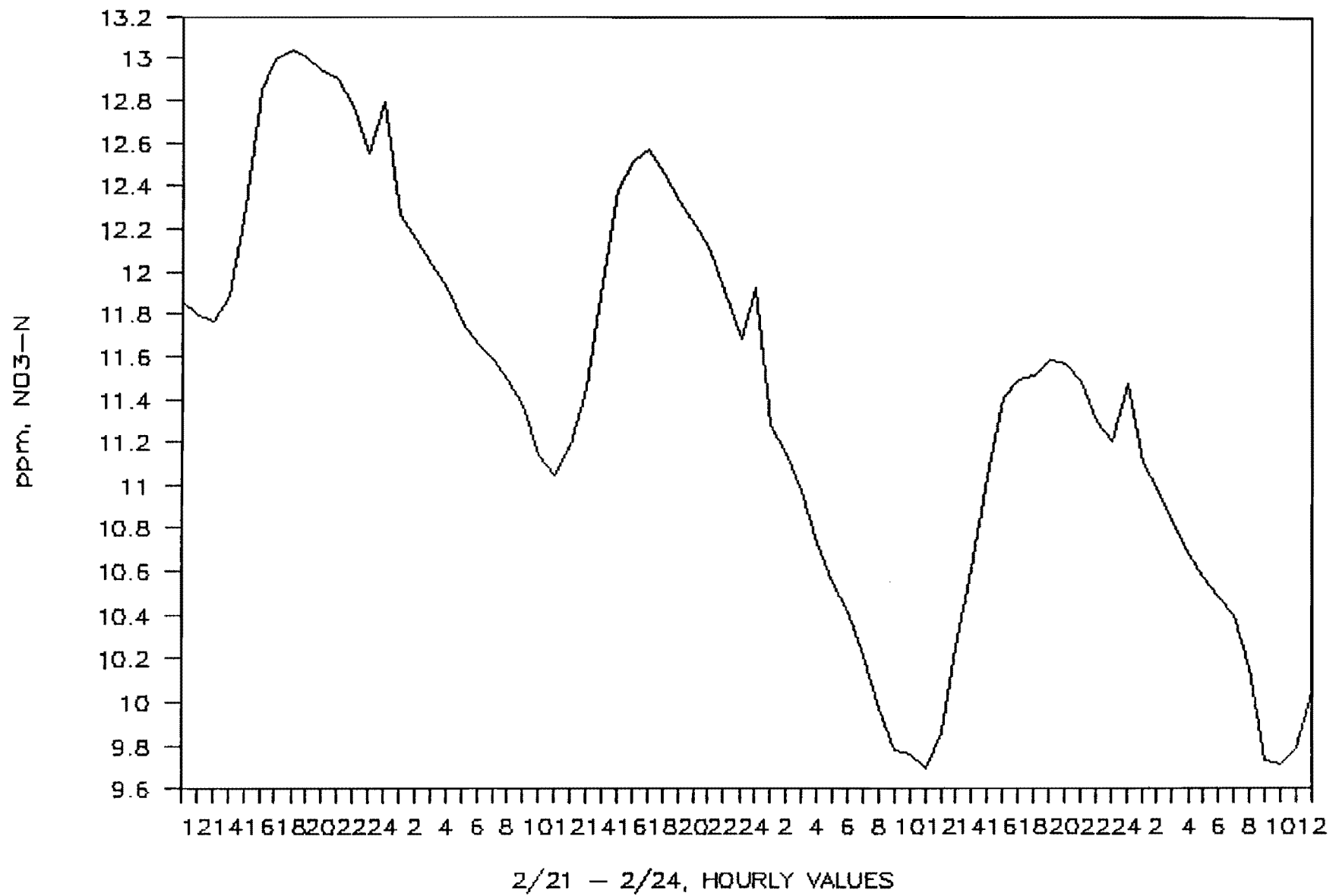
OCONOMOWOC, WI

WEEKLY DIURNAL PATTERN



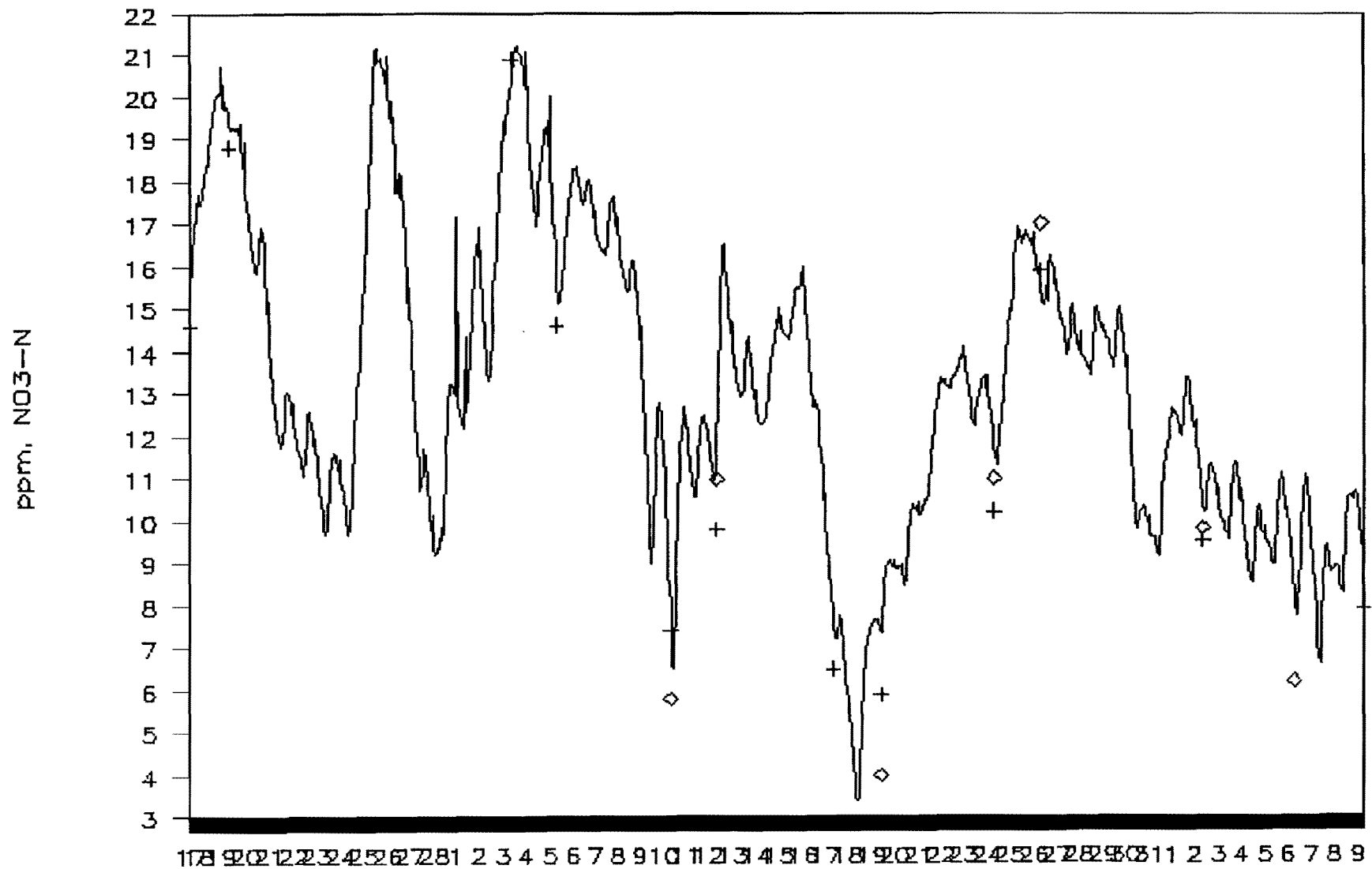
OCONOMOWOC, WI

DAILY DIURNAL PATTERN



OCONOMOWOC, WI

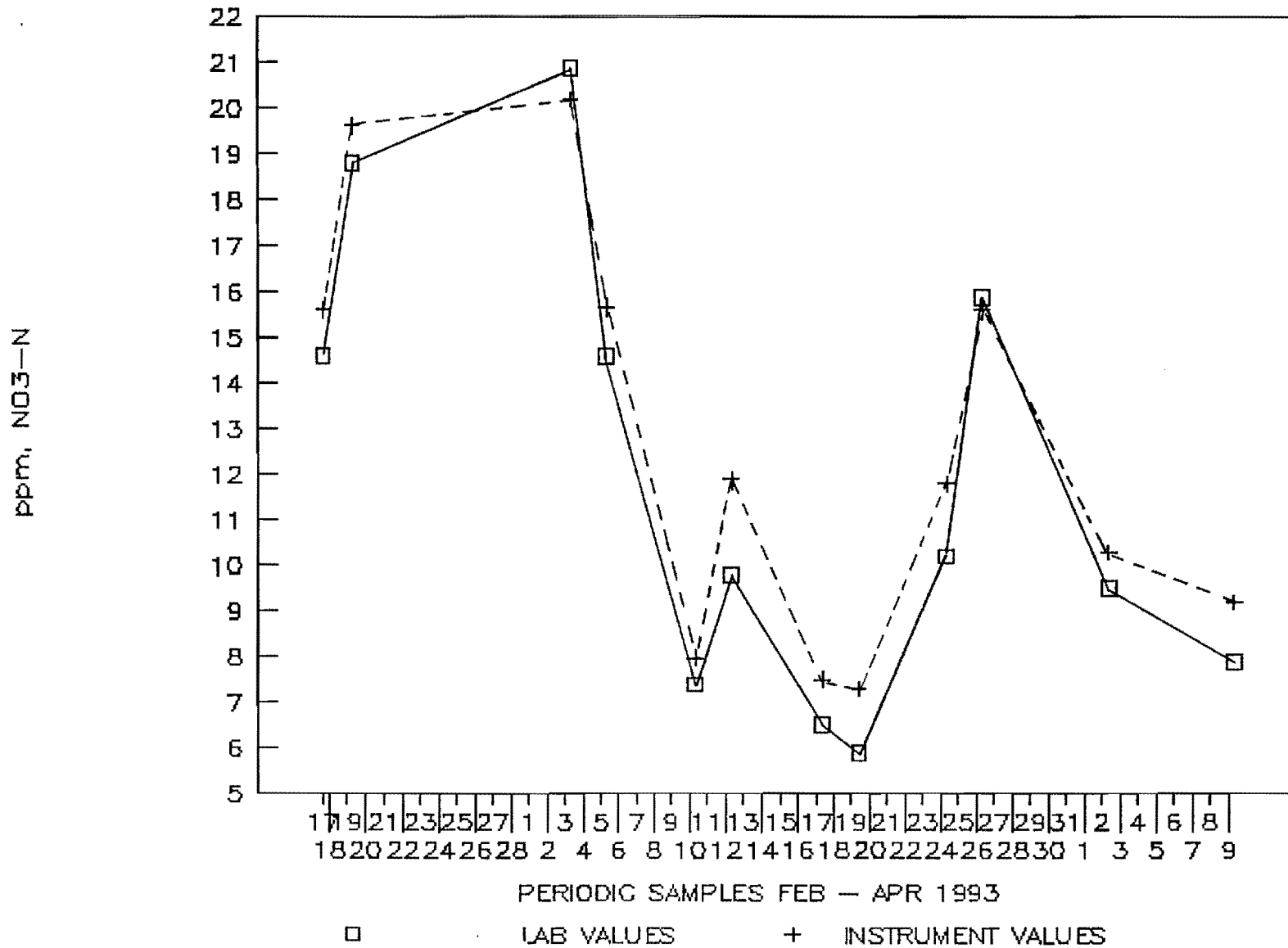
INSTRUMENT LOG WITH LAB VALUES



HOURLY LOG, STARTING 2-17-93

OCONOMOWOC, WI

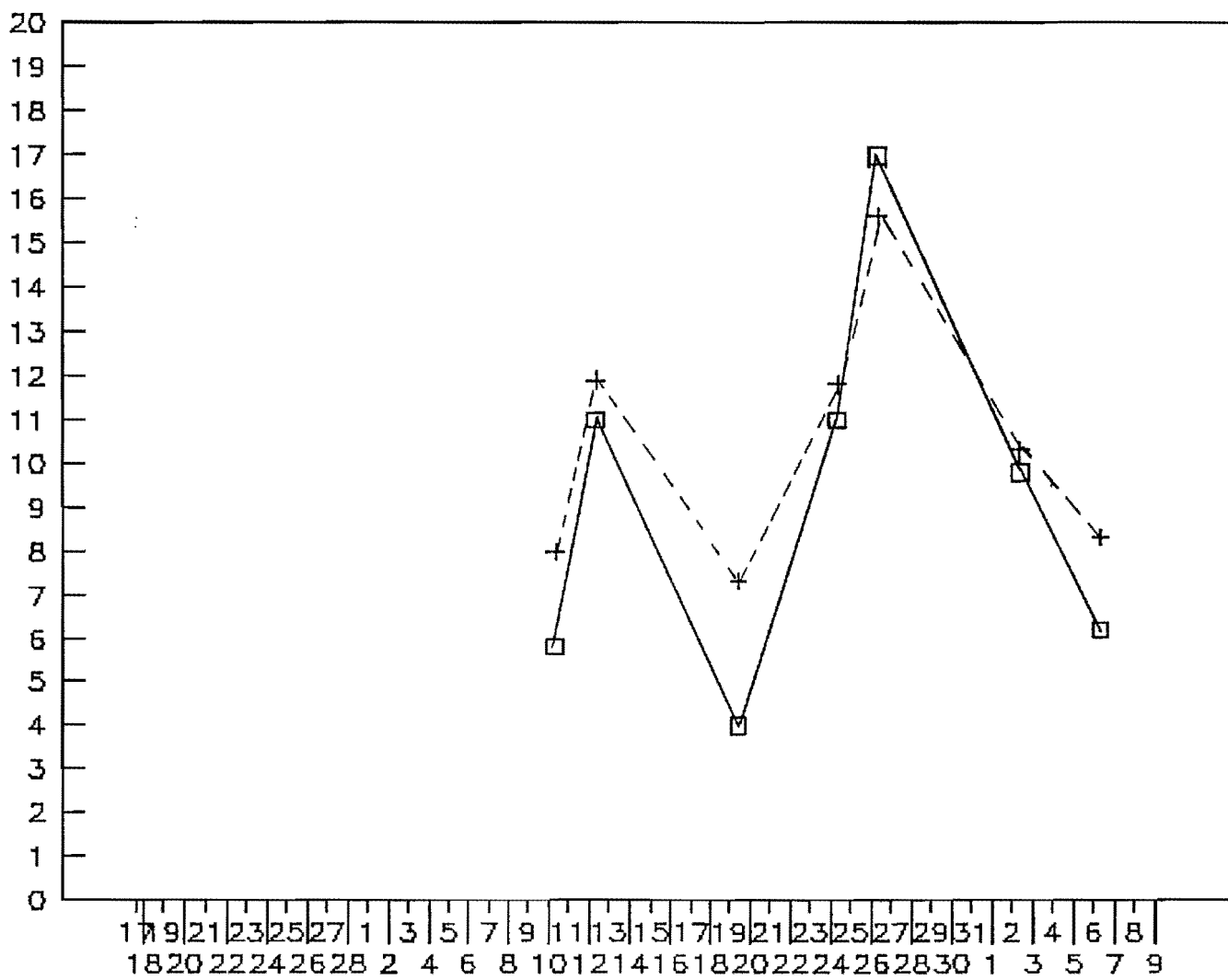
BTI LAB VS INSTRUMENT



OCONOMOWOC, WI

OUTSIDE LAB VS INSTRUMENT

ppm, NO₃-N



PERIODIC SAMPLES FEB - APR 1993

□ LAB VALUES + INSTRUMENT VALUES

OCONOMOWOC TEST SITE OBSERVATIONS AND CONCLUSIONS TO DATE

1. BASELINE CORRECTIONS COULD BE USED TO PERIODICALLY ADJUST FOR THE EFFECTS OF FLOW CELL FOULING. THIS PROCEDURE CAN BE PERFORMED IN ABOUT 15 MINUTES USING DI WATER AND THE "INSTRUMENT STANDARD" FEATURE OF THE ANALYZER.
2. THE UV-6100 PROCESS ANALYZER REFERENCE WAVELENGTH FEATURE WILL ALLOW ACCURATE ANALYSIS OVER EXTENDED PERIODS OF TIME, EVEN WHEN ROUTINE MAINTENANCE SUCH AS FLOW CELL CLEANING AND BASELINE CORRECTIONS HAVE NOT BEEN PERFORMED.
3. A 20% HCL SOLUTION COULD BE USED TO CHEMICALLY CLEAN THE FLOW CELL, EXTENDING THE INTERVALS BETWEEN MECHANICAL CLEANING.
4. THE EFFECTIVENESS OF CLEANING AND BASELINE CORRECTION PROCEDURES CAN BE VERIFIED BY RECORDING AND COMPARING SPECTRA BEFORE AND AFTER THE PROCEDURES.
5. THE STABILITY AND REPEATABILITY OF THE ANALYZER CAN BE VERIFIED BY RECORDING AND COMPARING SPECTRA FROM IDENTICAL SOLUTIONS.
6. THE USE OF AN IN LINE FILTER AHEAD OF THE ANALYZER HAS NOT BEEN NECESSARY.
7. SUCCESSFUL LONG TERM MECHANICAL, ELECTRICAL, ELECTRONIC AND OPTICAL PERFORMANCE CAN BE ACHIEVED IN A WASTEWATER TREATMENT PLANT ENVIRONMENT.
8. THE USE OF LABORATORY GENERATED CALIBRATION STANDARDS IN DI WATER CAN PROVIDE A REASONABLY GOOD STARTING POINT FOR THE ANALYSIS OF NITRATE IN A NITRIFIED WASTEWATER EFFLUENT FOLLOWING TERTIARY FILTRATION. THIS CAN REDUCE BUT NOT ELIMINATE THE NEED FOR SITE SPECIFIC CALIBRATION SOLUTIONS IN MANY WATER AND WASTEWATER APPLICATIONS.
9. ULTRAVIOLET ABSORBANCE SPECTROMETRY CAN SUCCESSFULLY DETECT NITRATE ON-LINE IN WASTEWATER WITHOUT REAGENTS.
10. THE UV-6100 PROCESS ANALYZER CAN BE USED TO FAITHFULLY TRACK NITRATE CONCENTRATIONS AT FREQUENT INTERVALS, PROVIDING RELIABLE ON-LINE INFORMATION FOR WASTEWATER TREATMENT PROCESS MONITORING AND CONTROL.