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# Environmental Technology Verification Report

OPSIS INC. AR-500  
ULTRAVIOLET  
OPEN-PATH MONITOR

Prepared by



Battelle

Under a cooperative agreement with



U.S. Environmental Protection Agency

US EPA ARCHIVE DOCUMENT

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September 2000

# Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

## Opsis Inc. AR-500 Ultraviolet Open-Path Monitor

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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 (ORD) 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 permittees, buyers, and users of the technology, thus substantially 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. At present, there are 12 environmental technology areas covered by ETV. Information about each of the environmental technology areas covered by ETV can be found on the Internet at <http://www.epa.gov/etv.htm>.

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. In 1997, through a competitive cooperative agreement, Battelle was awarded EPA funding and support 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/07/07\\_main.htm](http://www.epa.gov/etv/07/07_main.htm).

## Acknowledgments

The authors wish to acknowledge the support of all those who helped plan and conduct the verification test, analyze the data, and prepare this report. In particular we would like to thank Brian Canterbury and Paul Webb of Battelle. We also acknowledge the participation of Carl Kamme and Paul Stenberg of Opsis in this verification test.

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## List of Abbreviations

AMS	Advanced Monitoring Systems
CEM	continuous emission monitor
cm	centimeter
CO	carbon monoxide
CO <sub>2</sub>	carbon dioxide
DOAS	differential optical absorption spectroscopy
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
GC/FID	gas chromatography/flame ionization detection
GC/MS	gas chromatography/mass spectroscopy
HCHO	formaldehyde
HF	hydrogen fluoride
Hg <sup>o</sup>	elemental mercury
HNO <sub>2</sub>	nitrous acid
kg	kilogram
lb	pound
m	meter
MDL	minimum detection limit
NH <sub>3</sub>	ammonia
NIST	National Institute of Standards and Technology
NO	nitric oxide
NO <sub>2</sub>	nitrogen dioxide
NO <sub>x</sub>	nitrogen oxides (= NO + NO <sub>2</sub> )
O <sub>2</sub>	oxygen
O <sub>3</sub>	ozone
ppb	parts per billion
ppb*m	parts per billion meters
ppbv	parts per billion by volume
ppm	parts per million
ppm*m	parts per million meters
QA	quality assurance
QC	quality control
QMP	Quality Management Plan
RH	relative humidity
RSD	relative standard deviation

SO<sub>2</sub>  
TSA

sulfur dioxide  
technical systems audit

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## Chapter 1 Background

The U.S. Environmental Protection Agency (EPA) has created 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 substantially 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, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of regulators, buyers and vendor organizations; 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 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 recently evaluated the performance of optical open-path monitors for use in ambient air or fence line measurements. This verification report presents the procedures and results of the verification test for the Opsis Inc. (Opsis) AR-500 ultraviolet (UV) optical open-path monitor.

## 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 AR-500. The following description of the AR-500 is based on information provided by the vendor.

The AR-500 ultraviolet differential optical absorption spectroscopy (UV-DOAS) system uses a broad-band Xenon light-source that projects a narrow beam of light across a monitoring path ranging from 1 to 1,000 meters in length. The receiver telescope focuses the light into a quartz fiber optic cable that connects to the DOAS analyzer.

The AR-500 is a compact, tunable, and fast-scanning spectrometer that measures spectra in the wavelength regions of interest. The system can provide path-averaged measurements, from the light source to the receiver, of, e.g., SO<sub>2</sub>, NO, NO<sub>2</sub>, NH<sub>3</sub>, O<sub>3</sub>, benzene, toluene, p-, m- and o-xylene, styrene, HNO<sub>2</sub>, HCHO, Hg<sup>0</sup>, and hydrogen fluoride (HF). The AR-500 is designated by the U.S. EPA as an Equivalent Method for measuring the criteria pollutants SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub> in ambient air.



**Figure 2-1. Opsis AR-500 Optical Open-Path Monitor**

The AR-500 evaluated in this verification test was bi-static, with separate emitters and receivers and a light beam that passed through the gas volume once.

From the AR-500 monitor, the results are transferred to a data collection system for presentation and reporting. The Opsis EnviMan software suite (Windows™ 95, 98, NT, 2000), provides the necessary functions for data analysis, presentations, and reporting.

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The AR-500 is designed for continuous operation and is used in a variety of applications, including ambient air quality measurements; fence-line measurements at industrial plants and airports; street-level monitoring and tunnel measurements; and industrial continuous emission monitoring (CEM) and process applications at power plants, incinerators, cement plants, and aluminum smelters.

The AR-500 uses the Opsis ER-150 emitter/receiver unit for the monitoring path. Two temperature signals are logged through the signal unit: the temperature of the calibration cell and the ambient air temperature. The temperature values are used to normalize data, which are stored in the analyzer and can be extracted directly from the analyzer in ASCII format. Data also are available on a separate computer that connects to the system.

The AR-500 measures 60 x 44 x 26.6 cm (23.6 x 17.3 x 10.5 inches). It weighs (including the case) approximately 50 kg (110 lb).

## Chapter 3 Test Design and Procedures

### 3.1 Introduction

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Optical Open-Path Monitors*.<sup>(1)</sup> The test was designed to challenge the AR-500 in a manner similar to that which would be experienced in field operations and was modeled after Compendium Method TO-16.<sup>(2)</sup> The monitor was challenged using an optically transparent gas cell filled with known concentrations of a target gas. The gas cell was inserted into the optical path of the monitor during operation under field conditions, simulating a condition where the target gas would be present in the ambient air. The gas cell was used to challenge the monitor in a controlled and uniform manner.

The monitor was challenged with three target gases at known concentrations, and the measurement result was compared to the known concentration of the target gas. The gases and concentrations used for testing the AR-500 are shown in Table 3-1. The verification was conducted by measuring the gases in a fixed sequence over three days. The sequence of activities for testing the monitor for a single gas is shown in Table 3-2.

**Table 3-1. Target Gases and Concentrations for Testing the AR-500**

Gas	Concentration Level	Target Gas Concentration (ppm*m)	Gas Cell Concentration <sup>a</sup> (ppm)
Ammonia	c1	3	60
	c2	6	120
	c3	10	200
	c4	20	400
NO	c1	2	40
	c2	5	100
	c3	10	200
	c4	15	300
Benzene	c1	2	40
	c2	3	60
	c3	5	100
	c4	10	200

<sup>a</sup>Length of gas cell = 4.98 cm



Table 3-2. Optical Open-Path Monitor Verification: Measurement Order for Each Target Gas

Meas. #	Gas Cell Conc.	Activity	# of Measurements	Times (min.)		Path Length (m)	Verification Parameter Calculated
				Integrate	Equilibrate		
1	N <sub>2</sub>	Change gas & stabilize	25	1	10	100	Accuracy, Concentration linearity, MDL
	N <sub>2</sub> <sup>a</sup>	Collect spectra				100	
2	c1	Change gas & stabilize	5	1	10	100	Accuracy, Concentration linearity
3	c1	Collect spectra	5	1		100	Source strength linearity
4	c1	Collect spectra - ND 1	5	1		100	Source strength linearity
5	c1	Collect spectra - ND 2	5	1		100	Source strength linearity
6	N <sub>2</sub>	Change gas & stabilize	5	1	10	100	Accuracy, Concentration linearity
	N <sub>2</sub>	Collect spectra				100	
7	c2	Change gas & stabilize	5	1	10	100	Accuracy, Concentration linearity, Interference effect (Int.)
	N <sub>2</sub>	Collect spectra				100	
8	N <sub>2</sub>	Change gas & stabilize	5	1	10	100	Accuracy, Concentration linearity
	N <sub>2</sub>	Collect spectra				100	
9	c3	Change gas & stabilize	5	1	10	100	Accuracy, Concentration linearity
	N <sub>2</sub>	Collect spectra				100	
10	c3	Collect spectra - ND 1	5	1		100	Source strength linearity
11	c3	Collect spectra - ND 2	5	1		100	Source strength linearity
12	c3	Collect spectra - ND 3	5	1		100	Source strength linearity
13	N <sub>2</sub>	Change gas & stabilize	5	1	10	100	Accuracy, Concentration linearity
	N <sub>2</sub>	Collect spectra				100	
14	c4	Change gas & stabilize	25	1	10	100	Accuracy, Concentration linearity, Precision
14b	N <sub>2</sub>	Collect spectra	5			100	Accuracy, Concentration linearity
	N <sub>2</sub>	Change gas & stabilize	25	5	10	100	Concentration linearity, MDL
15	N <sub>2</sub>	Collect spectra				250	Int.
16	N <sub>2</sub>	Change gas & stabilize	5	5	10	250	Int., Accuracy, Concentration linearity
17	c2	Collect spectra	5	5		250	Int., Accuracy, Concentration linearity
	N <sub>2</sub>	Change gas & stabilize	5	5	10	250	Int., Accuracy, Concentration linearity
18	N <sub>2</sub>	Collect spectra	5	5		250	Int., Accuracy, Concentration linearity
	N <sub>2</sub>	Change to Path length 3				optimum <sup>b</sup>	
19	N <sub>2</sub>	Collect spectra	5	1	10	optimum	Int., Accuracy, Concentration linearity
20	c2	Change gas & stabilize	5	1	10	optimum	Int., Accuracy, Concentration linearity
	N <sub>2</sub>	Collect spectra				optimum	Int., Accuracy, Concentration linearity
21	N <sub>2</sub>	Change gas & stabilize	25	1	10	optimum	Int., MDL
	N <sub>2</sub>	Collect spectra				optimum	

<sup>a</sup> See Table 3-1 for values of c1-c4 for the three target gases.

<sup>b</sup> Vendor optimum of 250 meters was selected.

### 3.2 Test Design

The verification test was performed near West Jefferson, Ohio, at an outdoor testing area belonging to Battelle, between April 11 and April 16, 2000. This location provided sufficient length and a direct line of sight for each of the two path lengths used during the test, and provided an area that was away from major chemical sources that might affect the testing. The AR-500 receiver was mounted on top of an 8-foot-tall, concrete block column near the edge of a lightly traveled road and pointed toward the AR-500 source, which was on top of another concrete block column located along the road at a distance of 100 meters. Another column was located at 250 meters from the receiver, and the source was located on top of this second column for the measurements that required a longer path length. The power supply, the computer, and the optical bench were located inside a temperature-controlled trailer near the receiver. The open space in the foreground of Figure 3-1 shows the test site at Battelle's West Jefferson facility. The testing area was near the edge of several farm fields. It also was located near a set of train tracks, and periodically trains passing by affected the NO measurements. In those cases, the testing was suspended until the train passed. Occasionally vehicles traveled along the road next to the test site. Testing was not suspended when vehicles passed, which may have contributed to background levels of NO.

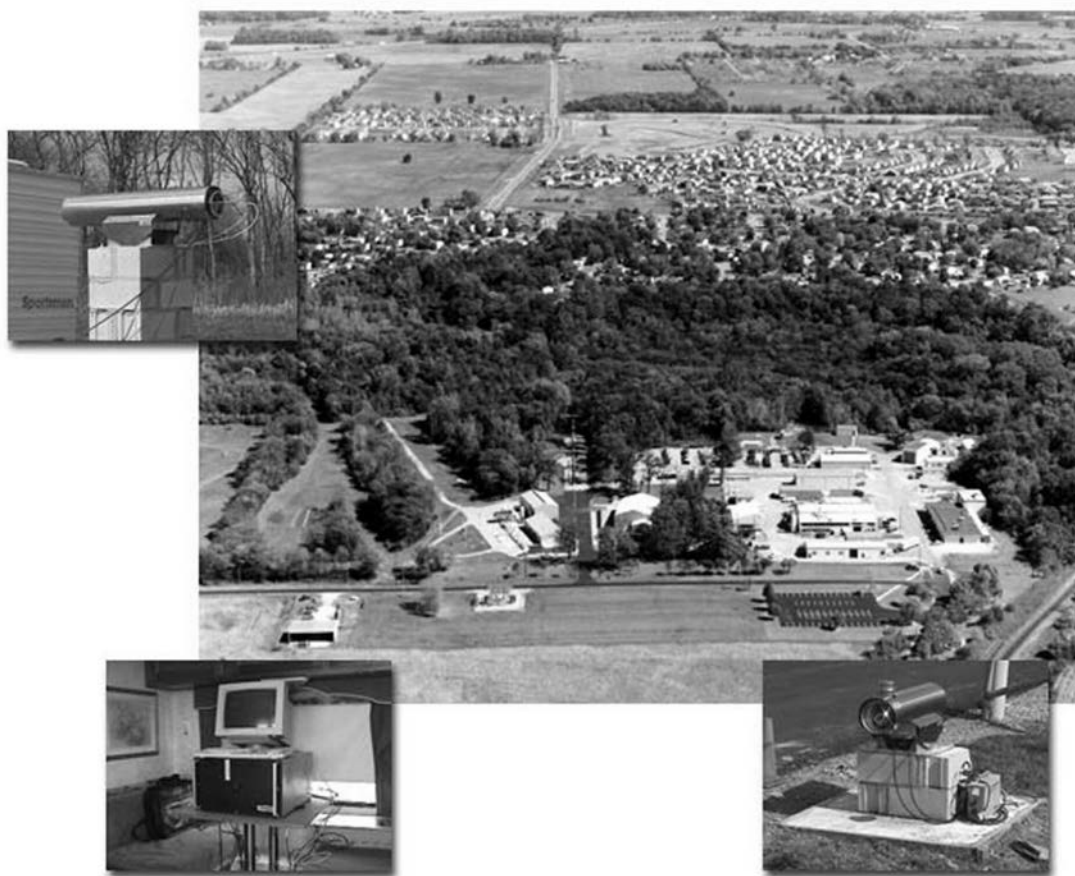


Figure 3-1. Test Site at West Jefferson Facility

The AR-500 was challenged with the target gases shown in Table 3-1 at known concentrations, and the AR-500 measurement was compared to the known concentration of the target gas. For each target gas, the monitor was set up as if it were operating in the field, except that an optically transparent gas cell was placed in the light beam's path (see Figure 3-2). National Institute of Standards and Technology (NIST) traceable or commercially certified standard gases, a calibrated gas diluter, and a supply of certified high-purity dilution gas were used to supply the target gases to the gas cell.

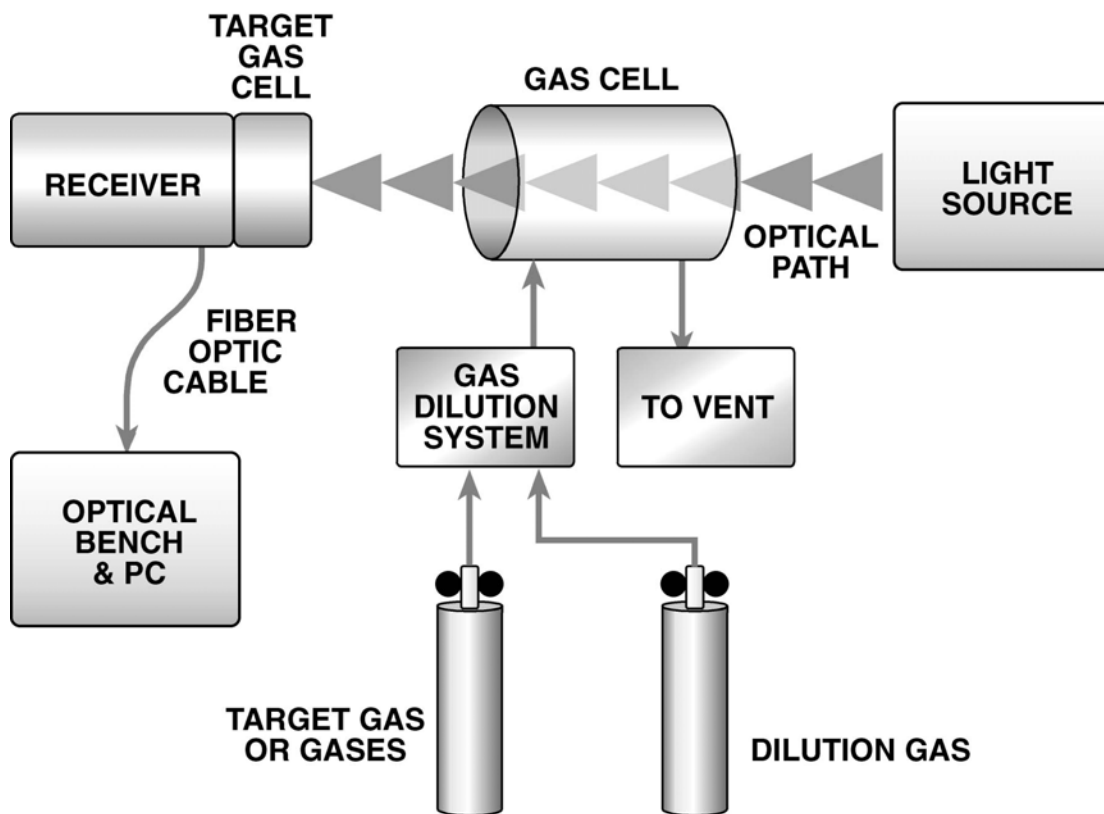


Figure 3-2. Optical Open-Path Monitor Setup

Target gases were measured at different path lengths, integration times, source intensities, and numbers of replicate measurements to assess

- Minimum detection limit (MDL)
- Source strength linearity
- Concentration linearity
- Accuracy
- Precision
- Sensitivity to atmospheric interferences.

The test procedures shown in Table 3-2 were nested, in that each measurement was used to evaluate more than one of the above parameters. In Table 3-2, N<sub>2</sub> in the gas cell concentration column denotes a period of cell flushing with high-purity nitrogen. The denotations c1, c2, c3,

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and c4 refer to the concentrations shown in Table 3-1. The last column shows the parameters to be calculated with the data from that measurement.

### **3.3 Experimental Apparatus and Materials**

#### **3.3.1 Standard Gases**

The standard gases diluted to produce target gas levels for the verification testing were NIST traceable gases or commercially certified gases. The gases were obtained in concentrations appropriate for dilution to the concentrations required for the test.

#### **3.3.2 Dilution Gas**

The dilution gas was ultra-high-purity nitrogen obtained from commercial suppliers.

#### **3.3.3 Gas Dilution System**

The dilution system used to generate known concentrations of the target gases was an Environics 2020 (Serial No. 2428). This system had mass flow capabilities with an accuracy of approximately  $\pm 1\%$ . The dilution system accepted a flow of compressed gas standard and could be diluted with high-purity nitrogen or air. It was capable of performing dilution ratios from 1:1 to at least 100:1.

#### **3.3.4 Gas Cell**

A vendor-provided quartz gas cell 4.98 centimeters in length was integrated into the end of the receiver. This cell had two 1/4-inch tube fittings that allowed the target gas to flow through.

#### **3.3.5 Temperature Sensor**

A thermocouple with a commercial digital temperature readout was used to monitor ambient air and test cell temperatures. This sensor was operated in accordance with the manufacturer's instructions and was calibrated against a certified temperature measurement standard within the 12 months preceding the verification test.

#### **3.3.6 Ozone Sensor**

The sensor used to determine ozone in ambient air was a commercial UV absorption monitor (ThermoEnvironmental Model 49) designated by U.S. EPA as an Equivalent Method for this measurement. The UV absorption method is preferred for this application over the Reference Method (which is based on ethylene chemiluminescence) because the UV method is inherently calibrated and requires no reagent gases or calibration standards. The sensor was operated in accordance with the manufacturer's instructions.

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### 3.3.7 *NO/NH<sub>3</sub> Monitor*

A chemiluminescent nitrogen oxides monitor [Advanced Pollution Instrumentation (API) Model 200, Serial No. 142] was used with a high-temperature ammonia converter (API Model 1000, Serial No. 100-233-120F-120H) to monitor the NO and NH<sub>3</sub> concentrations supplied to the optical cell for verification testing. This monitor sampled gas immediately downstream of the optical cell to confirm the NO or NH<sub>3</sub> concentrations prepared by dilution of high-concentration NO or ammonia standards. The API monitor was calibrated with a NIST-traceable commercial standard cylinder of NO in nitrogen. The conversion efficiency for NH<sub>3</sub> was checked by comparing the calibration slope for NO with that found in calibrations with NH<sub>3</sub>. All NH<sub>3</sub> measurements were corrected for the NH<sub>3</sub> conversion efficiency, which was generally greater than 95%.

### 3.3.8 *Benzene Measurement*

Benzene concentrations provided to the optical cell were checked by collecting a sample at the exit of the cell using pre-cleaned Summa® stainless steel air sampling canisters. The collected sample was then analyzed for benzene by gas chromatography with flame ionization detection (GC-FID), according to a method based on EPA Method 18. This method used certified commercial standards of propane in air for calibration.

## 3.4 Test Parameters

### 3.4.1 *Minimum Detection Limit*

The MDL was calculated for each target gas by supplying pure nitrogen to the test cell in the optical path of the monitor and taking a series of 25 measurements using integration times of 1 and 5 minutes. The MDL was defined as two times the standard deviation of the calculated target gas concentrations. The sequence of measurements was conducted at both integration times, twice at a 100-meter path length and once at a 250-meter path length.

### 3.4.2 *Linearity*

Two types of linearity were investigated during this verification: source strength and concentration. Source strength linearity was investigated by measuring the effects of reducing the source intensity on the monitor's performance. In the field, light signal levels can be attenuated by mist, rain, snow, or dirty optical components. As a constant concentration of target gas was introduced into the gas cell, the light intensity of the source was reduced by placing an aluminum wire mesh in the path of the light to determine how the monitor's measurements were affected by an attenuated light source. Three aluminum wire screens of various meshes were placed in the beam path. These screens were approximately 1 foot square and had a mesh spacing of approximately ¼, ½, and 1 inch. At each of these attenuation levels, a measurement was made, and the monitor analyzed for the target gas. The test was performed at two concentrations (2 ppm\*m and 10 ppm\*m) using NO.

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Concentration linearity was investigated by challenging the AR-500 with each target gas at the concentrations shown in Table 3-1, while the path length and integration time were kept constant. At each concentration, the monitor response was recorded and its linearity evaluated by comparing the recorded response with the input target gas concentration.

### **3.4.3 Accuracy**

Accuracy of the monitor relative to the gas standards was verified by introducing known concentrations of the target gas into the cell. The gas cell was first flushed with at least five cell volumes of nitrogen, and five zero measurements were recorded. The target gas was then introduced into the cell and, after flushing with at least five cell volumes, five measurements of the target gas were obtained. The cell was again flushed with at least five cell volumes of nitrogen, and five more zero measurements were recorded. The concentration of the target gas was the average value with the target gas in the cell, minus the average of the zero measurements.

The accuracy was evaluated at concentrations denoted as c1 through c4, using an integration time of 1 minute. The accuracy was then evaluated at concentration c2 using a longer integration time, and then again at concentration c2 during the interference measurements (Table 3-2). The percent relative accuracy for an experimental condition is the absolute value of the difference between the average monitor response and the reference monitor response, divided by the reference monitor response, times 100 (see Section 5.3).

### **3.4.4 Precision**

The procedure for determining precision was very similar to the procedure for determining accuracy. The gas cell was flushed with at least five cell volumes of nitrogen. The target gas was then introduced into the cell and, after flushing with at least five cell volumes, 25 measurements of the target gas were obtained. The relative standard deviation (RSD) of this set of measurements was the precision at the target gas concentration. Precision was evaluated by this procedure at one concentration of the target gas (see Table 3-2).

### **3.4.5 Interferences**

The effects of interfering gases were established by supplying the gas cell with a target gas and varying the distance (i.e., the path length) between the source and detector of the monitor. For the UV measurement of the target gases, the main interferences in ambient air are O<sub>2</sub> and O<sub>3</sub>, and changing the path length effectively changed the amount of interferants in the light path for the measurement. The purpose of the interference measurements was to determine the effects that the ambient atmospheric gases have on the accuracy and MDL of the AR-500. These tests were performed using two different integration times to determine the effect of integration time on the monitor's ability to perform measurements with interfering gases in the light path.

To determine the effect of the interferences, the path length was first set to 100 meters. Then, the gas cell was supplied with nitrogen and, after flushing with at least five cell volumes, five measurements were recorded. Next, the target gas was introduced into the cell; and, after



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similarly flushing the cell, five measurements were recorded. Finally, the cell was flushed again and five more measurements were recorded. Atmospheric concentrations of O<sub>2</sub> and O<sub>3</sub> were recorded at the beginning and the end of these measurements.

The path length was then set to 250 meters, which was the length that Opsis chose as optimum (i.e., the path length that theoretically yields the best signal-to-noise ratio), and the entire measurement procedure was repeated. The sensitivity of the monitor to the interferant was calculated by comparing the results at different path lengths (i.e., different ppm\*m levels of O<sub>2</sub> and O<sub>3</sub>).

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## Chapter 4 Quality Assurance/Quality Control

Quality assurance/quality control (QA/QC) procedures were performed in accordance with the quality management plan (QMP) for the AMS Center<sup>(3)</sup> and the test/QA plan<sup>(1)</sup> for this verification test.

### 4.1 Data Review and Validation

Test data were reviewed by the Verification Testing Coordinator and disclosed to the Verification Testing Leader. The Verification Testing Coordinator reviewed the raw data and the data sheets that were generated each day. Laboratory record notebook entries also were signed and dated.

### 4.2 Changes from the Test/QA Plan

Two types of changes from the test/QA plan could occur: planned changes to improve the test procedures for a specific vendor (amendments) and changes that occurred unexpectedly (deviations). Deviations from the test/QA plan were as follows:

- The test/QA plan called for a one-over-one data review within two weeks of generating the data. While the entire data set was reviewed within this two-week period, documentation of this task was not completed. Although this task was documented after the two-week period, no reduction in the quality of the data occurred.
- The thermocouple used in the verification test to monitor ambient air temperatures had not been calibrated within the previous six months, as specified in the test/QA plan. The thermocouple had been calibrated within one year, however, and was still within its calibration certification period. In addition, the thermocouple temperature measurement agreed with the mercury bulb thermometer temperature measurement during the performance audit.
- The test/QA plan calls for a performance evaluation audit of the NO measurement using a calibration standard obtained from an independent supplier. Instead, a separate NO standard obtained from the same manufacturer was used for the PE audit.



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- An additional measurement was recorded because trains and trucks in the area caused varying background levels of NO. The additional background measurement was taken to help overcome this problem of fluctuations in the background NO levels.
  - The test/QA plan called for acid rain CEM zero nitrogen to be used to flush the cell and as dilution gas. Instead, ultra-high-purity nitrogen was used.

Deviation reports have been filed for each deviation.

Before the verification test began, several planned amendments were made to the original test/QA plan to improve the quality or efficiency of the test. These procedural changes were implemented and, in each case, either increased the quality of the collected data set or removed inefficiencies in the test, ultimately resulting in a reduced test duration. A brief summary of these amendments is provided below:

- MDL was determined using twice the standard deviation, as described in section 3.4.1. The test/QA plan inadvertently called for the MDL to be determined by two different methods. The correct method was chosen and used during the verification test.
- The benzene analysis procedure was changed from that specified in the test/QA plan. The test/QA plan specified using Method 18, which is designed to determine the hydrocarbon emissions from combustion or other source facilities. This method broadly describes an analysis procedure, but does not specify how the analysis is to be done and calls for the use of Tedlar bags rather than Summa® canisters. Instead of as described in the test/QA plan, the analysis was done according to Battelle's GC/FID/MS analysis procedure for canister samples.
- The long and the short path lengths in the test/QA plan, which were specified as 100 and 400 meters, were changed to meet the specific technology requirements of the monitor tested.
- The order of testing in the test/QA plan was changed. The test order was originally developed to maximize the efficiency of the test procedure. Several improvements were made to the test matrix to further improve its efficiency. For example, instead of conducting all of the measurements for one gas then changing to the next gas, all of the short path measurements were conducted before moving to the long path. This was done because changing the path length was more time consuming than changing the target gas.
- One additional test was added to complete the data set collected. Originally, the test/QA plan lacked a nitrogen flush after measurement 14, under the same conditions as measurement 14. This additional measurement was added to the test matrix as measurement #14b (see Table 3-2).
- The test/QA plan specified that source strength linearity would be tested for each of the gases. The original intent was to conduct this test for one gas only. The source strength linearity test thus was conducted only for a single gas.

- 
- The original test/QA plan specified that the ambient oxygen concentration be monitored by an oxygen analyzer. Instead, the ambient oxygen concentrations were assumed to be 20.9%.
  - Although monitoring CO was part of the test/QA plan, it was decided that CO measurements would not add any useful information to the verification. No CO monitoring was conducted.
  - The test/QA plan called for determining ammonia converter efficiency by placing two converters in series with the NO monitor. Instead, conversion efficiency was calculated by comparing NO and NH<sub>3</sub> calibration curves.

Amendments required the approval of Battelle's Verification Testing Leader and Center Manager. A planned deviation form was used for documentation and approval of all amendments.

Neither the deviations nor the amendments had a significant impact on the test results used to verify the performance of the optical open-path monitors.

## **4.3 Calibration**

### ***4.3.1 Gas Dilution System***

Mass flow controllers in the Environics gas dilution system were calibrated prior to the start of the verification test by means of a soap bubble flow meter. Corrections were applied to the bubble meter data for pressure, temperature, and water vapor content.

### ***4.3.2 Temperature Sensor***

The thermocouple was calibrated by comparing it to a certified standard in September 1999. This instrument has a one-year calibration period, and so was still within its calibration interval.

### ***4.3.3 Ozone Sensor***

The UV absorption method of ozone measurement is inherently calibrated, relying as it does on the accurately determined absorption coefficient of ozone. As a result, routine calibration of the ozone monitor is not needed. However, the monitor was operated according to the manufacturer's directions, with careful attention to the diagnostic indicators that assure proper operation.

### ***4.3.4 NO/NH<sub>3</sub> Monitor***

The NO/NH<sub>3</sub> monitor was calibrated with both NO and NH<sub>3</sub> standards. The NO standard was a Certified Master Class Calibration Standard of 6,960 ppm NO in nitrogen, of ±1% analytical uncertainty (Scott Specialty Gases, Cylinder No. K026227). The NH<sub>3</sub> standard was also a Certified Master Class Calibration Standard, of 494 ppm NH<sub>3</sub> in air, of ± 2% analytical

uncertainty (Scott, Cylinder No. ALM 005256). The ratio of the slopes of the NH<sub>3</sub> and NO calibration curves established the NH<sub>3</sub> conversion efficiency.

A performance evaluation audit was also conducted once during the test, in which the API monitor’s response was tested with a different NO standard. For that audit, the comparison standard used was a NIST-traceable EPA Protocol Gas of 3,925 ppm NO in nitrogen, with ± 1% analytical uncertainty (Scott, Cylinder No. ALM 057210).

#### 4.3.5 Benzene Measurement

The GC/FID measurement for benzene was calibrated using two standard gases. One was an EPA Protocol Gas of 32.73 ppm propane in air, with analytical uncertainty of ± 2% (Cylinder No. AAL 20803, Scott Specialty Gases). The other was a Certified Working Class Calibration Standard of 340 ppm propane in air, with ± 5% analytical uncertainty (Cylinder No. ALM 025084, also from Scott).

#### 4.4 Data Collection

Data acquisition was performed primarily by Battelle and the vendor. Table 4-1 summarizes the type of data recorded (see also Appendix A); where, how often, and by whom the recording was made; and the disposition or subsequent processing of the data. Test records were then converted to Excel spreadsheet files.

**Table 4-1. Summary of Data Recording Process for the AR-500 Verification Test**

<b>Data Recorded</b>	<b>Recorded By</b>	<b>Where Recorded</b>	<b>When Recorded</b>	<b>Disposition of Data</b>
Dates, Times, Test Events	Battelle	Data Sheet	Start of each test, whenever testing conditions changed	Used to compile result, manually entered into spreadsheet as necessary
Test Parameters (temp., RH, etc.)	Battelle	Data Sheet	Every hour during testing	Transferred to spreadsheet
Interference Gas Concentrations	Battelle	Data Sheet	Before and after each measurement of target gas	Transferred to spreadsheet
Target Gas Concentrations	Battelle	Data Sheet	At specified time during each test	Transferred to spreadsheet
Optical Open-Path Monitor Readings	Battelle	Data Sheet	At specified time during each test	Transferred to spreadsheet

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## 4.5 Assessments and Audits

### 4.5.1 *Technical Systems Audit*

A technical systems audit (TSA) was conducted on April 13 and 14 for the open-path monitor verification test conducted in early 2000. The TSA was performed by Battelle's Quality Manager as specified in the AMS Center QMP. The TSA ensures that the verification test is conducted according to the test/QA plan<sup>(1)</sup> and that all activities associated with the test are in compliance with the AMS QMP.<sup>(3)</sup> Specifically, the calibration sources and methods used were reviewed and compared with test procedures in the test/QA plan. Equipment calibration records and gas certificates of analysis were reviewed. The conduct of the testing was observed, and the results were assessed.

All findings noted during the TSA on the above dates were documented and submitted to the Verification Testing Coordinator for correction. The corrections were documented by the Verification Testing Coordinator and reviewed by Battelle's Quality Manager, Verification Testing Leader, and Center Manager. None of the findings adversely affected the quality or outcome of this verification test, and all were resolved to the satisfaction of the Battelle Quality Manager. The records concerning the TSA are permanently stored with the Battelle Quality Manager.

In addition to the internal TSA performed by Battelle's Quality Manager, an external TSA was conducted by EPA on April 14, 2000. The TSA conducted by EPA included all the components listed in the first paragraph of this section. A single finding was noted in the external TSA, which was documented in a report to the Battelle Center Manager for review. A response and corrective action were prepared and returned to EPA. The finding did not adversely affect the quality or outcome of this verification test.

### 4.5.2 *Performance Evaluation Audit*

A performance evaluation audit was conducted to assess the quality of the measurements made in the verification test. This audit addressed only those measurements made by Battelle in conducting the verification test. The performance audit procedures (Table 4-2) were performed by the technical staff responsible for the measurements. Battelle's Quality Manager was present to assess the results. The performance evaluation audit was conducted by comparing test measurements to independent measurements or standards.

Each of the required procedures for the performance evaluation audit was conducted during the testing period in accordance with the direction specified in the test/QA plan, except for the deviation concerning the NO performance evaluation, listed in Section 4.2. The results from the performance evaluation are shown in Table 4-2. The temperature measurement agreed to within 0.4°C and the ozone to within 3 ppb. The monitor used for NO/NH<sub>3</sub> determination agreed with the performance evaluation standard within 4%, at a concentration of 75 ppm.

**Table 4-2. Summary of Performance Evaluation Audit Procedures**

<b>Measurement Audited</b>	<b>Audit Procedure</b>	<b>Expected</b>	<b>Actual</b>	<b>Difference</b>
Temperature	Compare to independent temperature measurement (Hg thermometer)	10°C	9.6°C	0.4°C
Ozone	Compare to independent ozone measurement	16.2 ppb	19 ppb	17.3%
NO/NH <sub>3</sub>	Compare using another NO standard from the same supplier	75 ppm	72 ppm	-4.0%
Benzene	Compare to results of gas chromatographic analysis of canister sample	0 ppm	0 ppm	0%
		40 ppm	37 ppm	-7.5%
		60 ppm	56 ppm	-6.7%
		200 ppm	168 ppm	-16.0%

The benzene concentrations were audited by independent analysis of the test gas mixture supplied to the optical cell during verification testing. The results of the performance audit for the benzene concentrations were within 10% (except one canister, which was within 16%) of the expected concentrations, which met the test/QA plan criterion.

**4.5.3 Data Quality Audit**

Battelle’s Quality Manager audited at least 10% of the verification data acquired in the verification test. The Quality Manager traced the data from initial acquisition, through reduction and statistical comparisons, to final reporting. All calculations performed on the data undergoing audit were checked.

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## Chapter 5 Statistical Methods

The following statistical methods were used to reduce and generate results for the performance factors.

### 5.1 Minimum Detection Limit

The MDL is defined as the smallest concentration at which the monitor's expected response exceeds the calibration curve at the background reading by two times the standard deviation ( $\sigma_o$ ) of the monitor's background reading.

$$MDL = 2\sigma_o$$

### 5.2 Linearity

Both concentration and source strength linearity were assessed by linear regression with the certified gas concentration as independent variable and the monitor's response as dependent variable. Linearity was assessed in terms of the slope, intercept, and correlation coefficient of the linear regression.

$$y = mx + b$$

where  $y$  is the response of the monitor to a target gas,  $x$  is the concentration of the target gas in the optical cell,  $m$  is the slope of the linear regression curve, and  $b$  is the zero offset.

### 5.3 Accuracy

The relative accuracy ( $A$ ) of the monitor with respect to the target gas was assessed by

$$A = \frac{|\bar{R} - \bar{T}|}{\bar{R}} \times 100$$

where the bars indicate the mean of the reference (R) values and monitor (T) results.

## 5.4 Precision

Precision was reported in terms of the percent RSD of a group of similar measurements. For a set of measurements given by  $T_1, T_2, \dots, T_n$ , the standard deviation ( $\sigma$ ) of these measurements is

$$\sigma = \left[ \frac{1}{n-1} \sum_{k=1}^n (T_k - \bar{T})^2 \right]^{1/2}$$

where  $\bar{T}$  is the average of the monitor's readings. The RSD is calculated from

$$RSD = \left| \frac{\sigma}{\bar{T}} \right| \times 100$$

and is a measure of the measurement uncertainty relative to the absolute value of the measurement. This parameter was determined at one concentration per gas.

## 5.5 Interferences

The extent to which interferences affected MDL and accuracy was calculated in terms of sensitivity of the monitor to the interferant species, relative to its sensitivity to the target gas, at a fixed path length and integration time. The relative sensitivity is calculated as the ratio of the observed response of the monitor to the actual concentration of the interferant. For example, a monitor that indicates 26 ppm of cyclohexane in air with an interference concentration of 100 ppm of  $\text{CO}_2$  indicates 30 ppm of cyclohexane when the  $\text{CO}_2$  concentration is changed to 200 ppm. This would result in an interference effect of  $(30 \text{ ppm} - 26 \text{ ppm})_{\text{cyclohexane}} / (200 \text{ ppm} - 100 \text{ ppm})_{\text{CO}_2} = 0.04$ , or 4% relative sensitivity.



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## Chapter 6 Test Results

The results of the verification test of the AR-500 are presented in this section, based upon the statistical methods described in Chapter 5. The monitor was challenged with nitric oxide (NO), benzene, and ammonia over path lengths of 100 to 250 meters. These gases were chosen because they are typical gases that this monitor would be used to detect in the field. Test parameters included MDL, linearity, accuracy, precision, and the effects of atmospheric interferants on concentration measurements. In many cases, verification results are based on comparing the test cell concentration of target gas calculated from the AR-500's open-path measurement to the actual gas cell concentration. In addition, where appropriate, the path-average concentrations are noted. The AR-500 reports concentration averages over the entire path length being monitored. In this report, a measured concentration of 1.5 ppb means that the path average concentration is 1.5 ppb over the entire 100 or 250 meters, depending upon the stated path length. The path-average concentration is determined by multiplying the gas cell concentration by the gas cell length and then dividing by the path length used during the given measurement.

While the measurements conducted during this verification test were done in as controlled a way as possible, several uncontrollable factors should be pointed out before the results are presented. There may have been sources of the target gases near the test site that could have affected the monitor's response during these measurements such as trains, highway traffic, and local vehicular traffic. Attempts were made to suspend testing during obvious periods of source activity; however, not all potential sources of the target gases could be eliminated.

### 6.1 Minimum Detection Limit

The MDL was calculated from measurements in which there were no target gases in the gas cell, but the monitor analyzed the absorption spectra for the presence of a target gas. The data used to determine the MDL were obtained under several experimental conditions, including different path lengths and integration times, as shown in Table 6-1. Table 6-2 shows the results of the MDL calculations, in terms of both the path-average MDL value in ppb and the integrated MDL value in ppb\*m over the total path.

The results in Table 6-2 show that the AR-500 has an MDL of between 0.9 and 1.4 ppb for NO, 0.4 and 1.5 ppb for benzene, and 2.8 and 5.8 ppb for ammonia, at the path lengths and integration times tested. Changing the path lengths between 100 and 250 meters and changing the integration



**Table 6-1. MDL Data for the AR-500**

Measurement Number	NO			Benzene			Ammonia		
	Path Length (m)			Path Length (m)			Path Length (m)		
	100	250	100	100	250	100	100	250	100
	Integration Time (min)			Integration Time (min)			Integration Time (min)		
	1	1	5	1	1	5	1	1	5
	Concentration (ppb)								
1	1.41	2.50	2.40	2.70	0.30	-0.30	-5.70	1.41	-0.40
2	1.43	1.60	4.28	2.70	0.20	0.30	-2.30	1.50	0.00
3	1.06	1.80	3.01	2.80	0.10	0.30	-6.30	1.00	-0.40
4	1.82	2.50	2.70	2.60	-0.10	0.10	-2.50	2.70	-0.50
5	0.59	1.50	2.35	2.70	0.00	0.30	-1.80	0.20	-0.50
6	1.94	2.00	2.79	2.90	0.30	0.30	1.20	2.80	-1.10
7	1.75	1.70	2.13	2.80	0.40	0.50	-3.50	3.90	2.50
8	1.68	1.00	5.63	2.90	0.60	0.30	-9.70	-0.10	-1.10
9	2.01	1.90	2.68	2.50	0.70	0.00	-1.60	1.30	-2.40
10	1.29	2.30	2.55	3.00	0.00	0.10	-2.90	0.20	-2.00
11	0.98	2.00	2.88	2.60	-0.10	0.00	-0.90	-0.20	0.60
12	1.73	1.80	2.47	2.50	-0.20	0.30	-1.00	0.20	2.60
13	1.39	1.90	2.89	3.40	0.10	0.30	0.40	1.20	-0.20
14	1.78	1.50	3.21	3.00	-0.10	0.30	-1.60	4.20	-0.60
15	1.23	1.30	2.82	-0.70	-0.20	0.50	-4.10	1.60	0.60
16	0.93	1.50	2.56	2.80	0.00	0.60	1.40	0.30	1.40
17	0.16	2.40	3.17	2.60	0.00	0.20	0.90	1.10	0.90
18	1.42	2.40	3.28	3.30	-0.20	0.00	0.00	-0.80	1.70
19	1.71	2.90	2.78	3.00	0.10	0.30	-0.30	-0.90	-1.60
20	0.51	2.50	2.64	2.50	-0.40	0.30	1.20	2.10	-0.80
21	1.07	2.00	2.64	2.10	0.10	0.30	2.60	3.50	-2.60
22	0.87	2.20	2.40	2.50	0.00	-0.10	-0.10	0.40	-2.60
23	1.06	1.60	2.39	2.70	0.00	-0.10	0.70	1.20	-0.30
24	0.43	1.50	2.61	2.40	0.10	0.10	2.50	2.60	1.90
25	0.76	2.10	2.59	3.30	0.20	0.00	-1.20	2.60	0.40

times between 1 and 5 minutes had little consistent effect on the MDL. For two of the three target gases, the MDL is lowest at the 250-meter path length, which is consistent with the vendor's claim of a better signal-to-noise ratio at longer path length.

**Table 6-2. Minimum Detection Limits of the AR-500**

Target Gas	Path Length (m)	Integration Time (min)	MDL (ppb)	MDL (ppb*m)
NO	100	1	1.01	100
NO	250	1	0.91	225
NO	100	5	1.42	140
Benzene	100	1	1.51	150
Benzene	250	1	0.50	125
Benzene	100	5	0.42	42.2
Ammonia	100	1	5.8	580
Ammonia	250	1	2.8	700
Ammonia	100	5	3.1	310

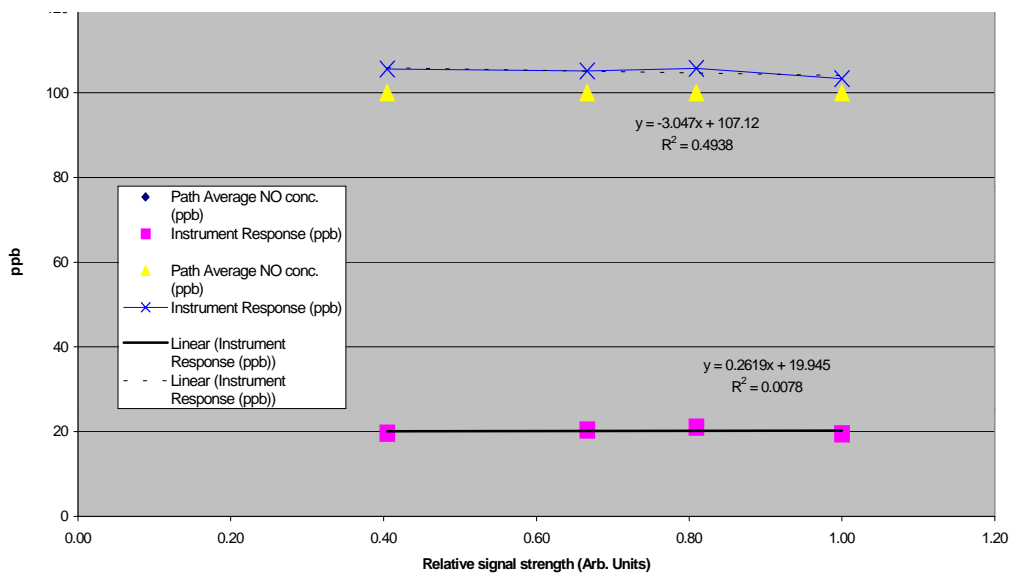
## 6.2 Linearity

### 6.2.1 Source Strength Linearity

Table 6-3 shows the results from this evaluation of source strength linearity, and Figure 6-1 shows a plot of the effect that the light signal level has on the monitor's measurements. In Table 6-3, the relative signal power is the measure of light attenuation during that measurement.

**Table 6-3. Source Strength Linearity of the AR-500**

Relative Signal Power	NO Concentration (ppb)	Monitor Response (ppb)
1.00	20	19.5
0.81	20	21.1
0.67	20	20.4
0.40	20	19.6
1.00	100	103
0.81	100	106
0.67	100	105
0.40	100	106



**Figure 6-1. Source Strength Linearity Plot of the AR-500**

For example, a relative signal power of 0.81 means that the light level for that test is 81% of what the light level is during normal operating conditions. The NO concentration is the concentration of gas being delivered to the gas cell during the measurement, and the monitor response is the resulting reading from the AR-500. The source strength results show that there is little degradation in monitor performance during conditions of declining source strength. The maximum differences between AR-500 response and the NO concentration were 1.1 ppb at 20 ppb NO and 6 ppb at 100 ppb NO. The data do not indicate any consistent effect of source strength on NO measurement, with source reductions of up to 60%. In addition, the coefficients of determination ( $r^2$ ) of 0.0078 and 0.4938, shown in Figure 6-1, indicate that reducing the source strength had little effect on the monitor's response over the range tested.

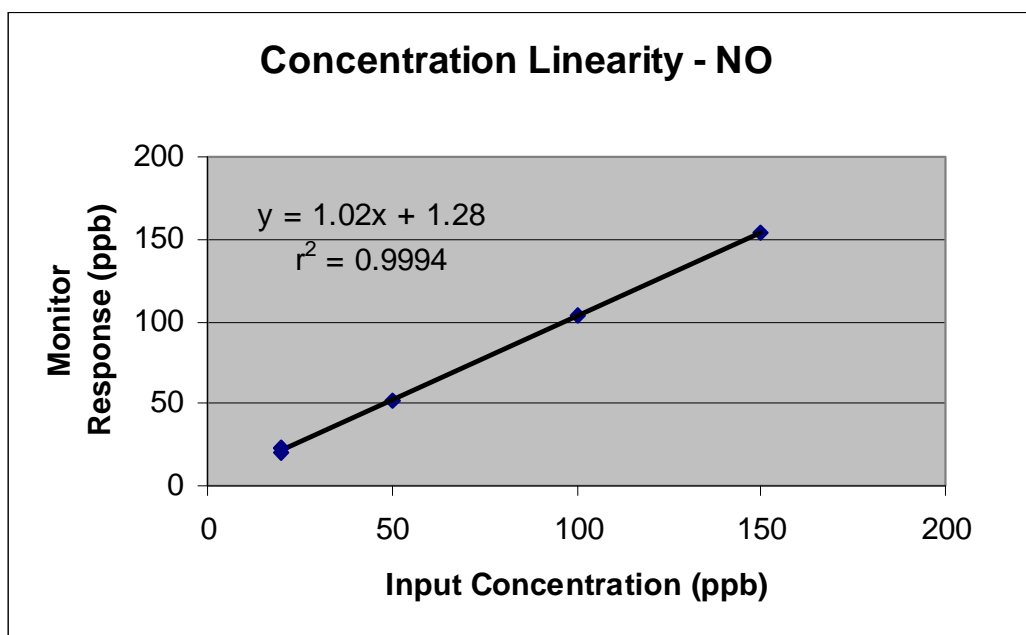
### 6.2.2 Concentration Linearity

Table 6-4 and Figures 6-2 through 6-4 show the path-average results of the evaluation of concentration linearity. The regression analysis results are shown on the individual figures.

The concentration linearity results show that the AR-500 has a linear response over the concentration ranges tested. The monitor response as given by the slope of the linear regression line is 1.02 for NO, with an  $r^2$  value of 0.9994; a slope of 0.95 for benzene, with an  $r^2$  value of 0.9992; and a slope of 1.11 for ammonia, with an  $r^2$  value of 0.9997.

**Table 6-4. Concentration Linearity Data for the AR-500**

Target Gas	Target Gas Concentration (ppb)	Monitor Response (ppb)
NO	20	19.5
NO	20	22.7
NO	50	51.6
NO	20	23.4
NO	100	103
NO	150	155
Benzene	20	18.9
Benzene	12	10.4
Benzene	30	29.4
Benzene	12	10.4
Benzene	50	48.3
Benzene	100	93.9
Ammonia	30	33.1
Ammonia	24	25.4
Ammonia	60	66.7
Ammonia	24	23.2
Ammonia	100	110
Ammonia	200	221



**Figure 6-2. Concentration Linearity Plot of the AR-500 Challenged with NO**

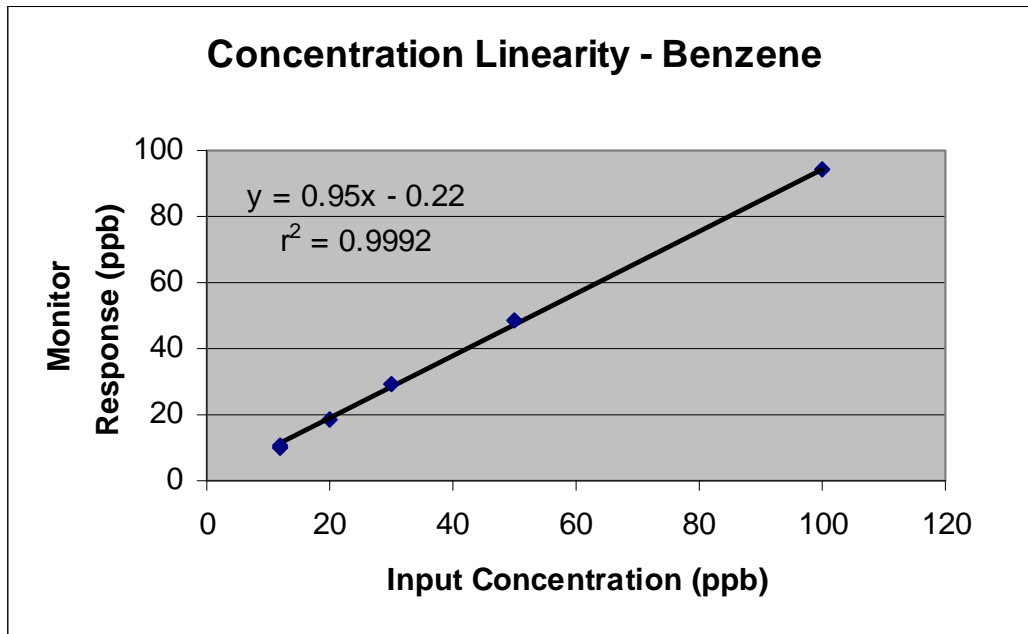


Figure 6-3. Concentration Linearity Plot of the AR-500 Challenged with Benzene

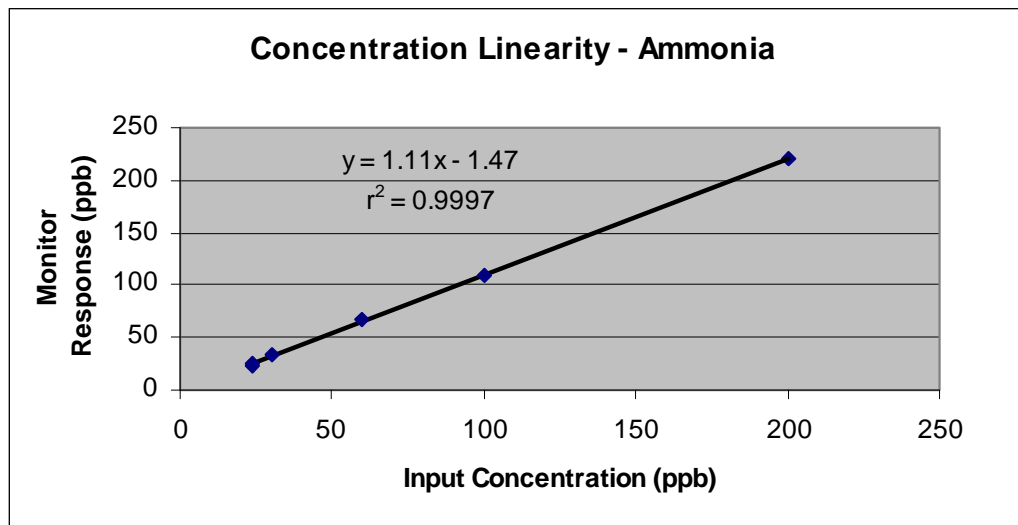


Figure 6-4. Concentration Linearity Plot of the AR-500 Challenged with Ammonia

### 6.3 Accuracy

The accuracy of the AR-500 was evaluated at each target gas concentration introduced into the cell. These concentrations were introduced at the path lengths and integration times shown in Table 6-5. The accuracy results compare the monitor response with the target gas concentration as delivered by the Environics 2020 diluter. The AR-500's relative accuracy ranges from 2.7 to 17% for NO, from 2.1 to 14% for benzene, and from 3.3 to 11% for ammonia. Integration time had little effect on accuracy of the AR-500. The longer path length improved accuracy for ammonia, but had the opposite effect for NO and benzene.

**Table 6-5. Results of Accuracy Tests for the AR-500**

Target Gas	Expected Concentration (ppb)	Path Length (m)	Integration Time (min)	Monitor Response (ppb)	Relative Accuracy (%)
NO	20	100	1	19.5	2.7
NO	20	250	1	22.7	14
NO	50	100	1	51.6	3.2
NO	20	250	5	23.4	17
NO	100	100	1	103	3.4
NO	150	100	1	155	3.0
Benzene	20	100	1	18.9	5.8
Benzene	12	250	1	10.4	14
Benzene	30	100	1	29.4	2.1
Benzene	12	250	5	10.4	14
Benzene	50	100	1	48.3	3.4
Benzene	100	100	1	93.9	6.1
Ammonia	30	100	1	33.1	10
Ammonia	24	250	1	25.4	5.6
Ammonia	60	100	1	66.7	11
Ammonia	24	250	5	23.2	3.3
Ammonia	100	100	1	110	9.5
Ammonia	200	100	1	221	10

### 6.4 Precision

Precision data were collected during measurement #14 (see Table 3-2) using an integration time of 1 minute and a path length of 100 meters. The target gas was introduced into the gas cell at a fixed concentration, and 25 successive analyses were made for the target gas. The data from these measurements are found in Table 6-6, and the results are shown in Table 6-7. In both tables, the data are shown in terms of the path-average concentration of the target gas. Table 6-7 shows precision of about 0.5% RSD for NO, 0.6% RSD for benzene, and 1.5% RSD for ammonia.

**Table 6-6. Data from Precision Tests on the AR-500**

Analysis	Target Gas		
	NO (ppb)	Benzene (ppb)	Ammonia (ppb)
1	168	96.7	219
2	168	96.9	221
3	166	97.6	220
4	167	97.4	221
5	167	97.2	220
6	167	96.6	214
7	166	95.8	221
8	167	96.1	228
9	168	96.2	220
10	168	96.6	222
11	169	96.8	225
12	167	96.2	220
13	167	97.0	219
14	167	96.4	221
15	168	96.4	223
16	168	96.2	219
17	168	96.2	223
18	169	96.2	227
19	167	95.8	231
20	166	96.2	219
21	168	95.6	219
22	167	97.2	221
23	168	96.8	223
24	168	97.5	224
25	168	97.0	221

**Table 6-7. Results of Precision Tests on the AR-500<sup>a</sup>**

Target Gas	Gas Cell Concentration (ppb)	AR-500 Average (ppb)	Standard Deviation (ppb)	Relative Standard Deviation (%)
NO	150	167	0.77	0.46
Benzene	100	96.8	0.55	0.57
Ammonia	200	222	3.40	1.53

<sup>a</sup> Integration time = 1 minute, path length = 100 meters.

## 6.5 Interferences

Interference tests of the AR-500 evaluated the effects that the common atmospheric interferants O<sub>2</sub> and O<sub>3</sub> have on the monitor's ability to determine the concentration of the target gases and on the MDL for the target gases. Tables 6-8 and 6-9 show the data used to determine the interference effects of ozone and oxygen on the concentration and MDL.

**Table 6-8. Concentration Data from Interference Tests on the AR-500**

Target Gas	Path Length (m)	Gas Cell		Concentration of Ozone (ppb*m)	Concentration of Target Gas (ppb)	Relative Accuracy (%)
		Concentration (ppb)	Concentration of Oxygen (%*m)			
NO	250	20	5225	500	22.7	14
NO	100	20	2090	3440	19.5	2.5
NO	250	20	5225	1075	23.4	17
Benzene	250	12	5225	6725	10.4	13
Benzene	100	30	2090	1270	29.4	2.0
Benzene	250	12	5225	7100	10.4	13
Ammonia	250	30	5225	4575	33.1	10
Ammonia	100	24	2090	1900	25.4	5.8
Ammonia	250	24	5225	4450	23.2	3.3

**Table 6-9. MDL Data from Interference Tests on the AR-500**

Target Gas	Path Length (m)	Concentration of Oxygen (%*m)	Concentration of Ozone (ppb*m)	MDL (ppb)
NO	250	5225	3400	0.91
NO	100	2090	3290	1.01
Benzene	250	5225	7325	0.50
Benzene	100	2090	530	1.51
Ammonia	250	5225	5900	2.81
Ammonia	100	2090	1150	5.75

Both ozone and oxygen have absorption features in the same spectral region that the AR-500 uses to analyze for the target compounds. Because the concentration of these two potential interferants is usually much greater than the concentration of the compounds of interest, the presence of these compounds can make analyzing for the target compounds difficult. The AR-500 uses various methods to deal with these interferants, and this test evaluated the effectiveness of these methods.



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Changing the total number of ozone and oxygen molecules in the path length had little effect on the monitor's ability to accurately calculate the concentrations of the target gas. The best accuracy for benzene was found with the lowest O<sub>2</sub> and O<sub>3</sub> levels, but this was not clearly the case for the other gases. Overall, no consistent effect on relative accuracy could be inferred. During these measurements, the ozone concentration in the path changed from 500 to 7100 ppb\*m, and the oxygen concentration varied from 2090 to 5225 %\*m.

These results did not permit calculation of relative sensitivity, as described in Section 5.5. Instead, a comparison of the measured concentrations was made to the input concentrations.

Likewise, changing the total number of ozone and oxygen molecules in the path length had little effect on the monitor's MDL for the target gas. The MDL varied from 0.91 to 1.01 ppb for NO, from 0.50 to 1.51 ppb for benzene, and from 2.81 to 5.75 ppb for ammonia; while the ozone concentration in the path changed from approximately 530 to 7325 ppb\*m, and the oxygen concentration varied from approximately 2090 to 5225%\*m.

## **6.6 Other Factors**

### **6.6.1 Costs**

The cost of the AR-500, as tested, was not available from the vendor. Costs for the AR-500 depend on the specific application and are established in discussion with the vendor.

### **6.6.2 Data Completeness**

All portions of the verification test were completed, and all data that were to be recorded were successfully acquired. Thus, data completeness was 100%.

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## Chapter 7 Performance Summary

The AR-500 detection limits ranged between 0.9 and 1.4 ppb for NO, between 0.4 and 1.5 ppb for benzene, and between 2.8 and 5.8 ppb for ammonia. While the variation in detection limits could be due to the changes in path length and integration time, there was no consistent trend. That is, longer integration times did not, in general, lead to lower detection limits, nor did the longer path lengths.

The tests of the effects of source strength on the measurement capability of the monitor showed that there was little to no degradation of monitor performance, with reductions in source strength of up to 60%. Coefficients of determination at two different test concentrations were low, indicating that reducing the source strength had little effect on the monitor's response over the range tested. The concentration linearity results showed that the AR-500 had a slope of 1.02 and an  $r^2$  value of 0.9994 for NO over a range of 20 to 150 ppb; a slope of 0.95 and an  $r^2$  value of 0.9992 for benzene over a range of 12 to 100 ppb; and a slope of 1.11 and an  $r^2$  value of 0.9997 for ammonia over a range of 24 to 200 ppb.

Percent relative accuracy was evaluated over the same ranges of concentration noted above for concentration linearity testing. Relative accuracy over these ranges was 2.7% to 17% for NO, 2.1 to 14% for benzene, and 3.3 to 11% for ammonia. The monitor performed about equally well at long and short integration times and at long and short path lengths.

Precision results showed that the AR-500 had an RSD of 0.46% for NO at a concentration of 150 ppb, an RSD of 0.57% for benzene at a concentration of 100 ppb, and an RSD of 1.53% for ammonia at a concentration of 200 ppb. This RSD was calculated at one experimental condition using a path length of 100 meters and an integration time of 1 minute.

Analysis of the effects of the interferences of oxygen and ozone on the measurement ability of the AR-500 showed that neither the accuracy nor the MDLs for the target gases were affected in a consistent way by the oxygen and ozone in the light path. Variations in MDL and accuracy were similar to those found during the other measurements made under normal operating conditions.

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## Chapter 8 References

1. *Test/QA Plan for Verification of Optical Open-Path Monitors*, Battelle, Columbus, Ohio, October 28, 1999.
2. *Compendium Method TO-16 Long-Path Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases*, EPA-625/R-96/010b, U.S. Environmental Protection Agency, Cincinnati, Ohio, January 1997.
3. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Pilot*, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, September 1998.

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**Appendix A  
Data Recording Sheet**

Sample Gas:	Date:				Operator:			
Measurement #								
Cell Temp (F)								
Ambient O <sub>2</sub> Concentrations (ppb)								
Ambient CO <sub>2</sub> Concentrations (ppb)								
Ambient RH (%)								
Ambient O <sub>3</sub> Concentrations (ppb)								
Ambient Temp (F)								
Integration Time								
Path Length								
Concentration in Cell								
Cell Length								
Time of Measurement								