

US EPA ARCHIVE DOCUMENT

**Environmental Technology  
Verification Program**  
Advanced Monitoring  
Systems Center

Generic Verification Protocol  
for Optical Open-Path  
Monitors

US EPA ARCHIVE DOCUMENT

ET ✓ ET ✓ ET ✓

**GENERIC VERIFICATION PROTOCOL**

**FOR**

**OPTICAL OPEN-PATH MONITORS**

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## ACRONYMS

<b>AMS</b>	Advanced Monitoring Systems
<b>CO</b>	carbon monoxide
<b>CO<sub>2</sub></b>	carbon dioxide
<b>EPA</b>	United States Environmental Protection Agency
<b>ETV</b>	Environmental Technology Verification
<b>FTIR</b>	Fourier transform infrared
<b>HF</b>	hydrogen fluoride
<b>MDL</b>	minimum detection limit
<b>min.</b>	minute
<b>ND</b>	neutral density
<b>NDIR</b>	non-dispersive infrared
<b>NIST</b>	National Institute of Standards and Technology
<b>NO<sub>x</sub></b>	nitrogen oxides
<b>SO<sub>2</sub></b>	sulfur dioxide
<b>O<sub>2</sub></b>	oxygen
<b>QA</b>	quality assurance
<b>QMP</b>	Quality Management Plan
<b>RH</b>	relative humidity
<b>RSD</b>	relative standard deviation
<b>TDL</b>	tunable diode laser
<b>TSA</b>	technical systems audit
<b>UV</b>	ultraviolet

## **1 INTRODUCTION**

### **1.1 Test Description**

This protocol provides generic procedures for implementing a verification test of optical open-path monitors for use in ambient air or fence-line measurements. Verification tests are conducted under the auspices of the U.S. Environmental Protection Agency (EPA) through the Environmental Technology Verification (ETV) program. The purpose of the ETV program is to provide objective and quality-assured performance data on environmental technologies, so that users, developers, regulators, and consultants can make informed decisions about these technologies.

The verification tests are coordinated by Battelle, of Columbus, Ohio, which is EPA's partner in the ETV Advanced Monitoring Systems (AMS) Center. The scope of the AMS Center covers verification of monitoring technologies for contaminants and natural species in air, water, and soil. In performing verification tests, Battelle follows procedures specified in this protocol and complies with the requirements in the "Quality Management Plan for the ETV Advanced Monitoring Systems Pilot"(QMP).<sup>(1)</sup>

### **1.2 Test Objective**

The purpose of verification tests of commercially available optical open-path monitors is to evaluate their performance for use at facilities concerned with emissions or ambient levels of volatile organic or inorganic chemicals. Verification tests involve challenging these monitors with known reference gas samples under realistic operating conditions.



### 1.3 Test Applicability

This generic protocol is applicable to verification testing of commercial optical open-path monitors capable of real-time monitoring of atmospheric pollutants. These monitors are typically used over greater than 100-meter path lengths and provide information about the concentrations of gases that are present in the air between the light source and the detector. In such applications, these open-path monitors can provide real-time continuous monitoring of air quality and allow early warning of potential non-compliance conditions or emergency release situations. In contrast, grab sample analysis by standard methods is both time-consuming and non-continuous.

## 2 TECHNOLOGY DESCRIPTION

The monitors verified under this protocol rely upon a radiation source (ultraviolet, visible, or infrared) and a detector used together to identify and quantify the levels of certain chemicals in the atmosphere. These monitors are typically used in a continuous monitoring mode and in many cases, are able to simultaneously monitor several compounds. Although the overall design requirements for the different spectral ranges are significantly different, the basic components of these technologies are similar.

In general, these monitors contain at least the following components:

- Radiation source
- Optics
- Detector
- Data processing algorithms.

The radiation sources for these technologies belong to one of three distinct groups. The monitors operating in the ultraviolet (UV) region of the spectrum use a continuous or non-continuous lamp that provides broad-band radiation in the UV and visible regions. The monitors using tunable diode laser (TDL) technology use a laser to provide radiation over a very narrow spectral range in the near infrared. That spectral range can be tuned over a small range with a

single TDL and is selectable over a wider range using multiple TDLs. The Fourier transform infrared (FTIR) monitors use a broadband infrared source.

The optical components of these monitors typically are used to project the radiation from the source, through the atmospheric path to be monitored, and to the detector. The detectors and configurations for these monitors vary according to specific applications. They are typically chosen to maximize signal-to-noise ratio for the spectral region and operating temperature.

### **3 VERIFICATION APPROACH**

#### **3.1 Scope of Test**

The objective of the verification test derived from this generic protocol is to provide quantitative verification of the performance of optical open-path monitors under realistic operational conditions. Specifically, the verification parameters to be verified are

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

#### **3.2 Roles and Responsibilities**

The verification test will be performed by Battelle with the participation of EPA and the vendors whose optical open-path monitors will be verified. The chart in Figure 1 shows the organization of responsibilities for Battelle, the vendor companies, and EPA. Specific responsibilities are detailed below.

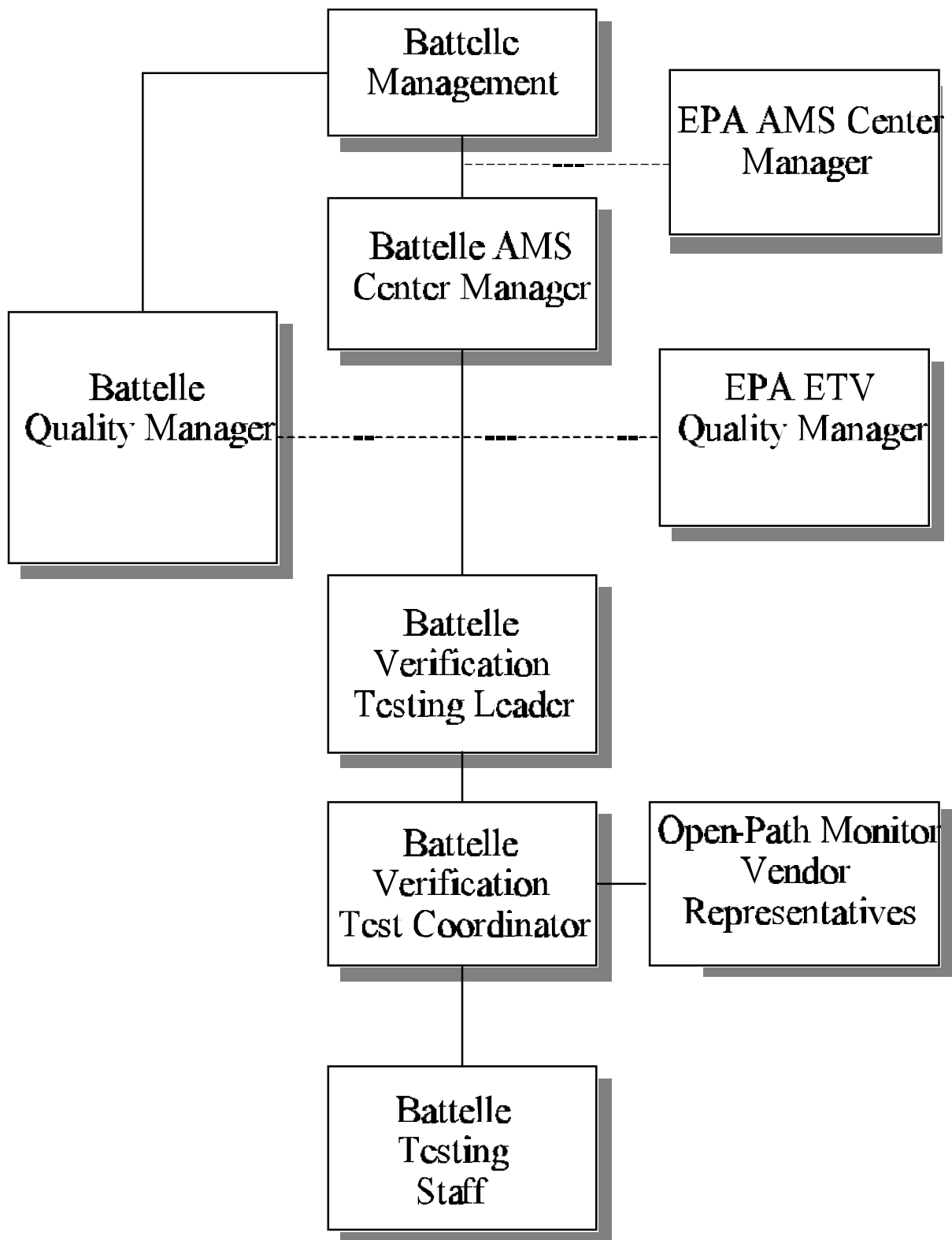


Figure 1. Organization Chart for Optical Open-Path Monitor Verification Test

### 3.2.1 Battelle

The Verification Test Coordinator has the overall responsibility for ensuring that the technical, scheduling, and cost goals established for the verification test are met. The Verification Test Coordinator shall

- Prepare a draft test/quality assurance (QA) plan, verification reports, and verification statements
- Revise the draft test/QA plan, verification reports, and verification statements in response to reviewers' comments
- Assemble the requisite equipment and a team of qualified technical staff to conduct the verification test
- Direct the team in performing the verification test in accordance with the test/QA plan
- Coordinate distribution of the final test/QA plan, verification reports, and verification statements
- Ensure that all quality procedures specified in the test/QA plan and in the QMP are followed
- Respond to any issues raised in assessment reports and audits, including instituting corrective action as necessary
- Serve as the primary point of contact for vendor representatives
- Establish a budget for the verification test and monitor staff effort to ensure that the budget is not exceeded
- Ensure that confidentiality of vendor information is maintained.

The Verification Testing Leader for the AMS Center provides technical guidance and oversees the various stages of the verification test. The Verification Testing Leader shall

- Support the Verification Test Coordinator in preparing the test/QA plan and organizing the test
- Review the draft test/QA plan
- Review the draft verification reports and verification statements
- Ensure that vendor confidentiality is maintained.

The Battelle AMS Center Manager shall

- Review the draft test/QA plan
- Review the draft verification reports and verification statements
- Ensure that necessary Battelle resources, including staff and facilities, are committed to the verification test
- Ensure that vendor confidentiality is maintained
- Support the Verification Test Coordinator in responding to any issues raised in assessment reports and audits
- Maintain communication with EPA's AMS Center and ETV Quality Managers.

The Battelle Quality Manager for the verification test shall

- Review the draft test/QA plan
- Conduct a technical systems audit (TSA) once during the verification test
- Review performance evaluation audit results as specified in the test/QA plan
- Audit at least 10% of the verification data
- Prepare and distribute an assessment report for each audit

- Verify implementation of any necessary corrective action
- Issue a stop work order if self-audits indicate that data quality is being compromised; notify the Battelle AMS Center Manager if a stop work order is issued
- Provide a summary of the audit activities and results for the verification reports
- Review the draft verification reports and statements
- Have overall responsibility for ensuring that the test/QA plan and AMS Center QMP is followed
- Ensure that Battelle management is informed if persistent quality problems are not corrected
- Interface with the EPA Quality Manager.

### 3.2.2 Vendors

Vendor representatives shall

- Review the draft test/QA plan and provide comments and recommendations
- Approve the revised test/QA plan
- Provide off-the-shelf models of the optical open-path monitors to be verified for the duration of the verification test
- Host verification testing of their monitors at their respective facilities or send the monitors and personnel to Battelle to conduct the test
- Install the test equipment and open-path monitors in the test facilities and ensure proper operation of the open-path monitors before and during the test
- Perform on-site maintenance as necessary if a monitor fails any time during the test
- Review and comment upon their respective draft verification reports and statements
- Provide measurement results from the verification test to Battelle in a readily accessible and previously agreed upon format
- Provide and operate the open-path monitors during testing

- Provide sample gas cells appropriate for the monitors being tested
- If the test is performed at Battelle, remove and ship the monitors from Battelle upon completion of test.

### 3.2.3 EPA

EPA's responsibilities in the AMS Center are based on the requirements stated in the "Environmental Technology Verification Program Quality and Management Plan for the Pilot Period (1995-2000)"<sup>(2)</sup> or the most current version of this document. The roles of the specific EPA staff are as follows:

EPA's ETV Quality Manager shall

- Review the draft test/QA plan
- Perform, at his/her option, one external TSA during the verification test
- Notify the Battelle AMS Center Manager to facilitate a stop work order if an external audit indicates that data quality is being compromised
- Prepare and distribute an assessment report summarizing the results of an external audit, if performed
- Review draft verification reports and statements.

EPA's AMS Center Manager shall

- Review the draft test/QA plan
- Approve the final test/QA plan
- Review the draft verification reports
- Approve the final verification reports
- Review the draft verification statements.

## 4 EXPERIMENTAL DESIGN

### 4.1 Overview

The verification test derived from this protocol is designed to challenge the monitors being verified in a manner similar to that which would be experienced in operation in the field. Reproducing many of the actual conditions and problems encountered in the field is beyond the scope of this project; however, a verification test should establish benchmarks that provide quantitative data on specific performance parameters. The basic theory used throughout a test involves challenging the monitors using an optically transparent gas cell that is filled with known concentrations of a target gas. A gas cell is inserted into the optical path of the monitor, thereby simulating a condition where the target gas would be present in the ambient air. The gas cell is used to challenge the monitor in a controlled and uniform manner.

### 4.2 General Experimental Approach

The verification test derived from this protocol is intended to be applicable to many types of open-path monitors. As such, the general approach is deliberately broad, with specific protocols for a technology type specified in Section 5, Test Procedures. In general, the experimental approach employed assumes that the monitor operates by sending a beam of radiation from a source, through the atmosphere, and to a detector. Then, measuring the absorption of the light by the target gas in the atmosphere, the monitor is able to identify and quantify the target gas or gases. The same basic technique is used to verify a variety of technology types. Each monitor shall be challenged with several target gases at known concentrations, and the measurement result shall be compared to the known concentration of the target gas. Since open-path monitors are often able to measure many different types of gases, it is not feasible to test all potential target gases. As a result, in this protocol only a few target gases have been suggested. For each target gas, the monitor is set up as it would be if it were operating in the field, with the exception that an optically transparent gas cell is placed in the light beam's path if the monitor does not already have a built-in gas reference cell. A known concentration of



the target gas is then introduced into the gas cell, and the monitor makes a measurement. Figure 2 is a schematic of a typical setup for the test. The optical open-path monitor and the gas cell are provided by the vendor. The gas dilution system is provided by Battelle. This system consists of National Institute of Standards and Technology-(NIST-) traceable, commercially certified, standard gases, a calibrated gas diluter, and a supply of certified high-purity dilution gas. All of the test equipment used to evaluate the monitors is provided by Battelle to ensure that the testing is conducted in a repeatable manner regardless of the test location. When testing is performed at a site other than Battelle, all appropriate equipment shall be transported to the test site.

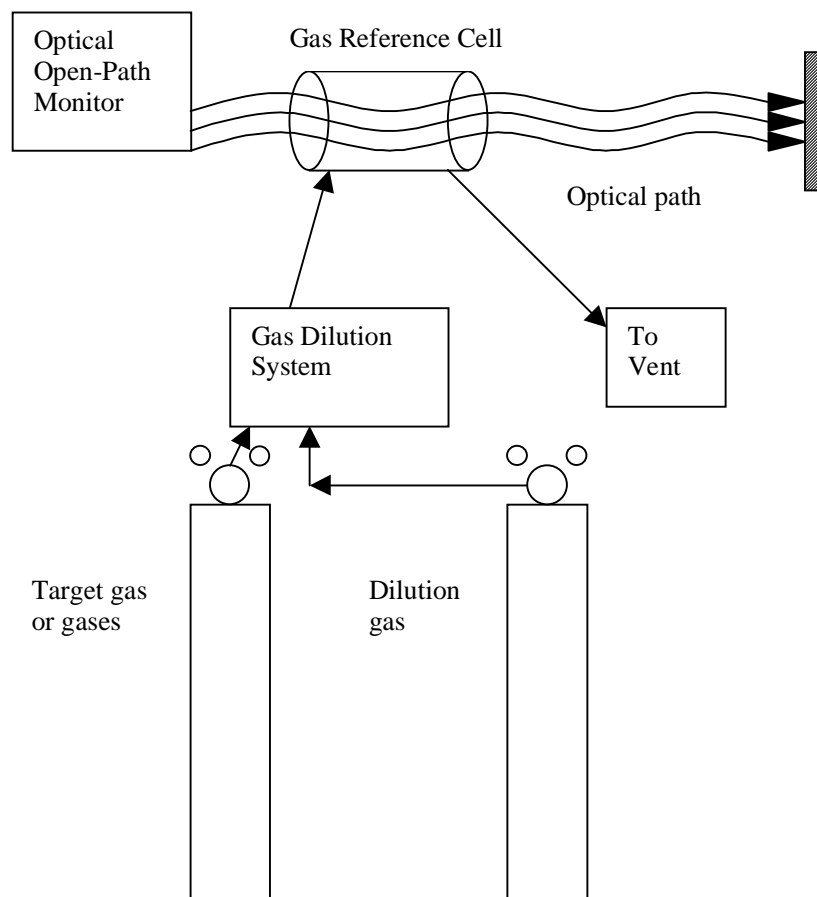


Figure 2. Schematic Showing Functional System and Setup for Verification Tests

The test procedures involve providing a range of known concentrations of various target gases to each monitor. Measurements are made with different path lengths, integration times, source intensities, and numbers of replicate measurements to assess the verification parameters listed in Section 3.1. The test procedures are nested, in that each measurement is used to evaluate more than one verification parameter. To the extent feasible with so diverse a group of technologies, verification test procedures rely on established procedures, such as EPA Method TO-16.<sup>(3)</sup> This method was developed to provide guidelines for gathering and analyzing data using an FTIR.

## 5 TEST PROCEDURES

### 5.1 General Procedural Description

The procedures to be used in the verification test are detailed in this section. The test procedures section is divided into three subsections—FTIR, TDL, and UV—each outlining the specific test procedures for a particular technology type.

The procedures detailed in this section can be carried out for many target gases. In an effort to be as efficient as possible with both time and materials, a specific order of measurements has been established that allows many of the verification parameters to be determined in as short a period as possible. Table 1 shows an efficient measurement order and the verification parameters associated with each measurement. The “Activity #” column provides a reference number for each activity during the test. This allows for easy reference later in the test/QA plan. The “Meas. #” column shows the number of times spectra are recorded. “Ref. Cell Conc.” describes the contents of the reference gas cell during the data acquisition. In these measurements, the content of the gas cell is either “N2” (nitrogen dilution gas) or a known concentration of the target gas “c1” through “c4.” Concentrations shown as c1, c2, etc. represent the target gas concentrations specified in Table 3 in this section for each technology type. The “Activity” column explains the activity taking place: collecting spectra, changing gases, or adjusting the path length. Several measurements are made (Meas. #3 through #5 and #10 through #12) using an inserted neutral density (ND) filter that allows the source strength (i.e., light intensity) to be varied in a controlled and repeatable manner. The “# of Measurements”

**Table 1. Optical Open-Path Monitor Verification Measurement Order for a Single Gas**

Activity #	Meas. #	Ref. Cell Conc. <sup>a</sup>	Activity	# of Measurements	Integration Time (min)	Path Length (m)	Verification Parameter Calculated
1		N <sub>2</sub>	Change gas & stabilize			short	
2	1	N <sub>2</sub>	Collect spectra	25	1	short	Accuracy., Concentration linearity, MDL
3		c1	Change gas & stabilize			short	
4	2	c1	Collect spectra	5	1	short	Acc., Concentration linearity
5	3	c1	Collect spectra - ND 1 <sup>b</sup>	5	1	short	Source strength linearity
6	4	c1	Collect spectra - ND 2 <sup>b</sup>	5	1	short	Source strength linearity
7	5	c1	Collect spectra - ND 3 <sup>b</sup>	5	1	short	Source strength linearity
8		N <sub>2</sub>	Change gas & stabilize			short	
9	6	N <sub>2</sub>	Collect spectra	5	1	short	Acc., Concentration linearity
10		c2	Change gas & stabilize			short	
11	7	c2	Collect spectra	5	1	short	Acc., Concentration linearity, Interference effect (Int.)
12		N <sub>2</sub>	Change gas & stabilize			short	
13	8	N <sub>2</sub>	Collect spectra	5	1	short	Acc., Concentration linearity
14		c3	Change gas & stabilize			short	
15	9	c3	Collect spectra	5	1	short	Acc., Concentration linearity
16	10	c3	Collect spectra - ND 1 <sup>b</sup>	5	1	short	Source strength linearity
17	11	c3	Collect spectra - ND 2 <sup>b</sup>	5	1	short	Source strength linearity
18	12	c3	Collect spectra - ND 3 <sup>b</sup>	5	1	short	Source strength linearity
19		N <sub>2</sub>	Change gas & stabilize			short	
20	13	N <sub>2</sub>	Collect spectra	5	1	short	Acc., Concentration linearity
21		c4	Change gas & stabilize			short	
22	14	c4	Collect spectra	25	1	short	Acc., Concentration linearity, MDL, Precision
23	15	N <sub>2</sub>	Collect spectra	5	1	short	Acc., Concentration linearity
24		N <sub>2</sub>	Change gas & stabilize			short	
25	15	N <sub>2</sub>	Collect spectra	25	5	short	Acc., Concentration linearity, MDL, Precision
26			Change to path length 2			long	
27	16	N <sub>2</sub>	Collect spectra	5	5	long	Interference Effect (Int.)
28		c2	Change gas & stabilize			long	
29	17	c2	Collect spectra	5	5	long	Int., Acc., Concentration linearity
30		N <sub>2</sub>	Change gas & stabilize			long	
31	18	N <sub>2</sub>	Collect spectra	5	5	long	Int., Acc., Concentration linearity
32			Change to path length 3			optimum	
33	19	N <sub>2</sub>	Collect spectra	5	1	optimum	Int., Acc., Concentration linearity
34		c2	Change gas & stabilize			optimum	
35	20	c2	Collect spectra	5	1	optimum	Int., Acc., Concentration linearity
36		N <sub>2</sub>	Change gas & stabilize			optimum	
37	21	N <sub>2</sub>	Collect spectra	25	1	optimum	Int., Precision. MDL

<sup>a</sup> See Table 3 for gas concentrations.

<sup>b</sup> Measurement performed for only one gas.

column explains how many individual spectra are collected at that experimental condition. The “Integration Time” column is the integration time to be used for that measurement. “Path Length” is the total length the beam will travel between the source and the detector. This is not the length of the gas cell used in these experiments. The “Verification Parameter Calculated” column relates each measurement to the verification parameters that will eventually be calculated.

### 5.2 Schedule

The verification is conducted by performing measurements in the fixed sequence shown in Table 1. The monitor provided by the vendor undergoes that full test sequence. It is anticipated that the testing will take place over three days, with a day for setup and a day for teardown. The recommended schedule for testing a single monitor is shown in Table 2.

**Table 2. Schedule of Verification Testing Activities**

<b>Activity #</b>	<b>Day</b>	<b>Gas</b>	<b>Approximate Time</b>
Travel and Setup	One	--	1 day
1-24	Two	One	08:00-13:00
25-36	Two	One	14:00-18:00
1-24	Three	Two	08:00-12:00
25-36	Three	Two	13:00-17:00
1-24	Four	Three	08:00-12:00
25-36	Four	Three	13:00-17:00
Teardown and Travel	Five	--	1 day

## 5.3 Fourier Transform Infrared

### 5.3.1 Gases

Example gases and concentrations to be used for testing FTIR open-path monitors are shown in Table 3. Gases may vary depending upon the specific technology verified. The gases listed in Table 3 were selected because they cover a broad spectral range.

**Table 3. Target Gases for Verification Testing of FTIR Open-Path Monitors**

Gas		Concentration Path Length (ppm-m)
Tetrachloroethylene	c1	5
	c2	10
	c3	25
	c4	50
Cyclohexane	c1	5
	c2	10
	c3	25
	c4	50
Ethylene	c1	5
	c2	10
	c3	25
	c4	50

### 5.3.2 Minimum Detection Limit

The MDL shall be determined for each target gas. This number represents the lowest obtainable value for detecting that specific gas. The MDL is calculated by removing the target gas from the optical path of the monitor, then a series of 26 single-beam spectra are taken using the appropriate averaging time (either 1 min. or 5 min.). The single-beam spectra are then used to

create absorption spectra, using each single beam spectrum as the background for the next spectrum. The absorption spectra are created by using the first and second single-beam spectra, the second and third, the third and fourth, etc. The resulting 25 absorption spectra are then analyzed for the target gas. The MDL is defined as two times the standard deviation of the calculated concentrations.

A summary procedure for determining MDL is as follows:

1. Remove the target gas from the optical path of the monitor
2. Choose an appropriate averaging time for the monitor
3. Acquire 26 single-beam spectra
4. Use the first single-beam spectrum as a background to create an absorption spectrum from the second single-beam spectrum
5. Use the second single-beam spectrum as a background to create an absorption spectrum from the third single-beam spectrum
6. Continue until 25 absorbance spectra are obtained
7. Analyze each absorption spectrum to determine the concentration of the target gas
8. Calculate the standard deviation of the set of concentrations
9. Multiply the standard deviation by two to obtain the MDL.

### 5.3.3 Linearity

Two types of linearity shall be evaluated. The first is the linearity of the monitor for a specific gas over a range of concentrations. The second is the linearity of the monitor as a series of ND filters are inserted into the beam path. This second evaluation of linearity is designed to simulate a reduction in source intensity and to measure the effect this intensity reduction has on the monitor's ability to maintain linear response.

Determining the concentration linearity of the monitor requires challenging the monitor with a target gas at several concentration levels. At each of these concentrations, a single-beam spectrum is acquired.

The procedure for determining concentration linearity is as follows:

1. Place the target gas cell in the optical path of the monitor
2. Set up a dilution system to provide the target gas to the gas cell by diluting a certified gas standard for each gas of interest
3. Perform dilutions with high-purity nitrogen
4. Provide diluent gas or a prepared dilution of the target gas to the gas cell
5. Choose an appropriate averaging time for the monitor
6. After at least five cell volumes of the gas have passed through the cell, acquire a single-beam spectrum
7. Record the concentration value given by the monitor
8. Flush the cell with at least five volumes of high-purity nitrogen and again acquire a single-beam spectrum
9. Repeat steps 4 through 6 with the next concentration of the target gas.

The source strength linearity is evaluated at two concentrations for each gas using three ND filters placed in the beam path. These three ND filters are used to determine the monitor's ability to maintain a linear response with an attenuated source. These filters attenuate the source strength by approximately 10%, 25%, and 50%. The procedure for this evaluation is identical to steps 1 through 7 above, except that one of the ND filters is placed in the optical path.

#### **5.3.4 Accuracy**

Accuracy of the monitors relative to the gas standards shall be verified by introducing known concentrations of the target gas into the cell. The gas cell is flushed with at least five cell volumes of nitrogen, and a single-beam spectrum is recorded. The target gas is then introduced into the cell and, after flushing with at least five cell volumes, a single-beam spectrum of the target gas is obtained. The cell is flushed with at least five cell volumes of nitrogen, and a third spectrum is

recorded. The three spectra are analyzed for the target gas using the background selected by the vendor. The concentration of the target gas is the result of analyzing the second spectrum minus the average of the first and third (flushed cell) spectra.

The accuracy is evaluated at concentrations c1 through c4 using an integration time of 1 min. The accuracy is then evaluated at concentration c2 using a longer integration time, and then again at a concentration of c2 during the interference measurements (Activity #26 through #34 in Table 1). The percent accuracy is the average value of all the measurements at the same conditions, divided by the concentration of the gas in the reference cell, times 100.

### **5.3.5 Precision**

The precision of the monitor is a quantification of its ability to make repeatable measurements when challenged with the same gas sample. The procedure for determining precision is essentially identical to the procedure for determining accuracy. The gas cell is flushed with at least five volumes of nitrogen. The target gas is then introduced into the cell and, after flushing with at least five cell volumes, 25 single-beam spectra of the target gas are obtained. These spectra are analyzed for the target gas. The relative standard deviation of this set of measurements is the precision at the target gas concentration. Precision is evaluated by this procedure at two different concentrations of each of the target gases (see Table 1). Additional precision information shall be obtained from the replicate analysis conducted in the interferences test (Section 5.3.6).

### **5.3.6 Interferences**

The effects of interfering gases shall be established by supplying the reference cell with a target gas and varying the distance between the source and detector of the monitor. The main interferences in ambient air are H<sub>2</sub>O and CO<sub>2</sub>, and, if the measurements are made outdoors, changing the path length will effectively change the amount of interferences in the measurement. The purpose of the interference measurements (Activity #26 through #34 in Table 1) is to determine the effects that the interfering gases have on accuracy, precision, and MDL. These



tests are performed using two different integration times to determine the effect that integration time has on the monitor's ability to make measurements with interfering gases in the light path.

The effect of the interferences shall be measured by setting up the monitor outdoors or in an area where the light path passes through ambient air levels of H<sub>2</sub>O and CO<sub>2</sub> that are consistent with those outdoors, as measured by a relative humidity monitor and a CO<sub>2</sub> monitor (for example, in an airplane hangar). First, the path length is changed to approximately 400 meters. Then, the reference cell is supplied with nitrogen; and, after flushing with at least five cell volumes, five single-beam spectra will be recorded. Next, the target gas is introduced into the cell, and, after similarly flushing the cell, five single-beam spectra are recorded. Finally, nitrogen is again introduced into the cell and five spectra are recorded.

Then the path length is set to the length that the vendor chooses as optimum (i.e., the path length that would theoretically yield the best signal-to-noise ratio). The entire measurement procedure is repeated. Atmospheric concentrations of H<sub>2</sub>O and CO<sub>2</sub> are recorded at the beginning and the end of these measurements. The extent of interference is calculated in terms of sensitivity of the monitor to the interferent. The relative sensitivity is reported.

## **5.4 Tuneable Diode Laser**

### **5.4.1 Gases**

Example gases and concentrations to be used for testing TDL open-path monitors are shown in Table 4.

### **5.4.2 Minimum Detection Limit**

The MDL shall be determined for each target gas. This number represents the lowest obtainable value for detecting that specific gas. The MDL is calculated by removing the target gas from the optical path of the monitor, then a series of 25 measurements are taken using the appropriate averaging time (either 1 min. or 5 min.). The resulting values are then analyzed for the target gas. Two times the standard deviation of the calculated concentrations is defined as the MDL.

**Table 4. Gases for Verification Testing of TDL Open-Path Monitors**

Gas		Concentration Path Length (ppm-m)
NH <sub>3</sub>	c1	5
	c2	25
	c3	50
	c4	100
HF	c1	25
	c2	50
	c3	100
	c4	500
Methane	c1	5
	c2	25
	c3	50
	c4	100

The procedure for determining the MDL is as follows:

1. Remove the target gas from the optical path of the monitor
2. Choose an appropriate averaging time for the monitor
3. Acquire 25 measurements
4. Analyze each absorption spectrum for the target gas
5. Calculate the standard deviation of the set of concentrations
6. Multiply the standard deviation by two to obtain the MDL.

#### 5.4.3 Linearity

Two types of linearity shall be evaluated. The first is the linearity of the monitor for a specific gas over a range of concentrations. The second is the linearity of the monitor as a series of ND filters are inserted into the beam path. This second evaluation of linearity is designed to simulate a reduction in source intensity and to measure the effect this intensity reduction has on the monitor's ability to maintain linear response.

Determining the concentration linearity of the monitor requires challenging the monitor with a target gas at several concentration levels. At each of these concentrations, a measurement is made.

The procedure for determining concentration linearity is as follows:

1. Place the target gas cell in the optical path of the monitor
2. Set up a dilution system to provide the calibration gas to the gas cell by dilution of a certified gas standard for each gas of interest
3. Perform dilutions with high-purity nitrogen
4. Provide a target gas or a prepared dilution of the target gas to the gas cell
5. Choose an appropriate averaging time for the monitor
6. After at least five cell volumes of the gas have passed through the cell, make measurements
7. Record the concentration value given by the monitor
8. Flush the cell with at least five volumes of high-purity nitrogen and again make measurements
9. Repeat steps 4 through 6 with the next concentration.

The source strength linearity is evaluated at two concentrations for each gas using three ND filters placed in the beam path. These three ND filters are used to determine the monitor's ability to maintain a linear response with an attenuated source. These filters will attenuate the source strength by approximately 10%, 25%, and 50%. The procedure for this evaluation is identical to steps 1 through 7 above, except that one of the ND filters is placed in the optical path.

#### **5.4.4 Accuracy**

Accuracy of the monitors relative to the gas standards shall be verified by introducing the target gas into the cell. The gas cell is flushed with at least five cell volumes of nitrogen, and a measurement is recorded. The target gas is then introduced into the cell; and, after flushing with

at least five cell volumes, a measurement of the target gas is obtained. The cell is flushed with at least five cell volumes of nitrogen, and a third measurement is recorded. The three measurements are analyzed for the target gas using the background selected by the vendor. The concentration of the target gas is the result of analyzing the second measurement, minus the average of the first and third (flushed cell) measurements.

The accuracy is evaluated at concentrations  $c_1$  through  $c_4$ , using an integration time of 1 min. The accuracy is then evaluated at concentration  $c_2$  using a longer integration time and then again at a concentration of  $c_2$  during the interference measurements (Activities #26 through #34). The percent accuracy is the average value of all the measurements at the same conditions, divided by the concentration of the gas in the reference cell, times 100.

#### **5.4.5 Precision**

The precision of the monitor is a quantification of its ability to make repeatable measurements when challenged with the same gas sample. The procedure for determining precision is essentially identical to the procedure for determining accuracy. The gas cell is flushed with at least five volumes of nitrogen. The target gas is then introduced into the cell; and, after flushing with at least five cell volumes, 25 measurements of the target gas are obtained. The relative standard deviation of this set of concentrations is the precision at the target gas concentration. Precision is evaluated by this procedure at two different concentrations of each of the target gases (see Table 1). Additional precision information will be obtained from the replicate analysis conducted in the interference measurements (Section 5.4.6)

#### **5.4.6 Interferences**

The effects of interfering gases shall be established by supplying the reference cell with a target gas and varying the distance between the source and detector of the monitor. The main interferences in ambient air are  $H_2O$  and  $CO_2$ ; and, if the measurements are made outdoors, changing the path length will effectively change the amount of interferences in the measurement. The purpose of the interference measurements (Activities #26 through #34 in Table 1) is to determine the effects that the interfering gases have on accuracy, precision, and MDL. These

tests are performed using two different integration times to determine the effect that integration time has on the monitor's ability to make measurements with interfering gases in the light path.

The effect of the interferences shall be measured by setting up the monitor outdoors or in an area where the light path passes through ambient air levels of H<sub>2</sub>O and CO<sub>2</sub> that are consistent with those outdoors, as measured by the relative humidity monitor and the CO<sub>2</sub> monitor (for example, in an airplane hangar). First, the path length is changed to approximately 400 meters. Then, the reference cell is supplied with nitrogen; and, after flushing with at least five cell volumes, five single-beam spectra are recorded. Next, the target gas is introduced into the cell; and, after similarly flushing the cell, five single-beam spectra are recorded. Finally, nitrogen is again introduced into the cell, and five spectra are recorded.

Then the path length is set to the length that the vendor chooses as optimum (i.e., the path length that would theoretically yield the best signal-to-noise ratio). The entire measurement procedure is repeated. Atmospheric concentrations of H<sub>2</sub>O and CO<sub>2</sub> are recorded at the beginning and the end of these measurements. The extent of interference is calculated in terms of sensitivity of the monitor to the interferent. The relative sensitivity is reported.

## **5.5 Ultraviolet Open-Path Monitors**

### **5.5.1 Gases**

Example gases and concentrations to be used for testing UV open-path monitors are shown in Table 5.

### **5.5.2 Minimum Detection Limit**

The MDL shall be determined for each target. This number represents the lowest obtainable value for the detection of that specific gas. The MDL is calculated by removing the target gas from the optical path of the monitor, then a series of 25 measurements are taken using

**Table 5. Gases for Verification Testing of UV Open-Path Monitors**

Gas		Concentration Path Length (ppm-m)
NH <sub>3</sub>	c1	3
	c2	6
	c3	10
	c4	20
NO	c1	2
	c2	5
	c3	10
	c4	15
Benzene	c1	2
	c2	3
	c3	5
	c4	10

the appropriate averaging time (either 1 min. or 5 min.). The resulting values are then analyzed for the target gas. Two times the standard deviation of the calculated concentrations is defined as the MDL.

The procedure for determining MDL is as follows:

1. Remove the target gas from the optical path of the monitor
2. Choose an appropriate averaging time for the monitor
3. Acquire 25 measurements
4. Analyze each measurement for the target gas
5. Calculate the standard deviation of the set of measurements
6. Multiply the standard deviation by two to obtain the MDL.

Additional MDL information will be obtained from the replicate analysis conducted in the interference measurement (Section 5.5.6).

### 5.5.3 Linearity

Two types of linearity shall be evaluated. The first is the linearity of the monitor for a specific gas over a range of concentrations. The second is the linearity of the monitor as a series of ND filters are inserted into the beam path. This second evaluation of linearity is designed to simulate a reduction in source intensity and to measure the effect this intensity reduction has on the monitor's ability to maintain linear response.

Determining concentration linearity requires challenging the monitor with a target gas at several concentration levels. At each of these concentrations, a measurement is made.

The procedure for determining concentration linearity is as follows:

1. Place the gas cell in the optical path of the monitor
2. Set up the dilution system to provide the calibration gas to the gas cell by diluting a certified gas standard for each gas of interest
3. Perform dilutions with high-purity nitrogen
4. Provide target gas or a prepared dilution of the target gas to the gas cell
5. Choose an appropriate averaging time for the monitor
6. After five cell volumes of the gas have passed through the cell, make a measurement
7. Record the concentration value given by the monitor
8. Flush the cell with five volumes of high-purity nitrogen and again make a measurement
9. Repeat with the next concentration
10. Repeat steps 4 through 6 with the next concentration.

The source intensity linearity is evaluated at two concentrations for each gas using three ND filters placed in the beam path. These three ND filters are used to determine the monitor's

ability to maintain a linear response with an attenuated source. These filters will attenuate the source strength by approximately 10%, 25%, and 50%. The procedure for this evaluation is identical to steps 1 through 7 above, except that one of the ND filters is placed in the optical path.

#### **5.5.4 Accuracy**

Accuracy of the monitors relative to the gas standards shall be verified by introducing the target gas into the cell. The gas cell is flushed with at least five cell volumes of nitrogen and a measurement is recorded. The target gas is then introduced into the cell; and, after flushing with at least five cell volumes, a target gas is measured. The cell is flushed with at least five cell volumes of nitrogen, and a third measurement is recorded. The three measurements are analyzed for the target gas using the background selected by the vendor. The concentration of the target gas is the result of analyzing the second measurement, minus the average of the first and third (flushed cell) measurements.

The accuracy is evaluated at concentrations  $c_1$  through  $c_4$ , using an integration time of 1 min. The accuracy is then evaluated at concentration  $c_2$ , using a longer integration time, and then again at a concentration of  $c_2$  during the interference measurements (Activities #26 through #34 in Table 1). The percent accuracy is the average value of all the measurements at the same conditions, divided by the concentration of the gas in the reference cell, times 100.

#### **5.5.5 Precision**

The precision of the monitor is a quantification of its ability to make repeatable measurements when challenged with the same gas sample. The procedure for determining precision is essentially identical to the procedure for determining accuracy. The gas cell is flushed with at least five volumes of nitrogen. The target gas is then introduced into the cell; and, after flushing with at least five cell volumes, 25 measurements of the target gas are obtained. The relative standard deviation of this set of concentrations is the precision at the target gas concentration. Precision is evaluated by this procedure at two different concentrations of each of the target gases (see Table 1). Additional precision information shall be obtained from the replicate analysis conducted in the interference measurements (Section 5.5.6)



### 5.5.6 Interferences

The effects of interfering gases shall be established by supplying the reference cell with a target gas and varying the distance between the source and detector (path length) of the monitor. The main interferences in ambient air are O<sub>2</sub> and O<sub>3</sub>; and, if the measurements are made outdoors, changing the path length will effectively change the amount of interferents in the measurement. The purpose of the interference measurements (Activities #26 through #34 in Table 1) is to determine the effects that the interfering gases have on the accuracy, precision, and MDL. These tests are performed using two different integration times to determine the effect that integration time has on the monitor's ability to make measurements with interfering gases in the light path.

The effect of the interferences is measured by setting up the monitor outdoors or in an area where the ambient levels of O<sub>2</sub> and O<sub>3</sub> are consistent with those outdoors, as measured by the O<sub>2</sub> and O<sub>3</sub> monitors. First, the path length is changed to approximately 400 meters. Then, the reference cell is supplied with nitrogen; and, after flushing with at least five cell volumes, five measurements are recorded. Next, the target gas is introduced into the cell; and, after similarly flushing the cell, five measurements are recorded. Finally, the cell is flushed again, and five more spectra are recorded. Atmospheric concentrations of O<sub>2</sub> and O<sub>3</sub> are recorded at the beginning and the end of these measurements.

Then the path length is set to the length that the vendor chooses as optimum (i.e., the path length that would theoretically yield the best signal-to-noise ratio). The entire measurement procedure is repeated. The extent of interference is calculated in terms of sensitivity of the monitor to the interferent. The relative sensitivity is reported.

## 6 SITE DESCRIPTION

Under this generic protocol, the verification of each monitor should occur at Battelle's Columbus facilities or at a location near the vendor's establishment. If the test is to be performed at the vendor's location, the specific test site shall be identified by the vendor and reviewed with Battelle prior to Battelle staff traveling to the vendor's location to initiate the test.

At either location, the test site shall be outside in an open field or parcel of land where a line of sight is available that meets the maximum path length required (400 meters). The site needs to be away from local sources of emissions and yet easily accessible and able to be reached conveniently throughout the test period. If the test site has limited access, the host (either Battelle or the vendor) shall make appropriate arrangements to ensure that all non-host staff have access. Sufficient lighting shall be available in the event that the test runs into the evening, and there shall be access to appropriate electrical power.

## **7 MATERIALS AND EQUIPMENT**

### **7.1 Standard Gases**

The standard gases diluted to produce target gas levels for the verification testing shall be NIST-traceable gases when possible. Alternatively, commercially certified gas shall be used if NIST-traceable gases are not available for a particular analyte. The gases shall be obtained in concentrations appropriate for dilution to the concentrations required for the tests.

### **7.2 Dilution Gas**

The dilution gas for the verification testing shall be high-purity nitrogen and shall be supplied by Battelle. The dilution gas should have the following specifications: Acid Rain CEM Zero Nitrogen or equivalent (i.e., having the following purity specifications: total hydrocarbons, SO<sub>2</sub> and NO<sub>x</sub> <0.1 ppm, CO and O<sub>2</sub>, <0.5 ppm, CO<sub>2</sub> <1 ppm, and water <5 ppm).

### **7.3 Dilution System**

The dilution system used for preparing the target gases shall have mass flow capabilities with an accuracy of approximately  $\pm 1\%$ . The dilution system shall be capable of accepting a flow of compressed gas standard and diluting it with high-purity nitrogen or air. It shall be able to perform dilution ratios from 1:1 to at least 100:1. The dilution system may be commercially available or assembled from separate commercial components.

#### **7.4 Temperature Sensor**

The temperature sensor used to monitor the ambient air and test cell temperatures shall be a thermocouple with a commercial digital temperature readout. This sensor shall be operated in accordance with the manufacturer's instructions and must have been calibrated against a certified temperature measurement standard within the six months preceding the verification test.

#### **7.5 Relative Humidity Sensor**

The relative humidity (RH) sensor used to determine the humidity of ambient air shall be a commercial RH/dew point monitor that uses the chilled mirror principle. This sensor shall be operated in accordance with the manufacturer's instructions, which call 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 for this monitor must be approximately  $\pm 5\%$  RH.

#### **7.6 Carbon Dioxide Sensor**

A commercial non-dispersive infrared (NDIR) instrument shall be used to monitor the level of CO<sub>2</sub> in ambient air during interference measurements. This sensor shall be operated in accordance with the manufacturer's instructions and shall be calibrated with a commercially prepared cylinder standard of CO<sub>2</sub> in air.

#### **7.7 Ozone Sensor**

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

## 7.8 Monitor for NO and NH<sub>3</sub>

The concentrations of NO and NH<sub>3</sub> prepared by the dilution system during testing shall be checked using a commercial EPA reference chemiluminescent NO/NO<sub>x</sub> monitor, equipped with a high-temperature converter for oxidizing NH<sub>3</sub> to NO for detection. The monitor and converter shall be operated according to the manufacturer's instructions, and the conversion efficiency of the NH<sub>3</sub> converter shall be determined in the laboratory before each use in verification testing.

# 8 QUALITY ASSURANCE/QUALITY CONTROL

## 8.1 Calibration

### 8.1.1 Gas Dilution System

The gas dilution system shall be the responsibility of Battelle. Flow controllers in this system shall be calibrated prior to the start of the verification test for each monitor by means of a soap bubble flow meter. Corrections shall be applied to the bubble meter data for temperature and water content.

### 8.1.2 Temperature Sensor

The thermocouple calibration shall be based upon its comparison to a certified standard within the six months preceding the test. The accuracy of the thermocouple also shall be checked at least once during verification testing by comparison to a standard mercury-in-glass type thermometer. Agreement within 3°C is required or the thermocouple shall be replaced. That comparison shall be conducted as part of the performance evaluation audit described in Section 8.2.2.

### 8.1.3 Relative Humidity Sensor

The RH sensor shall be operated according to the manufacturer's directions and shall employ the manufacturer's calibration. The accuracy of the monitor for RH also shall be checked at least once during verification testing for each monitor by comparison to a standard wet/dry bulb measurement. Accuracy within  $\pm 5\%$  RH is required, or the calibration of the monitor will be adjusted. That comparison shall be conducted as part of the performance evaluation audits described in Section 8.2.2.

### 8.1.4 Carbon Dioxide Sensor

The NDIR CO<sub>2</sub> monitor shall be calibrated before testing each vendor's open-path monitor, using a commercially prepared certified standard of CO<sub>2</sub> in air. Also, at least once during the verification test for each open-path monitor, the CO<sub>2</sub> monitor shall be challenged with an equally certified independent calibration standard obtained from another supplier. Agreement must be within  $\pm 10\%$ , or the monitor shall be recalibrated. That comparison shall be conducted as part of the performance evaluation audits described in Section 8.2.2.

### 8.1.5 Ozone Sensor

The UV absorption method of ozone measurement is inherently calibrated, relying as it does on the accurately determined absorption coefficient of ozone. As a result, routine calibration of the ozone monitor is not needed. However, the monitor shall be operated according to the manufacturer's directions, with careful attention to the diagnostic indicators that assure proper operation of the monitor. In addition, at least once during the verification test of each open-path monitor, the ozone monitor shall be checked in a side-by-side comparison with a different ozone monitor while sampling ambient air. Agreement within 5 parts per billion volume or 10% of reading, whichever is greater, is required. Failure to meet this specification shall result in investigation of the diagnostics of both monitors.

### 8.1.6 Monitor for NO and NH<sub>3</sub>

The NO monitor shall be calibrated using a commercial standard of NO in nitrogen, the concentration of which has been established by direct comparison to a standard reference material of NO in nitrogen, obtained from the NIST. A multipoint calibration is performed before any verification testing takes place, and a single-point span check is performed before testing each vendor's open-path monitor. If that single-point check differs from the original multipoint result by more than 5%, then a new multipoint calibration is performed. In addition, at least once during the verification testing of each open-path monitor, using NO or NH<sub>3</sub> as a target gas, the NO calibration is checked by measuring an independent NO calibration standard obtained from an independent supplier. That comparison is conducted as part of the performance evaluation audits in Section 8.2.2.

The conversion efficiency of the NH<sub>3</sub> converter is established before testing each open-path monitor for which NH<sub>3</sub> is a target compound. The efficiency test consists of operating the NO monitor with the NH<sub>3</sub> converter, while supplying a known NH<sub>3</sub> concentration. All NH<sub>3</sub> measurements are corrected for the conversion efficiency determined in this way.

## 8.2 Audits

### 8.2.1 Technical Systems Audits

Battelle's Quality Manager shall perform a TSA at least once during the verification test. The purpose of this TSA is to ensure that the verification test is being performed in accordance with the AMS Center QMP<sup>(1)</sup> and this protocol and to ensure that all QA/quality control procedures are being implemented. During this audit, the Battelle Quality Manager reviews the calibration sources and methods used, compares actual test procedures to those specified in this protocol, and reviews data acquisition and handling procedures. The Quality Manager also reviews instrument calibration records and gas certificates of analysis.

At EPA's discretion, EPA QA staff may also conduct an independent on-site TSA during the verification test. The TSA findings will be communicated to testing staff at the time of the audit and documented in a TSA report.

### 8.2.2 Performance Evaluation Audits

Performance evaluation audits shall be conducted to assess the quality of the measurements made in the verification test. These audits address only those measurements made by Battelle in conducting the verification test, i.e., the monitors being verified and the vendors operating these analyzers are not the subject of the performance evaluation audits. These audits are performed by comparing Battelle measurements with a standard or a reference that is independent of the standards used during the testing. These audits are performed once during the verification test of each monitor. The audit procedures, which are listed in Table 6, are performed by the technical staff responsible for the measurements being audited. Battelle's Quality Manager shall be present during at least one of the performance evaluation audits to assess the results.

The measurements (physical or chemical) shall undergo the performance evaluation audit by comparison to independent measurements or standards, as indicated in Sections 8.1.2 through 8.1.6 and summarized in Table 6. If during the performance evaluation audit, the measurement being audited does not meet the specified performance criteria, the verification test shall be stopped until the cause of the failed audit is determined.

Table 6 indicates that performance auditing of the prepared hydrogen fluoride (HF) and organic gas concentrations shall be conducted by independent analysis of the test gas mixture supplied to the optical cell during verification testing. For the target organic compounds (i.e., methane, benzene, ethylene, cyclohexane, and tetrachloroethylene), this procedure involves collecting a sample of the test gas mixture exiting the cell using a pre-cleaned and evacuated Summa-polished sampling canister. This gas sample is returned to Battelle and analyzed using EPA Method 18<sup>(5)</sup> or an equivalent method for the target hydrocarbons (methane, benzene, ethylene, and cyclohexane) using gas chromatography with flame ionization detection.

**Table 6. Summary of Performance Evaluation Audit Procedures<sup>a</sup>**

<b>Measurement to be Audited</b>	<b>Audit Procedure</b>
Ammonia	Compare with independent NO standard.
Temperature	Compare with independent temperature measurement (Hg thermometer)
Relative humidity	Compare with independent RH measurement (wet/dry bulb device)
Carbon dioxide	Compare with independent carbon dioxide standard
Ozone	Compare with independent ozone measurement (different analyzer)
NO	Compare with independent NO standard
Organic gases (e.g., benzene, methane)	Compare with results of gas chromatographic analysis of canister sample
Hydrogen fluoride	Compare with results of ion selective electrode or ion chromatography analysis of impinger sample

<sup>a</sup> Each audit procedure will be performed at least once during the verification test.

For HF, the performance audit involves passing a known volume of the gas mixture exiting the optical cell through an impinger containing deionized water. The collected HF solution is then analyzed at Battelle by either of two techniques: an ion selective electrode, as is the basis for EPA Method 13B<sup>(6)</sup>, or ion chromatography for fluoride ion. In either case, calibration is based on fluoride solution standards prepared gravimetrically from high-purity water and reagents.

For both the organic compounds and HF, the analytical results of the performance audit samples shall indicate concentrations in the optical cell within 10% of the expected concentrations. If not, the target gas source and dilution system shall be assembled at Battelle, and additional samples shall be collected and analyzed to re-establish the output of the gas source and



dilution system. The same optical cell used in the verification test shall be obtained from the technology vendor for use in this effort.

### **8.2.3 Audits of Data Quality**

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

## **8.3 Assessment Reports**

Each assessment and audit will be documented in accordance with Section 2.9.7 of the QMP for the AMS Center.<sup>(1)</sup> Assessment reports include the following:

- Identification of any adverse findings or potential problems
- Response to adverse findings or potential problems
- Possible recommendations for resolving problems
- Citation of any noteworthy practices that may be of use to others
- Confirmation that solutions have been implemented and are effective.

## **8.4 Corrective Action**

The Battelle Quality Manager, during the course of any assessment or audit, shall identify to the technical staff performing experimental activities any immediate corrective action that should be taken. If serious quality problems exist, the Battelle Quality Manager is authorized to stop work. Once the assessment report has been prepared, the Verification Test Coordinator ensures that a response is provided for each adverse finding or potential problem and implements

any necessary follow-up corrective action. The Battelle Quality Manager shall ensure that follow-up corrective action has been taken.

## **9. DATA ANALYSIS AND REPORTING**

### **9.1 Data Acquisition**

Data acquisition in this verification test includes recording response data from the monitors undergoing testing, operational data such as ambient RH and temperatures, times of test activities, etc. Data acquisition for the commercial monitors undergoing verification is primarily performed by the vendors themselves during the test. Each monitor shall have some form of data acquisition device, such as a digital display whose readings can be recorded manually, a printout of the monitor's response, or an electronic data recorder that stores individual monitor results. Throughout the test, the vendor is responsible for reporting the response of the monitor to the sample gases provided. Forms for this purpose are provided as needed by Battelle.

Other data are recorded in laboratory record books maintained by each Battelle staff member involved in the testing. These records are reviewed on a daily basis to identify and resolve any inconsistencies.

In all cases, strict confidentiality of data from each vendor's monitor, and strict separation of data from different monitors, is maintained. Separate files (including manual records, printouts, and/or electronic data files) are kept for each monitor. At no time during verification testing will Battelle staff engage in any comparison or discussion of test data or of different monitors.

Table 7 summarizes the types of data to be recorded; where, how often, and by whom the data shall be recorded; and the disposition or subsequent processing of the data. The general approach is to record all test information immediately and in a consistent format throughout all tests. Data recorded by the vendors are to be turned over to Battelle staff immediately upon completion of the test procedure. Test records shall then be converted to Excel spreadsheet files by a designated Battelle staff member. Identical file formats are used for the data from all analyzers tested to assure uniformity of data treatment. This process of data recording and compiling is overseen by the Verification Test Coordinator.

**Table 7. Summary of Data Recording Process for the Verification Tests**

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

<sup>a</sup> Sample data sheet provided in Appendix A.

## 9.2 Statistical Calculations

Performance characterization is based on statistical comparisons of continuous open-path monitor results to the known concentrations of the target gases. The following statistical procedures shall be used to make those comparisons.

### 9.2.1 Minimum Detection Limit

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

$$MDL = +2 \sigma_o \quad (1)$$

### 9.2.2 Linearity

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

$$y = Mx + b \quad (2)$$

where  $y$  is the response of the monitor to a reference 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.

### 9.2.3 Accuracy

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

$$A = \frac{|\bar{T} - \bar{R}|}{\bar{R}} \times 100 \quad (3)$$

where the bars indicate the mean of the reference ( $R$ ) values and monitor ( $T$ ) results. This parameter is determined at each concentration.

### 9.2.4 Precision

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

$$\sigma = \left[ \frac{1}{n-1} \sum_{k=1}^n (T_k - \bar{T})^2 \right]^{1/2} \quad (4)$$

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

$$RSD = \left| \frac{\sigma}{\bar{T}} \right| \times 100 \quad (5)$$

and is a measure of the measurement uncertainty relative to the absolute value of the measurement. This parameter is determined at each concentration.

### 9.2.5 Interferences

The extent of interference is calculated by comparing the relative accuracy of the target gas for each measurement.

## 9.3 Data Review

Records generated by Battelle staff in the verification test shall receive one-over-one review within two weeks after generation before these records are used to calculate, evaluate, or report verification results. These records include laboratory record books, equipment calibration records, and data sheets used to record the monitor's response. This review is performed by a Battelle technical staff member involved in the verification test, but not the staff member that originally generated the record. The review is documented by the person performing the review by adding his/her initials and date to a hard copy of the record being reviewed. This hard copy then is returned to the Battelle staff member who generated or who will be storing the record.

In addition, data calculations performed by Battelle will be spot-checked by Battelle technical staff to ensure that calculations are performed correctly. Calculations to be checked include determination of each monitor's precision, accuracy, minimum detection limit, and other statistical calculations identified in Section 9.2.

## 9.4 Reporting

Statistical data calculations that result from each of the tests described above are conducted separately for each optical open-path monitor. Separate verification reports are prepared, each addressing the monitor provided by one commercial vendor. For each parameter evaluated in the verification test, the verification report presents the measurement data, as well as the results of the statistical evaluation of those data.

The verification report shall briefly describe the ETV program, the AMS Center, and the procedures used in the verification test; but will include specific requirements or departures from procedure necessitated in testing the individual monitor in question. These sections shall be common to each verification report resulting from the verification test. The results of the verification test shall then be stated quantitatively, without comparison to any other monitor tested or any comment on the acceptability of the monitor's performance. The preparation of draft verification reports, review of reports by vendors and others, revision of the reports, final approval, and distribution of the reports shall be conducted as stated in the "Generic Verification Protocol for the Advanced Monitoring Systems Pilot."<sup>(4)</sup> Preparation, approval, and use of verification statements summarizing the results of this test also are subject to the requirements of that same protocol.

## 10. HEALTH AND SAFETY

### 10.1 General

The health and safety officer of the test facility, whether Battelle's or a technology vendor's, shall review the necessary health and safety requirements and guidelines for the facility with Battelle and vendor staff before the verification test begins. Battelle staff involved in this verification test shall operate under these established requirements and guidelines, as well as under appropriate procedures covered in the Battelle Safety Manual. Specifically, personal protective equipment, as defined in procedure SIH-PP-01, shall be used; and the chemical safety protocols set forth in SIH-PP-05 shall be followed. It is expected that while on Battelle's site, all vendor representatives shall operate according to the Battelle site requirements.

## 10.2 Potential Hazards

Vendor staff shall only operate their open-path monitors during the verification test. They are not responsible for generating, nor will they be permitted to generate dilution gases or perform any other verification activities identified in this protocol. Operating the open-path monitors does not pose any known chemical, fire, mechanical, electrical, noise, or other potential hazard.

## 10.3 Training

Before installing and operating their monitors in Battelle laboratories, all vendor staff shall be given a safety briefing. This briefing shall include a description of emergency operating procedures (i.e., in case of fire, tornado, bomb, laboratory accident) and the identification, location, and operation of safety equipment (e.g., fire alarms, fire extinguishers, eye washes, exits). Similar instruction shall be provided by the vendor to all Battelle staff members traveling to the vendor's site.

## 11 DEFINITIONS

**Accuracy**—The degree of agreement between the response of the optical open-path monitor and actual gas concentration.

**Dilution System**—An instrument or apparatus equipped with mass flow controllers, capable of flow control to  $\pm 1\%$  accuracy and used to dilute the target gas to concentrations suitable for testing the monitors.

**Monitor**—System provided by the vendor, consisting of a radiation source and detector, used to measure atmospheric pollutants.

**Minimum Detection Limit**—The concentration at which the response of an optical open-path monitor equals two times the standard deviation of the noise level at the monitor background.

**Linearity**—The linear proportional relationship expected between analyte concentration and monitor response over the full measuring range of the monitor.

**Precision**—The degree of mutual agreement among successive readings of the same sample gas.

**Neutral Density Filter**—An optical filter that attenuates an incident beam of radiation without changing its spectral distribution; that is, it has a constant transmittance over a wide spectral range.

**Interference**—The response of a monitor to a constituent of the sample gas other than the target gas.

**Path Length**—The linear distance over which the radiation from the optical open-path monitor travels between the source and detector.

**Target Gas**—The gas measured by the monitor.

## 12 REFERENCES

1. “Quality Management Plan for the ETV Advanced Monitoring Systems Center,” U. S. EPA, Environmental Technology Verification Program, Battelle, Columbus, Ohio, December 2001.
2. “Environmental Technology Verification Program Quality and Management Plan for the Pilot Period (1995-2000)”, U. S. Environmental Protection Agency, EPA-600/R-98/064, Cincinnati, Ohio, May 1998.
3. “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 1999.
4. “Generic Verification Protocol for the Advanced Monitoring Systems Pilot,” U. S. EPA Environmental Technology Verification Program, prepared by Battelle, Columbus, Ohio, October 1998.



5. “Method 18–Measurement of Gaseous Organic Compound Emissions by Gas Chromatography,” U.S. EPA, Research Triangle Park, North Carolina, February 2000.
6. “Method 13B–Determination of Total Fluoride Emissions from Stationary Sources (Specific Ion Electrode Method),” U.S. EPA, Research Triangle Park, North Carolina, February 2000.

**APPENDIX A**  
**EXAMPLE DATA SHEET**

ETV Advanced Monitoring Systems Pilot  
 Verification of Optical Open-Path Monitor  
 Vendor \_\_\_\_\_  
 Instrument \_\_\_\_\_

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