

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

Test/QA Plan for Verification  
of Optical Open-Path  
Monitors

ET ✓ ET ✓ ET ✓

**TEST/QA PLAN**

**FOR**

**VERIFICATION OF  
OPTICAL OPEN-PATH MONITORS**

**October 28, 1999**

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**TEST/QA PLAN FOR VERIFICATION OF  
OPTICAL OPEN-PATH MONITORS**

**October 28, 1999**

**APPROVAL**

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**Vendor Name**

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**Approval**

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**Date**

## TABLE OF CONTENTS

	<u>Page</u>
1. Introduction .....	6
1.1. Test Description .....	6
1.2. Test Objective .....	6
1.3. Applicability .....	7
2. Technology Description .....	7
3. Verification Approach .....	8
3.1. Scope of Test .....	8
3.2. Organization and Responsibilities .....	8
3.2.1 Battelle .....	10
3.2.2 Vendors .....	12
3.2.3 EPA .....	13
4. Experimental Design .....	14
4.1. Overview .....	14
4.2. General Experimental Method .....	14
5. Test Procedures .....	15
5.1. General Procedural Description .....	15
5.2. Schedule .....	17
5.3. FTIR .....	19
5.3.1 Gases .....	19
5.3.2 Minimum Detection Limit .....	19
5.3.3 Linearity .....	21
5.3.4 Accuracy .....	22
5.3.5 Precision .....	23
5.3.6 Interferences .....	23
5.4. Tuneable Diode Laser .....	24
5.4.1 Gases .....	24
5.4.2 Minimum Detection Limit .....	25
5.4.3 Linearity .....	25
5.4.4 Accuracy .....	26
5.4.5 Precision .....	27
5.4.6 Interferences .....	27
5.5. Ultra Violet (UV) Open Path Monitors .....	28
5.5.1 Gases .....	28

5.5.2 Minimum Detection Limit ..... 28  
5.5.3 Linearity ..... 30  
5.5.4 Accuracy ..... 31  
5.5.5 Precision ..... 31

## TABLE OF CONTENTS (CONTINUED)

	<u>Page</u>
5.5.6 Interferences .....	32
6. Site Description .....	33
7. Materials and Equipment .....	33
7.1. Standard Gases .....	33
7.2. Dilution Gas .....	33
7.3. Dilution System .....	34
7.4. Temperature Sensor .....	34
7.5. Relative Humidity Sensor .....	34
7.6. Oxygen Sensor .....	34
7.7. Carbon Dioxide Sensor .....	35
7.8. Ozone Sensor .....	35
7.9. Monitor for NO and NH <sub>3</sub> .....	35
7.10. Carbon Monoxide Sensor .....	35
8. Quality Assurance/Quality Control .....	37
8.1. Calibration .....	37
8.1.1 Gas Dilution System .....	37
8.1.2 Temperature Sensor .....	37
8.1.3 Relative Humidity Sensor .....	37
8.1.4 Oxygen Sensor .....	38
8.1.5 Carbon Monoxide Sensor .....	38
8.1.6 Carbon Dioxide Sensor .....	38
8.1.7 Ozone Sensor .....	39
8.1.8 Monitor for NO and NH <sub>3</sub> .....	39
8.2. Assessments and Audits .....	40
8.2.1 Technical Systems Audit .....	40
8.2.2 Performance Evaluation Audits .....	40
8.2.3 Data Quality Audit .....	42
8.3. Assessment Reports .....	43
8.4. Corrective Action .....	43
9. Data Analysis and Reporting .....	43
9.1. Data Acquisition .....	43
9.2. Statistical Calculations .....	44
9.2.1 Minimum Detection Limit .....	45

9.2.2 Linearity ..... 45  
9.2.3 Accuracy ..... 46  
9.2.4 Precision ..... 46  
9.2.5 Interferences ..... 47

## TABLE OF CONTENTS (CONTINUED)

	<u>Page</u>
9.3. Data Review .....	47
9.4. Reporting .....	48
10. Health and Safety .....	48
10.1. General .....	48
10.2. Potential Hazards .....	49
10.3. Training .....	49
11. Definitions .....	50
12. References .....	52
APPENDIX A - Example Data Sheet .....	53

## LIST OF FIGURES

1. Organizational chart for optical open-path monitor verification test .....	9
2. Schematic showing functional system and setup for verification tests.....	16

## LIST OF TABLES

1. Optical Open-Path Monitor Verification Measurement Order for a Single Gas .....	18
2. Schedule of Verification Testing Activities .....	19
3. Target Gases for Verification Testing of FTIR Open-Path Monitors .....	20
4. Target Gases for Verification Testing of TDL Open-Path Monitors .....	24
5. Target Gases for Verification Testing of UV Open-Path Monitors .....	29



6. Summary of Performance Evaluation Audit Procedures . . . . . 41  
7. Summary of Data Recording Process . . . . . 45

**1. INTRODUCTION**

**1.1. Test Description**

This test/QA plan provides detailed procedures for a verification test of optical open-path monitors for use in ambient air or fenceline measurements. The verification test will be conducted under the auspices of the U.S. Environmental Protection Agency (EPA) through the Environmental Technology Verification (ETV) program. The purpose of ETV is to provide objective and quality assured performance data on environmental technologies, so that users, developers, regulators, and consultants have an independent and credible assessment of what they are buying and permitting.

The verification test will be performed by Battelle, of Columbus, Ohio, which is managing the ETV Advanced Monitoring Systems (AMS) pilot through a cooperative agreement with EPA (CR826215). The scope of the AMS pilot covers verification of monitoring methods for contaminants and natural species in air, water, and soil. In performing the verification test, Battelle will follow procedures specified in this test/QA plan, and will comply with the quality requirements in the “Quality Management Plan for the ETV Advanced Monitoring Systems Pilot” (QMP).<sup>1</sup>

**1.2. Test Objective**

The goal of this verification test is to quantify the verification parameters of commercially available optical open-path monitors for use at facilities concerned with emissions or ambient levels of volatile organic or inorganic chemicals. This verification will involve challenging these monitors with known reference gas samples under realistic operational conditions.

### **1.3. Applicability**

The technologies tested under this plan are 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 present the users with 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 to be verified under this test/QA plan 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 provide simultaneous monitoring of 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**

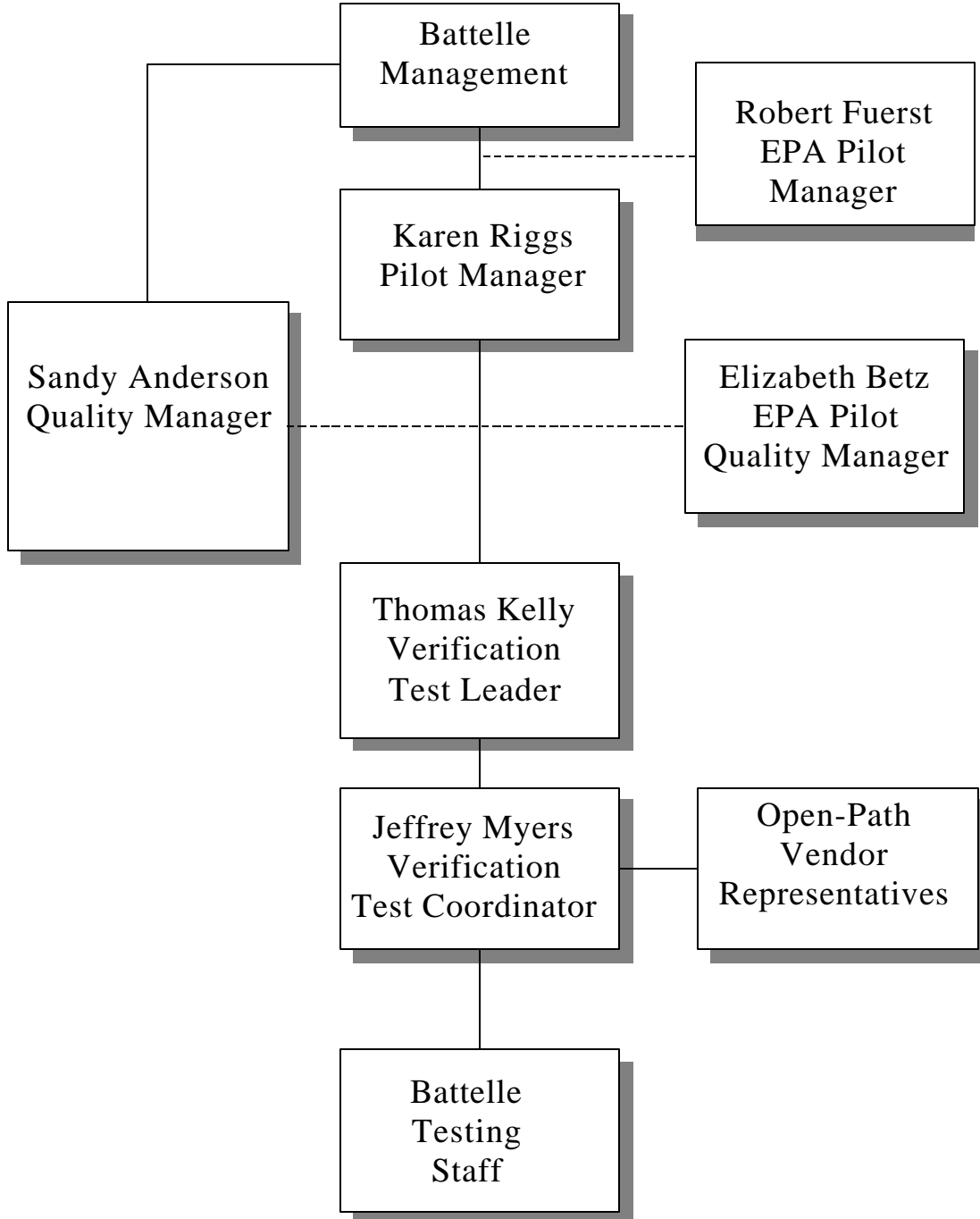
#### **3.1. Scope of Test**

The overall objective of the verification test 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. Organization 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 organizational chart in Figure 1 shows the individuals from Battelle, the vendor companies, and EPA who will have responsibilities in the verification test. The specific responsibilities of these individuals are detailed below.



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

### 3.2.1 Battelle

Mr. Jeffrey D. Myers is the Verification Test Coordinator for the testing of optical open-path monitors through the AMS pilot. In this role, Mr. Myers will have the overall responsibility for ensuring that the technical, scheduling, and cost goals established for the verification test are met. Mr. Myers will:

- Prepare the draft test/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.

Dr. Thomas J. Kelly is the Verification Testing Leader for the AMS pilot. As such, Dr. Kelly will provide technical guidance and oversee the various stages of the verification test. He will:

- Support Mr. Myers 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.

Ms. Karen Riggs is Battelle's ETV pilot manager. As such, Ms. Riggs will:

- 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 Mr. Myers in responding to any issues raised in audits
- Maintain communication with EPA's Pilot Manager.

Ms. Sandy Anderson will serve as the Quality Manager for this verification test. As such Ms. Anderson or her designate will:

- Review the draft test/QA plan
- Conduct a technical system audit 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 Battelle Pilot Manager if stop work order is issued
- Provide a summary of the QA/QC 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 pilot QMP is followed
- Ensure that Battelle management is informed if persistent quality problems are not corrected
- Maintain communication with EPA's Pilot Quality Manager

### **3.2.2 Vendors**

Vendor representatives will:

- Review the draft test/QA plan
- 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 monitor and personnel to Battelle to conduct test
- Install the test equipment and open-path monitor in the test facilities and ensure proper operation of the open-path monitor before and during the test

- Perform on-site maintenance as necessary if monitor fails any time during the test
- Review 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 monitor during testing
- Provide sample gas cell appropriate for the monitor being tested
- If test is performed at Battelle, remove and ship monitor from Battelle upon completion of test

### **3.2.3 EPA**

EPA's responsibilities in the AMS pilot are based on the requirements stated in the "Environmental Technology Verification Program Quality and Management Plan of the Pilot Period (1995-2000)" (QMP). The roles of the specific EPA staff are as follows:

Ms. Elizabeth Betz is EPA's Pilot Quality Manager. For the verification test, Ms. Betz will:

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

- Review draft verification reports and statements.

Mr. Robert Fuerst is EPA's Pilot Manager. As such, Mr. Fuerst will:

- 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 outlined in this document 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 this verification test establishes benchmarks that provide quantitative data on specific performance parameters. The basic theory used throughout these tests involves challenging the monitors using an optically transparent gas cell that is filled with known concentrations of a target gas. The 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**

This verification test is intended to be applicable to many types of open-path monitors. As such, the general approach is deliberately broad, allowing specific protocols for a technology type to be specified in the Test Procedures section. In general, the experimental approach employed in this test 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 each of the technology types as each of the monitors is challenged with several target gases at known concentrations, and the measurement result from the monitor is then compared to the known concentration of the target gas. Since these 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 verification test only a few target gases have been chosen. 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 instrument 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 shows a schematic of the setup to be used for the test. The optical open-path monitor and the gas cell will be provided by the vendor. The gas dilution system will be 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 will be 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 will be transported to the test site.

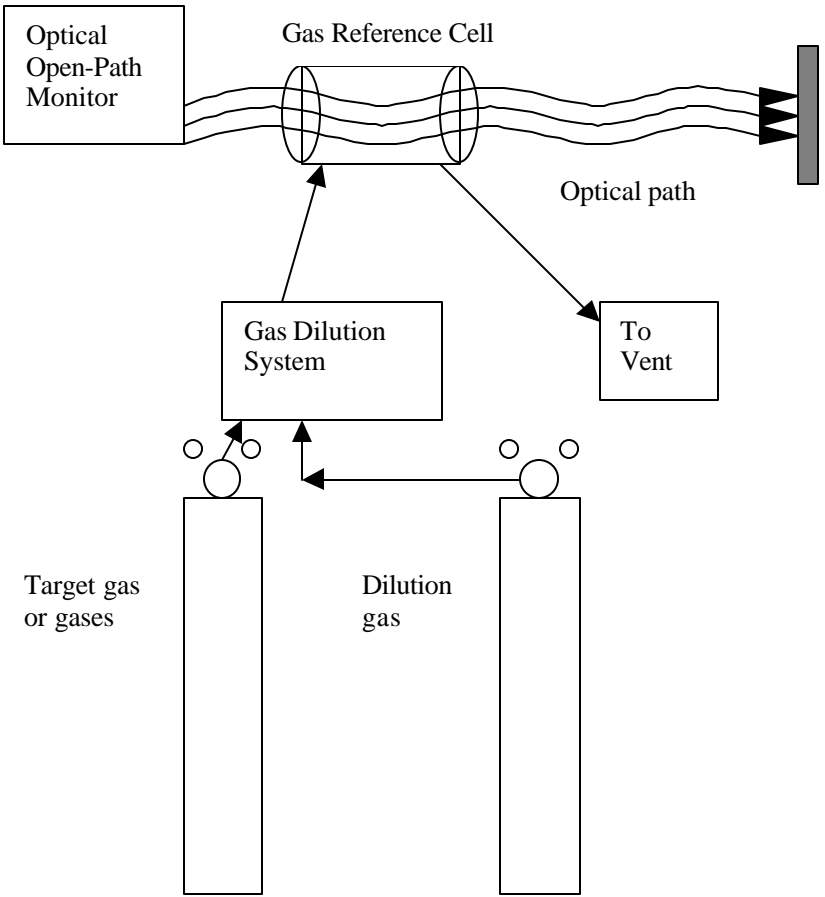
The test procedures involve providing a range of known concentrations of various target gases to each monitor. Measurements are made with different path lengths, integration times, source intensities, and numbers of replicate measurements to assess the verification parameters listed in Section 3.1. The test procedures are 'nested', in that each measurement is used for the evaluation of 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>2</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. This test procedure section is divided into three sub sections - FTIR, TDL, and UV - each outlining the specific test procedures required for a particular technology type.



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

The procedures detailed in this section can be carried out for many different target gases. In an effort to be as efficient as possible with both time and materials a specific order of measurements has been established which allows many of the verification parameters to be determined in as short a period as possible. Table 1 shows the 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 plan. The “Meas. #” column is listed to show 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 later in this section for each technology type. The “Activity” column explains the activity taking place: collecting spectra, changing gases, or adjusting the pathlength. Several measurements are made (Meas. #3 through #5 and #10 through #12) using an inserted neutral density (ND) filter which allows the source strength (i.e. light intensity) to be varied in a controlled and repeatable manner. The “# of Spectra” column explains how many individual spectra are collected at that experimental condition. The “Integrate Time” column is the integration time to be used for that measurement and “Equilibrate Time” expresses the length of time allowed to flow gas through the cell in order to obtain a stable measurement from the monitor. “Pathlength” 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. From the “Elapsed Time” column it can be seen that the test will require about 8.25 hours for the first gas. The subsequent gases take an half an hour less since the replicate tests for the ND filter are not conducted. The “Verification Parameter Calculated” column relates each measurement to the verification parameters that will eventually be calculated.

## 5.2. Schedule

The verification will be conducted by performing measurements in a fixed sequence. The monitor provided by the vendor will undergo that full test sequence. It is anticipated that the



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

Activity #	Meas #	Ref. Cell Conc.	Activity	# of Spectra	Times		Pathlength (m)	Elapsed Time (hrs)	Verification Parameter Calculated
					Integrate	Equilibrate			
1		N2	Change gas & stabilize			10	100	1/4	
2	1	N2	Collect spectra	26	1		100	2/4	Accuracy., Concentration linearity, MDL, Precision
3		c1	Change gas & stabilize			10	100	3/4	
4	2	c1	Collect spectra	5	1		100	3/4	Acc., Concentration linearity
5	3	c1	Collect spectra - ND 1	5	1		100	1	Source strength linearity
6	4	c1	Collect spectra - ND 2	5	1		100	1	Source strength linearity
7	5	c1	Collect spectra - ND 3	5	1		100	1	Source strength linearity
8		N2	Change gas & stabilize			10	100	1 1/4	
9	6	N2	Collect spectra	5	1		100	1 1/4	Acc., Concentration linearity
10		c2	Change gas & stabilize			10	100	1 2/4	
11	7	c2	Collect spectra	5	1		100	1 2/4	Acc., Concentration linearity
12		N2	Change gas & stabilize			10	100	1 3/4	
13	8	N2	Collect spectra	5	1		100	1 3/4	Acc., Concentration linearity
14		c3	Change gas & stabilize			10	100	2	
15	9	c3	Collect spectra	5	1		100	2	Acc., Concentration linearity
16	10	c3	Collect spectra - ND 1	5	1		100	2 1/4	Source strength linearity
17	11	c3	Collect spectra - ND 2	5	1		100	2 1/4	Source strength linearity
18	12	c3	Collect spectra - ND 3	5	1		100	2 1/4	Source strength linearity
19		N2	Change gas & stabilize			10	100	2 2/4	
20	13	N2	Collect spectra	5	1		100	2 2/4	Acc., Concentration linearity
21		c4	Change gas & stabilize			10	100	2 3/4	
22	14	c4	Collect spectra	26	1		100	2 3/4	Acc., Concentration linearity, MDL, Precision
23		N2	Change gas & stabilize			10	100	3	
24	15	N2	Collect spectra	26	5		100	5 1/4	Acc., Concentration linearity, MDL, Precision
25			Change to Pathlength 2			20	400	5 2/4	
26	16	N2	Collect spectra	5	5		400	6	Interference Effect (Int.)
27		c2	Change gas & stabilize			10	400	6	
28	17	c2	Collect spectra	5	5		400	6 2/4	Int., Acc., Concentration linearity
29		N2	Change gas & stabilize			10	400	6 3/4	
30	18	N2	Collect spectra	5	5		400	7	Int., Acc., Concentration linearity
31			Change to Pathlength 3			20	optimum	7 2/4	
32	19	N2	Collect spectra	5	1		optimum	7 2/4	Int., Acc., Concentration linearity
33		c2	Change gas & stabilize			10	optimum	7 3/4	
34	20	c2	Collect spectra	5	1		optimum	7 3/4	Int., Acc., Concentration linearity

Optical Open-Path Monitors

Test/QA Plan

Revision 1

Date: 10/28/99

Page: 25 of 67

35		N2	Change gas & stabilize			10	optimum	8	
36	21	N2	Collect spectra	26	1		optimum	8 1/4	Int., Precision, MDL

testing will take place over three days, with a day for set up and a day for teardown. An example schedule of testing a single monitor is shown in Table 2.

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

Activity #	Day	Gas	Approximate Time
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. FTIR

#### 5.3.1 Gases

The gases and concentrations to be used for testing FTIR open-path monitors are shown in Table 3.

#### 5.3.2. Minimum Detection Limit

The minimum detection limit (MDL) is to be determined for each target gas. 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 26 single beam spectra are taken using the appropriate averaging time (either 1 min. or 5 min.). The

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

Gas		Concentration Pathlength (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

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 minimum detection limit is defined as two times the standard deviation of the calculated concentrations.

The procedure for determining MDL is as follows:

1. Remove the target gas from the optical path of the monitor
2. Choose appropriate averaging time for the monitor
3. Acquire 26 single beam spectra
4. Use first single beam spectrum as a background to create absorption spectrum from the second single beam spectrum
5. Use second single beam spectrum as a background to create 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 minimum detection limit.

### **5.3.3 Linearity**

Two types of linearity will be evaluated. The first will be the linearity of the monitor for a specific gas over a range of concentrations. The second will be the linearity of the monitor as a series of neutral density 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 dilution system to provide the target 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 diluent gas or a prepared dilution of the target gas to the gas cell
5. Choose 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 cell with at least five volumes of high purity nitrogen, and again acquire a single beam spectrum
9. Repeat steps 4-6 with next concentration of the target gas.

The source strength linearity will be evaluated at two concentrations for each gas using three neutral density (ND) filters placed in the beam path. These three neutral density filters will be 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 the 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 will 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  $c_1$  through  $c_4$  using an integration time of 1 minute. The accuracy is then evaluated at concentrations  $c_2$  using a longer integration time, and then again at a concentration of  $c_2$  during the interference measurements (Activity #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.

### **5.3.5 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 the determination of precision is essentially identical to the procedure for the determination of 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 will be obtained from the replicate analysis conducted in the interference test (Section 5.3.6).

### **5.3.6 Interferences**

The effects of interfering gases will 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 pathlength will

effectively change the amount of interferents 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 will 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 pathlength will be changed to approximately 400 meters. Then, the reference cell will be supplied with nitrogen, and after flushing with at least five cell volumes, 5 single beam spectra will be recorded. Next, the target gas will be introduced into the cell and after similarly flushing the cell, 5 single beam spectra will be recorded. Finally, nitrogen will again be introduced into the cell and 5 spectra will be recorded.

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

## **5.4. Tuneable Diode Laser (TDL)**

### **5.4.1. Gases**

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

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



Gas		Concentration Pathlength (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

### **5.4.2. Minimum Detection Limit**

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

The procedure for determining the MDL is as follows:

1. Remove the target gas from the optical path of the monitor.
2. Choose 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 minimum detection limit.

### **5.4.3 Linearity**

Two types of linearity will be evaluated. The first will be the linearity of the monitor for a specific gas over a range of concentrations. The second will be the linearity of the monitor as a series of neutral density 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 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 target gas or a prepared dilution of the target gas to the gas cell
5. Choose 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 cell with at least five volumes of high purity nitrogen, and again make a measurements
9. Repeat steps 4-6 with next concentration.

The source strength linearity will be evaluated at two concentrations for each gas using three neutral density (ND) filters placed in the beam path. These three neutral density filters will be 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 will 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 minute. The accuracy is then evaluated at concentrations  $c_2$  using a longer integration time, and then again at a concentration of  $c_2$  during the interference measurements (Activity #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 the determination of precision is essentially identical to the procedure for the determination of 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 will 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 pathlength will

effectively change the amount of interferents in the measurement. The purpose of the interference measurements (#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 will 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 pathlength will be changed to approximately 400 meters. Then, the reference cell will be supplied with nitrogen, and after flushing with at least five cell volumes, 5 single beam spectra will be recorded. Next, the target gas will be introduced into the cell and after similarly flushing the cell, 5 single beam spectra will be recorded. Finally, nitrogen will again be introduced into the cell and 5 spectra will be recorded.

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

## **5.5. Ultra Violet (UV) Open Path Monitors**

### **5.5.1 Gases**

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

### **5.5.2 Minimum Detection Limit**

The minimum detection limit (MDL) is to 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 the appropriate averaging time (either 1 min. or 5 min.). The

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

Gas		Concentration Pathlength (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

resulting values are then to be analyzed for the target gas. Two times the standard deviation of the calculated concentrations is defined as the minimum detection limit.

The procedure for determining MDL is as follows:

1. Remove the target gas from the optical path of the monitor
2. Choose 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 minimum detection limit.

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 will be evaluated. The first will be the linearity of the monitor for a specific gas over a range of concentrations. The second will be the linearity of the monitor as a series of neutral density 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 gas cell in the optical path of the monitor
2. Set up 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 target gas or a prepared dilution of the target gas to the gas cell

5. Choose 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 cell with five volumes of high purity nitrogen, and again make a measurement
9. Repeat with next concentration
10. Repeat steps 4-6 with next concentration.

The source intensity linearity will be evaluated at two concentrations for each gas using three neutral density (ND) filters placed in the beam path. These three neutral density filters will be 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 the 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 will 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 minute. The accuracy is then evaluated at concentrations  $c_2$  using a longer integration time, and then again at a



concentration of  $c_2$  during the interference measurements (Activity #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.

### **5.5.5 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 the determination of precision is essentially identical to the procedure for the determination of 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 5.5.6)

### **5.5.6 Interferences**

The effects of interfering gases will be established by supplying the reference cell with a target gas and varying the distance between the source and detector (pathlength) of the monitor. The main interferences in ambient air are  $O_2$  and  $O_3$  and if the measurements are made outdoors, changing the pathlength will effectively change the amount of interferences in the measurement. The purpose of the interference measurements (#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 will be 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> that are consistent with those outdoors as measured by the O<sub>2</sub> and O<sub>3</sub> monitors. First, the pathlength will be changed to approximately 400 meters. Then, the reference cell will be supplied with nitrogen, and after flushing with at least five cell volumes, 5 measurements will be recorded. Next, the target gas will be introduced into the cell and after similarly flushing the cell, 5 measurements will be recorded. Finally, the cell will be flushed again and 5 more spectra will be recorded. Atmospheric concentrations of O<sub>2</sub> and O<sub>3</sub> will be recorded at the beginning and the end of these measurements.

Then pathlength will be set to the length that the vendor chooses as optimum, the pathlength that would theoretically yield the best signal to noise ratio, and the entire measurement procedure will be repeated. The extent of interference will be calculated in terms of sensitivity of the monitor to the interferent. The relative sensitivity will be reported.

## **6. SITE DESCRIPTION**

Under this test/QA plan, the verification of each monitor will 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 will 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 will be outside in an open field or parcel of land where a line of sight is available that meets the maximum pathlength required (400 m). 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) must take appropriate arrangements to ensure that all non-host staff have access. Sufficient lighting must be available in the event that the test runs into the evening.

## **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 will be used if NIST traceable gases are not available for a particular analyte. The gases will 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 will be high purity nitrogen and will be supplied by Battelle. The dilution gas must 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 preparation of the target gases must have mass flow capabilities with an accuracy of approximately  $\pm 1$  percent. The dilution system must be capable of accepting a flow of compressed gas standard and diluting it with high purity nitrogen or air. It must 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 will be a thermocouple with a commercial digital temperature readout. This sensor will 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 (RH) Sensor**

The RH sensor used to determine the ambient air humidity will be a commercial RH/Dew Point monitor that uses the chilled mirror principle. This sensor will be operated in accordance with the manufacturer's instructions, which call for cleaning of the mirror and re-balancing of the optical path when necessary, as indicated by the diagnostic display of the monitor. The manufacturer's accuracy specification of this monitor must be approximately  $\pm 5$  percent RH.

### **7.6. Oxygen Sensor**

A commercial electrochemical oxygen sensor will be used to measure the oxygen content of the ambient air during interference measurements. The sensor will be operated according to the

manufacturer's directions, which call for zeroing with nitrogen and calibrating with ambient air (i.e., oxygen content of 20.9 percent).

### **7.7. Carbon Dioxide Sensor**

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

### **7.8. Ozone Sensor**

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

### **7.9. Monitor for NO and NH<sub>3</sub>**

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

### **7.10. Carbon Monoxide Sensor**

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

## **8. QUALITY ASSURANCE/QUALITY CONTROL**

### **8.1. Calibration**

#### **8.1.1 Gas Dilution System**

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

#### **8.1.2 Temperature Sensor**

The thermocouple calibration will be based upon its comparison to a certified standard within the six months preceding the test. The accuracy of the thermocouple will also 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 will be replaced. That comparison will be conducted as part of the Performance Evaluation Audit procedure in Section 8.2.2.

#### **8.1.3 Relative Humidity (RH) Sensor**

The relative humidity sensor will be operated according to the manufacturer's directions, and will employ the manufacturer's calibration. The accuracy of the monitor for RH will also be checked at least once during verification testing for each monitor, by comparison to a standard wet/dry bulb measurement. Accuracy within +/- 5 percent RH is required, or the calibration of the monitor will be adjusted. That comparison will be conducted as part of the Performance Evaluation Audits in Section 8.2.2.



#### **8.1.4 Oxygen Sensor**

The oxygen monitor will be calibrated on each day of use by zeroing with high purity nitrogen and calibrating with ambient air (i.e., 20.9 percent O<sub>2</sub>), per the manufacturer's directions. This procedure assures that the monitor calibration accounts for the effects of day-to-day variations in air temperature and humidity. Also, at least once during the verification test of each monitor, the oxygen monitor will be checked by comparison with another oxygen monitor. Agreement within 0.5 percent oxygen is required when sampling ambient air, or the monitor will be recalibrated. That comparison will be conducted as part of the Performance Evaluation Audits in Section 8.2.2.

#### **8.1.5 Carbon Monoxide Sensor**

The NDIR CO monitor will be calibrated before testing of each vendor's open-path system, using a commercially prepared certified standard of CO. Also, at least once during the verification test for each open-path monitor, the CO monitor will be challenged with an equally certified independent calibration standard obtained from another supplier. Agreement must be within +/- 10 percent, or the monitor will be recalibrated. That comparison will be conducted as part of the Performance Evaluation Audits described in Section 8.2.2.

#### **8.1.6 Carbon Dioxide Sensor**

The NDIR CO<sub>2</sub> monitor will be calibrated before testing of each vendor's open-path system, 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 will be challenged with an equally certified independent calibration standard obtained from another supplier. Agreement must be within +/- 10 percent, or the monitor will be recalibrated. That comparison will be conducted as part of the Performance Evaluation Audits described in Section 8.2.2.

### **8.1.7 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 will 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 will be checked in a side-by-side comparison with a different ozone monitor while sampling ambient air. Agreement within 5 ppbv or 10 percent of reading, whichever is greater, is required. Failure to meet this specification will result in investigation of the diagnostics of both monitors.

### **8.1.8 Monitor for NO and NH<sub>3</sub>**

The NO monitor will 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 will be performed before any verification testing takes place, and a single point span check will be performed before testing of each vendor's open-path system. If that single-point check differs from the original multipoint result by more than 5 percent, then a new multipoint calibration will be 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 will be checked by measurement of an independent NO calibration standard obtained from an independent supplier. That comparison will be conducted as part of the Performance Evaluation Audits in Section 8.2.2.

The conversion efficiency of the NH<sub>3</sub> converter will be established before testing each open-

path system for which  $\text{NH}_3$  is a target compound. The efficiency test will consist of operating the NO monitor with the  $\text{NH}_3$  converter, while sampling a constant  $\text{NH}_3$  concentration in clean dilution gas. A second  $\text{NH}_3$  converter will then be inserted into the sampling line downstream of the first, and the conversion efficiency of the first converter will be assessed by the increase (if any) in response. This approach requires a stable  $\text{NH}_3$  source, but does not require a certified or even known  $\text{NH}_3$  concentration. All  $\text{NH}_3$  measurements will be corrected for the conversion efficiency determined in this way.

## **8.2 Assessment and Audits**

### **8.2.1 Technical Systems Audit**

Battelle's Quality Manager, Ms. Sandy Anderson or her designee, will perform a technical systems audit once during a verification test. The purpose of this technical systems audit is to ensure that the verification test is being performed in accordance with this test/QA plan and that all QA/QC procedures are being implemented. During this audit, Ms. Anderson will review the calibration sources and methods used, compare actual test procedures to those specified in this plan, and review data acquisition and handling procedures. She will also review instrument calibration records and gas certificates of analysis.

### **8.2.2 Performance Evaluation Audits**

Performance evaluation audits will be conducted to assess the quality of the measurements made in this 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 will be performed by analyzing a standard or comparing to a reference that is independent of standards used during the

testing. These audits will be performed once during the verification test of each monitor. The audit procedures, which are listed in Table 6, will be performed by the technical staff responsible for the measurements being audited. Battelle's Quality Manager will be present during at least one of the performance evaluation audits to assess the results.

The measurements (physical or chemical) will undergo the performance evaluation audit by comparison to independent measurements or standards, as indicated in Sections 8.1.2 through 8.1.8, and summarized in Table 6. If during the performance evaluation audit, the measurement

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

<b>Measurement to be Audited</b>	<b>Audit Procedure</b>
Ammonia	Compare measurements using an independent NO standard.
Temperature	Compare to independent temperature measurement (Hg thermometer)
Relative humidity	Compare to independent RH measurement (wet/dry bulb device)
Oxygen	Compare to independent oxygen measurement (different analyzer)
Carbon Monoxide	Compare measurement using an independent carbon monoxide standard
Carbon Dioxide	Compare measurement using an independent carbon dioxide standard
Ozone	Compare to independent ozone measurement (different analyzer)
NO	Compare measurements using an independent NO standard
Other target gases (e.g. benzene, methane, etc.)	Comparison to results of gas chromatographic analysis of canister sample
HF	Comparison to results of ion selective electrode or ion chromatography analysis of impinger sample

- (a) Each audit procedure will be performed at least once during the verification test.

being audited does not meet the specified performance criteria, the verification test will be stopped until the cause of the failed audit is determined.

Table 6 indicates that performance auditing of the prepared HF and hydrocarbon concentrations will 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 will involve collecting a sample of the test gas mixture exiting the cell using a pre-cleaned and evacuated Summa-polished sampling canister. This gas sample will be returned to Battelle, and analyzed using EPA Method 18 when applicable for the target hydrocarbons (methane, benzene, ethylene, and cyclohexane) using gas chromatography with flame ionization detection (GC/FID). Calibration of the FID response will be based on a NIST propane standard containing 9 ppm carbon. Analysis for tetrachloroethylene will be by GC with mass selective detection (GC/MS), using a gravimetrically prepared standard of the target compound for calibration.

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

For both the organics and HF, the analytical results of the performance audit samples must indicate concentrations in the optical cell within 10 percent of the expected concentrations. If not, the target gas source and dilution system will be assembled at Battelle, and additional samples will 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 will be obtained from the technology vendor for use in this effort.

### **8.2.3 Data Quality Audit**

Battelle's Quality Manager will audit at least 10 percent of the verification data acquired in the

verification test. The Quality Manager will trace the data from initial acquisition, through reduction and statistical comparisons, and to final reporting. All calculations performed on the data undergoing audit will be 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 pilot.<sup>(1)</sup> Assessment reports will include the following:

- C Identification of any adverse findings or potential problems
- C Response to adverse findings or potential problems
- C Possible recommendations for resolving problems
- C 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 Quality Manager during the course of any assessment or audit will 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 will ensure that a response is provided for each adverse finding or potential problem, and will implement any necessary follow-up corrective action.

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

### **9.1. Data Acquisition**

Data acquisition in this verification test includes recording of 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 must 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 will be responsible for reporting the response of the monitor to the sample gases provided. Forms for this purpose will be provided as needed by Battelle.

Other data will be recorded in laboratory record books maintained by each Battelle staff member involved in the testing. These records will be 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, will be maintained. Separate files (including manual records, printouts, and/or electronic data files) will be 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 recording is made, 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 is to be turned over to Battelle staff immediately upon completion of the test procedure. Test records will then be converted to Excel spreadsheet files by a designated Battelle staff member. Identical file formats will be used for the data from all analyzers tested, to assure uniformity of data treatment. This process of data recording and compiling will be overseen by the Verification Test Coordinator.

## **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 will be used to make those comparisons.

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

Data to be Recorded	Recorded By	Where Recorded	When Recorded	Disposition of Data
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.

### 9.2.1 Minimum Detection Limit

The minimum detection limit (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.

$$MDL = \bar{x}_o + 2\sigma_o$$

### 9.2.2 Linearity

Both concentration and source strength linearity will be assessed by linear regression with the certified gas concentration as independent variable and the monitor's response as dependent variable. Linearity will be 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 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 will be 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. This parameter will be determined at each concentration.

### 9.2.4 Precision

Precision will be 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 ( $s$ ) of these measurements is:

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

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

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

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

### 9.2.5 Interferences

The extent of interference will be calculated in terms of sensitivity of the monitor to the interferent species, relative to its sensitivity to the target gas at a fixed integration time. The relative sensitivity is calculated as the ratio of the observed response of the monitor to the actual concentration of the interferent. For example, a monitor that reports 26 ppb of cyclohexane in air with an interference concentration of 100 ppb of CO<sub>2</sub> may report 30 ppb of cyclohexane when the CO<sub>2</sub> concentration is changed to 200 ppb. This would result in an interference effect of  $(30 \text{ ppb} - 26 \text{ ppb})_{\text{cyclohexane}} / (200 \text{ ppb} - 100 \text{ ppb})_{\text{CO}_2}$  or 4 percent.

## 9.3. Data Review

Records generated by Battelle staff in the verification test will receive one-over-one review within two weeks after generation, before these records are used to calculate, evaluate, or report verification results. These records may include laboratory record books; equipment calibration records; and data sheets used to record the monitor's response. This review will be performed by a Battelle technical staff member involved in the verification test, but not the staff member that originally generated the record. The review will be 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 will then be 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 of this test/QA plan.

#### **9.4. Reporting**

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

The verification report will briefly describe the ETV program and the AMS pilot, and will describe the procedures used in the verification test, but will include specific requirements or departures from procedure necessitated in testing of the individual monitor in question. These sections will be common to each verification report resulting from this verification test. The results of the verification test will 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, the review of reports by vendors and others, the revision of the reports, final approval, and the distribution of the reports, will be conducted as stated in the Generic Verification Protocol for the Advanced Monitoring Systems Pilot.<sup>3</sup> Preparation, approval, and use of verification statements summarizing the results of this test will also be 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 or one of the monitor vendors, will 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 will operate under these established requirements and guidelines as well as under appropriate procedures covered in the Battelle Safety Manual. Specifically, the use of personal protective equipment, as defined in

procedure SIH-PP-01, will be used, and the chemical safety

protocols set forth in SIH-PP-05 will be followed. It is expected that while on Battelle's site, all vendor representatives will operate according to the Battelle site requirements.

### **10.2. Potential Hazards**

Vendor staff will only be operating their open-path monitors during the verification test. They are not responsible for, nor permitted to, generate dilution gases, or perform any other verification activities identified in this test/QA plan. Operation of the open-path monitors does not pose any known chemical, fire, mechanical, electrical, noise, or other potential hazard.

### **10.3. Training**

All vendor staff will be given a safety briefing prior to their installation and operation of their monitors in Battelle laboratories. This briefing will include a description of emergency operating procedures (i.e., in case of fire, tornado, bomb, laboratory accident) and identification and location and operation of safety equipment (e.g., fire alarms, fire extinguishers, eye washes, exits). Similar instruction will 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  $\pm 1$  percent accuracy, and used for dilution of the target gas to concentrations suitable for the testing of the monitors.

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

**Minimum Detection Limit** - The concentration at which the response of the 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 the monitor to a constituent of the sample gas other than the target gas.



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

**Target gas** - The gas for which the monitor is making its measurement.

## **12. REFERENCES**

1. Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Pilot, U. S. EPA Environmental Technology Verification Program, prepared by Battelle, Columbus, Ohio, September 1998.
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. Generic Verification Protocol for the Advanced Monitoring Systems Pilot, U. S. EPA Environmental Technology Verification Program, prepared by Battelle, Columbus, Ohio, October 1998.

**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 <sub>2</sub> 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								