September 2005

Environmental Technology Verification Report

ZAPS TECHNOLOGIES, INC. MULTI-PARAMETER ANALYZER (MP-1) FOR NUTRIENT MONITORING

Prepared by
Battelle

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ETV ETV ETV

September 2005

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ETV Advanced Monitoring Systems Center

ZAPS TECHNOLOGIES, INC. MULTI-PARAMETER ANALYZER (MP-1) FOR NUTRIENT MONITORING

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Notice

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six verification centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. Under a cooperative agreement, Battelle has received EPA funding to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

Acknowledgments

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List of Abbreviations

AMS	Advanced Monitoring Systems
PPA	aminomethyl phosphonic acid
BQL	below quantitation limit
C	carbon
CI	confidence interval
m^3/min	cubic meters per minute
°C	degrees Celsius
DOC	dissolved organic carbon
DI	deionized
DMA	dimethyl amine
DC	direct current
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
F&R	Froehling & Robertson, Inc.
LCS	laboratory control standard
L	liter
LOD	limit of detection
µg	microgram
mA	milliamp
mg	milligram
mL	milliliter
mm	millimeter
MS	matrix spike
MSD	matrix spike duplicate
NIST	National Institute of Standards and Technology
N	nitrogen
NA	not applicable
OMI	Operations Management International, Inc.
PE	performance evaluation
%D	percent difference
%R	percent recovery
%RSD	percent relative standard deviation
P	phosphorus

QA	quality assurance
QC	quality control
QMP	quality management plan
QL	quantitation limit
RPD	relative percent difference
RS	Raman scattering
SD	standard deviation
TSA	technical systems audit
TKN	total Kjeldahl nitrogen
TN	total nitrogen
TOC	total organic carbon
TP	total phosphorus
UV	ultraviolet

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA’s National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center, in collaboration with the DuPont Company, recently evaluated the performance of the ZAPS Technologies, Inc. Multi-Parameter Instrument (MP-1) in quantifying nitrate concentrations in wastewater at an industrial wastewater treatment plant.

Chapter 2
Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This verification report provides results for the verification testing of the MP-1 for nitrate. Following is a description of the MP-1, based on information provided by the vendor. The information provided below was not verified in this test.

The MP-1, shown in Figure 2-1, was designed to serve as a first-alert system for water treatment plants and can also be used for routine monitoring of source and product waters. The MP-1 provides high-quality, continuous, in-line monitoring of water quality, using a combination of measured and calculated parameters. Data are captured 25 times per second and processed in real time. The MP-1 is a sequential fiber-optic spectrometer that measures nitrate by its absorption at 220 nanometers. In unfiltered natural water, two artifacts affect this absorption band: blocking of light by particles in the water (turbidity) and absorption by natural organic matter. The MP-1 minimizes these artifacts by making corrections using light measurements at other wavelengths.

Figure 2-1. ZAPS Technologies, Inc., MP-1

Since it can operate from 200 to 800 nanometers, the MP-1 can be programmed to measure standard laboratory water-quality parameters, including those in the ultraviolet (UV) range. The MP-1 is capable of providing over 100 channels of optical data by monitoring absorption, fluorescence, and total reflection bands. It can control and acquire data from other sensors such as thermistors and pH probes, as well as for MP-1 satellite units and single element analyzers. The MP-1 used in this verification test was configured to measure corrected nitrate absorption, temperature, and several other channels related to dissolved organic carbon, complex hydrocarbons, bacterial abundance, and chlorophyll *a*. Only MP-1 measurements of nitrate were verified in this test. The MP-1 sequentially measured each of nine channels (including nitrate absorbance, UV absorbance, and others) for approximately 13 seconds, for a total loop time of approximately two minutes. The MP-1 measured value displayed on-screen was updated after each channel measurement, and the MP-1 reported a nitrate concentration value in units of milligrams (mg) nitrogen (N) per liter (L) at the end of each loop. Thus, a nitrate measurement was reported every two minutes.

Data from the MP-1 were written to a computer in real time and stored as a comma separated values file format (*.csv), and a new file was written every 24 hours with the following file name format: ZAPS_MP1_yyyymmddHHmmss.csv, where the file name includes the start date and time. Each file was approximately 58 kilobytes in size and included values for the date and time of each measurement loop, the nine channel values for each loop, and the sample temperature within the flow cell. Nitrate measurement values were not stored in the data files, but were recalculated in Microsoft Excel using an equation provided by ZAPS Technologies. Over the duration of the verification test, the MP-1 produced approximately 1.5 megabytes of data.

The MP-1 verified in this test utilized the prototype configuration, shown in Figure 2-2, which consisted of a rack-mounted personal computer and analog board (A), an instrument enclosure (B), and a plumbing board (C), which held the MP-1 flow cell (D) and inlet valve system. (The current configuration of the MP-1 is shown in Figure 2-1, with all three components packaged in a single unit.) Nutrient standards and other test samples were delivered to the MP-1 by gravity-feeding the standard through the flow cell, using the off-line measurement sample bottle (E). For on-line monitoring, the sample was supplied at positive pressure through the valve shown at the bottom, right side of the plumbing board, filling the flow cell, and discharging through the outlet at the upper left corner of the plumbing board. The angle of the flow cell allowed it to be drained (back-flushed) by opening the inlet drain valve (Figure 2-2, bottom right). Subsequent to this verification test, the valve system was upgraded to facilitate cleaning the flow cell and its components.

The computer rack was approximately 1.7 meters tall (66 inches) and was positioned within two feet of the instrument enclosure for connecting power and computer cables. The instrument enclosure weighs approximately 14 kilograms (30 pounds) and was 508 millimeters (mm, 20 inches) wide, 610 mm (24 inches) tall, and 229 mm (9 inches) deep. The plumbing board was 737 mm (29 inches) tall. The MP-1 has full network capabilities; allowing results to be forwarded to a remote location. The node MP-1, with the full data acquisition system, costs $54,900. Satellite MP-1 units and single-element analyzers that can be controlled by node MP-1 units cost $45,540 and $33,630, respectively.

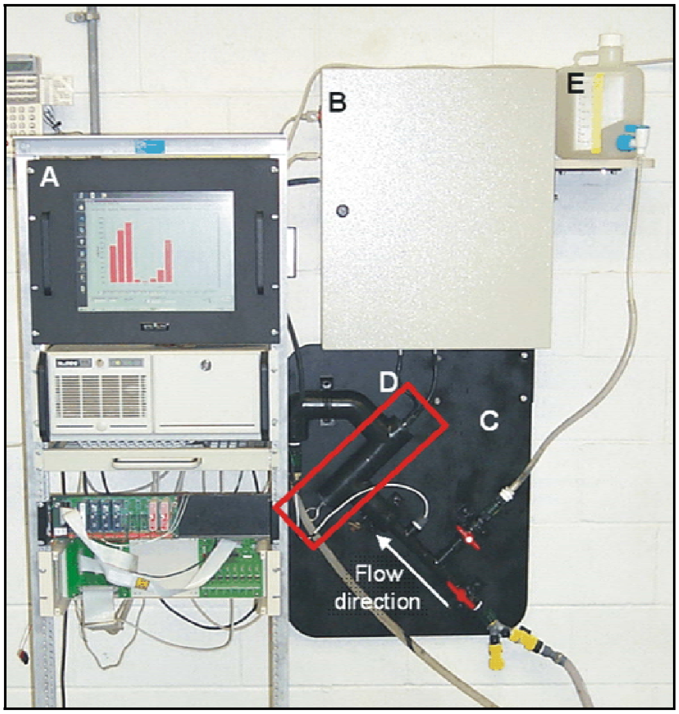


Figure 2-2. MP-1 in Configuration for This Verification Test

Chapter 3
Test Design and Procedures

3.1 Introduction

High nutrient concentrations reduce the quality of water in lakes, rivers, and estuaries. Excess nutrient levels, including nitrate, reduce water quality by causing harmful algal blooms and hypoxia, create declines in wildlife habitat, and may increase human pathogen levels. EPA is developing region-specific nutrient criteria to reduce the nutrient loading of the nation's aquatic environment. On-line monitoring of nutrients in wastewater is a critical component in reducing nutrient loading because the composition of wastewater varies considerably depending upon the sampling location, source, and/or treatment methods. Using wastewater from the DuPont Company's industrial wastewater treatment facility at the Spruance Plant in Richmond, Virginia, as a sample matrix in this test provided a single example (not a comprehensive overview) of possible matrix effects associated with wastewater monitoring.

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Nutrient Analyzers at a Wastewater Treatment Plant.*(1) Testing was conducted for six weeks between May 5 and June 16, 2005, during which time the MP-1 measured nitrate concentrations in wastewater and prepared nutrient standards of known concentration. The performance of the MP-1 was evaluated in terms of

- Accuracy
- Bias
- Linearity
- Limit of detection (LOD)
- Reproducibility
- Span and zero drift
- Interference effects
- Matrix effects
- Data completeness
- Operational factors.

3.2 Site Description

The host facility for the nutrient analyzer verification test was the DuPont Spruance Plant in Richmond, Virginia. At this plant, DuPont manufactures engineering polymers/plastics and fibers (e.g., NOMEX® flame retardant and KEVLAR®). Operations Management International

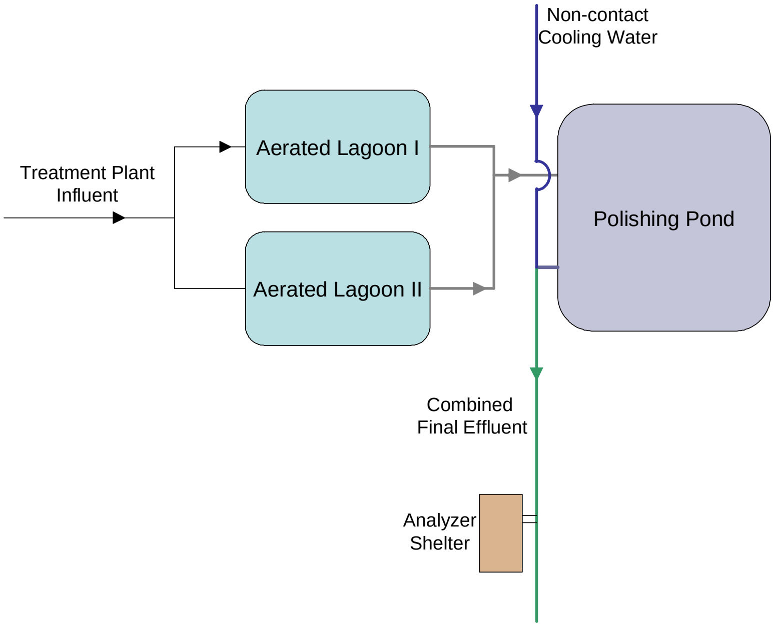


Figure 3-1. Test Site (not drawn to scale)

(OMI), Inc., operates the wastewater treatment plant at the Spruance Plant under contract with DuPont and provided the day-to-day logistical support for this verification test. The generalized layout of the test site with respect to the treatment facility is shown in Figure 3-1 (not drawn to scale). The waste treatment processes used at the plant include aerated lagoons and a polishing pond. Flow leaving the polishing pond joins a flow of non-contact cooling water from the plant in an open drainage ditch, shown in Figure 3-2, that empties into the James River. Table 3-1 summarizes the characteristics of the final effluent stream at the Spruance Plant, based on data provided by DuPont and OMI for the previous year. The test site was located along the final effluent stream. Figure 3-3 shows the temperature-regulated shelter where the MP-1 was installed. The final effluent was pumped out of the open drainage ditch into the shelter through 1-inch Tygon® tubing. A multi-spigot tap was installed in the shelter to supply the final effluent to the MP-1 at a flow rate sufficient to maintain flow through the MP-1 flow cell. (Valves on each spigot allowed for manual adjustment of the flow rate by apportioning the final effluent flow to the MP-1 and the overflow drain.) An in-line filter screen was installed upstream of the multi-spigot tap to catch larger debris before reaching the MP-1. The in-line filter screen is shown in Figure 3-4, pictured at the beginning and end of the verification test prior to back-flushing. To reduce build-up of debris in the in-line filter screen, it was back-flushed twice daily and hand-cleaned if necessary (Monday through Friday).

Figure 3-2. DuPont Spruance Final Effluent

Table 3-1. Effluent Characteristics at the Test Site

Parameter	Range	Average	Standard Deviation
Temperature (°C)	18 - 39	27	7
Total organic carbon [mg carbon (C)/L]	6.6 - 20	8.8	2.5
pH	6.8 - 7.8	7.4	0.3
Total nitrogen (mg N/L)	0.6 - 6.4	3.0	1.6
Nitrate-N (mg N/L)	<0.1 - 2.7	1.3	0.8
Nitrite-N (mg N/L)	0.05 - 1.06	0.11	0.08
Ammonia-N (mg N/L)	0.2 - 1.6	0.6	0.5
Total phosphorus (mg P/L)	0.09 - 0.26	0.14	0.03

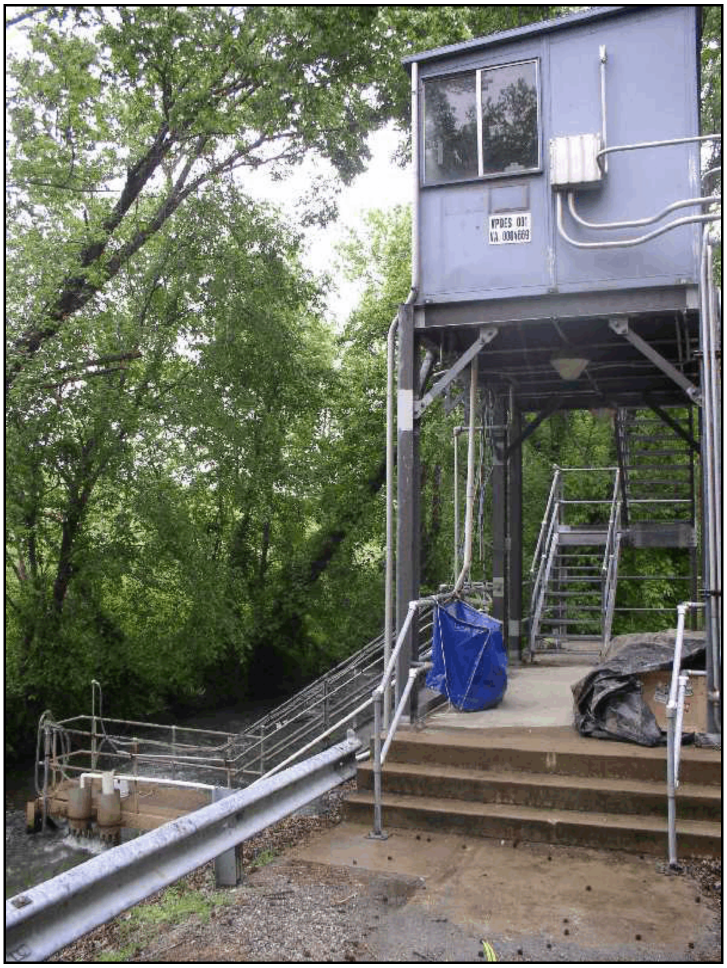


Figure 3-3. Test Site Showing Analyzer Shelter

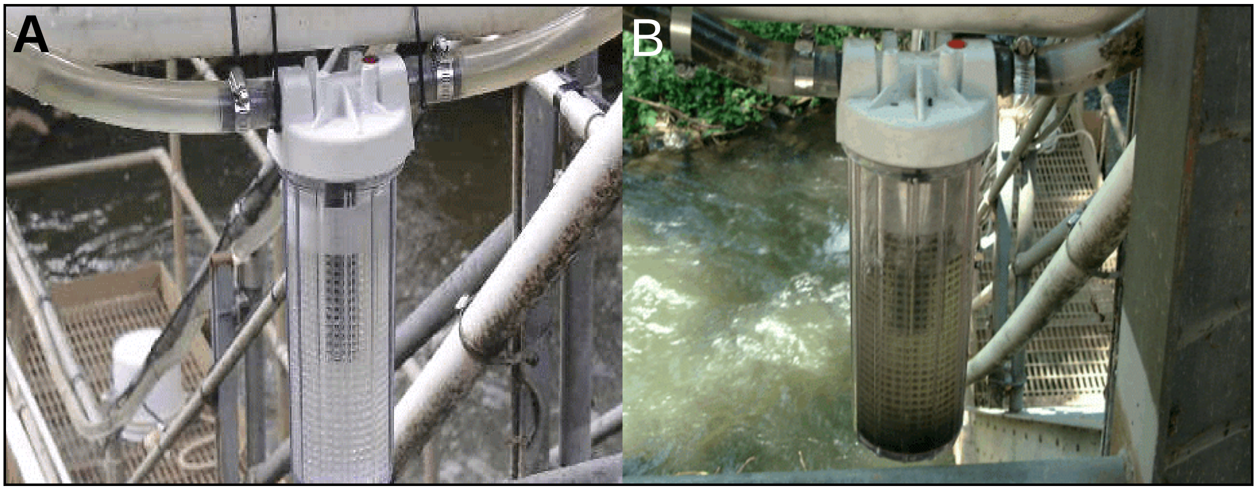


Figure 3-4. In-line Filter Screen and Inlet Tubing Before (A) and After (B) the Verification Test

3.3 Test Design

Table 3-2 shows the activities involved in preparing for and conducting the verification test. All testing activities, which are described in the following sections, were conducted by Battelle and/or OMI staff.

The MP-1 was installed and calibrated at the test site by a vendor representative. No additional calibrations of the MP-1 were performed during the verification test. Battelle and OMI staff worked with the vendor representative to establish procedures for operating the MP-1 during this verification test. Instructions for operating the MP-1 in off-line and on-line measurement modes were provided by the vendor representative and included in this report as Appendix A. The vendor representative trained Battelle and OMI staff to check several instrument parameters to verify the operation of the MP-1 and identify signs of malfunction. A checklist was provided by the vendor representative and was completed daily (Monday through Friday) by Battelle or OMI staff. The checklist was revised by Battelle staff to include additional daily maintenance activities that were determined to be necessary during the first week of on-line monitoring (cleaning of the flow cell) and is included as Appendix B. In general, Battelle or OMI staff verified that the power was on and the lamp was firing, back-flushed the effluent feed system, and cleaned the flow cell (during on-line effluent monitoring). In the event of a malfunction, Battelle and/or OMI staff could contact the vendor representative and conduct minor trouble-shooting procedures as necessary, but were not expected to make any major repairs. MP-1 measurement data files, containing data collected every two minutes, were opened in Microsoft Excel, where the results were analyzed using the procedures outlined in Chapter 5 of this report.

Table 3-2. Test Activities

Week of	Activities
May 2, 2005 Analyzer Installation Off-Line Phase I (Week 1)	• Test preparations by OMI and Battelle staff • MP-1 installation • Training of OMI and Battelle staff by vendor representatives • Conduct trial operations • Nutrient standard challenges for reproducibility, span/zero drift baseline response, and interference effects • Deionized (DI) water challenges for LOD determination
May 9, 2005 Off-line Phase I (Week 2)	• Multi-level nutrient standard challenges for accuracy, bias, and linearity • pH-adjusted nutrient standard challenges for matrix effects • Chlorophyll *a*-containing nutrient standard challenges for matrix effects • DI water challenges for LOD determination
May 16, 2005 On-line Effluent Monitoring (Week 1)	• Nutrient standard and DI water challenges for span/zero drift and LOD • On-line monitoring of wastewater effluent • Three reference samples collected and submitted for analysis • Routine operation
May 23, 2005 On-line Effluent Monitoring (Week 2)	• Nutrient standard and DI water challenges for span/zero drift and LOD • On-line monitoring of wastewater effluent • Three reference samples collected and submitted for analysis • Routine operation
May 30, 2005 On-line Effluent Monitoring (Week 3)	• Nutrient standard and DI water challenges for span/zero drift and LOD • On-line monitoring of wastewater effluent • Three reference samples collected and submitted for analysis • Routine operation
June 6, 2005 On-line Effluent Monitoring (Week 4)	• Nutrient standard and DI water challenges for span/zero drift and LOD • On-line monitoring of wastewater effluent • Three reference samples collected and submitted for analysis • Routine operation
June 13, 2005 Off-line Phase II	• One span/zero drift check • Multi-level nutrient standard challenges for accuracy, bias, and linearity (repeated due to unsatisfactory operation of the MP-1 during Phase I) • Plant effluent challenges for matrix effects • Plant process challenges for matrix effects • Plant influent challenges for matrix effects
June 20, 2005	• Remove MP-1 from test site

The MP-1 was evaluated for the performance parameters summarized in Table 3-3 and discussed in detail in the following sections. The test had two components: off-line testing (two phases) and on-line effluent monitoring. During off-line Phase I testing, the MP-1 was challenged with nutrient standards and other samples in a DI water matrix. During off-line Phase II, the MP-1 was challenged with wastewater samples. Grab samples of the final effluent (reference samples) were collected from the multi-spigot tap three times per week during the on-line effluent monitoring portion of the verification test. All nutrient standards used to challenge the MP-1 and reference samples were analyzed by a reference laboratory, Froehling and Robertson (F&R), Inc., of Richmond, Virginia, using standard methods.

Table 3-3. Verification Test Performance Parameters

Performance Parameter	Method of Evaluation
Accuracy	Closeness of analyzer response to nitrate standards compared to reference method value
Bias	Systematic error in analyzer response to nitrate standards compared to reference method value
Linearity	Analyzer response to multi-level nitrate standards compared to reference value
LOD	Calculated from analyzer response to repeated measurements of DI water
Reproducibility	Percent relative standard deviation (SD) (%RSD) of repeated analysis of the same nitrate standard
Span and zero drift	Stability of analyzer response to DI water and nitrate standards over time
Interference effects	Analyzer response to non-nitrate compounds containing N and/or P compared to the reference value
Matrix effects	Analyzer response to nitrate in several sample matrices (chlorophyll *a*, varied pH, wastewater, on-line sampling of final effluent) compared to response to nitrate in DI water
Data completeness	Percentage of maximum data return over field period
Operational factors	Operator observations, records of needed and performed maintenance, vendor activities, use of expendable supplies

Nutrient standards used to perform the testing activities were prepared from high-purity solids (e.g., potassium nitrate, potassium dihydrogenphosphate) diluted in DI water (Millipore Milli-Q Academic Ultrapure Water Purification system, 18.2 megaohm · centimeter resistivity) or wastewater (influent, process, and effluent) samples. The total volume prepared for each nutrient solution varied from 5 L to more than 25 L. The nutrient solutions were not prepared quantitatively since each performance evaluation (PE) used the reference laboratory analysis result for each nutrient standard or wastewater sample, rather than the nominal concentration calculated from the sample preparation. However, the solutions were prepared as close to the target concentrations outlined in the test/QA plan(1) as possible.

When conducting off-line measurements, test samples (nutrient standards and wastewater samples) were supplied to the MP-1 by gravity-feeding approximately 5 L of each sample from the off-line measurement sample bottle (Figure 2-2, E) into the MP-1 flow cell. The gravity feed was initiated when the MP-1 was measuring Channel 5 or 6 so that the cell would be completely filled before the next measurement loop began (i.e., Channel 1). Whenever possible, the sample flow through the MP-1 was maintained for three full measurement loops (approximately 6 minutes). Between samples, the MP-1 flow cell was emptied by opening the inlet valves and allowing the contents to gravitationally flow into a waste container; the off-line sample measurement bottle was rinsed three times with the next sample before filling. The average of up to three nitrate measurements reported for each sample was used for the analyses described in Chapter 5 of this verification report.

During Week 2 of off-line testing (Phase I), it was discovered that the MP-1 sensitivity to nitrate had decreased significantly since the beginning of the verification test. The measurement data were provided to the vendor representative, who determined that the number of photons in the MP-1 flow cell had become too low. The flow cell components had become coated with a brown residue (visible on the tubing shown in Figure 3-4, B) and needed to be cleaned. The vendor representative provided instructions for cleaning the cell, included in this report as Appendix C. Once the flow cell components were cleaned, the photon count [Raman scattering (RS) channel value] in the cell increased to the values observed at the beginning of the verification test (RS >20). The RS channel value was then used as a diagnostic tool to determine whether the MP-1 was working properly. Values for the RS channel less than 20 indicated that residue in the flow cell had accumulated on the internal components and was blocking the UV radiation, while RS values greater than 70 were caused by entrained air bubbles in the flow cell. The flow cell was cleaned daily during on-line effluent monitoring before reference samples were collected or other testing activities were performed. However, the testing performed during Week 2 of Phase I off-line testing (i.e., before regular cleaning of the flow cell was instituted by the vendor representative) was affected by the residue in the cell. The accuracy, bias, and linearity checks were repeated during the last week of the verification test. The chlorophyll *a* and pH matrix effects checks could not be repeated due to time constraints, so an additional analysis method was employed for these checks, as described in Section 5.8 (Matrix Effects).

3.3.1 Accuracy, Bias, Linearity, and Limit of Detection

During off-line Phase I and off-line Phase II testing, the MP-1 was challenged with multi-level nitrate standards and DI water. Three non-consecutive measurements were recorded at each of five nominal concentrations (including zero); the three measurements at each concentration were conducted within the same day. As previously mentioned, each measurement typically consisted of three complete measurement loops. Table 3-4 shows the approximate concentration values for the multi-level nutrient standards supplied to the MP-1 and the order in which the standards were supplied. The MP-1 sampled DI water to obtain an additional blank measurement at least once each day during off-line Phase I testing to evaluate the instrumental LOD. Since the method detection limit will vary depending on the sample matrix, the LOD provides a more general measure of performance.

Table 3-4. Nitrate Concentrations and Sequence of Multi-level Challenges

Target Concentration (mg N/L)(a)	0	0.1	0.5	2	5
Measurement Number	1	2	3	4	5
	6	10	8	7	9
	11	15	14	13	12
	16				

(a) From potassium nitrate.

3.3.2 Reproducibility

The reproducibility of the MP-1 results was evaluated during off-line Phase I testing (on the first day of testing). The MP-1 was challenged with a mixed standard containing potassium nitrate and potassium dihydrogenphosphate at approximately 5 mg N/L and 3 mg P/L, respectively. The mixed nutrient standard was delivered five times sequentially.

3.3.3 Span and Zero Drift

The “baseline” response of the MP-1 to a mixed nutrient standard and DI water was determined during the reproducibility check on the first day of testing. The average and standard deviations (SDs) of the MP-1 response to the mixed nutrient standard supplied for the reproducibility checks were calculated from the five average nitrate readings. Similarly, the average and SDs of the MP-1 response to DI water were calculated from the first five DI water measurements obtained during the verification test.

Once each week during the on-line monitoring and off-line Phase II of the verification test, DI water and the mixed nutrient standard were supplied to the MP-1 for a total of five span/zero drift checks. The drift checks were performed immediately following a cleaning of the MP-1 flow cell. Each response was compared to the baseline response to determine whether drift had occurred in the MP-1 response to DI water or the nutrient standard.

3.3.4 Interference Effects

The MP-1 was challenged with the nutrient standards shown in Table 3-5 for the determination of interference effects for several forms of N and P. A nitrate standard was included to verify the MP-1 sensitivity to nitrate during the check.

3.3.5 Matrix Effects

During off-line Phase I and Phase II testing, the MP-1 was challenged with a series of samples containing altered matrices. In off-line Phase I, synthetic samples containing nitrate at three pH levels and in the presence and absence of chlorophyll *a* (present in algal blooms) were prepared in DI water and delivered to the MP-1. In off-line Phase II, wastewater samples were collected

Table 3-5. Nutrient Standards for Interference Effects

Nutrient	Nutrient Source	Target Nutrient Concentration	
		Nitrogen (mg N/L)	Phosphorus (mg P/L)
Total Nitrogen	"Ammonia" Ammonium chloride (NH_4Cl)	5	NA
	"Nitrite" Sodium nitrite ($NaNO_2$)	5	NA
	"Nitrate" Potassium nitrate (KNO_3)	5	NA
	"Organic Nitrogen" Dimethyl amine (DMA) ($((CH_3)_2NH)$)	5	NA
	"Mixed Nitrogen" (Approximately equally apportioned NH_4Cl, $NaNO_2$, KNO_3, DMA)	10	NA
Total Phosphorus	"Inorganic Phosphorus" Potassium dihydrogenphosphate (KH_2PO_4)	NA	3
	"Organic phosphorus" Aminomethyl phosphonic acid (PPA) ($H_2NCH_2P(O)(OH)_2$)	1.4[a]	3
	"Mixed Phosphorus" Approximately equally apportioned (ortho-phosphate and PPA)	1.1[a]	5

NA = not applicable

[a] This form of organic P also contains N. The N concentration in the standard at the target PPA concentration is listed here for reference purposes.

from three points in the treatment process—effluent, process, and influent—and delivered to the MP-1 both unspiked and after spiking with nitrate and ortho-phosphate. Off-line Phase II measurements of the wastewater samples were conducted at the end of the verification test to minimize the potential impact of analyzer fouling from potentially high total suspended solids levels in the influent samples. Table 3-6 summarizes the samples that were delivered to the MP-1. MP-1 responses were compared to reference laboratory analysis results for the same samples to determine the percent recovery (%R) for each sample.

Table 3-6. Sample Specifications for Evaluation of Matrix Effects

Matrix (Variable)	Sample Description	Number of Measurements	Target Nutrient and Spike Concentration	
			Nitrogen(a) (mg/L)	Phosphorus(b) (mg/L)
pH	pH = 5	1	5	NA
	pH = 7	1	5	NA
	pH = 9	1	5	NA
Chlorophyll *a* (pH 7)	120 microgram (µg)/L Chlorophyll *a*	1	0	0
	0 µg/L Chlorophyll *a*	1	5	NA
	120 µg/L Chlorophyll *a*	1	5	NA
Effluent sample	Effluent	3	0	0
	Effluent spike	3	5	3
Process sample	Process	3	0	0
	Process spike	3	5	3
Influent sample	Influent	3	0	0
	Influent spike	3	5	3

(a) KNO_3
(b) KH_2PO_4
NA = not applicable

During on-line effluent monitoring, MP-1 matrix effects were evaluated for the final effluent. The MP-1 sampled the final plant effluent for a period of approximately four weeks. Three times per week, reference samples of the plant effluent were collected for analysis in coordination with MP-1 on-line measurement times and immediately after the daily cleaning of the MP-1 flow cell.

The samples were collected from the drain valve of the multi-spigot tap, which was just upstream of the tee to the MP-1 inlet valve. The MP-1 response to the final effluent at the time of the reference sample collection was compared to the reference laboratory result to determine the %R for each sample. A total of 12 reference samples were collected and analyzed; reference results from 10 samples that met quality control (QC) requirements were used to determine matrix effects.

3.3.6 Data Completeness

Data completeness was assessed based on the overall data return achieved by the MP-1.

3.3.7 Operational Factors

Operational factors such as maintenance needs, calibration frequency, data output, consumables used, ease of use, and repair requirements were evaluated based on the observations of Battelle and OMI staff.

3.4 Reference Method

One aliquot of each nutrient standard and wastewater sample described in Sections 3.3.1 through 3.3.5 was submitted to a local commercial laboratory (F&R) for analysis. F&R is state-certified in Virginia, North Carolina, and South Carolina and is inspected yearly by the Virginia Department of Environmental Quality. Samples [either 250 milliliters (mL) or 500 mL] were collected in high-density polyethylene bottles and stored at 4°C until transfer to the commercial laboratory, for analysis. Preservative (2 mL concentrated sulfuric acid per L) was added to sample bottles for all analyses except for nitrate or nitrite only (samples for nitrate+nitrite analysis were acid-preserved). Samples were transported to the laboratory on ice in coolers and were stored at 4°C at the laboratory until analysis. Table 3-7 provides the methods that were used for each analysis, method quantitation limits (QL), preservation methods, and maximum holding times. The preservation methods listed in the table are standard procedures,(2) but are different from those listed in the test/QA plan.(1) A deviation report was filed to address the use of different preservation methods; the quality of the reference method data was not impacted by the deviation.

Table 3-7. Reference Methods

Parameter	Method	Method QL mg/L	Preservation and Storage Conditions	Maximum Holding Time
Ammonia	4500-NH3 H (Parts B and C) (Distillation and Nesslerization Method)(2)	0.05	2 mL H_2SO_4/L; 4°C	28 days
Nitrate	4500-(NO3F and NO2B) minus NO2B(2)	0.02	4°C for nitrate or nitrite individually	48 hours
Nitrite	4500-NO2B(2)		2 mL H_2SO_4/L; 4°C for nitrate + nitrite	28 days
Total Nitrogen	sum of total Kjeldahl nitrogen (TKN) (EPA 351.1),(3) nitrate, and nitrite	0.52	2 mL H_2SO_4/L; 4°C	48 hours
Organic Nitrogen	TKN minus ammonia	0.5	2 mL H_2SO_4/L; 4°C	28 days
Total Phosphorus	4500-P, Parts B and F(2)	0.05	2 mL H_2SO_4/L; 4°C	28 days
Dissolved Inorganic Phosphorus	4500-P, Parts B and E(2) total phosphorus minus organic phosphorus	0.05	2 mL H_2SO_4/L; 4°C	28 days
Organic Phosphorus	4500-P, Parts B and E(2) total phosphorus minus reactive and acid hydrolyzable phosphorus)	0.05	2 mL H_2SO_4/L; 4°C	28 days

Chapter 4
Quality Assurance/Quality Control

QA/QC procedures were performed in accordance with the quality management plan (QMP) for the AMS Center(4) and the test/QA plan for this verification test,(1) with the exception of two deviations, which have been addressed in this report. Briefly, the preservation methods used by the reference laboratory were different from those listed in the test/QA plan(1) and the statistical approach for determination of matrix effects was modified. These deviations are changes to the procedures outlined in the test/QA plan(1) that did not negatively impact the quality of this verification test. All QA/QC results for this verification test are included in the following sections, although not all results directly impact the verification of the MP-1.

4.1 Reference Method Quality Control Results

F&R followed their standard QA/QC protocols, which included analysis of blanks, laboratory control samples (LCS), matrix spikes (MS), and MS duplicates (MSDs). The tolerances for each analysis and QA/QC sample are listed in Table 4-1. LCS and MS results were evaluated in terms of the %R; MSDs were evaluated in terms of relative percent difference (RPD). All of the blanks and LCS results were within the tolerances listed in Table 4-1. Nine of the MS samples [four for nitrate+nitrite (%R values of 116%, 119%, 84%, and 119%), two for ammonia (80% and 128%), two for TKN (498% and 80.4%), and one for TP analysis (70%)] did not meet the acceptance criterion. Of those samples, five were performed on samples from other clients (i.e., not from this verification test). Since the LCSs from the same analysis batches were within tolerances, these failed MS samples did not indicate a problem with the reference analyses. The MSD results for the two failed TKN MS samples were 46.8% (%D) and 50.1%; all other MSD results were within the 20% tolerance. For the one failed MS sample that was from the set for this verification test, the unspiked measurement was suspected to be incorrect, based on knowledge of the sample and the MS results. The MS sample analysis was conducted on a blank sample (i.e., DI water) and the unspiked analysis result was 0.37 mg P/L. The sample was spiked with 1.00 mg P/L, and the two MS results were 1.09 and 1.07, which is consistent with an initial sample concentration near zero. Thus, none of the discrepancies for the QC results indicated that the reference analyses for this verification test were affected.

Table 4-1. Reference Method QA/QC Protocols and Tolerances

Analysis	Blank	LCS (%R)	Matrix Spike (%R)	Matrix Spike Duplicate (RPD)
Nitrate	BQL	86.5 – 110	85 – 115	<20
Nitrite	BQL	85 – 115	85 – 115	<20
Ammonia	BQL	80.9 – 114.8	85 – 115	<20
TKN	BQL	78.6 – 121.4	85 – 115	<20
Total P	BQL	84.5 – 115.5	85 – 115	<20
Inorganic P	BQL	84.5 – 115.5	85 – 115	<20

BQL = below quantitation limit.

4.2 Audits

4.2.1 Performance Evaluation Audits

PE audit samples were submitted to F&R for analysis to assess the quality of nutrient reference method measurements. The PE audit of the nutrient reference methods was performed by supplying for each reference method a blind National Institute of Standards and Technology (NIST)-traceable nutrient standard independent of those used for testing the MP-1. The PE samples were analyzed in the same manner as all other samples, and the analytical results for the PE samples were compared to the nominal concentration. The target criterion for the PE audit samples was agreement of the analytical result within 25% of the nominal nutrient concentration by percent difference (%D). If the PE audit results did not meet the tolerances required, they were repeated. PE audits were required to be performed once prior to the verification test and once during the verification test; audits were performed once prior to and twice during the verification test. The PE audit samples submitted to F&R for analysis are summarized in Table 4-2.

As shown in Table 4-2, several of the PE audit samples submitted on April 14, April 20, and May 6, all of which were prepared with the same NIST-traceable nutrient standards, did not meet the acceptance criterion. However, the laboratory QA/QC samples analyzed during the same sample batches were within acceptable tolerances. New standards intended specifically for nutrient analysis were purchased (the standards used for the April and May PE audit samples were intended for ion chromatography) and the PE audits repeated. The simple and complex nutrient standards were diluted in DI water and effluent wastewater and submitted to F&R on June 17 for analysis. All analyses of the PE audit samples that were prepared from the simple and complex nutrient standards were within 25% of the nominal concentration. The April and May PE audit failures were attributed to unreliable/inaccurate standards and did not impact the results of this verification test.

Table 4-2. PE Audit Sample Results

Sample Submission Date	Spiked Nutrient	Analysis	Sample Matrix	Expected Result (mg/L)	F&R Result (mg/L)	%D	Pass/ Fail
4/14/2005	Phosphate	TP	DI Water	0.75	0.86	14	Pass
4/14/2005	Nitrate Nitrite Ammonia	Nitrate + Nitrite	DI Water	8.00	8.08	1	Pass
		TN	DI Water	10.0	16.20	62	Fail
4/20/2005	Nitrate	Nitrate	DI Water	2.00	2.00	0	Pass
5/6/2005	Nitrate	Nitrate	Wastewater	4.72	6.20	31	Fail
5/6/2005	Phosphate	TP	Wastewater	8.01	7.70	4	Pass
5/6/2005	Nitrate Nitrite Ammonia	Nitrate + Nitrite	Wastewater	8.77	8.02	9	Pass
		TN	Wastewater	19.75	29.30	48	Fail
5/17/2005	Simple Nutrients	Ammonia	DI Water	6.96	6.38	8	Pass
		Nitrate	DI Water	8.44	8.28	2	Pass
		TP	DI Water	0.336	0.29	14	Pass
5/17/2005	Complex Nutrients	TKN	DI Water	7.76	7.9	2	Pass
		TP	DI Water	2.87	2.82	2	Pass
5/17/2005	Simple Nutrients	Ammonia	Wastewater	3.92	3.46	12	Pass
		Nitrate	Wastewater	4.52	4.46	1	Pass
		TP	Wastewater	0.25	0.24	3	Pass
5/17/2005	Complex Nutrients	TKN	Wastewater	5.28	5.80	10	Pass
		TP	Wastewater	1.52	1.45	4	Pass

4.2.2 Technical Systems Audits

The Battelle Quality Manager performed a technical systems audit (TSA) on May 10, 2005, to ensure that the verification test was being performed in accordance with the AMS Center QMP,(4) the test/QA plan,(1) published reference methods, and any standard operating procedures used by DuPont or OMI. In the TSA, the Battelle Quality Manager visited the test site, observed the nutrient reference method sampling and sample recovery, inspected documentation of nutrient sample chain of custody, and reviewed analyzer-specific record books. The Battelle Quality Manager also toured F&R's laboratories, viewed the reference methods used by F&R, compared actual test procedures to those specified by the test/QA plan,(1) and reviewed data acquisition and handling procedures.

Observations and findings from this audit were documented and submitted to the Battelle Verification Test Coordinator for response. No findings were documented that required any corrective action. The records concerning the TSA are stored for at least seven years with the Battelle Quality Manager.

4.2.3 Audit of Data Quality

At least 10% of the data acquired during the verification test were audited. To ensure the integrity of the reported results, Battelle's Quality Manager or his designee traced the data from the initial acquisition, through reduction and statistical analysis, to final reporting. All calculations performed on the data undergoing the audit were checked.

4.3 Quality Assurance/Quality Control Reporting

Each assessment and audit was documented in accordance with Sections 3.3.4 and 3.3.5 of the QMP for the ETV AMS Center.(4) Once the assessment report was prepared, the Battelle Verification Test Coordinator ensured that a response was provided for each adverse finding or potential problem and implemented any necessary follow-up corrective action. The Battelle Quality Manager ensured that follow-up corrective action was taken. The results of the TSA were sent to the EPA.

4.4 Data Review

Records generated in the verification test were reviewed before these records were used to calculate, evaluate, or report verification results. Table 4-3 summarizes the types of data recorded. The review was performed by a technical staff member involved in the verification test, but not the staff member who originally generated the record. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed.

Table 4-3. Summary of Data Recording Process

Data to Be Recorded	Where Recorded	How Often Recorded	By Whom	Disposition of Data
Dates, times, and details of test events, analyzer maintenance, down time, etc.	ETV laboratory record books or data recording forms	Start/end of test procedure, and at each change of a test parameter or change of analyzer status	Battelle if on-site; DuPont or OMI at other times	Used to organize and check test results; manually incorporated in data spreadsheets as necessary
Analyzer calibration information	ETV laboratory record books or electronically	At analyzer calibration or recalibration	Electronic data by vendor; Battelle if on-site; DuPont or OMI at other times	Incorporated in verification report as necessary
Analyzer nutrient readings	Recorded electronically by the MP-1 and downloaded to disk and e-mailed to Battelle at least weekly.	Recorded continuously	Analyzer vendor, for transfer to Battelle	Converted to spreadsheet for statistical analysis and comparison
Sample collection and reference method analysis procedures, calibrations, QA, etc.	Laboratory record books or data recording forms	Throughout sampling and analysis processes	Battelle if on-site, DuPont or OMI at other times, and reference laboratory	Retained as documentation of reference method performance
Reference method nutrient analysis results	Electronically from analytical method	Every sample analysis	Reference laboratory	Transferred to spreadsheets for statistical analysis and comparison to MP-1 results

Chapter 5
Statistical Methods and Reported Parameters

The statistical methods presented in this chapter were used to evaluate the performance parameters listed in Section 3.1.

5.1 Accuracy

Accuracy of the MP-1 with respect to the individual nutrient standards was assessed as the %R, using Equation 1:

$$\%R = \left[1 + \left(\frac{Y - X}{X}\right)\right] \times 100 \qquad (1)$$

where Y is the measured MP-1 (average for up to three measurement loops) value and X is the reference laboratory nutrient concentration. The average, minimum, and maximum %R values were reported for each series of multi-level nutrient challenges. A %R value of 100% indicates perfect agreement between the MP-1 result and the reference laboratory nutrient concentration.

5.2 Bias

Bias of the MP-1 was defined as a systematic error in measurement that resulted in measured error that was consistently positive or negative compared to the reference value. The bias was calculated as the average %D of the MP-1 compared to the reference laboratory nutrient concentration and was calculated for the entire series of multi-level nitrate standard challenges, using Equation 2:

$$\%\overline{D} = \frac{1}{k}\sum_{j=1}^{k}\left(\frac{Y - X}{X}\right)_j \times 100 \qquad (2)$$

where *k* is the number of valid comparisons, and Y and X are the same as in Equation 1. A %D value of 0% indicates that no bias was present in the MP-1 measurements.

5.3 Linearity

Linearity was assessed by a linear regression analysis using the nutrient concentration determined by the reference laboratory as the independent variable and results from the MP-1 as the dependent variable. Linearity was expressed in terms of slope, intercept, and coefficient of determination (r^2). The 95% confidence interval (CI) was also calculated for the slope and intercept using Microsoft Excel's Analysis Toolpack.

5.4 Limit of Detection

The LOD is the minimum nitrate concentration that is significantly different from the blank or background signal and is defined for this verification test as the average blank signal $(\overline{Y}_b)$ plus three times the SD_b, where SD_b is the standard deviation of the blank measurements. Based on this definition, there is a 99.7% probability that samples at or above the LOD represent concentrations truly above the background noise. The LOD was calculated from at least 15 blank (DI water) measurements using Equations 3 and 4:

$$SD_b = \sqrt{\frac{\sum\left(Y_b - \overline{Y}_b\right)^2}{n-1}} \tag{3}$$

$$LOD = \overline{Y}_b + 3SD_b \tag{4}$$

where Y_b is an individual blank measurement and *n* is the number of blank measurements used to determine the LOD.

5.5 Reproducibility

The reproducibility of the MP-1 was evaluated from six repeated measurements of a mixed nutrient standard. Reproducibility was defined as the %RSD of the six measurements, using Equation 5:

$$\%RSD = \frac{SD}{\overline{Y}} \times 100 \tag{5}$$

where $\overline{Y}$ is the average MP-1 concentration for the mixed nutrient standard, and SD is the SD of the MP-1 measurements.

5.6 Span and Zero Drift

The baseline response of the MP-1 to DI water and the mixed nutrient standard was established early in the verification test. The mean ($\overline{Y}$) and SD of the MP-1 response to DI water and the mixed nutrient standard were calculated from the six replicate measurements conducted for the reproducibility checks. From these values, a control chart was constructed, and the $\overline{Y}$ ± 2SD "warning limit" and the $\overline{Y}$ ± 3SD "action limit" were calculated. Span drift was defined as having occurred if three consecutive span checks fell either above or below the warning limit. Zero drift was defined as having occurred if three consecutive zero checks fell either above or below the warning limit. However, if the SD from the baseline DI water challenge was equal to zero, the absolute difference to the zero air baseline mean was reported for each zero check. Since the actual baseline response and span drift check standard concentrations varied over the five drift checks (ranged from 4.56 to 5.41 mg N/L), the MP-1 span measurements for the baseline response and drift checks were normalized to the target concentration, as shown in Equation 6:

$$Y_{norm} = Y_{span} \times \frac{X_{target}}{X_{span}} \tag{6}$$

where Y_{norm} is the normalized MP-1 measurement, Y_{span} is the MP-1 measurement value for the drift check, X_{target} is the target nutrient concentration standard concentration, and X_{span} is the actual reference method measurement.

5.7 Interference Effects

The interference effects of the MP-1 were calculated in terms of the ratio of its response to the non-nitrate nutrient relative to the measured reference laboratory concentration. For example, if 5 mg N/L of ammonia resulted in a 0.5 mg N/L response of the MP-1, the interference effect was reported as 10% (i.e., 0.5 mg N/L ÷ 5 mg N/L × 100). Interference effects were reported separately for each non-nitrate nutrient, for a mixed N sample, and for a mixed P sample.

5.8 Matrix Effects

Matrix effects on the MP-1 with respect to each matrix sample were assessed based on the %R value for each sample. The basis for this comparison was changed from that in the test/QA plan,(1) which described determination of matrix effects relative to the average ± 2SD range calculated for the on-line effluent measurements conducted during on-line monitoring. The %D was also calculated for pH and chlorophyll *a* matrix effects test samples relative to nutrient samples at pH = 7 in the absence of chlorophyll *a* since the matrix variable could be isolated. For on-line effluent monitoring results, a two-tailed paired *t*-test was applied to determine whether the reference method and MP-1 gave significantly different values for the mean nitrate concentration. The experimental *t* value (t_{exp}) was calculated using Equation 7:

$$t_{exp} = \frac{\sum_i (\mathrm{Y} - \mathrm{X})_i}{n} \times \frac{\sqrt{n}}{\mathrm{SD}} \qquad (7)$$

where Y is the measured MP-1 value, X is the corresponding reference method measurement, *n* is the number of measurement pairs, and SD is the standard deviation of the absolute differences. The critical values of *t* (t_{crit}) for (n-1) degrees of freedom at the 95% confidence level were calculated in Microsoft Excel software for the number (*n*) of nitrate measurement pairs used to calculate t_{exp}. Values for t_{exp} that are less than t_{crit} indicate that the two methods do not give significantly different values for the mean nitrate concentration. A deviation report was filed to address this change from the test/QA plan.(1)

5.9 Data Completeness

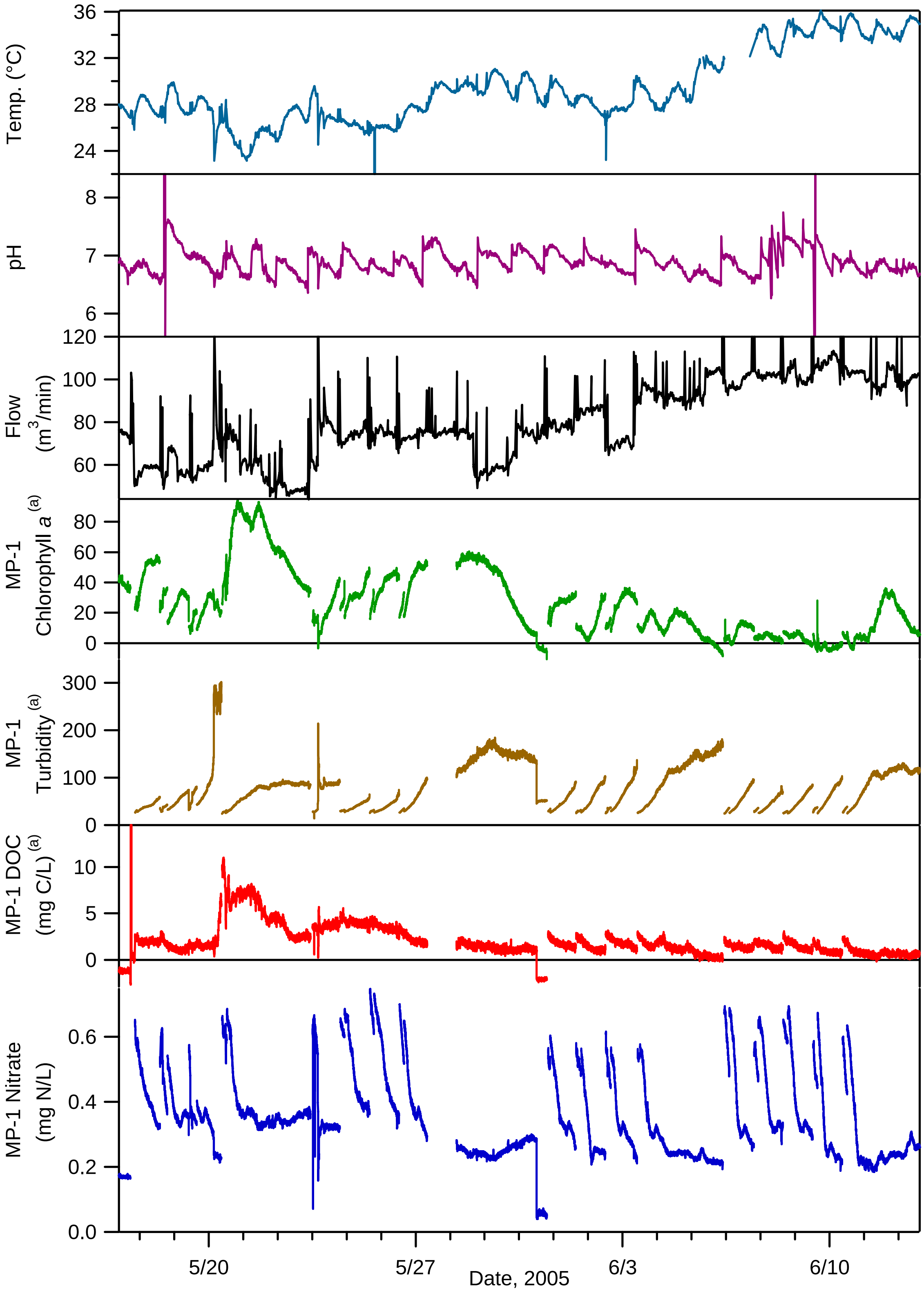
Data completeness was calculated as the percentage of the total possible data return achieved over the entire field period. This calculation used the total hours of data recorded from the MP-1, divided by the total hours of data in the entire field period. The field period was defined as beginning at 8:00 a.m. on May 5, 2005, and ending at 9:00 p.m. on June 16, 2005. No distinction was made in this calculation between data recorded during a specific test activity (e.g., data recorded for off-line testing) and that recorded during on-line effluent monitoring.

Chapter 6
Test Results

The results of the verification test of the MP-1 are presented in this section. The MP-1 was calibrated by the vendor representative prior to the start of the verification test for operation in the range from <0.01 to 7 mg N/L nitrate. The analyzer was not recalibrated during the verification test.

The MP-1 was set up to monitor effluent wastewater during the evenings after off-line Phase I testing activities were completed and over the weekend preceding the accuracy, bias, linearity, and off-line Phase I matrix effects challenges. As discussed in Section 3.3, buildup in the MP-1 flow cell necessitated regular cleaning. During on-line effluent monitoring, the MP-1 “target” was cleaned daily, and the fiber assembly tip was cleaned weekly or when cleaning the target did not improve the RS value to acceptable levels (greater than 20). According to ZAPS Technologies, Inc., the RS value for a clean cell containing only DI water should be approximately 50 to 60 and, for a cell with a wastewater sample, the value should be approximately 30 to 40. When the RS value drops below 20, it is an indication that buildup in the flow cell is too thick for the MP-1 to perform properly. The residue in the flow cell impacted the results for the following checks: accuracy, bias, linearity, and chlorophyll *a* and pH matrix effects. Checks for accuracy, bias, and linearity were repeated during the last week of the verification test, but the chlorophyll *a* and pH matrix effects checks could not be repeated due to time constraints. However, the impact of chlorophyll *a* and pH on MP-1 nitrate measurements could still be evaluated using the data collected during the verification test by correcting for the overall nitrate sensitivity change (see Section 6.8, Matrix Effects).

The temperature and pH of the final effluent were monitored by DuPont at the same site where this verification test was conducted; and the effluent flow rate, reported in units of cubic meters per minute (m^3/min), was monitored approximately 200 meters upstream of the test site. The MP-1 nitrate, dissolved organic carbon (DOC), turbidity, and chlorophyll *a* measurement data during on-line effluent monitoring are shown in Figure 6-1 with the effluent temperature, pH and flow rate. (Turbidity and chlorophyll *a* measurements are shown with arbitrary units.) The average nitrate concentration of the effluent stream measured by the MP-1 over the four-week on-line monitoring phase was 0.35 mg N/L, with a range of 0.04 to 0.75 mg N/L. The large-scale variations in the MP-1 measurement data are due to the rapid buildup of residue in the MP-1 flow cell. Several days of MP-1 RS values and nitrate measurements performed during on-line effluent monitoring are shown in Figure 6-2. The flow cell cleanings and first in-line filter strainer back-flushes (discussed in Section 3.3) are marked by solid vertical black lines in the figure. The dashed vertical lines mark the second in-line filter back-flush each day. The RS value increased dramatically when the cleaning activities were performed; cleaning the flow



[a] Not verified in this test.

Figure 6-1. Water Quality Parameters and MP-1 Nitrate, DOC, Turbidity, and Chlorophyll *a* Measurements

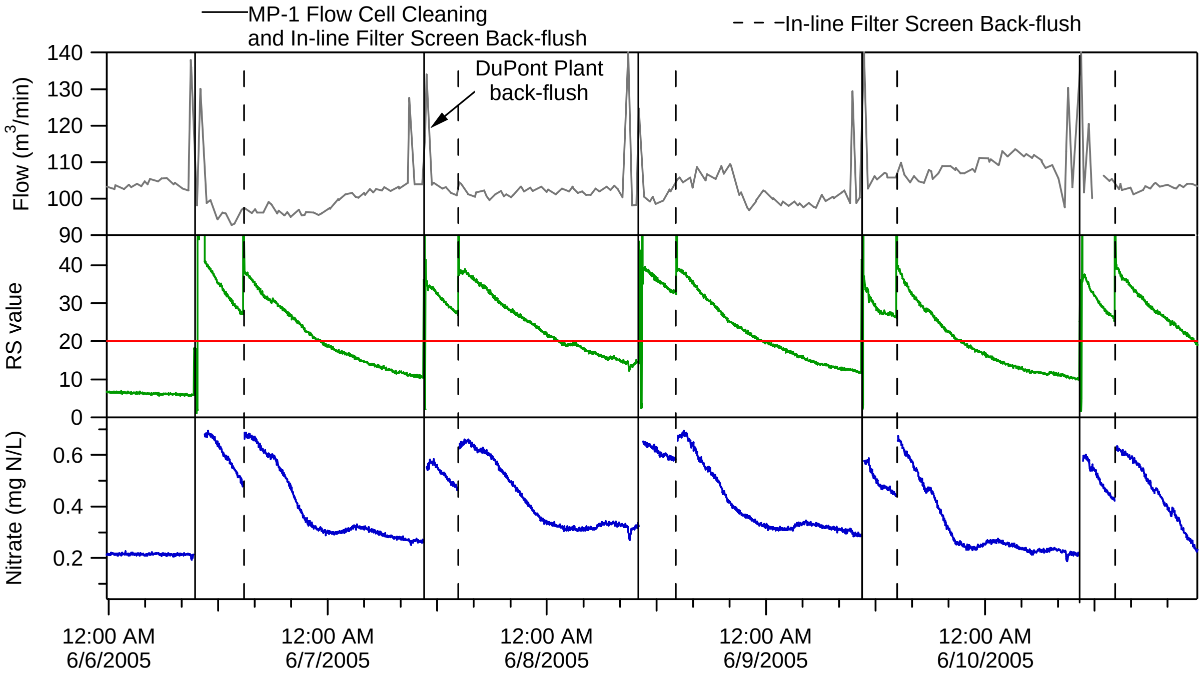


Figure 6-2. MP-1 Nitrate Measurements and RS Values with Effluent Flow

cell was more effective at increasing the RS value than back-flushing the in-line filter screen. As shown in the figure, the RS value frequently dropped below 20 (marked by the horizontal red line), indicating that the MP-1 was no longer making valid measurements. The flow cell cleanings and filter screen back-flushes were coordinated with regular back-flushes of the Spruance Plant's non-contact cooling water filters, which are evident as spikes in the effluent flow rate shown in Figure 6-2 (gray trace). Since the MP-1 was rapidly affected by the build-up of residue in the flow cell, reference samples for matrix effects checks (Section 6.8) were collected immediately after cleaning the flow cell.

6.1 Accuracy

The MP-1 was challenged with nutrient standards at several concentrations (0.1 to 5 mg N/L), as listed in Table 3-4. Table 6-1 presents the average nitrate concentrations measured by the MP-1 and the corresponding %R values relative to the reference method results. Data presented here are for the repeated checks performed during the last week of the verification test. The number of nitrate readings (*n*) used for each average, RS values, and the MP-1 responses to DI water are also presented for reference purposes. The high RS values (greater than 70) for three of the nitrate challenges indicate the presence of bubbles in the flow cell, resulting in invalid measurements. Because of constraints in the sample volume, these measurements could not be repeated. The %R values for the invalid measurements were not calculated and the results were excluded for the accuracy, bias, and linearity evaluations. As shown in Table 6-1, nitrate %R values ranged from 98% to 251%, with an average of 157%.

Table 6-1. Accuracy Results for Multi-level Nitrate Challenges

Measurement Number	Nitrate Concentration (mg N/L)(a)			RS Value	*n*	%R
	Target	Reference Method	Average MP-1			
1	0	BQL	0.04	59	3	NA
2	0.1	0.14	0.15	55	3	110
3	0.5	0.44	0.43	57	3	98
4	2	2.04	3.74	57	3	183
5	5	4.82	6.04	56	3	125
6	0	BQL	0.20	56	3	NA
7	2	2.04	3.38	78(b)	2	(b)
8	0.5	0.44	0.24	93(b)	3	(b)
9	5	4.82	6.40	59	3	133
10	0.1	0.14	0.35	60	3	251
11	0	BQL	0.09	58	3	NA
12	5	4.82	3.48	89(b)	3	(b)
13	2	2.04	4.20	60	3	206
14	0.5	0.44	0.55	61	3	126
15	0.1	0.14	0.25	61	3	177
16	0	BQL	0.11	60	3	NA
Average						157
SD						51
Minimum						98
Maximum						251
Bias (% $\overline{D}$)						+57

(a) N in the form of nitrate (from potassium nitrate).

(b) RS values greater than 70 for a DI water matrix are indicative of the presence of air bubbles entrained in the flow cell during measurement. These results were not valid and were excluded from the accuracy, bias, and linearity evaluations.

NA = not applicable.

6.2 Bias

Bias in the MP-1 response to nitrate standards was assessed for the multi-level nitrate challenges presented in Table 6-1. Bias of +57% was observed for the MP-1 nitrate measurements.

6.3 Linearity

Figure 6-3 shows the linearity results for the nitrate multi-level accuracy checks. For each check, a linear regression was calculated from the results presented in Table 6-1 (MP-1 versus reference method) over the range of 0 to 5 mg N/L (excluding the measurements with high RS values described in Section 6.1). The 95% CI for the slope and intercept regression were also calculated (and are shown in the following text in parenthesis). The slope of the regression line was 1.34 (± 0.37), with an intercept of 0.19 (± 0.77) and an r^2 value of 0.9574.

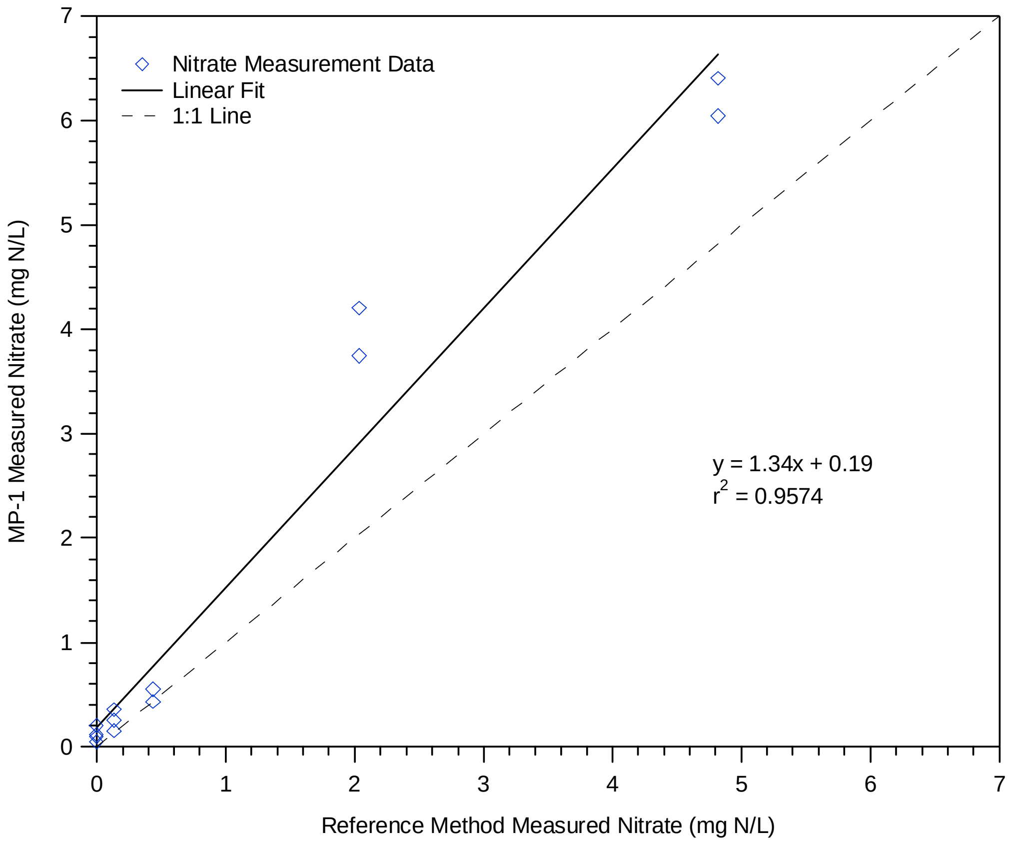


Figure 6-3. MP-1 Linearity Results for Nitrate

6.4 Limit of Detection

The MP-1 measured DI water blanks 15 times throughout the verification test. The average ($\overline{Y}_b$) and SD_b were calculated and used to determine the MP-1 LOD for nitrate measurement. The average MP-1 nitrate measurement for DI water blanks was 0.043 mg N/L, with an SD of 0.063 mg N/L, resulting in a nitrate LOD of 0.232 mg N/L. It should be noted that the reference laboratory results for DI water ranged from < 0.04 to 0.08 mg N/L during the verification test. The presence of nitrate in the DI water supply at concentrations consistent with the MP-1 measurement results cannot be ruled out. The vendor-reported MP-1 nitrate LOD is 0.05 mg N/L (determined as three times the signal-to-noise ratio). Since the LOD can be influenced by a number of factors, it is suggested that a method detection limit be determined by the user for each sample matrix.

6.5 Reproducibility

The reproducibility results from replicate challenges of a mixed nutrient standard (~5 mg N/L nitrate and ~3 mg P/L ortho-phosphate) for the MP-1 are shown in Table 6-2. The mixed nutrient standard was delivered five times sequentially. The reproducibility, determined as the %RSD, for MP-1 nitrate measurements was 14%. As indicated by reduced RS channel values shown in Table 6-2, the flow cell components were partially coated with residue, which may have affected the MP-1's reproducibility. (For spiked DI water, RS values were generally greater than 50 for a clean flow cell.)

Table 6-2. Reproducibility Results

Nitrate Concentration (mg N/L)			
Target	**Reference Method**	**MP-1[a]**	**RS**
5	5.41	2.69	33.8
		3.06	35.5
		3.24	35.9
		3.60	38.2
		3.82	39.4
Average		3.28	36.6
SD		0.45	2.2
%RSD		14	6

[a] Each MP-1 nitrate value is the average of three results (sample loops) measured for each replicate.

6.6 Span and Zero Drift

The baseline response of the MP-1 to the mixed nutrient standard used in the reproducibility checks (Section 6.5) and DI water blanks was determined during the first week of testing. It should be noted that the MP-1 RS value during the determination of the average baseline response for the mixed nutrient standard and DI water was between 30 and 40 (RS values for DI water are generally greater than 50), indicating that residue was partially blocking photons in the flow cell. Since this was discovered during the on-line monitoring portion of the verification test, the baseline response could not be redetermined. Therefore, the span baseline response values were corrected by multiplying the values by the target concentration (×5.00) and dividing by the average baseline response (÷ 3.28). This effectively normalized the average MP-1 span response values to the target concentration. The SD for the normalized average baseline response was also calculated. The nitrate measurements for each replicate are shown in Table 6-3. The $\overline{Y} \pm 2SD$ warning and $\overline{Y} \pm 3SD$ action limits were calculated for the mixed nutrient span standard and DI water blanks and are also shown in the table.

Span and zero drift checks were performed once per week beginning with the on-line effluent monitoring portion of the verification test, for a total of five drift checks. The results of the span and zero drift checks are shown in Table 6-4. Control charts were prepared from the data shown in Tables 6-3 and 6-4, to demonstrate graphically whether drift occurred over the duration of the verification test. The control charts are shown in Figures 6-4 and 6-5 for nitrate span and zero drift, respectively. Drift in the normalized nitrate span response was not observed for the MP-1 relative to the corrected baseline response, although the last span drift check result was 1.22 mg N/L greater than the target concentration. However, if the uncorrected baseline response data were used to evaluate drift, none of the span check results fell within the warning limit. The last two zero drift checks were within the warning limits, thus drift did not occur in the MP-1 response to DI water blanks. The final drift check result was 0.04 mg N/L less than the average baseline zero response.

Table 6-3. Span and Zero Baseline Response

Span Response (mg N/L)					Zero Response (mg N/L)			
Week and Day	**Reference Method**	**MP-1[a]**	**Corrected MP-1[b]**	***n***	**Week and Day**	**Reference Method**	**MP-1[a]**	***n***
Week 1 Thursday	5.41	2.69	4.09	3	Week 1 Thursday	0.08	0.02	1
Week 1 Thursday	5.41	3.06	4.66	3	Week 1 Thursday	0.08	0.03	1
Week 1 Thursday	5.41	3.24	4.94	3	Week 1 Thursday	0.08	0.05	1
Week 1 Thursday	5.41	3.60	5.49	3	Week 1 Thursday	0.08	0.06	1
Week 1 Thursday	5.41	3.92	5.82	3	Week 1 Thursday	0.08	0.09	1
Baseline Response		3.28	5.00				0.05	
SD		0.45	0.68				0.03	
Warning Limit			3.64 to 6.36				0.00 to 0.10	
Action Limit			2.96 to 7.04				-0.03 to 0.13	

[a] Invalid measurements; low RS value.

[b] Concentrations corrected using the response factor (5.00/3.28) normalized to target concentration of 5 mg N/L.

Table 6-4. Span and Zero Drift Check Results

	Nitrate Span				Nitrate Zero			
Check Date	Reference Method (mg N/L)	MP-1[(a)] (mg N/L)	Within Warning Limit? (3.64 to 6.36)	Within Action Limit? (2.96 to 7.04)	Reference Method (mg/L)	MP-1 (mg/L)	Within Warning Limit? (0.00 to 0.10)	Within Action Limit? (-0.03 to 0.13)
5/17/05 Tuesday	4.76	5.72	Yes	Yes	< 0.04	0.00	Yes	Yes
5/23/05 Monday	4.67	5.72	Yes	Yes	< 0.04	-0.00	No	Yes
5/31/05 Tuesday	4.80	6.10	Yes	Yes	< 0.04	-0.03	No	Yes
6/6/05 Monday	4.87	6.11	Yes	Yes	< 0.04	0.04	Yes	Yes
6/13/05 Monday	4.56	6.22	Yes	Yes	< 0.04	0.01	Yes	Yes

(a) Concentration normalized to target nitrate concentration of 5 mg N/L.

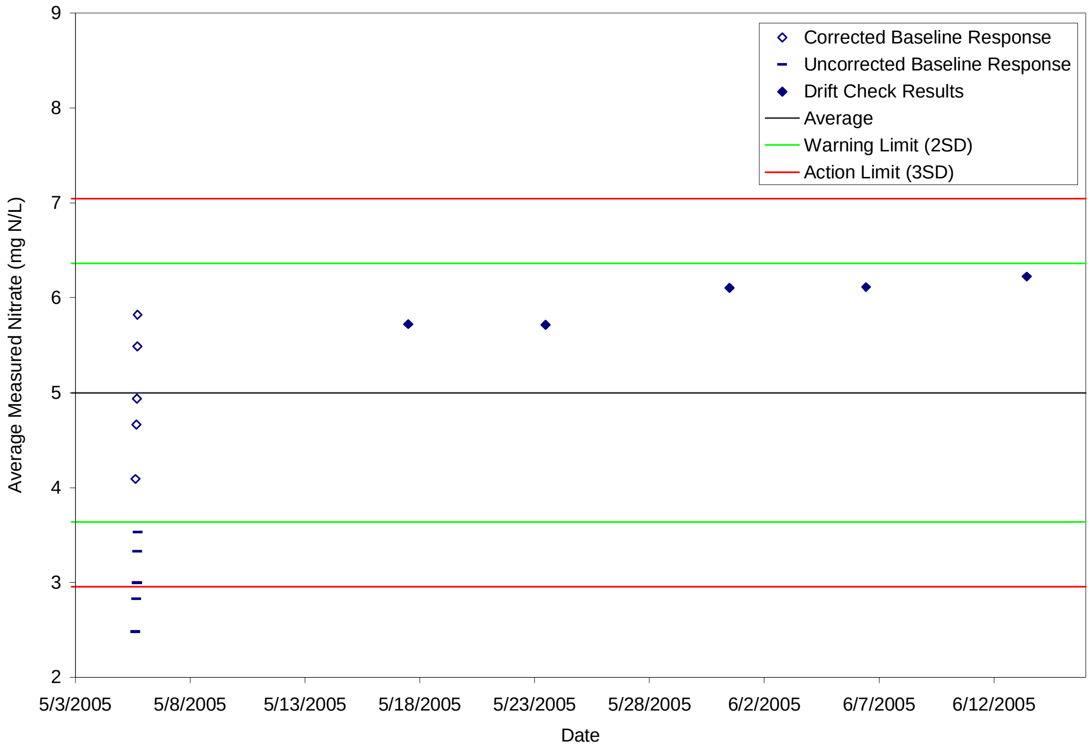


Figure 6-4. MP-1 Span Drift Control Chart

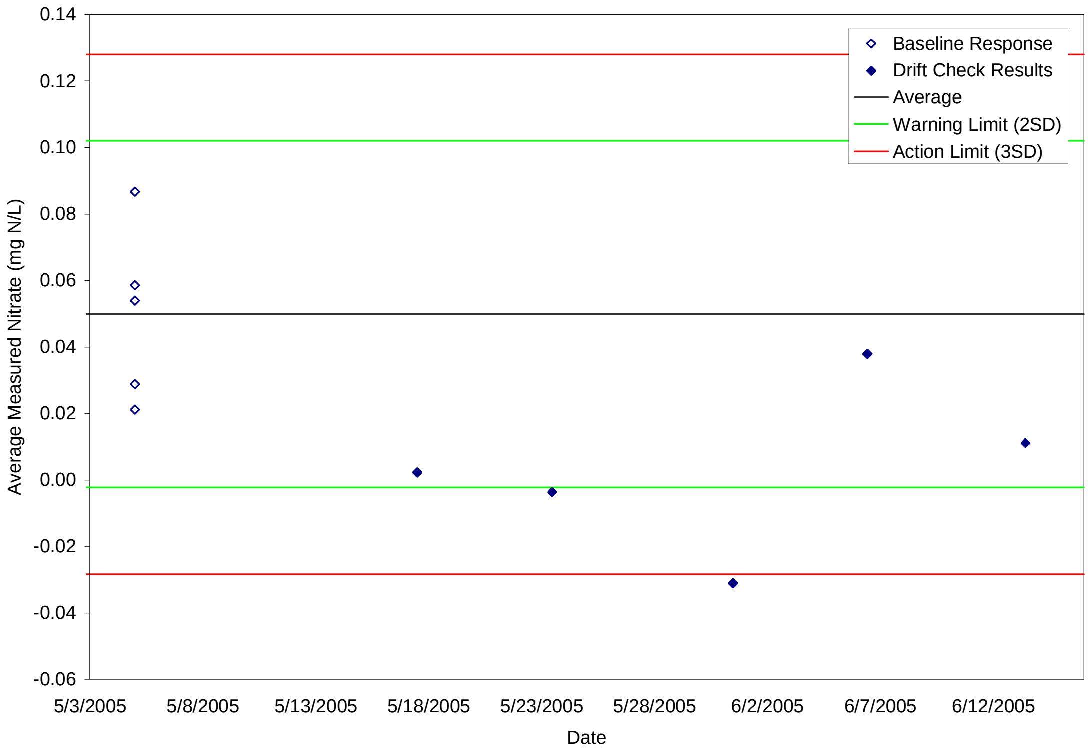


Figure 6-5. MP-1 Zero Drift Control Chart

6.7 Interference Effects

The effect of non-nitrate nutrients on the MP-1 response was assessed by challenging the MP-1 with the series of nitrogen- and phosphorus-containing compounds listed in Table 3-5. The response of the MP-1 to each compound is summarized in Table 6-5, which shows the MP-1 average response and the MP-1 non-nitrate response determined by subtracting the reference method nitrate result. All of the non-nitrate nutrients produced an interference effect less than or equal to 7% except for nitrite, for which a 97% interference effect was observed. The MP-1 response to nitrite is expected since the MP-1 measures absorbance of UV light by the nitrogen-oxygen bond, which occurs in nitrate and nitrite ions. Therefore, the MP-1 cannot distinguish between these two species of nitrogen. The MP-1 reading represents a sum of nitrate plus nitrite.

6.8 Matrix Effects

Matrix effects were evaluated during off-line Phases I and II and during on-line effluent monitoring by calculating the %R value for each sample. Some test samples were analyzed by the MP-1 more than once. In these cases, the average response was used to calculate the %R. The number of replicates (*n*) for each test sample is shown in Table 6-6. The off-line matrix effects results are shown in Table 6-6. The MP-1 RS values during the pH and chlorophyll *a* matrix effects challenges ranged from 5 to 7, indicating that the measurement accuracy was

Table 6-5. MP-1 Interference Effects Results

			Reference Method							
Nutrient Source	**N Target (mg N/L)**	**P Target (mg P/L)**	**N**	**N Result (mg N/L)**	**Nitrate Result (mg N/L)**	**P**	**P Result (mg P/L)**	**MP-1 Result (mg N/L)**	**MP-1 Non-nitrate Result(a) (mg N/L)**	**Inter-ference Effect (%)**
Ammonia	5	0	Ammonia	4.70	0.03	–(b)	–(b)	0.15	0.12	3
Nitrite	5	0	Nitrite	4.55	0.09	–(b)	–(b)	4.51	4.42	97
Organic Nitrogen	5	0	Organic Nitrogen	4.40	<0.04	–(b)	–(b)	0.11	0.11	2
Mixed Nitrogen	10	0	TN	12.0 8.43(c)	3.57 2.25(d)	–(b)	–(b)	4.12	0.55	7
Inorganic Phosphorus	0	3	–(b)	–(b)	–(b)	TP	3.00	0.14	0.14	5
Organic Phosphorus	1.4(e)	3	TN	1.45	0.05	TP	3.04	0.10	0.05	2
Mixed Phosphorus	1.1(e)	5	TN	–(b)	< 0.04	TP	5.08	0.21	0.21	4

(a) MP-1 non-nitrate result is equal to the average MP-1 response minus the reference method nitrate result.
(b) This reference analysis was not requested.
(c) Non-nitrate reference method TN result.
(d) Reference method value for nitrite.
(e) This form of organic P also contains N. The N concentration in the standard at the target concentration is listed here for reference purposes.

greatly impacted by residue on the flow cell components and, therefore, the MP-1 was not operating properly. Thus, the %R values for these measurements (8% to 9%) do not accurately indicate the presence or absence of matrix effects, but rather point to the reduced sensitivity of the MP-1 due to residue buildup. For these checks, a %D value was calculated relative to the nitrate standard at pH 7 in the absence of chlorophyll *a* and is a better representation than the % R value of the impact of adjusted pH and chlorophyll *a*-containing matrices on the MP-1 nitrate measurements. The low %D values (-1% and 1% for pH effects and 4% for the presence of chlorophyll *a*) indicate that the MP-1 response was not affected by pH over the range of 5 to 9 or in the presence of chlorophyll *a*. However, given the MP-1's reduced sensitivity during the measurement of these samples, it is not known whether a change in the MP-1 response could have been detected. The RS values for the wastewater samples were between 22 and 55, indicating that the measurements were not impacted by residue in the flow cell and, therefore, the %R values were used to evaluate matrix effects. Percent recovery values for wastewater samples ranged from 33% to 162%.

Table 6-6. Matrix Effects Results for Off-Line Testing

		Nitrate Concentration (mg N/L)				
Matrix (Variable)	**Sample Description**	**Reference Method**	**MP-1**	***n***	**%D**	**%R**
pH	pH = 5	5.16	0.40(a)	1	−1(a)	8
	pH = 7	5.17	0.40(a)	1	NA(a)	8
	pH = 9	5.20	0.41(a)	1	1(a)	8
Chlorophyll *a* (pH 7)	0 µg/L Chlorophyll *a* nitrate spike	4.88	0.41(b)	1	NA(b)	8
	120 µg/L Chlorophyll *a* nitrate spike	4.66	0.43(b)	1	4(b)	9
Effluent sample	Effluent	0.42	0.68	3	NA	162
	Effluent spike	4.70	5.76	3	NA	123
Process sample	Process	< 0.04	0.76	3	NA	NA
	Process spike	< 0.04(c)	5.78	3	NA	100(c)
Influent sample	Influent	0.61	0.59	3	NA	97
	Influent spike	5.26	1.76	3	NA	33

NA = not applicable.

(a) Inaccurate measurements as indicated by low RS values. MP-1 responses to nitrate at pH = 5 and pH = 9 compared to pH = 7 by %D.

(b) Inaccurate measurements as indicated by low RS values. MP-1 responses to nitrate in the presence of chlorophyll *a* compared to nitrate in the absence of chlorophyll *a* by %D.

(c) Reference method result for the spiked process sample was<0.04 (BQL), indicating a possible reference method interference. The MP-1 %R was calculated relative to the target spike concentration [unspiked process MP-1 nitrate measurement (0.76 mg N/L) plus target spike nitrate concentration (5.00 mg N/L)].

The MP-1 on-line effluent wastewater nitrate measurements are shown in Figure 6-6 with the reference method data. The MP-1 and reference method data are also presented in Table 6-7 with the corresponding %R values. The %R values for the on-line nitrate measurements ranged from 38% to 208%, with an average of 143%. A paired *t*-test was applied to the on-line effluent monitoring results to determine if the two analytical methods (reference method versus the MP-1) for nitrate gave significantly different values for the mean concentration. For the 11 nitrate measurement pairs, the SD of the absolute differences was 0.39 mg N/L, giving a value for t_{exp} of 0.625. The value for t_{crit} for the 95% confidence level and 10 degrees of freedom is 2.228. Since t_{crit} was greater than t_{exp} for nitrate measurements, the differences between the mean nitrate concentration measured by the two methods are not considered to be significant. It should be noted that, because of the small sample size and high variance in the nitrate measurements, the probability of detecting a true difference in the mean concentrations measured by the MP-1 and reference method is relatively low (less than 10%). Other statistical tests, including the non-parametric Wilcoxon signed rank test, were applied to the nitrate measurements. Since the results were the same as the *t*-test, only the *t*-test was presented.

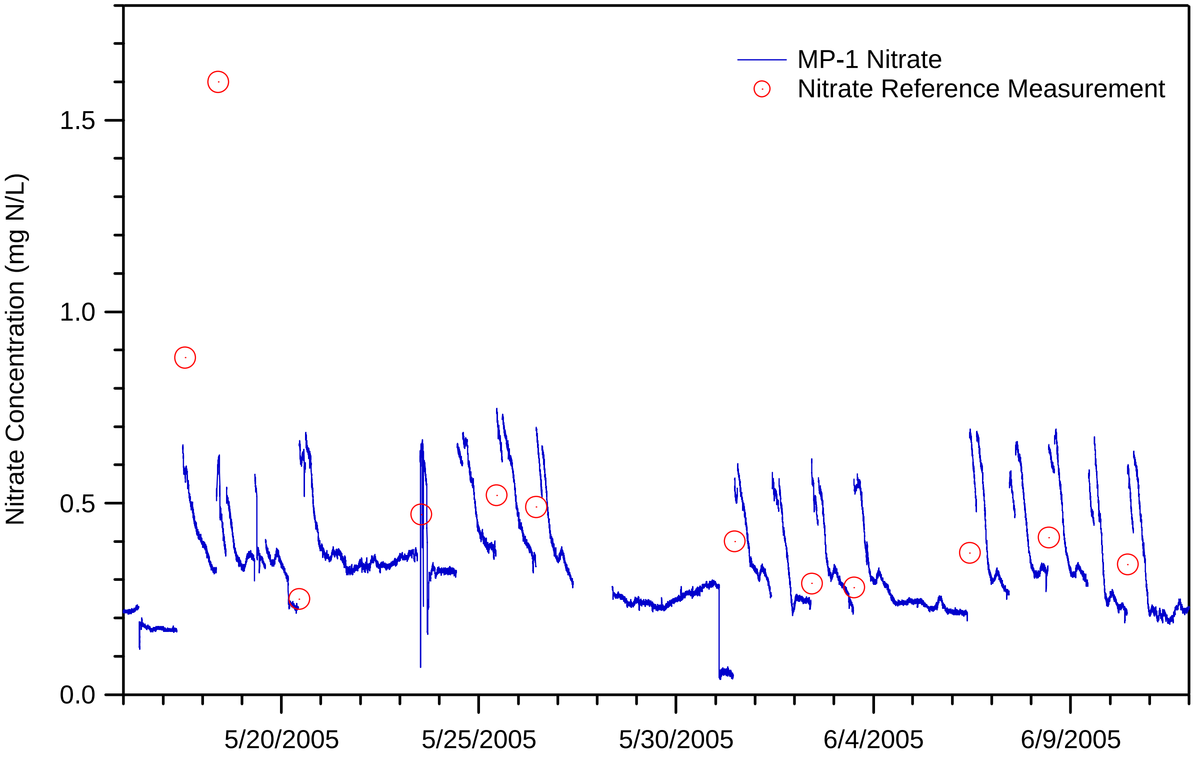


Figure 6-6. On-line MP-1 and Reference Method Nitrate Results

6.9 Data Completeness

The MP-1 was operating during 100% of the verification test, with the exception of two power losses at the plant that occurred for a total of approximately 38 hours. Over the duration of the verification test, the MP-1 conducted 26,057 nitrate measurements (including both on-line and

Table 6-7. Matrix Effects Results for On-Line Testing

	Nitrate Concentration (mg N/L)			
Sample Date and Time	Reference Method (X)	MP-1 (Y)	Y−X	%R
5/17/05 13:32	0.88	0.57	−0.31	65
5/18/05 9:32	1.60	0.61	−0.99	38
5/20/05 10:55	0.25[(a)]	0.65	NA	NA
5/23/05 13:03	0.47	0.64	0.17	135
5/25/05 11:01	0.52	0.74	0.22	143
5/26/05 11:02	0.49	0.70	0.21	142
5/31/05 11:45	0.40	0.55	0.15	137
6/2/05 10:34	0.29	0.60	0.31	208
6/3/05 12:23	0.28	0.55	0.27	195
6/6/05 10:37	0.37	0.68	0.31	183
6/8/05 10:47	0.41	0.65	0.24	158
6/10/05 10:45	0.34	0.59	0.25	174
Average	0.55	0.62	0.07	143
SD	0.39	0.06	0.39	52
Minimum	0.28	0.55		38
Maximum	1.60	0.74		208

NA = not applicable.
(a) Reference sample holding time was greater than 48 hours.

off-line measurements). The RS value was between 20 and 70 for 31% of all measurements recorded during the verification test. Measurements outside of this optimal range were caused by residue or entrained bubbles in the flow cell and include nitrate measurements recorded while the flow cell was being cleaned. Any testing activities for which the RS values were outside the optimal range (between 20 and 70) and the data used to evaluate the MP-1's performance were specified in this verification report.

6.10 Operational Factors

The MP-1 was installed at the test site by a vendor representative, and the installation was completed in less than two days. Data were recorded on the MP-1 personal computer every two minutes. The MP-1 could be operated by a user with minimal experience. A checklist was provided by the vendor representatives to establish whether the analyzer was in proper working order during the verification test. The checklist, shown in Appendix B, was completed by Battelle or OMI staff during daily checks of the MP-1 operating status. The checks were simple and quick, requiring approximately five minutes each day to complete. However, the daily cleaning of the MP-1 flow cell components (target and, less frequently, fiber assembly tip) took approximately 15 minutes to complete. Because of the large sample volumes needed to flush the MP-1 cell, testing of the MP-1 generated approximately 300 L of waste (5 L per off-line sample). The waste consisted of the nutrient standards and wastewater samples used to test the MP-1; no chemicals were added in the process of conducting measurements. After the two power losses at the test site, the MP-1 began conducting measurements again with little user intervention. Hand-recording of the individual channel values and nitrate concentrations during off-line testing was labor intensive, since the flow from the off-line measurement sample bottle needed to be adjusted during each sample, and the screen could not be read from the sample bottle location. The off-line testing was more manageable with two operators: one to manage the sample flow and one to hand-record the MP-1 channel values and nitrate concentrations.

Chapter 7
Performance Summary

The performance of the MP-1 was evaluated for its accuracy, bias, linearity, LOD, reproducibility, span and zero drift, interference effects, matrix effects, data completeness, and operational factors while sampling prepared nutrient standards and wastewater. The MP-1 measurement data were compared to reference measurements for the same samples to evaluate each performance parameter. The results of this evaluation are described below.

The accuracy of the MP-1 nitrate measurements was assessed over the range of 0.1 to 5 mg N/L in terms of %R relative to reference method measurements. Nitrate %R values ranged from 98% to 251%, with an average of 157%.

Bias of +57% was observed for the MP-1 nitrate measurements, calculated using data from the multi-level nitrate standards.

Linearity was evaluated in terms of slope, intercept, and r^2 over the nitrate range from 0 to 5 mg N/L. The 95% CIs for the slope and intercept of each regression were also calculated (and are shown in the following text in parenthesis). The slope of the regression line was 1.34 (± 0.37), with an intercept of 0.19 (± 0.77) and an r^2 value of 0.9574.

The MP-1 LOD for nitrate was determined from 15 DI water blank measurements conducted over the duration of the verification test. The average MP-1 nitrate measurement for DI water blanks was 0.043 mg N/L, with an SD of 0.063 mg N/L, resulting in a nitrate LOD of 0.232 mg N/L. The vendor-reported MP-1 nitrate LOD is 0.05 mg N/L (determined as three times the signal-to-noise ratio). Reference method DI water nitrate measurements ranged from < 0.04 to 0.08 mg N/L. Variability in the nitrate content of the DI water used for testing would be reflected in the calculated MP-1 LOD.

The reproducibility of the MP-1 was evaluated as the %RSD from five replicate challenges of a mixed nutrient standard (~5 mg N/L nitrate and ~3 mg P/L ortho-phosphate). The reproducibility for MP-1 nitrate measurements was 14%.

Drift, defined as three consecutive drift check results that fell either above or below the warning limit (± 2SD), was calculated for the MP-1 span (~5 mg N/L nitrate) response and zero response (to DI water). Drift in the normalized nitrate span response was not observed for the MP-1 relative to the corrected baseline response, although the last span drift check result was 1.22 mg N/L greater than the target concentration. However, if the uncorrected baseline response data were used to evaluate drift, none of the span check results fell within the warning limit. Drift was not observed in the MP-1 response to DI water blanks. The final drift check result was 0.04 mg N/L less than the average baseline zero response.

The effect of non-nitrate nutrients on the MP-1 response was assessed by challenging the MP-1 with the series of N- and P-containing compounds. All of the non-nitrate nutrients tested produced an interference effect less than or equal to 5% except for nitrite, for which a 97% interference effect was observed.

Matrix effects were evaluated by calculating the %R value for several matrices. The percent difference (%D) was calculated for test samples with varied pH and in the presence of chlorophyll a. The MP-1 RS values during the pH and chlorophyll *a* matrix effects challenges ranged from 5 to 7, indicating that the measurement accuracy was greatly impacted by residue on the flow cell components and, therefore, the MP-1 was not operating properly. The MP-1 nitrate measurements at pH 5 and 9 were within 1% (by %D) of measurements at pH 7. The nitrate measurement in the presence of chlorophyll *a* was 4% higher than the measurement at the same nitrate concentration in the absence of chlorophyll *a*. Given the MP-1's reduced sensitivity during the measurement of these samples, it is not known whether a change in the MP-1 response could have been detected. Percent recovery values for off-line measurements of effluent, process, and influent wastewater samples ranged from 33% to 162%. The %R values for the on-line nutrient measurements of effluent wastewater ranged from 38% to 208%, with an average of 143%. A paired *t*-test applied to the on-line effluent monitoring results indicated that differences in the mean nitrate concentration measured by the MP-1 and the reference method were not significant at the 95% confidence level. Because of the small sample size and high variance in the nitrate measurements, the probability of detecting a true difference in the mean concentration measured by the MP-1 and reference method is relatively low (less than 10%).

The MP-1 was operating during 100% of the verification test, with the exception of two power losses at the plant that occurred for a total of approximately 38 hours. Over the duration of the verification test, the MP-1 conducted 26,057 nitrate measurements (including both on-line and off-line measurements). The RS value was between 20 and 70 for 31% of all measurements recorded during the verification test. Measurements outside this optimal range were caused by residue or entrained bubbles in the flow cell and include nitrate measurements recorded while the flow cell was being cleaned. Any testing activities for which the RS values were outside the optimal range (between 20 and 70) and the data used to evaluate the MP-1's performance were specified in this verification report.

A user with minimal experience could operate the MP-1. The only maintenance required during the verification test included the daily cleaning of the flow cell components (target and, less frequently, fiber assembly tip), which required approximately 15 minutes to complete. Daily checks of the MP-1 were simple and quick, requiring less than five minutes per day.

Chapter 8
References

1. *Test/QA Plan for Verification of Nutrient Analyzers at a Wastewater Treatment Plant*, Battelle, Columbus, Ohio, April 2005.

2. *Standard Methods for the Examination of Water and Wastewater,* 18th Edition, American Public Health Association, Washington, DC, 1992.

3. *EPA Method 351.1 for Total Kjeldahl Nitrogen by Automated Colorimetry*, Issued 1971; Editorial Revision 1974 and 1978.

4. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center,* Version 5.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, March 2004.

APPENDIX A
MP-1 Measurement Instructions

Instructions for Operating the MP-1
During the ETV Nutrient Monitor Verification Test

1. Make sure the power strip has power and that the instrument is turned on−this is the red toggle switch on the left side of the instrument enclosure. The toggle lights up when the instrument is powered up.
2. The computer will boot up to a login window. Simply hit return, there is no password active.
3. At this point the MP.1 software will run automatically. Start the acquisition setup by clicking on the run arrow in the upper left. The arrow will go from white to black. This action will open the "measurements" window. Double click "LOAD" and select "DuPontConfig." Then click on "DONE."

   **At this point the instrument will begin sampling. After 30 seconds there should be a muffled clicking sound coming from inside the enclosure.

4. Move to the "channel view" window. Data will start appearing from left to right in data boxes at the bottom of the channel graphic as the instrument moves through its sampling loop. Once 9 data boxes are filled with numbers sampling will pause and an error message will appear (this is a glitch in the software). Close the error message box 4 times. After the 4th time sampling will resume and a number will appear in the "real-time measurement" box at the bottom of the screen. Once this error box sequence is complete it will not appear again unless data acquisition is restarted.
5. The number in the real time measurement box will be the nitrate concentration in mg/L N, if the cell is full of sample. Return to the "channel view" window. The real time measurement box will still be at the bottom of the window.

   **The 9 channels of data are used to measure nitrate by the absorption of UV radiation and to correct for matrix and turbidity effects. The channel designations as listed in the "measurements" window and values are displayed from left to right in the data boxes in "channel view":
   1 = 5Micron
   2 = nitrate
   3 = uv254
   4 = bac
   5 = hf
   6 = tf
   7 = RS
   8 = t600
   9 = cf
   **It's OK to run the cell dry for short periods of time (a few minutes), but if the instrument is left on for longer periods the cell should be filled with water (flow optional).

   **There is no need to ever start a data file. A new file will be created automatically when acquisition begins. A new file will also be created automatically every 24 hours if the instrument is left on. A new file will also be created if acquisition is halted then restarted. Data files are stored in C\data\ ; files are designated as a year-date-time stamp.

6. Halt acquisition at any time by clicking the STOP box in the bottom right.

Off-line Sample Feed

1. Close the intake and drain valves (both sides of the yellow Y-valve at the intake) with the small black valves. The brass stopcock can remain closed at all times.
2. Open the large red valve that points to the calibration shelf. This calibration valve can remain open during the entire manual feed process, but needs to be closed when sampling with the pump (see below). The other red valve on the intake line can be left open at all times.
3. If necessary, drain the cell and line through the drain valve (at the Y) before filling the cell.
4. The cell holds about 0.8 liters. Fill the cell quickly until water flows from the discharge tube, then back off and chase air from the line. Reduce flow to a drip to conserve sample (standard).

   **Flow rate has no effect on the measurement, unless bubbles are entrained in the system.

5. Wait until the instrument steps-through an entire loop AFTER the cell is filled. Record the data in each of the 9 channels and the nitrate concentration that appears in the real time measurement box along with the date and time. Write down the channel data each time the nitrate concentration is recorded. This record is important in the sense that the nitrate concentration is not stored in the file, only the raw data. While it is a simple matter to calculate the concentration in a spreadsheet later, this real-time record is useful for testing purposes.

   **The nitrate concentration only updates at the end of a loop and erroneously high or low values can appear in the real time measurement box if the cell was partially filled during the loop. Please disregard these values. Once water begins flowing from the outlet wait one full loop before recording data.

6. Remove the tube from the carboy before going on to the next solution, then drain the line, replace the tube, and refill the cell.

Sampling with the Pump

1. Close the red calibration valve. Leave this valve closed.
2. Open the intake valve at the yellow Y.
3. Check the outlet to make sure sample is flowing. Low and steady flow is best.
4. Record data in the 9 channels and the nitrate concentration in the real time measurement window as required. Remember to let one loop of data appear after initiating flow.

Maintenance

No maintenance is required unless sample flowing through the cell for long periods of time is highly turbid. Then it would be a good idea to drain the cell and line once a day.

APPENDIX B
MP-1 Daily Checklist

ZAPS MP-1 Daily Checklist

ETV Verification Test of Nutrient Analyzers for Plant Wastewater Monitoring

Observe Analyzer/Computer

☐ Verify that power is on
☐ Verify lamp is firing
☐ Check for error messages on computer screen (Error message:________________)

Morning Inspection:

☐ Visually inspect sample outlet flow
    ☐ Outlet stream is low steady flow
    ☐ No flow through system

☐ Record "RS" value: ____________________

☐ Perform back flush of feed system, drain MP-1 cell, and clean canister
    ☐ Time flow Stopped: ____________

☐ Clean target with optical cleaning solution and cloth (daily)

☐ Clean fiber assembly tip with optical cleaning solution and cloth wrapped around cleaning rod (weekly)

☐ Set sample stream flow for low steady flow
    ☐ Time flow Started: ____________ ☐ Record "RS" value: ____________

Afternoon Inspection:

☐ Visually inspect sample outlet flow
    ☐ Outlet stream is low steady flow
    ☐ No flow through system

☐ Record "RS" value: ____________________

☐ Perform back flush of feed system, drain MP-1 cell, and clean canister
    ☐ Time flow stopped: ____________

☐ Set sample stream flow for low steady flow
    ☐ Time flow started: ____________ ☐ Record "RS" value: ____________

Data File Transfer:

☐ Download Data
☐ E-mail data file to Battelle (daily M-F)
☐ Fax Data Sheets, Chain-of-Custodies, LRB entries, and Check Lists to Battelle (daily M-F)

Action: If any of the above issues fail or other problems occur, note below and contact:

Operator Name: __________________ Signature: __________________ Date: __________________
Comments: ____
____
____
____

Note: Please remember to sign and date this form in non-erasable ink.

APPENDIX C
MP-1 Flow Cell Cleaning Instructions

CLEANING THE FLOW CELL OF THE MP-1

Items required:

1. small alan wrench (provided)

2. optical cleaning clothes (provided)

3. cleaning solution (alcohol provided).

4. cleaning rod (a 11-12" long, 1-1.25" diameter wooden dowel rod, provided)

5. wash bottle of clean water.

6. rubber band.

Procedure:

1. Open the calibration valve. This will prevent suction that might dislodge the target lens. There should never be water behind the lens.

2. As you look at the plumbing board of the MP-1, the black wishbone fiber optic assembly is on the top left and sticks into the top of the flow cell. The BOTTOM of the flow consists of a cap with an eye-bolt handle. The cap is held in position with one alan screw. Remove this screw and grabbing the cap and handle, pull the cap out with a firm twisting motion. This cap has o-rings which have been greased so it should come out fairly easily. Don't worry about losing something; the cap and associated bits are one piece.

3. Once the cap is out of the flow cell you will see a black inner cell which screws into the cap base. Unscrew (normal counterclock) the black inner cell. Don't worry about touching the outside -just grab it and turn. Once you have the inner cell removed, clean the inside of the cell with clean water.

4. Once the inner cell is removed you will see the “target” which is a 3" long piece of plastic with a ball lens at the end. You can leave the target on the end cap. Just give the ball a squirt with the wash bottle and clean off any residue with a cleaning cloth wetted with cleaning solution. Once the ball is clean, screw back on the inner cell.

5. Place a piece of cleaning cloth over the flat end of the cleaning rod, holding it in place with the rubber band. Wet the cleaning cloth thoroughly with the cleaning fluid and insert the rod into the flow cell, cleaning cloth end first, until the cloth comes up against the fiber assembly tip. (Since the tip is in the middle of the cell, this will happen automatically if the rod is the proper diameter.) Don't worry about using a little force. The fiber assembly is silica, but it’s potted in a stainless steel tube so its plenty tough. Rotate the dowel and thus cleaning cloth against the fiber assembly tip several times. Check the cleaning cloth after you withdraw it from the flow cell. (You might want to repeat this bit with a second piece of cloth the first time, if the cloth is extremely dirty.)

6. Replace the cap assembly into the flow cell, lining up the witness line on the cap with the line on the flow-cell. This will ensure that the assembly is replaced at the same orientation every time, and also that the screw holes line up. Replace the alan screw.

7. Record the readings of the dry cell. Fill the cell with Milli-Q and record these readings as well.

*** It is important not to touch the inside of the inner cell, fiber assembly tip (accessed with the dowell), or the lens with anything but optical cleaning material.