

Environmental Technology Verification Report

BOREAL LASER INC.
GASFINDER 2.0
TUNABLE DIODE LASER
OPEN-PATH MONITOR

Prepared by



Battelle

Under a cooperative agreement with



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September 2000

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

**Boreal Laser Inc.
GasFinder 2.0
Tunable Diode Laser
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.

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 Paul Webb and Adam Abby of Battelle and Jim Bauer of Boreal Laser.

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List of Abbreviations

AMS	Advanced Monitoring Systems
CEM	continuous emission monitor
cm	centimeter
CO ₂	carbon dioxide
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
GC/FID	gas chromatography/flame ionization detection
HF	hydrogen fluoride
H ₂ O	water
kg	kilogram
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
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 Boreal Laser Inc. GasFinder 20 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 GasFinder 2.0 monitor. The following description of the GasFinder 2.0 is based on information provided by the vendor.

The GasFinder 2.0 measures gas concentration over an open path and consists of an integrated transmitter/receiver unit and a remote, passive retroreflector array. The remote retroreflector is initially targeted by the operator using a two-axis monitor mount, assisted by a telescopic sight and an on-board visible aiming laser. The transceiver houses the laser diode source, drive electronics, detector module, and microcomputer subsystems. The transceiver unit is in a weatherproof enclosure and has connectors for power input and data input/output.

The laser light emitted from the transceiver unit propagates through the atmosphere to the retroreflector and returns, where it is focused onto a photodiode detector. Simultaneously, a portion of the laser beam is passed through an onboard gas cell to provide a continuous calibration update. These two optical signals are converted into electrical waveforms, which the microcontroller processes to determine the actual concentration of the target gas along the optical path. The computed gas concentration is then displayed on the back panel of the monitor, as well as transmitted to a central coordinating computer where the data are collected, stored, and displayed.



Figure 2-1. Boreal Laser Inc. GasFinder 2.0 TDL Open-Path Monitor

By selecting the appropriate diode laser, the monitor can measure the concentration of methane, ammonia, carbon dioxide,

hydrogen sulphide, or hydrogen fluoride in the presence of other gases. Atmospheric gases, such as water vapor, have a negligible effect on the laser system.

The self-contained, automatic, self-calibrating monitor can be used as a portable tool, or it can be permanently installed with a path length up to 1,000 meters. It displays average gas concentrations either in parts per million (ppm) or, for low gas concentrations, in parts per million meters (ppm*m).

The GasFinder 2.0 weighs 5 kg and measures 26 x 20 x 15 cm (LxWxH) (10.2 x 7.9 x 5.9 inches). It uses 12Vdc power and operates in the range of -30° C to +50° C.

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 GasFinder 2.0 monitor 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 1-meter 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 GasFinder 2.0 are shown in Table 3-1. The verification was conducted by measuring the 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 and Concentrations for Testing the GasFinder 2.0

Gas	Concentration Level	Target Gas Concentration (ppm*m)	Gas Cell Concentration (ppm) ^a
Methane	c1	25	25
	c2	50	50
	c3	100	100
	c4	500	500
HF	c1	25	25
	c2	50	50
	c3	100	100
	c4	320	320
Ammonia	c1	25	25
	c2	50	50
	c3	100	100
	c4	475	475

^a Length of gas cell = 1 m.

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

Meas. #	Gas Cell Conc.	Activity	Collected # of Measurements	Times (min)		Path Length ^c (m)	Verification Parameter Calculated
				Integrate	Equilibrate		
1	N ₂	Change gas & stabilize	2.5	1	10	220	Accuracy, Concentration linearity, MDL
	N ₂	Collect spectra				220	
	c1 ^a	Change gas & stabilize		1	10	220	Accuracy, Concentration linearity
2	c1	Collect spectra	5	1		220	Source strength linearity ^b
3	c1	Collect spectra - ND 1	5	1		220	Source strength linearity ^b
4	c1	Collect spectra - ND 2	5	1		220	Source strength linearity ^b
5	c1	Collect spectra - ND 3	5	1		220	Source strength linearity ^b
	N ₂	Change gas & stabilize			10	220	
6	N ₂	Collect spectra	5	1		220	Accuracy, Concentration linearity
	c2	Change gas & stabilize		1	10	220	Accuracy, Concentration linearity, Interference effect (Int.)
7	c2	Collect spectra	5	1		220	
	N ₂	Change gas & stabilize			10	220	
8	N ₂	Collect spectra	5	1		220	Accuracy, Concentration linearity
	c3	Change gas & stabilize		1	10	220	
9	c3	Collect spectra	5	1		220	Accuracy, Concentration linearity
10	c3	Collect spectra - ND 1	5	1		220	Source strength linearity ^b
11	c3	Collect spectra - ND 2	5	1		220	Source strength linearity ^b
12	c3	Collect spectra - ND 3	5	1		220	Source strength linearity ^b
	N ₂	Change gas & stabilize			10	220	
13	N ₂	Collect spectra	5	1		220	Accuracy, Concentration linearity
	c4	Change gas & stabilize		1	10	220	
14	c4	Collect spectra	2.5	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	2.5	5		220	Concentration linearity, MDL
	N ₂	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
	N ₂	Change to Path length 3			20	480	
19	N ₂	Collect spectra	5	1		480	Int., Accuracy, Concentration linearity
	c2	Change gas & stabilize			10	480	
20	c2	Collect spectra	5	1		480	Int., Accuracy, Concentration linearity
	N ₂	Change gas & stabilize			10	480	
21	N ₂	Collect spectra	2.5	1		480	Int., MDL

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

^b Measurements for source strength linearity only made for ammonia.

^c Accuracy and MDL calculations only done for methane at 2 meters.

3.2 Test Design

The verification test was performed near West Jefferson, Ohio, at an outdoor testing area belonging to Battelle between April 22 and April 28, 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 GasFinder 2.0 receiver 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.

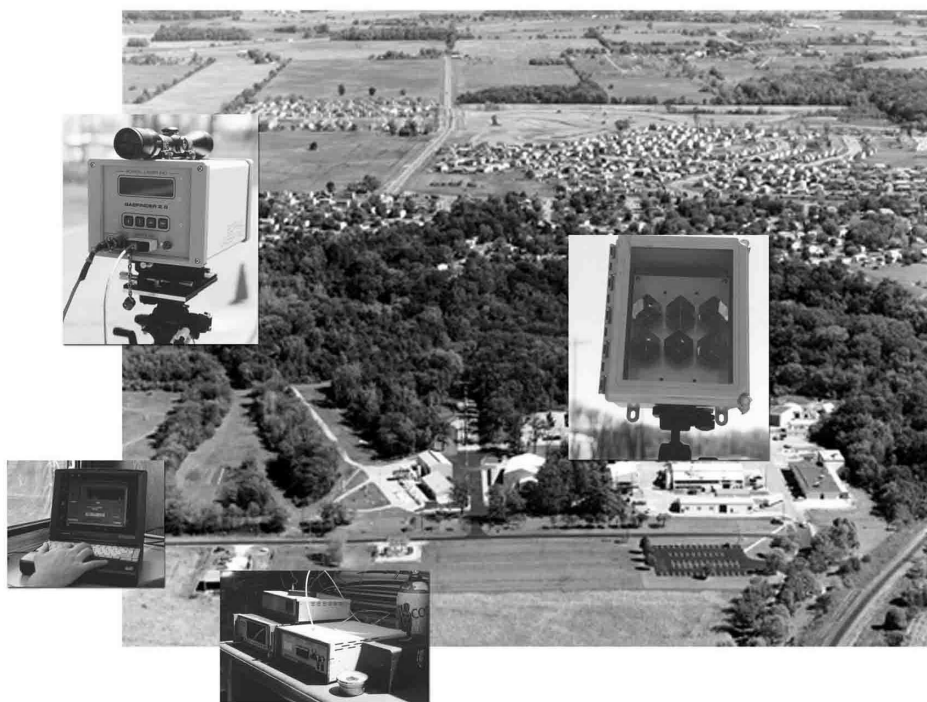


Figure 3-1. Test Site at Battelle's West Jefferson Facility

The GasFinder 2.0 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.

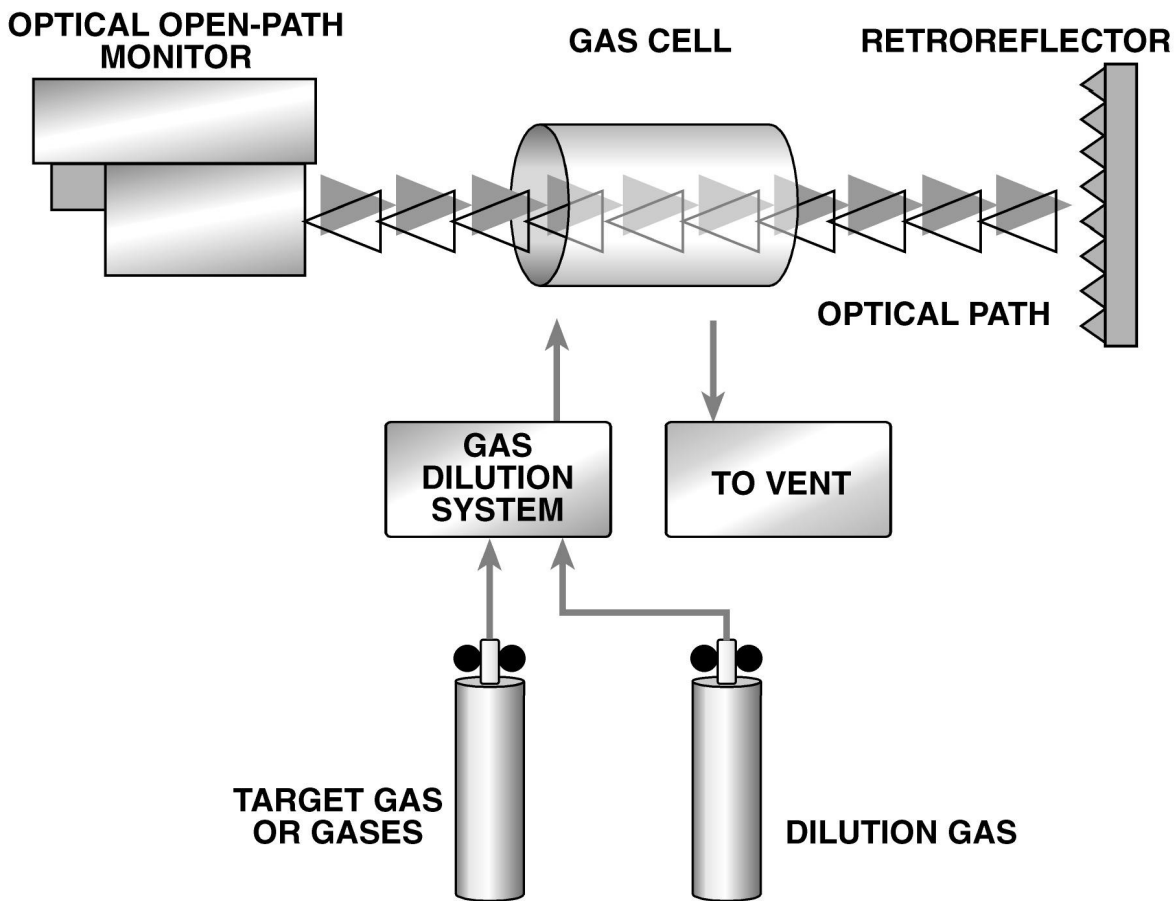


Figure 3-2. Optical Open-Path Monitor Setup

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 generate known concentrations of 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 (UHP) obtained by 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.

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

A quartz gas cell 1 meter in length and 10 centimeters in diameter was placed between the monitor and the retroreflector.

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 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 $\pm 5\%$ RH.

3.3.7 Carbon Dioxide Monitor

A commercial nondispersive infrared (NDIR) monitor (Gastech Model RI-411 infrared CO₂ monitor, Serial No. 9350211) was used to monitor the level of CO₂ 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 CO₂ in air. The limit of resolution of this monitor was 25 ppm.

3.3.8 NO/NH₃ 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 NH₃ concentrations supplied to the optical cell for verification testing. This monitor sampled gas immediately downstream of the optical cell to confirm the NH₃ concentrations prepared by dilution of a high-concentration ammonia standard. The API monitor was calibrated with a NIST-traceable commercial standard cylinder of NO in nitrogen. The conversion efficiency for NH₃ was checked by comparing the calibration slope for NO with that found in calibrations with NH₃. All NH₃ measurements were corrected for the NH₃ 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 flushing the target gas from the gas cell 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 target gas 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, various attenuations were achieved. At each of these attenuation levels, a measurement was made, and the monitor analyzed for the target gas. The test was performed at two different concentrations in the gas cell (25 ppm and 100 ppm) using ammonia.

Concentration linearity was determined by challenging the GasFinder 2.0 with each target gas at cell 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 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 GasFinder 2.0 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, using an integration time of 1 minute and a path length of 220 meters. 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. In addition, methane was tested at a 2-meter path

length to eliminate contributions from ambient methane fluctuations. The open-path measurements of the GasFinder 2.0 were used to infer the cell gas concentration. 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 two different concentrations of each of the target gases (see Table 3-2). Additional precision information was obtained from the replicate analyses conducted in the interference test.

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. The purpose of the interference measurements was to determine the effects of the ambient atmospheric gases on accuracy and MDL of the GasFinder 2.0. 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 GasFinder's open-path measurements and compared to the input cell gas concentrations.

This procedure was conducted with path lengths of both 220 and 480 meters, the latter being the length that Boreal chose as optimum. Atmospheric concentrations of H₂O and CO₂ 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 H₂O and CO₂). For methane only, additional measurements were also made with a 2-meter path length (i.e., the gas cell only) to avoid the effect of the ambient methane background concentration.

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). 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 N₂ was used.

-
- The test/QA plan stated that the CO₂ measurement would undergo a performance evaluation audit using a calibration standard obtained from an independent supplier. Instead, a separate CO₂ standard obtained from the same manufacturer was used for the audit.
 - The gas concentrations used in the verification test of the GasFinder 2.0 differ from those stated in Section 5.4 of the test/QA plan. The concentrations stated in the test/QA plan were based on the best knowledge of the monitors to be tested at the time the plan was written. In actuality, the instrument provided for testing was not designed to handle the methane and ammonia concentrations stated in the plan; and, therefore, different concentrations were used. For HF, the ability to deliver the target concentrations to the gas cell was the limiting factor, and consequently all HF concentrations used for testing were determined by actual measurement. Therefore, the gas concentrations used in the verification test of the GasFinder 2.0 differ from those stated in Section 5.4 of the test/QA plan.
 - The approach established in the test/QA plan was to dilute and deliver HF to the test cell in a flowing gas stream and to confirm the effectiveness of that delivery by a performance evaluation audit using impinger sampling. However, delivery of HF in known concentrations to the test cell was found to be very difficult. As a result, impinger sampling was adopted for all HF tests as a means to establish the test cell concentration. That is, the planned performance evaluation method was adopted as a routine part of each HF test and not used as a performance evaluation audit method.

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 that ultimately resulted 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.
 - The test/QA plan specified that neutral density filters would be used for each of the gases. The original intent was to use the filters for one gas only. The neutral density filters only were used during the measurements 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.

4.3.2 Temperature Sensor

The thermocouple was calibrated by comparing it to a certified standard. This instrument has a one-year calibration period.

4.3.3 RH Sensor

The RH sensor used the manufacturer's calibration.

4.3.4 Carbon Dioxide Monitor

The NDIR CO₂ monitor was calibrated before testing using a commercially prepared, certified standard of CO₂ in air.

4.3.5 NO/NH₃ Monitor

The NO/NH₃ monitor was calibrated with both NO and NH₃ 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 NH₃ standard was also a Certified Master Class Calibration Standard, of 494 ppm NH₃ in air, of ± 2% analytical uncertainty (Scott, Cylinder No. ALM 005256). The ratio of the slopes of the NH₃ and NO calibration curves established the NH₃ 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 the 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 all activities associated with the tests 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 TDL Monitor 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 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 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 assessed 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. The results from the performance evaluation are shown in Table 4-2.

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)	55 F	54.1 F	-0.9 F
CO ₂	Compare measurement using an independent carbon dioxide standard	700 ppm	700 ppm	0.0 ppm
RH	Compare to independent RH measurement (wet/dry bulb device)	34% RH	35.4% RH	4.1%
Methane	Compare to results of gas chromatographic analysis of canister samples	50 ppm	46 ppm	-8.0%
NO/NH ₃	Compare to measurement using an independent NO standard	50 ppm	47 ppm	-6.0%

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/NH₃ 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 3 ppm at 50 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

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

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, \dots, T_n , the standard deviation (σ) 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 methane in air with an interference concentration of 100 ppm of CO₂, indicates 30 ppm of methane when the CO₂ concentration is changed to 200 ppm. This would result in an interference effect of $(30 \text{ ppm} - 26 \text{ ppm})_{\text{methane}} / (200 \text{ ppm} - 100 \text{ ppm})_{\text{CO}_2} = 0.04$, or 4% relative sensitivity.

Chapter 6

Test Results

The results of the verification test of the GasFinder 2.0 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 2, 220, and 480 meters, which is a typical path length range 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 GasFinder's open-path measurement to the actual test cell concentration.

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. 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 around 1.7 ppm and removing the effect of the atmospheric methane could only be accomplished by placing the retroreflector immediately at the end of the 1-meter target gas cell. Therefore, for this target gas, only the integration time was varied.

The MDL calculations (which are based on the variability with zero concentration) may incorrectly estimate the actual MDL, since the majority of the data recorded were at a level below the monitor's ability to detect and, as a result, the output of the monitor was numerically zero. 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.

The stated MDL, shown in Table 6-2, was calculated using the method described in Section 3.4.1, and for the HF monitor is much larger than that claimed by the vendor. This was due to nonoptimal performance with the gas cell in the optical path. Several factors adversely affect measurements when an object (e.g., gas cell) is introduced into the optical path, such as diffraction caused by the edges of the cell, which may change due to slight misalignment as a result of wind or vibration and condensation on the tube windows during night-time operation. As a result of the exceptionally high values recorded during these measurements and the numerical

Table 6-1. MDL Data for the GasFinder 2.0

Measurement Number	Methane		HF			Ammonia		
	Path Length (m)		Path Length (m)			Path Length (m)		
	2	2	220	480	220	220	480	220
	Integration Time (min)		Integration Time (min)			Integration Time (min)		
	1	5	1	1	5	1	1	5
Concentration (ppm*m)								
1	1.4	1.5	0.0	0.0	0.0	0.0	0.0	0.0
2	1.4	1.6	0.0	0.0	0.0	0.0	0.0	0.0
3	1.3	1.1	0.0	0.0	0.0	0.0	0.0	0.0
4	1.6	1.4	0.0	0.0	0.0	0.0	0.0	0.0
5	1.5	1.3	0.0	0.0	0.0	0.0	0.0	0.0
6	1.6	1.7	0.0	0.0	0.0	0.0	0.0	0.0
7	1.6	1.7	0.8	0.0	0.0	0.0	0.0	0.0
8	1.6	1.7	0.8	0.0	0.0	0.0	0.0	0.0
9	1.5	1.5	0.6	0.0	0.0	0.0	0.0	0.0
10	1.5	1.4	0.9	0.0	0.0	0.0	0.0	0.0
11	1.3	1.9	0.9	0.0	0.0	0.0	0.0	0.0
12	1.4	1.7	0.8	0.0	0.0	0.0	0.0	0.0
13	1.5	1.7	0.9	0.0	0.0	0.0	0.0	0.0
14	1.4	2.1	0.0	0.0	0.0	0.0	0.0	0.0
15	1.4	1.9	0.0	0.0	1.8	0.0	0.0	0.0
16	1.3	2.0	0.0	0.0	2.2	0.0	0.0	0.0
17	1.3	2.1	0.0	0.0	2.7	0.0	0.0	0.0
18	1.3	1.4	0.0	0.0	3.9	0.0	0.0	0.0
19	1.1	1.3	0.0	0.0	4.2	0.0	0.0	0.0
20	1.2	1.3	0.0	0.0	3.7	0.0	0.0	0.0
21	1.3	1.3	0.0	0.0	2.2	0.0	0.0	0.0
22	1.4	1.2	0.0	0.0	1.0	0.0	0.0	0.0
23	1.6	1.5	0.0	0.0	0.0	0.9	0.0	0.0
24	1.5	1.4	0.0	0.0	0.0	0.0	0.0	0.0
25	1.6	1.3	0.7	0.0	0.0	0.0	0.0	0.0
Data used for alternate MDL calculation			4.7			22.7		
			3.6			19.3		
			3.7			23.5		
			3.7			26.3		
			3.7			20.9		

Table 6-2. Minimum Detection Limits of the GasFinder 2.0

Target Gas	Path Length (m)	Integration Time (min)	MDL (ppm*m)
Methane	2	1	0.29
Methane	2	5	0.56
HF	220	1	0.77
HF	480	1	0.00
HF	220	5	2.86 ^a
HF ^b	220	1	0.09 ^b
Ammonia	220	1	0.36
Ammonia	480	1	0.00
Ammonia	220	5	0.00
Ammonia ^b	220	1	5.32 ^b

^a Stated MDL is much larger than that claimed by the vendor - this was due to non-optimal performance with the calibration tube in the optical path. See explanation in Section 6.1

^b Calculated using alternate, peer review suggested, method described in Section 6.1

zeroes recorded for HF and ammonia, an alternate method of calculating the MDL is presented as well. This method, which was requested by peer review, substitutes the smallest tested concentrations of HF and ammonia (25 ppm*m and 3.0 ppm*m respectively) for an empty cell. Two times the standard deviation of these measurements is reported as the alternate MDL. These tests, were done at a path length of 220 meters and 1-minute integration time.

The results in Table 6-2 show that the GasFinder 2.0 exhibited detection limits of 0.29 to 0.56 ppm*m for methane. The detection limits for HF and ammonia were calculated using two methods. The method described in Section 3.4.1 resulted in an detection limits between 0.00 and 2.86 ppm*m for HF and between 0.00 and 0.36 ppm*m for ammonia. Since these results were calculated based upon data that were not appropriate for MDL measurements, a second method of calculating the MDL was used. This method resulted in an a detection limit of 0.09 ppm*m for HF and 5.32 ppm*m for ammonia at a path length of 220 meters and a 1-minute integration time.

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. The relative signal power is the measure of light attenuation during that measurement. For example, a relative signal power of 0.82 means that the light level for the test is 82% of the light level during normal operating conditions. The ammonia concentration is the amount of gas (in ppm) being delivered to the 1-meter cell during the measurement, and the monitor response is the resulting reading from the GasFinder 2.0.

Table 6-3. Source Strength Linearity of the GasFinder 2.0

Relative Signal Power	Ammonia Concentration (ppm)	Monitor Response (ppm)
1.00	25	22.5
0.82	25	25.2
0.60	25	24.8
0.48	25	25.1
1.00	100	96.0
0.90	100	95.4
0.65	100	102
0.45	100	92.5

The GasFinder 2.0 showed a maximum departure from the known ammonia concentration of approximately 1.3 ppm at 25 ppm and 7.5 ppm at 100 ppm. The linear regression results in Figure 6-1 indicate a correlation coefficient of 0.56 and a slope of -4.04 at 25 ppm and a near-zero correlation ($r^2 = 0.01$) and a minimal slope (1.82) at 100 ppm. These results show that over the attenuation range tested, the GasFinder 2.0 measurements are independent of source strength.

6.2.2 Concentration Linearity

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

The concentration linearity results show that the GasFinder 2.0 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 of known concentrations in the gas cell.

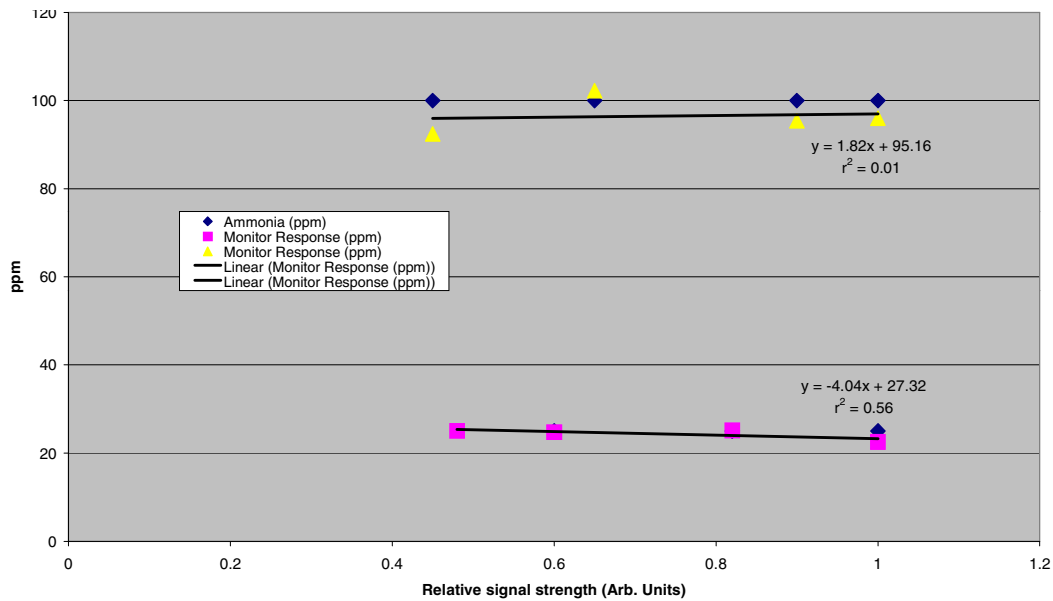


Figure 6-1. Source Strength Linearity Plot for the GasFinder 2.0

Table 6-4. Concentration Linearity Data for the GasFinder 2.0

Target Gas	Gas Cell Concentration (ppm)	Monitor Response ^a (ppm)
Methane	25	26.3
Methane	50	47.2
Methane	50	44.4
Methane	50	32.8
Methane	100	95.3
Methane	500	470
HF	2.6	3.0
HF	25.1	29.7
HF	3.6	6.4
HF	24.8	29.3
HF	13.8	22.6
HF	320	413
Ammonia	25	22.5
Ammonia	50	68.3
Ammonia	50	49.4
Ammonia	50	59.1
Ammonia	100	96.0
Ammonia	475	514

^a Measurements were conducted over path lengths of 220 and 480 meters, including the 1-meter gas cell.

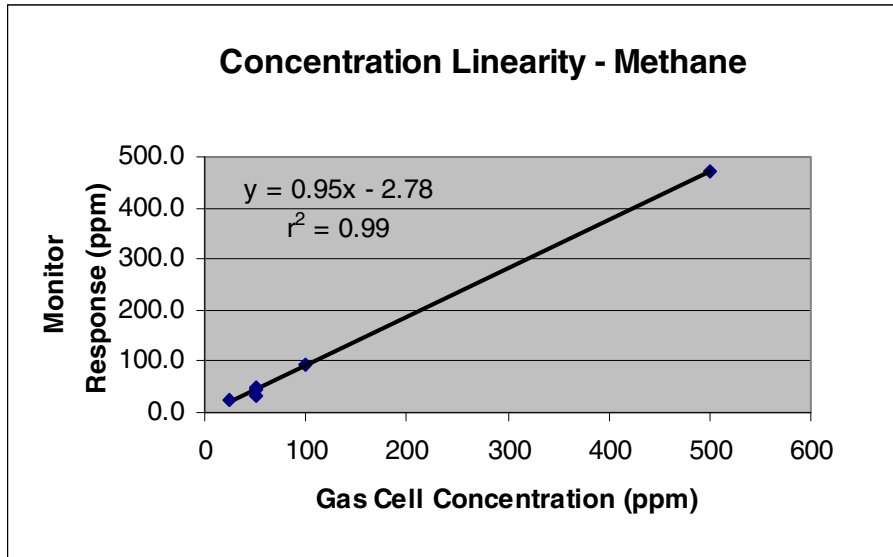


Figure 6-2. Concentration Linearity Plot of the GasFinder 2.0 Challenged with Methane

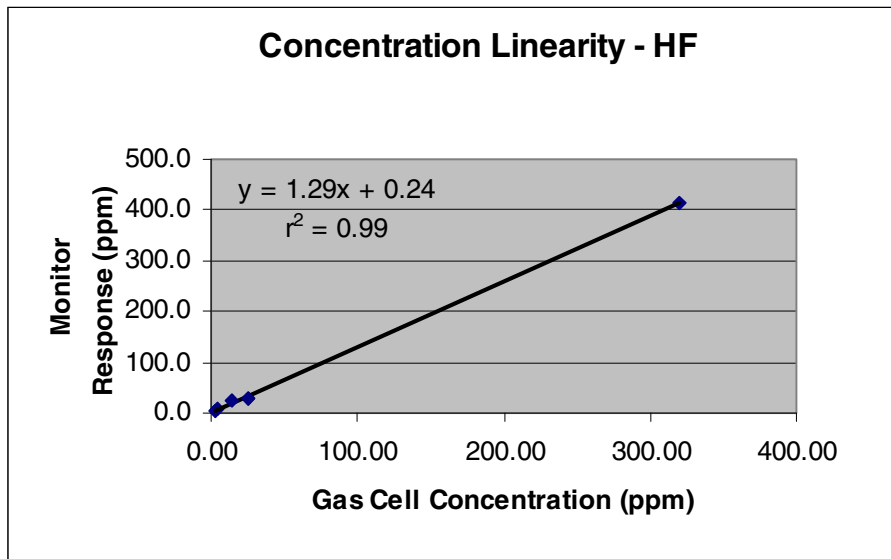


Figure 6-3. Concentration Linearity Plot of the GasFinder 2.0 Challenged with HF

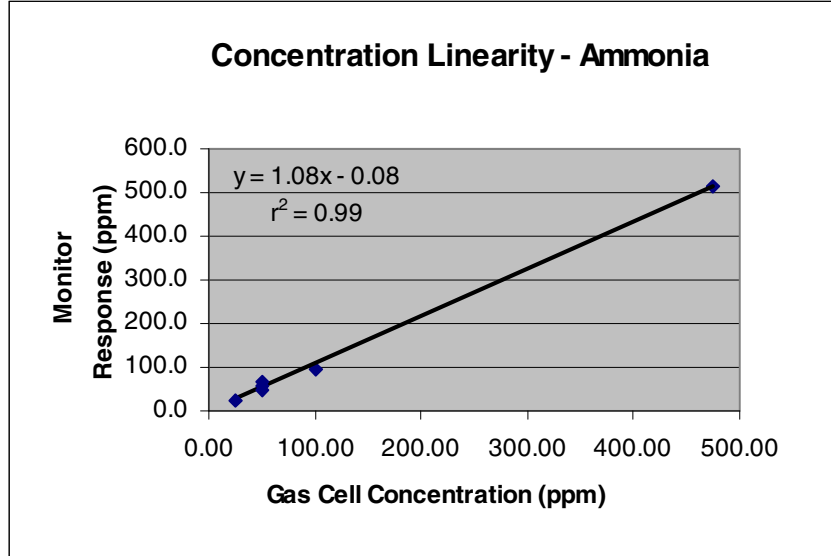


Figure 6-4. Concentration Linearity Plot of the GasFinder 2.0 Challenged with Ammonia

6.3 Accuracy

The accuracy of the GasFinder 2.0 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.

The percent relative accuracy for methane ranged between 5.2 and 34%, with 5.5% accuracy at a path length of 2 meters and a concentration of 50 ppm. Because a component of the longer path lengths of 220 and 480 meters was methane in the ambient air, these measurements are likely to be affected by fluctuations in ambient methane concentrations. This effect was generally small, as can be seen by the relative accuracies of 5.2 to 11% found at the 220-meter path lengths. However, the measurement at the longest path length and longest integration time (5 minutes) would be the most affected by the ambient background and variations of methane; and, in fact, the percent relative accuracy is highest for this condition.

The gas cell concentrations for HF listed in Table 6-5 are based upon impinger sample results. Because of difficulties with the transfer of HF gas, these concentrations may not exactly represent the concentration in the gas cell during the measurements. Results from impinger samples taken while flushing the cell with HF gas (554 ppm) directly from the certified tank through the gas cell showed that 320 ppm of HF was collected in the gas stream exiting the gas cell. This 42% reduction in concentration can be attributed to the reactive nature of HF. Impinger samples taken of the certified HF tank without the gas cell in place resulted in an tank HF concentration of 549 ppm, confirming that there were significant losses of HF on the gas cell walls.

Table 6-5. Results of Accuracy Tests for the GasFinder 2.0

Target Gas	Gas Cell		Integration Time (min)	Monitor Response (ppm)	Relative Accuracy (%)
	Concentration (ppm)	Path Length (m)			
Methane	25	220	1	26.3	5.2
Methane	50	2	1	47.2	5.5
Methane	50	220	1	44.4	11
Methane	50	480	5	32.8	34
Methane	100	220	1	95.3	4.7
Methane	500	220	1	470	6.1
HF	3	220	1	3.0	18
HF	25	480	1	29.7	19
HF	4	220	5	6.4	77
HF	25	480	5	29.3	18
HF	14	220	1	22.6	64
HF	320	220	1	413	29
Ammonia	25	220	1	22.5	9.8
Ammonia	50	480	1	68.3	37
Ammonia	50	220	1	49.4	1.3
Ammonia	50	480	5	59.1	18
Ammonia	100	220	1	96.0	4.0
Ammonia	475	220	1	527	11

The HF percent relative accuracy ranged between 18 and 77%. In each case, the measurement read from the GasFinder 2.0 was greater than that measured by impinger sampling, which was done downstream of the target gas cell. Because of the reactive nature of HF, some HF was lost on the walls of the sampling train and connecting Teflon tubes, leading to the consistent differences seen.

The percent relative accuracy for ammonia ranged between 1.3 and 37%, with better accuracy (1.3 to 9.8%) at the 220-meter path length. There were no obvious problems with the delivery of ammonia during these measurements. The longer integration time improved relative accuracy considerably with the 480-meter path length.

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. The target gas was introduced into the gas cell, and 25 successive analyses were made for the target gas. The actual concentrations delivered during these tests were 500 ppm for methane, 320 ppm for HF, and 475 ppm for ammonia, respectively. The data from these measurements are shown in Table 6-6, and the results are shown in Table 6-7. These results show that the monitor had an RSD of 1.24% for methane, of 1.75% for HF, and of 3.14% for ammonia.

Table 6-6. Data from Precision Tests on the GasFinder 2.0

Analysis	Target Gas		
	Methane (ppm)	HF (ppm)	Ammonia (ppm)
1	457	399	505
2	457	402	538
3	461	405	562
4	460	405	562
5	462	404	564
6	463	404	562
7	467	404	561
8	471	405	557
9	470	405	552
10	470	407	541
11	473	409	526
12	466	412	520
13	464	413	515
14	461	415	514
15	458	416	537
16	461	417	540
17	460	418	537
18	463	419	538
19	464	421	540
20	465	421	536
21	467	420	531
22	470	418	526
23	475	419	530
24	476	419	525
25	475	420	522

Table 6-7. Results of Precision Tests on the GasFinder 2.0^a

Target Gas	Gas Cell Concentration (ppm)	GasFinder 2.0 (ppm)	Standard Deviation (ppm)	Relative Standard Deviation (%)
Methane	500	465	5.75	1.24
HF	320	412	7.22	1.75
Ammonia	475	538	16.9	3.14

^a Integration time = 1 minute; path length = 220 m.

6.5 Interferences

Interference tests of the GasFinder 2.0 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 the 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.

Table 6-8. Concentration Data from Interference Tests on the GasFinder 2.0

Target Gas	Path Length (m)	Gas Cell Concentration (ppm*m)	Concentration of CO ₂ (ppm*m)	Concentration of H ₂ O (ppm*m)	Calculated	Relative Accuracy (%)
					Concentration of Target Gas (ppm*m)	
Methane	2	50	1.20E+03	1.60E+04	47.2	5.5
Methane	220	50	1.27E+05	1.54E+06	44.4	11
Methane	480	50	2.76E+05	3.61E+06	34.4	34
HF	480	25	2.64E+05	3.19E+06	29.7	19
HF	220	4	1.38E+05	1.49E+06	6.42	61
HF	480	25	2.76E+05	3.04E+06	29.3	17
Ammonia	480	50	2.64E+05	2.66E+06	68.3	37
Ammonia	220	50	1.32E+05	1.36E+06	49.4	1.3
Ammonia	480	50	2.88E+05	3.34E+06	59.1	18

Table 6-9. MDL Data from Interference Tests on the GasFinder 2.0

Target Gas ^a	Path Length (m)	Concentration of	Concentration	MDL (ppm*m)
		CO ₂ (ppm*m)	of H ₂ O (ppm*m)	
HF	480	2.64E+05	4.15E+06	2.86 ^b
HF	220	1.49E+05	1.43E+06	0.77
Ammonia	480	2.28E+05	3.11E+06	0.00
Ammonia	220	1.05E+05	1.04E+06	0.36

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

^b Stated MDL is much larger than that claimed by the vendor - this was due to non-optimal performance with the calibration tube in the optical path. See explanation in Section 6.1

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 GasFinder 2.0's ability to accurately determine the concentrations of the target gas. The measured gas concentrations were 34.4 to 47.2 ppm for methane delivered to the target gas cell at 50 ppm; 6.4 and about 29.5 ppm for HF delivered at 4 and 25 ppm, respectively; and from 49.4 to 68.3 ppm for ammonia delivered at 50 ppm, while the water concentration in the path changed from approximately 1.6×10^4 to 3.6×10^6 ppm*m, and the carbon dioxide concentration varied from approximately 1.2×10^3 to 2.9×10^5 ppm*m. For both methane and ammonia the best accuracy, relative to the 50-ppm gas cell concentrations, occurred at the lowest H₂O and CO₂ levels in the light path. However, the results were in opposite directions: high H₂O and CO₂ produced a low methane measurement (34.4 ppm), whereas for ammonia, high H₂O and CO₂ produced high measurement results (59 and 68 ppm). The HF results give no clear indication, having been done at two different concentrations. Here, again, the measurements for methane also would have been affected by any changes in ambient methane concentrations.

Changing the total number of water carbon and dioxide molecules in the path length had no clear effect on the monitor's MDL for the target gas. As shown in Tables 6-9 and 6-11, the MDL varied from 0.77 to 2.86 ppm for HF and from 0.0 ppm to 0.36 ppm for ammonia, while the water concentration in the path varied from approximately 1.0×10^6 to 4.2×10^6 ppm*m and the carbon dioxide concentration varied from approximately 1.1×10^5 to 2.6×10^5 ppm*m. However, the MDL for HF increases with greater H₂O and CO₂ in the light path, whereas that for ammonia decreases. Thus, no consistent interference effect on MDLs is evident. As in the MDL measurements and results, these results may be misleading, since the majority of the data recorded during these tests were at a level below the monitor's ability to detect. As a result, the output of the monitor was numerically zero (see Section 6.1).

6.6 Other Factors

6.6.1 Costs

The total cost of the GasFinder 2.0, as tested, is approximately \$36,500, according to Boreal Laser.

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 GasFinder 2.0 detection limits were 0.29 to 0.56 ppm*m for methane. Because the original data were not appropriate for MDL measurements, detection limits for HF and ammonia were calculated using the alternate approach described in Section 6.1. This approach resulted in an a detection limit of 0.09 ppm*m for HF and 5.32 ppm*m for ammonia at a path length of 220 meters and a 1-minute integration time.

The tests of the GasFinder 2.0 to determine the effects of source strength showed that there was little to no degradation of the monitor's performance with a decrease in source strength of up to 55%. The GasFinder 2.0 showed a maximum deviation from the known ammonia concentration in the gas cell of about 1.3 ppm at 25 ppm ammonia, and 7.5 ppm at 100 ppm ammonia, under this range of source reduction.

The concentration linearity results showed that the GasFinder 2.0 had a response slope of 0.95 and an r^2 value of 0.99 for methane; a slope of 1.29 and an r^2 of 0.99 for HF; and a slope of 1.08 and an r^2 of 0.99 for ammonia.

The accuracy of the GasFinder 2.0 ranged from 5.2 to 11% for methane at a 220-meter path length, and at a 480-meter path, the accuracy was 34%. For HF, accuracy was 18 to 77% at path lengths of 220 and 480 meters. With a cell concentration of 25 ppm and a path length of 480 meters, accuracy was 18%. In all cases, HF results from the GasFinder 2.0 were higher than those determined by impinger samples. Losses on the gas cell wall (as great as 42% in one case) contribute significantly to the bias observed. For ammonia, accuracy was 1.3 to 9.8% at a 220-meter path length. With a 480-meter path, accuracy was 18 and 37%.

Using a path length of 220 meters and cell concentrations of methane, HF, and ammonia of 500, 320, and 475 ppm, respectively, the GasFinder 2.0 exhibited precision in repetitive measurements of 1.24% RSD for methane, 1.75% RSD for HF, and 3.14% RSD for ammonia.

Analysis of the effects of ambient water vapor and carbon dioxide on the GasFinder's measurements showed no consistent effect of these species on the accuracy of measurement of the target gases, or on the MDLs for those gases.

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

Sample Gas:	Date:				Operator:			
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								