September 2000

Environmental Technology Verification Report

UNISEARCH ASSOCIATES
LASIR® TUNABLE DIODE LASER
OPEN-PATH MONITOR

Prepared by

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EPA U.S. Environmental Protection Agency

ETV ETV ETV

September 2000

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

UNISEARCH Associates
LasIR® Tunable Diode Laser
Open-Path Monitor

By

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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 permitters, 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.

Acknowledgments

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List of Abbreviations

AMS	Advanced Monitoring Systems
CEM	continuous emission monitor
C_2H_2	acetylene or ethenylidene radical
C_2H_4	ethylene or polyethylene
CH_4	methane
cm	centimeter
CO	carbon monoxide
CO_2	carbon dioxide
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
GC/FID	gas chromatography/flame ionization detection
HCl	hydrochloric acid
HF	hydrogen fluoride
H_2	hydrogen
H_2O	water
m	meter
MDL	minimum detection limit
NDIR	nondispersive infrared
NH_3	anhydrous ammonia
NIST	National Institute of Standards and Technology
N_2	nitrogen
NO_x	nitrogen oxides (= NO + NO_2)
NO_2	nitrogen dioxide
O_2	oxygen
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_2	sulfur dioxide
TDL	tunable diode laser
TSA	technical systems audit

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 UNISEARCH Associates LasIR tunable diode laser (TDL) 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 LasIR. The following description of the LasIR is based on information provided by the vendor.

The LasIR uses a TDL to measure concentrations of HF, HCl, CH_4, H_2, CO, CO_2, NH_3, C_2H_2, C_2H_4, NO, and NO_2. The LasIR controller houses the laser, its temperature and current control circuits, a reference cell used to lock the absorption feature to line center, an audit cell into which a known concentration of the gas being measured may be introduced for calibration purposes, and a computer to operate the system and process and store the measurement data. The controller can be placed indoors or outdoors and is connected by a fiber optic cable to the measurement sensors, which can be located kilometers away. A number of sensors can be operated from the controller simultaneously. The response of the system for most gases is in the range of a few parts per million per meter.

The light from the laser, which is mounted, with its focusing optics, in a thermoelectric cooler, is transferred by a fiber optic cable to a telescope, through the open path, onto a retroreflector, and back to the telescope. About 10% of the light is split off before entering the telescope and directed through a small internal cell containing the gas being measured and then to the reference detector. This reference signal is used to lock the laser to the selected absorption feature and may also act as a transfer calibration standard.

Figure 2-1. UNISEARCH Associates LasIR TDL Open-Path Monitor, Controller, Telescope, and Retroreflector

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*.(1) The test was designed to challenge the LasIR in a manner similar to that which would be experienced in field operations, and was modeled after Compendium Method TO-16.(2) 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 LasIR are shown in Table 3-1. The verification was conducted by measuring each gas in a fixed sequence over three days. The sequence of activities for testing the monitor for each gas is shown in Table 3-2.

Table 3-1. Target Gases for Testing the LasIR

Gas	Concentration Level	Target Gas Concentration Path Length (ppm*m)	Gas Cell Concentration (ppm)[a]
Methane	c1	4	40
	c2	8	80
	c3	40	400
	c4	80	800
HF	c1	8.3	67
	c2	23.0	165-182
	c3	61.8	498
	c4	68.0	549
Ammonia	c1	7.5	75
	c2	15.0	150
	c3	25.0	250
	c4	49.4	494

[a] Length of gas cell = 0.100 m for methane, 0.124 m for HF, and 0.100 m for ammonia.

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

Meas. #	Gas Cell Conc.	Activity	Collected # of Measure-ments	Times (min) Integrate	Times (min) Equilibrate	Path Length[b] (m)	Verification Parameter Calculated
	N_2	Change gas & stabilize			10	220	
1	N_2	Collect spectra	25	1		220	Accuracy, Concentration linearity, MDL
	c1[a]	Change gas & stabilize			10	220	
2	c1	Collect spectra	5	1		220	Accuracy, Concentration linearity
3	c1	Collect spectra - ND 1	5	1		220	Source strength linearity[c]
4	c1	Collect spectra - ND 2	5	1		220	Source strength linearity[c]
5	c1	Collect spectra - ND 3	5	1		220	Source strength linearity[c]
	N_2	Change gas & stabilize			10	220	
6	N_2	Collect spectra	5	1		220	Accuracy, Concentration linearity
	c2	Change gas & stabilize			10	220	
7	c2	Collect spectra	5	1		220	Accuracy, Concentration linearity, Interference Effect (Int.)
	N_2	Change gas & stabilize			10	220	
8	N_2	Collect spectra	5	1		220	Accuracy, Concentration linearity
	c3	Change gas & stabilize			10	220	
9	c3	Collect spectra	5	1		220	Accuracy, Concentration linearity
10	c3	Collect spectra - ND 1	5	1		220	Source strength linearity[c]
11	c3	Collect spectra - ND 2	5	1		220	Source strength linearity[c]
12	c3	Collect spectra - ND 3	5	1		220	Source strength linearity[c]
	N_2	Change gas & stabilize			10	220	
13	N_2	Collect spectra	5	1		220	Accuracy, Concentration linearity
	c4	Change gas & stabilize			10	220	
14	c4	Collect spectra	25	1		220	Accuracy, Concentration linearity, Precision
14b	N_2	Collect spectra	5			220	Accuracy, Concentration linearity
	N_2	Change gas & stabilize			10	220	
15	N_2	Collect spectra	25	5		220	Concentration linearity, MDL
		Change to Path length 2			20	480	
16	N_2	Collect spectra	5	5		480	Int.
	c2	Change gas & stabilize			10	480	
17	c2	Collect spectra	5	5		480	Int., Accuracy, Concentration linearity
	N_2	Change gas & stabilize			10	480	
18	N_2	Collect spectra	5	5		480	Int., Accuracy, Concentration linearity
		Change to Path length 3			20	optimum[d]	
19	N_2	Collect spectra	5	1		optimum	Int., Accuracy, Concentration linearity
	c2	Change gas & stabilize			10	optimum	
20	c2	Collect spectra	5	1		optimum	Int., Accuracy, Concentration linearity
	N_2	Change gas & stabilize			10	optimum	
21	N_2	Collect spectra	25	1		optimum	Int., MDL

[a] See Table 3-1 for values of c1–c4 for the three target gases.

[b] Because of the presence of ambient methane, path lengths of 1.5 and 220 meters were used for the accuracy and MDL measurements for methane.

[c] Measurements for source strength linearity only made for methane.

[d] Optimum path length chosen by the vendor was 220 meters for methane, 220 meters for NH_3, and 480 meters for HF.

3.2 Test Design

The verification test was performed from May 22 to May 26, 2000, near West Jefferson, Ohio, at an outdoor testing area belonging to Battelle. 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 LasIR telescope was mounted on a 3-foot-tall tripod near the edge of a lightly traveled road and pointed toward a retroreflector on another tripod located along the road at a distance of 110 meters. This arrangement produced a total light path of 220 meters. The tripod was subsequently moved down the road to a distance of 240 meters, producing a light path of 480 meters. The open space in the foreground of Figure 3-1 shows the test site at Battelle's West Jefferson facility.

Figure 3-1. Test Site at Battelle's West Jefferson Facility

The LasIR was challenged with the target gases shown in Table 3-1 at known concentrations, and the gas measurement by the monitor 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.

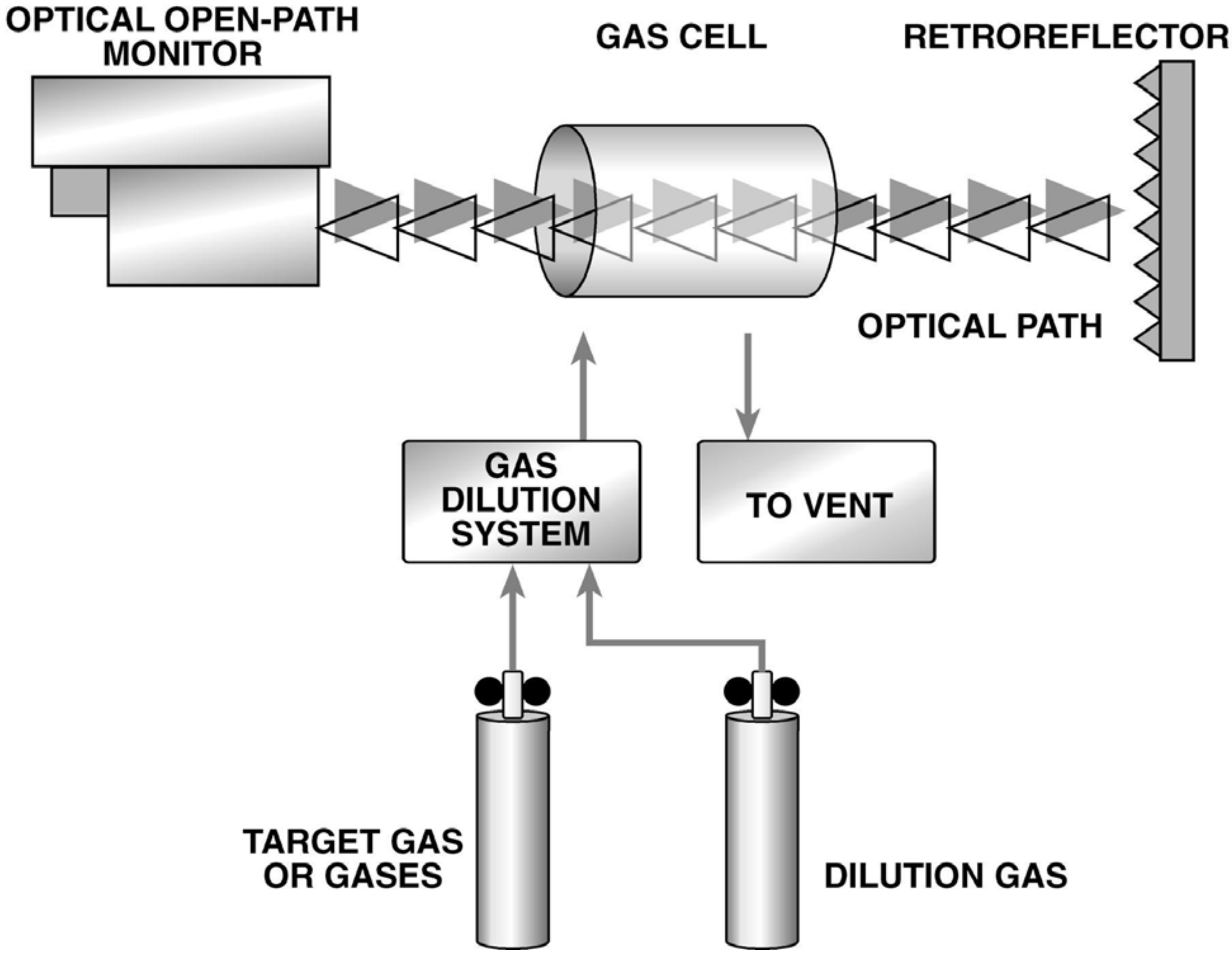

Figure 3-2. Optical Open-Path Monitor Setup

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_2 in the Gas Cell Concentration column denotes a period of cell flushing with high-purity nitrogen. The denotations c1, c2, c3, 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 (UHP) nitrogen obtained from commercial suppliers.

3.3.3 Gas Dilution System

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

The dilution system for HF consisted of a valved Teflon manifold that added the HF gas to the dilution gas flow from the Environics diluter downstream of the diluter, to avoid damage to the Environics from the HF. Because this system did not give the close control of concentrations that was achieved for the ammonia and methane, each of the HF concentrations delivered to the gas cell was sampled downstream of the cell as described in Section 3.3.9.

3.3.4. Gas Cell

Acrylic or Pyrex gas cells 0.100 in length for methane, 0.124 meter for HF, and 0.100 meter for ammonia were integrated into the monitor.

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 six months preceding the verification test.

3.3.6 Relative Humidity (RH) Sensor

The RH sensor used to determine the ambient air humidity was a commercial RH/Dew Point monitor that used the chilled mirror principle. This sensor was operated in accordance with the manufacturer’s instructions, which called for cleaning the mirror and rebalancing the optical path when necessary, as indicated by the diagnostic display of the monitor. The manufacturer’s accuracy specification of this monitor was ± 5% RH.

3.3.7 Carbon Dioxide Monitor

A commercial nondispersive infrared (NDIR) monitor (Gastech Model RI-411 infrared CO_2 monitor, Serial No. 9350211) was used to monitor the level of CO_2 in ambient air during interference measurements. This monitor was operated in accordance with the manufacturer's instructions and was calibrated with a commercially prepared cylinder standard of CO_2 in air. The limit of resolution of this monitor was 25 ppm.

3.3.8 NO/NH_3 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 NH_3 concentrations supplied to the optical cell for verification testing. This monitor sampled gas immediately downstream of the optical cell to confirm the NH_3 concentrations prepared by dilution of a high-concentration ammonia standard. The API monitor was calibrated with a NIST-traceable commercial standard cylinder of nitric oxide (NO) in nitrogen. The conversion efficiency for NH_3 was checked by comparing the calibration slope for NO with that found in calibrations with NH_3. All NH_3 measurements were corrected for the NH_3 conversion efficiency, which was generally greater than 95%.

3.3.9 HF Measurement

The test/QA plan(1) specified that impinger sampling and ion chromatographic analysis would be used as a performance evaluation method in selected tests, to confirm the HF concentrations supplied to the optical cell. However, the difficulty of delivering known HF concentrations to the optical cell made it necessary to apply this HF measurement in all tests, rather than as a PE method.

HF was measured by drawing a measured flow of about 2 l/min of gas, from a "T" fitting at the outlet of the optical cell, through a series of two impingers containing a total of 100 ml of deionized water. Sampling durations were 5 to 25 minutes, depending on the HF concentration provided to the cell. The impinger solutions were then analyzed for fluoride ion by ion chromatography, and the HF concentrations in the optical cell were calculated from the measured F^- concentrations, sampling durations, and sample flow rates.

3.3.10 Methane Measurement

Methane 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 methane 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 resulting measurements were then analyzed for the target gas. The MDL was defined as two times the standard deviation of the calculated concentrations.

3.4.2 Linearity

Two types of linearity were investigated during this verification: source strength and concentration. Reduction in light intensity is a common occurrence in the field. Rain, fog, snow, and dirty optics are some of the reasons that the light intensity would change. The source strength linearity was investigated by measuring the effects of reducing the source intensity on the monitor's performance. With a constant concentration of methane in the gas cell, and a constant total path length of 220 meters, the light intensity of the source was reduced by placing an aluminum wire mesh in the path of the light. These screens were approximately 1 foot square and had mesh spacings of approximately ¼, ½, and 1 inch, respectively. By placing different mesh sizes in the path, attenuation of the source intensity by as much as 72% was achieved. At each of these attenuation levels, a measurement was made, and the monitor analyzed for methane.

Concentration linearity was determined by challenging the LasIR with each target gas at cell concentrations between 40 and 800 ppm, while the path length and integration time were kept constant. At each concentration, the monitor response was recorded and used to infer the cell gas concentration. Linearity was evaluated by comparing the inferred cell gas concentration from the open-path measurement to the input target gas concentration.

3.4.3 Accuracy

Accuracy of the LasIR 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 a measurement was recorded. The target gas was then introduced into the cell and, after flushing with at least five cell volumes, a measurement of the target gas was obtained. The cell was again flushed with at least five cell volumes of nitrogen, and a third measurement was recorded. The three measurements were analyzed for the target gas, using the background selected by the vendor. The concentration of the target gas was calculated as the second measurement minus the average of the first and third (flushed cell) measurements.

The accuracy was evaluated at concentrations c1 through c4 for each of the three target gases (Table 3-1). Using an integration time of 1 minute and a path length of 220 meters, ammonia and HF were evaluated. The accuracy was then evaluated at concentration c2 with the same path length, but using a 5-minute integration time, and then again at concentration c2 during the interference measurements (Table 3-2), with 5-minute integration and a 480-meter path. The accuracy was evaluated for methane using an integration time of 1 min and a path length of

1.5 meters. The path length was then changed to 220 meters and the integration time changed to 5 minutes, and the accuracy was evaluated again. The open path measurements of the LasIR were used to infer the cell gas concentration. The percent accuracy is the difference between the average value of all the resulting measurements at the same conditions and the concentration in the gas cell divided by the concentration of the gas in the gas cell, 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 each of the target gases (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 path length between the source and detector of the monitor. The purpose of the interference measurements was to determine the effects of the ambient atmospheric gases on accuracy and MDL of the LasIR. Using two different integration times, these tests were also conducted to determine the effect of integration time on the measurements with interfering gases in the light path.

To determine the effect of the interferences, 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 similarly flushing the cell, five measurements were recorded. Finally, nitrogen was again introduced into the cell, and five measurements were recorded. As in other tests, the cell gas concentration was calculated from the LasIR’s open-path measurements and compared to the input cell gas concentrations.

For HF, this procedure was conducted with path lengths of both 220 and 480 meters, the latter being the length that UNISEARCH chose as optimum, given that 480 meters was the maximum length available at the test site. Atmospheric concentrations of H_2O and CO_2 were recorded at the beginning and end of these measurements. The monitor’s sensitivity to the interferant was calculated by comparing the results at different path lengths (i.e., different ppm*m levels of H_2O and CO_2). For methane, measurements were made with a 1.5-meter path length (i.e., the gas cell only) to avoid the effect of the ambient methane background concentration. Interference tests were not conducted for ammonia because the TDL light source used for that target gas did not allow variation of the path length beyond 220 meters.

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(3) and the test/QA plan(1) 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 reviewed, 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). The deviations from the test/QA plan were as follows:

- The test/QA plan calls for a on-over-one data review within two weeks of generating the data. While the entire data set was reviewed within this two-week period, no documentation of this task was generated. 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 was not calibrated within the previous six months, as specified in the test/QA plan. The thermocouple used 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 called for acid rain CEM zero nitrogen to be used to flush the cell and as dilution gas. Instead, ultra-high-purity N_2 was used.

- The gas concentrations used in the verification test of the LasIR differ from the original concentrations stated in the test/QA plan. The concentrations stated in the test/QA plan were based upon the best knowledge of the monitors to be tested at the time the test plan was written. In actuality, the monitor provided required a different gas concentration range.

- No independent performance evaluation was conducted for HF. The method planned for the performance evaluation (impinger sampling) was adopted for all HF measurements as a means of establishing the gas cell concentration.

- The CO_2 monitor performance evaluation audit was conducted in April, 2000, and not during the Unisearch test in May, 2000.

- The test/QA plan called for a performance evaluation audit of the NO/NH_3 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.

- The test/QA plan stated that the CO_2 measurement would undergo a performance evaluation audit using a calibration standard obtained from an independent supplier. Instead, a separate CO_2 standard obtained from the same manufacturer was used for the audit.

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 or removed inefficiencies in the test, ultimately resulting in a reduced test duration. A brief summary of these variations is provided below:

- 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 Summa® canister analysis procedure was changed from that specified in the test/QA plan. The test/QA plan specified using Method 18 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.

- 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 schedule of steps in testing (as indicated in Table 3-2 of the test/QA plan) was modified for this test because of the need to use a 1.5 meter path length in some tests to avoid atmospheric methane background. Additional tests were performed, to obtain the needed test data at both short and long paths.

- The test/QA plan for verification of optical open-path monitors (Revision 1, dated 10/28/99) contains a contradiction. Sections 5.3.2, 5.4.2, and 5.5.2 all correctly indicate that the minimum detection limit (MDL) will be calculated as twice the standard deviation of a series of measurements taken at zero target gas concentration. However, Section 9.2.1 states an incorrect equation to calculate the MDL. This revision changes Section 9.2.1 to eliminate the contradiction.

- 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.

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, when necessary.

4.3.2 Temperature Sensor

The thermocouple was calibrated by comparing it to a certified standard within the six months preceding the test.

4.3.3 RH Sensor

The RH sensor used the manufacturer’s calibration.

4.3.4 Carbon Dioxide Monitor

The NDIR CO_2 monitor was calibrated before testing using a commercially prepared, certified standard of CO_2 in air.

4.3.5 NO/NH_3 Monitor

The NO/NH_3 monitor was calibrated with both NO and NH_3 standards before verification testing of each open-path monitor. 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_3 standard was also a Certified Master Class Calibration Standard, of 494 ppm NH_3 in air, of ± 2% analytical uncertainty (Scott, Cylinder No. ALM 005256). The ratio of the slopes of the NH_3 and NO calibration curves established the NH_3 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).

4.3.6 HF Measurement

Calibration for HF was performed by preparing solutions of known fluoride content by serial dilution, using deionized water and ACS reagent grade sodium fluoride. These standards were analyzed with each batch of impinger samples, along with blank samples collected at the verification test site.

4.3.7 Methane Measurement

The GC/FID measurement for methane 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 both by Battelle and the vendor during the test. Table 4-1 summarizes the type of data recorded (see also Appendix A); where, how often, and by whom the recording is made; and the disposition or subsequent processing of the data. Data recorded by the vendor were turned over to Battelle staff immediately upon completion of the test procedure. Test records were then converted to Excel spreadsheet files.

4.5 Performance Systems 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(1) and that all activities associated with the test are in compliance with the ETV Center QMP.(3) 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 compared to the test/QA plan. The performance evaluation audit conducted by the staff was observed, and the results were assessed.

Table 4-1. Summary of Data Recording Process for the LasIR Verification Test

Data Recorded	Recorded By	Where Recorded	When Recorded	Disposition of Data
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	Vendor	Data Sheet	At specified time during each test	Transferred to spreadsheet

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 Pilot 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 this external TSA, which was documented in a report to the Battelle Center Manager for review. A response and corrective actions were prepared and returned to EPA. The findings 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 Battelle 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.

The results from the performance evaluation audit are shown in Table 4-2. The temperature measurement agreed to within 0.5°C and the relative humidity agreed to within 0.1% RH. The carbon dioxide monitor was calibrated before the test and agreed to within 25 ppm (i.e., within the resolution of the monitor) at 600 ppm.

Table 4-2. Summary of Performance Evaluation Audit Procedures

Measurement Audited	Audit Procedure	Expected Reading	Actual Reading	Difference
Temperature	Compare to independent temperature measurement (Hg thermometer)	9.6°C	10.1°C	0.5°C
CO_2	Compare measurement using an independent carbon dioxide standard	600 ppm	625 ppm	4.2%
RH	Compare to independent RH measurement (wet/dry bulb device)	70% RH	70.1% RH	0.14%
Methane	Compare to results of gas chromatographic analysis of canister samples	80 ppm	88 ppm	10%
NO/NH_3	Compare to measurement using an independent NO standard	150 ppm	152 ppm	1.3%

The methane concentrations were audited by independent analysis of the test gas mixture supplied to the gas cell during verification testing. The results of the performance audit for the target gas concentrations were within 10% of the expected concentrations, which met the test/QA plan criterion.

The performance evaluation of the NO/NH_3 monitor was based on analysis of a different NO standard than that ordinarily used for calibration. As Table 4-2 shows, the agreement of the performance evaluation standard with the calibration of the monitor was within 2 ppm at 150 ppm NO.

No performance evaluation audit was conducted for HF, because the impinger sampling procedure planned for use as a PE method was instead used routinely to determine HF concentrations in all verification tests with that gas. This change in procedure was necessitated by the difficulty of supplying accurately known HF concentrations to the test cell, using dilution of a commercial HF standard.

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.

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 (σ_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

$$A = \frac{\left|\overline{R} - \overline{T}\right|}{\overline{R}} \times 100$$

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, ..., T_n, the standard deviation (σ) of these measurements is

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

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

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

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 methane in air with an interference concentration of 100 ppm of CO_2 indicates 30 ppm of methane when the CO_2 concentration is changed to 200 ppm. This would result in an interference effect of $(30\text{ ppm} - 26\text{ ppm})_{\text{methane}}/(200\text{ ppm} - 100\text{ ppm})_{CO2} = 0.04$, or 4% relative sensitivity.

Chapter 6
Test Results

The results of the verification test of the LasIR are presented in this section, based upon the statistical methods shown in Chapter 5. The monitor was challenged with methane, HF, and ammonia over path lengths of 1.5, 220, and 480 meters, which cover typical path lengths for this monitor. These gases were chosen because they are targeted in key market areas for the vendor. Test parameters include minimum detection limit, 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 LasIR's open-path measurement to the actual gas cell concentration. In addition, where appropriate, the path-average concentrations are noted. The path-average concentration is determined by multiplying the gas cell concentration by the gas cell length and then dividing by the total path length used during the given measurement.

6.1 Minimum Detection Limit

The MDL was calculated from the variability of measurements in which there were no target gases in the gas cell, but in which the monitor analyzed the absorption data for the presence of a target gas. In the case of methane, it is not possible to eliminate the methane from the atmospheric measurement path, so scatter would result in the data from variation in the ambient methane. Therefore, the MDL measurements for methane were performed at a path length of 1.5 meters, i.e., by excluding atmospheric methane entirely. 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. As is common practice, units of ppm*m are shown in Table 6-2. This is the path length of the measurement times the path-average concentration for that measurement.

Table 6.2 summarizes the LasIR MDL measurements. Based on measurements made with path lengths of 1.5 m (methane), 220 m (ammonia and HF), and 480 m (HF) and integration times of 1 minute and 5 minutes, the LasIR has an MDL between 0.09 and 1.21 ppm*m for methane, between 0.13 and 0.23 ppm*m for HF, and between 1.05 and 13.7 ppm*m for ammonia. The MDL tests for methane were not conducted under the same experimental conditions as those for HF and ammonia because the background concentration of methane in the air is typically around 1.7 ppm, and removing the effect of the variation in atmospheric methane could only be

Table 6-1. MDL Data for the LasIR

	Methane		HF			Ammonia		
	Path Length (m)		Path Length (m)			Path Length (m)		
	1.5	1.5	220	220	480	220	220	220
	Integration Time (min)		Integration Time (min)			Integration Time (min)		
Measurement Number	1	5	1	5	1	1	5	1
	Concentration							
	ppm	ppm	ppb	ppb	ppb	ppb	ppb	ppb
1	1.67	1.91	0.64	-1.30	-0.38	-3.60	-15.5	5.70
2	1.70	2.09	0.38	-1.40	-0.42	-1.60	-9.11	1.90
3	1.71	1.95	0.08	-1.30	-0.34	1.90	-7.37	1.90
4	1.72	1.63	-0.58	-0.90	-0.30	-3.40	-2.77	4.10
5	1.72	1.30	-0.76	-0.70	-0.30	3.20	-3.37	-0.60
6	1.71	1.14	0.23	-0.50	-0.23	2.40	8.05	-2.30
7	1.76	1.21	0.66	-0.30	-0.25	1.90	8.82	-3.70
8	1.77	1.47	0.38	-0.30	-0.21	3.90	11.2	-7.80
9	1.75	1.78	0.13	-0.20	-0.21	1.40	9.75	-10.5
10	1.74	2.08	0.52	-0.10	-0.15	3.90	9.36	-20.6
11	1.76	2..28	0.27	0.00	-0.28	5.40	2.72	-77.8
12	1.75	2.35	-0.19	0.00	-0.27	5.30	-4.49	-77.8
13	1.75	2.31	0.02	-0.10	-0.27	3.20	5.55	-71.0
14	1.74	2.15	0.30	-0.50	-0.34	3.50	3.90	-57.0
15	1.73	1.89	0.26	-0.50	-0.39	4.50	1.57	-47.0
16	1.73	1.63	-0.31	-0.70	-0.49	3.30	-4.55	-47.5
17	1.73	1.37	-0.14	-0.60	-0.43	0.20	-12.4	-41.0
18	1.73	1.18	0.22	-1.00	-0.49	1.80	-12.0	-29.0
19	1.70	1.10	-0.05	-1.10	-0.53	2.70	-15.0	-27.0
20	1.66	1.10	-0.32	-1.10	-0.56	-0.20	-11.2	-21.0
21	1.70	1.15	-0.35	-1.20	-0.59	1.60	-6.20	-8.00
22	1.69	1.25	-0.36	-1.50	-0.60	2.60	-3.41	2.90
23	1.66	1.38	-0.57	-1.50	-0.65	4.00	0.69	11.80
24	1.69	1.55	-0.62	-1.40	-0.66	1.70	-9.05	26.00
25	1.68	1.74	-1.07	-0.78	-0.40	-0.50	-19.4	38.00

Table 6-2. Minimum Detection Limits of the LasIR

Target Gas	Path Length (m)	Integration Time (min)	MDL (ppm)	MDL (ppm*m)
Methane	1.5	1	0.063	0.09
Methane	1.5	5	0.095	1.21
HF	220	1	0.00091	0.20
HF	220	5	0.0010	0.23
HF	480	1	0.00030	0.13
Ammonia	220	1	0.0048	1.05
Ammonia	220	5	0.018	3.90
Ammonia	220	1	0.062	13.7

accomplished by placing the retroreflector near the target gas cell. Therefore, for this target gas, only the integration time was varied, with the shorter integration time giving the better detection limit. The MDL tests for ammonia were conducted at a single path length of 220 meters because a 480-meter path length was too long for the laser diode being used (the only laser available to the vendor at the time of the testing was of very low power). At the 220-meter path length and the one-minute integration time, the MDL varied between 1.05 and 13.7 ppm*m. During these measurements, it began raining and approximately half of the data obtained was collected during that period. During the rain, the power was significantly reduced due to scattering of the laser beam, which resulted in a significant increase in the relative noise of the system. This is reflected in the greater MDL for this species. Stable readings and low MDLs were seen during the HF measurements, with the lowest MDL occurring at the 480-meter path length.

6.2 Linearity

6.2.1 Source Strength Linearity

Table 6-3 shows the results from this evaluation of source strength linearity. Figure 6-1 shows a plot of the effect that the light signal level has on the monitor's measurements of methane in the gas cell. The average power determined from the background measurement, and the subsequent measurement with added methane for each pair of measurements at a particular power attenuation is used in the figure. The relative signal power is the measure of light attenuation during that measurement. For example, a relative signal power of 0.60 means that the light level for the test is 60% of the light level during normal operating conditions. The methane concentration is the path-average concentration at 220 meters during the measurement, and the monitor response is the resulting reading from the LasIR. The LasIR showed a maximum departure from the known added methane concentration of 0.019 ppm (4%) of the path-average concentration of 0.454 ppm over 220 meters. The linear regression results in Figure 6-1 indicate a near-zero correlation (r^2=0.09) and minimal slope (-0.01). These results show that, over the attenuation range tested, the LasIR measurements are independent of source strength.

Table 6-3. Source Strength Linearity of the LasIR

Relative Signal Power	Path-Average Methane Concentration from Added Methane (ppm)	Path-Average Monitor Response with Empty Cell (ppm)	Path Average Monitor Response with Methane in Cell (ppm)	Monitor Response Difference (ppm)
1.00	0.454	1.65	2.09	0.445
0.67	0.454	1.62	2.08	0.458
0.56	0.454	1.58	2.05	0.473
0.32	0.454	1.49	1.94	0.449

6.2.2 Concentration Linearity

Table 6-4 and Figures 6-2 through 6-4 show the results of the concentration linearity tests. The linear regression results are shown on the individual figures.

The concentration linearity results show that the LasIR responds linearly to all three target gases. This performance is especially noteworthy for HF and ammonia because of the nature of these gases, which introduces uncertainty in the preparation and delivery of known concentrations in the gas cell.

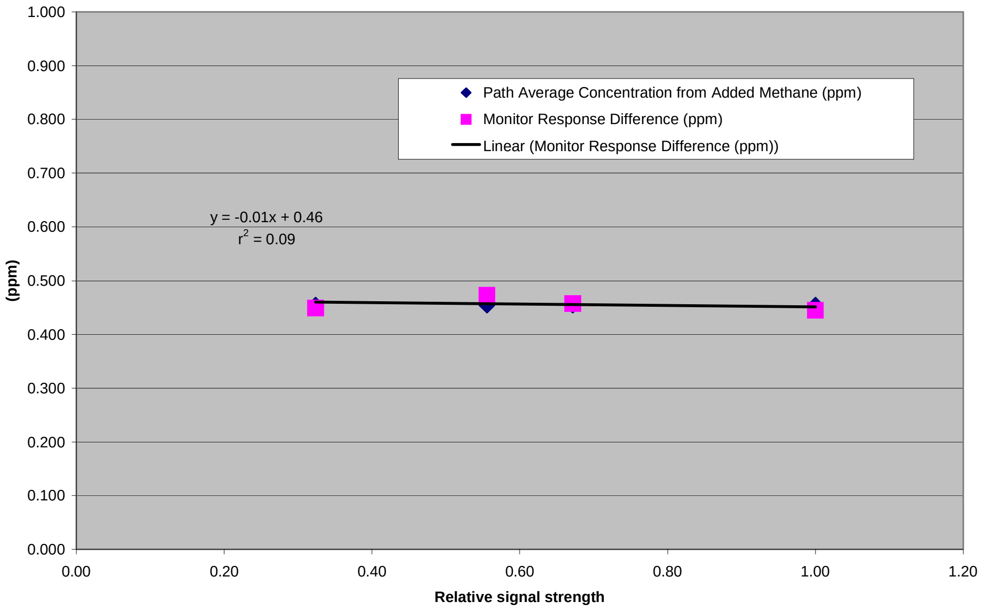

Figure 6-1. Source Strength Linearity Plot for the LasIR

Table 6-4. Concentration Linearity Data for the LasIR

Target Gas	Gas Cell Concentration (ppm)	Monitor Response[a] (ppm)
Methane	40	44.9
Methane	80	72.4
Methane	400	399
Methane	800	800
HF	67	79.8
HF	165	188
HF	182	173
HF	182	170
HF	498	355
HF	549	469
Ammonia	75	60.2
Ammonia	250	286
Ammonia	150	145
Ammonia	250	243.
Ammonia	250	261
Ammonia	494	551

[a] Test cell concentration calculated from open path readings of the LasIR.

[b] Determined from dilution of standard cylinder gas with nitrogen. In the case of HF, the concentration was determined from impinger samplers taken downstream of the gas cell. Errors associated with the dilution and impinger methods contribute to differences between the monitor response and the target gas cell concentration.

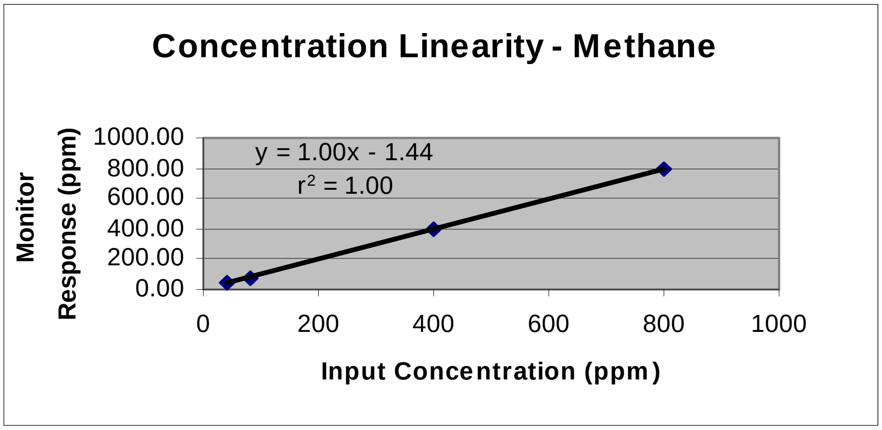

Figure 6-2. Concentration Linearity Plot of the LasIR Challenged with Methane

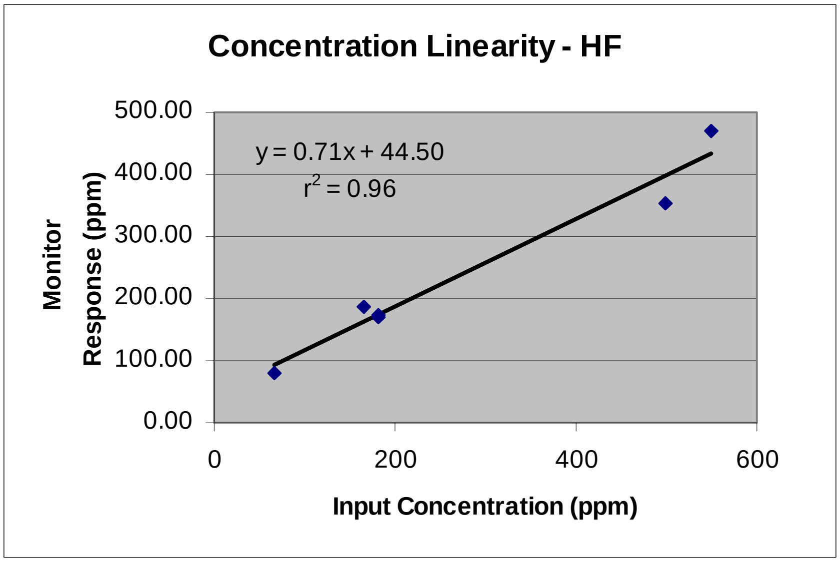

Figure 6-3. Concentration Linearity Plot of the LasIR Challenged with HF

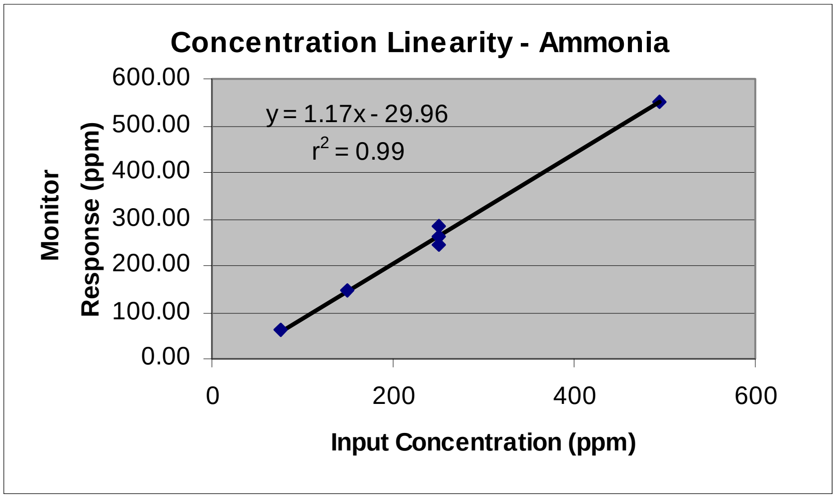

Figure 6-4. Concentration Linearity Plot of the LasIR Challenged with Ammonia

6.3 Accuracy

The relative accuracy of the LasIR 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 cell gas concentration inferred from the open-path monitor response with the target gas concentration as delivered by the Environics 2020 diluter for methane and ammonia, and with impinger sample results for HF.

It should be noted that the relative accuracy includes the uncertainty in the delivery and determination of the target gas. This is particularly true for ammonia and HF, which are both sticky gases and difficult to dilute accurately.

Table 6-5. Results of Accuracy Tests for the LasIR

Target Gas	Gas Cell Concentration (ppm)	Path Length (m)	Integration Time (min)	Monitor Response (ppm)	Relative Accuracy (%)
Methane	40	1.5	1	44.9	12.3
Methane	80	1.5	1	72.4	9.60
Methane	400	1.5	1	399	0.38
Methane	800	1.5	1	800	0.02
HF	67	220	1	79.8	19.1
HF	165	480	1	188	13.7
HF	182	220	1	173	5.15
HF	182	480	5	170	6.54
HF	498	220	1	355	28.7
HF	549	220	1	469	14.6
Ammonia	75	220	1	60.2	19.7
Ammonia	250	220	1	286	14.2
Ammonia	150	220	1	145	3.66
Ammonia	250	220	5	243	3.64
Ammonia	250	220	1	261	4.23
Ammonia	494	220	1	551	11.5

[a] No assessment of the accuracy associated with the determination of the standard gas concentration has been included.

The percent relative accuracy for methane ranges between 0.02 and 12.3%, with the lower value occurring at a gas cell concentration of 800 ppm.

The HF percent relative accuracy ranged between 5.2 and 28.7%, relative to the results of impinger sampling, at gas cell concentrations of 67 to 549 ppm. Overall, the LasIR achieved very good results considering the difficulties encountered when attempting to deliver known concentrations of HF gas.

The percent relative accuracy for ammonia ranged between 3.64 and 19.7% at the 220-meter path length, with gas cell concentrations of 75 to 494 ppm.

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 220 meters (except methane, for which data were collected at 1.5 meters). The target gas was introduced into the gas cell, and 25 successive analyses were made for the target gas. The input concentrations delivered during these tests were 800 ppm for methane, 549 ppm for HF, and 494 ppm for ammonia (i.e., path-average concentrations of 309 ppb for HF and 225 ppb for ammonia). The data from these measurements are found in Table 6-6, and the results are shown in Table 6-7. These results show that the LasIR had an RSD of 0.63% for methane, of 1.19% for HF, and of 1.84% for ammonia.

6.5 Interferences

Interference tests of the LasIR evaluated the effect that the common atmospheric interferants, water and carbon dioxide, have on the monitor's ability to determine the concentration of the target gases and on the MDL for the target gases. Both water and carbon dioxide have absorption features in the same infrared region that the monitor 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 water and carbon dioxide can make analyzing for target compounds difficult. The monitor uses various methods to deal with these interferants, and this test evaluated the effectiveness of these methods. Tables 6-8 and 6-9 show the data used to determine the interference effect of water vapor and carbon dioxide on the concentration and MDL determination.

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.

Changing the total number of water and carbon dioxide molecules in the path length had a small effect on the LasIR's ability to accurately determine the concentrations of the target gas. The measured gas concentrations were 72.4 to 103 ppm for methane delivered to the target gas cell at 80 ppm and from 173 to 188 ppm for HF delivered at 165 and 182 ppm, while the water concentration in the path changed from approximately 2.4×10^4 to 5.2×10^6 ppm*m, and the carbon dioxide concentration varied from approximately 8.1×10^2 to 1.6×10^5 ppm*m. For methane, the best accuracy, relative to the gas cell concentrations, occurred at the lower water and carbon dioxide levels in the light path. Accuracy for HF was within 14% at all water and carbon dioxide path concentrations.

Table 6-6. Data from Precision Tests on the LasIR

	Target Gas		
Analysis	**Methane (ppm)**	**HF (ppm)**	**Ammonia (ppm)**
1	818.6	452.1	552.2
2	819.3	447.8	556.6
3	819.3	455.3	558.8
4	819.5	455.1	569.8
5	820.5	458.6	569.8
6	821.0	454.9	569.8
7	822.0	458.1	563.2
8	821.3	456.0	572.0
9	821.1	458.8	569.8
10	822.1	460.9	563.2
11	822.1	460.1	576.4
12	825.3	463.2	567.6
13	829.0	460.8	574.2
14	831.9	460.0	567.6
15	834.4	463.2	567.6
16	834.5	460.1	565.4
17	832.1	463.2	556.6
18	832.3	467.3	554.4
19	831.5	468.0	556.6
20	831.4	466.6	547.8
21	827.5	469.8	536.8
22	826.3	467.0	545.6
23	821.9	467.0	552.2
24	822.3	465.1	550.0
25	826.4	465.4	547.8

Table 6-7. Results of Precision Tests on the LasIR[a]

Target Gas	Test Cell Concentration (ppm)	LasIR Average (ppm)	Standard Deviation (ppm)	Relative Standard Deviation (%)
Methane[b]	800	826[c]	4.2	0.63
HF	549	461	5.5	1.19
Ammonia	494	560	10.3	1.84

[a] Integration time = 1 minute, path length = 220 meters

[b] 1.5-meter path length

[c] Includes contribution from ambient methane

Table 6-8. Concentration Data from Water Interference Tests on the LasIR

Target Gas	Path Length (m)	Concentration of CO_2 (ppm*m)	Concentration of H_2O (ppm*m)	Input Gas Cell Concentration (ppm)	Calculated Concentration of Target Gas (ppm)	Relative Accuracy (%)
Methane	1.5	8.1E+02	2.4E+04	80	72.4	9.6
Methane	220	1.2E+05	1.6E+06	80	103	28.8
HF	480	1.6E+05	5.0E+06	165	188	13.5
HF	220	6.6E+04	1.8E+06	182	173	5.2
HF	480	1.3E+05	5.2E+06	182	170	6.4

Table 6-9. MDL Data from Water Interference Tests on the LasIR

Target Gas[a]	Path Length (m)	Concentration of CO_2 (ppm*m)	Concentration of H_2O (ppm*m)	MDL (ppm*m)
HF	480	1.7E+05	6.3E+06	0.13
HF	220	7.2E+04	2.4E+06	0.20

[a] MDL tests were conducted with zero concentration of target gas in the test cell.

Increasing the total number of water carbon and dioxide molecules in the path length had no significant deleterious effect on the monitor's MDL for HF. In fact, as shown in Table 6-9, the MDL varied from 0.13 to 0.20 ppm for HF, while the water concentration in the path varied from approximately 2.4×10^6 to 6.3×10^6 ppm*m and the carbon dioxide concentration varied from approximately 7.2×10^4 to 1.7×10^5 ppm*m. That is, the MDL for HF actually decreased with greater H_2O and CO_2 in the light path.

6.6 Other Factors

6.6.1 Costs

The total cost of the LasIR, as tested, is approximately $80,000, according to UNISEARCH.

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%.

Chapter 7
Performance Summary

The LasIR exhibited detection limits of 0.09 and 1.21 ppm*m for methane, 0.13 to 0.23 ppm*m for HF, and 1.05 to 13.7 ppm*m for ammonia. In these field tests, there was no strong trend in detection limits with either path length or integration time for the target gases.

The tests of the LasIR to determine the effects of source strength showed that there was no consistent degradation of the monitor's performance with a decrease in source strength of up to 72%. The LasIR showed a maximum deviation of 0.019 ppm at a path-average concentration of approximately 0.454 ppm over 220 meters, under this range of source reduction.

The concentration linearity results showed that the LasIR had a response slope of 1.00 and an r^2 value of 1.00 for methane over a gas cell concentration range of 40 to 800 ppm; a response slope of 0.71 and an r^2 value of 0.96 for HF over a gas cell concentration of 66 to 549 ppm; and a slope of 1.17 and an r^2 value of 0.99 for ammonia over a gas cell concentration of 75 to 494 ppm.

The percent relative accuracy for methane ranged between 0.02 and 12.2%, with the best accuracy found at a gas cell concentration of 800 ppm. The HF percent relative accuracy ranged between 5.1 and 28.7%, at a path length of 220 meters. The percent relative accuracy for ammonia ranged between 3.66 and 19.7% at the 220-meter path length. Note that these results are subject to uncertainties in the delivery and determination of the target gases, especially for NH_3 and HF. In particular, it should be noted that the reference concentration was determined by impinger sampling downstream of the optical cell, which is subject to potential uncertainty from losses of HF, adding to uncertainty

Using a path length of 220 meters for HF and ammonia and 1.5 meters for methane, the LasIR exhibited precision in repetitive measurements of 0.63% RSD for methane, 1.19% RSD for HF, and 1.84% RSD for ammonia at target gas cell concentrations of 800, 549, and 494 ppm, respectively.

Analysis of the effects of ambient water vapor and carbon dioxide on the LasIR's measurements showed no consistent effect of these species on the accuracy of measurement for methane and HF. The MDL for HF was also not significantly affected with increased levels of H_2O and CO_2 in the light path.

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.

Appendix A
Data Recording Sheet

	Date:	**Operator:**	
Sample Gas:		**Reviewed by:**	

Measurement #												
Cell Temp (F)												
Ambient O_2 Concentrations (ppb)												
Ambient CO_2 Concentrations (ppb)												
Ambient RH (%)												
Ambient O_3 Concentrations (ppb)												
Ambient Temp (F)												
Integration Time												
Path Length												
Concentration in Cell												
Cell Length												
Time of Measurement												