September 2000

# Environmental Technology Verification Report

# AIL SYSTEMS INC. RAM 2000 FOURIER TRANSFORM INFRARED OPEN-PATH MONITOR

Prepared by

Battelle

. . . Putting Technology To Work

Battelle

Under a cooperative agreement with

EPA

U.S. Environmental Protection Agency

ETV ETV ETV

September 2000

# Environmental Technology Verification Report

## ETV Advanced Monitoring Systems Center

## AIL Systems Inc. RAM 2000 Fourier Transform Infrared Open-Path Monitor

By

Jeffrey Myers
Thomas Kelly
Charles Lawrie
Karen Riggs

Battelle
Columbus, Ohio 43201

# Notice

# Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development (ORD) provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification Organizations oversee and report verification activities based on testing and Quality Assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. At present, there are 12 environmental technology areas covered by ETV. Information about each of the environmental technology areas covered by ETV can be found on the Internet at http://www.epa.gov/etv.htm.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. In 1997, through a competitive cooperative agreement, Battelle was awarded EPA funding and support to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/07/07_main.htm.

# Acknowledgments

The authors wish to acknowledge the support of all those who helped plan and conduct the verification test, analyze the data, and prepare this report. In particular we would like to thank Darrell Joseph of Battelle. We also acknowledge the participation of William Walter of Laser Consultants Inc., Bill Woturski of AIL Systems, Inc., and Steve Perry of Kassay Field Services Inc. in this verification test.

# Contents

## Figures

## Tables

# List of Abbreviations

| | |
|---|---|
| ac | alternating current |
| AMS | Advanced Monitoring Systems |
| CEM | continuous emission monitor |
| cm | centimeter |
| CO | carbon monoxide |
| $CO_2$ | carbon dioxide |
| dc | direct current |
| EPA | U.S. Environmental Protection Agency |
| ETV | Environmental Technology Verification |
| FTIR | Fourier transform infrared |
| GC/FID | gas chromatography/flame ionization detection |
| Hg | mercury |
| $H_2O$ | water |
| m | meter |
| MDL | minimum detection limit |
| NDIR | nondispersive infrared |
| NIST | National Institute of Standards and Technology |
| $N_2$ | nitrogen |
| $NO_x$ | nitrogen oxides (= NO + $NO_2$) |
| $O_2$ | oxygen |
| ppb | parts per billion |
| ppm | parts per million |
| ppm*m | parts per million meters |
| QA | quality assurance |
| QC | quality control |
| QMP | Quality Management Plan |
| RH | relative humidity |
| RSD | relative standard deviation |
| $SO_2$ | sulfur dioxide |
| TSA | technical systems audit |

# Chapter 1
# Background

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high quality, peer-reviewed data on technology performance to those involved in the design, distribution, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of regulators, buyers and vendor organizations; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA’s National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of optical open-path monitors for use in ambient air or fence line measurements. This verification report presents the procedures and results of the verification test for the AIL Systems Inc. (AIL) RAM 2000™ Fourier transform infrared (FTIR) optical open-path monitor.

# Chapter 2
# Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This verification report provides results for the verification testing of the RAM 2000. The following description of the RAM 2000 is based on information provided by the vendor.

The RAM 2000 detects, identifies, and measures the concentrations of unwanted, dangerous, or life-threatening gases. It provides standoff air quality monitoring and detects and identifies the presence of more than 250 chemical species in the local atmosphere. In situ measurements enable quantification of polar and unstable species. The RAM 2000 automatically determines the concentration and significance of each chemical detected and provides real-time results to facilitate an early warning system for unexpected releases.

The RAM 2000's active open-path FTIR technology uses light from a silicon carbide glower within the monitor to project a modulated infrared light beam to a retroreflector. The retroreflector directs the modulated beam back to a mercury cadmium telluride detector within the monitor. The projected infrared beam is modulated by a Michelson interferometer, which allows the detection electronics to be ac coupled and insensitive to dc contributions from any stray background source of infrared light. The return signal is analyzed for absorbed frequencies that act as fingerprints for any chemical species present. An autopositioner accessory enables a single RAM 2000 to address multiple beam paths and provide protection over many acres.

**Figure 2-1. AIL RAM 2000 FTIR Optical Open-Path Monitor and Retroreflector**

An integrated meteorological station supplies the weather data to facilitate identification of the source of the chemical species and enable modeling to project downwind concentrations at receptor sites. Weather parameter recording is synchronized with spectral data taking and archived in a common file that retains all of the conditions under which the data were taken. Computer displays of concentrations and concentration histories, wind speed and wind direction, trend charts, and concentration of pollution wind roses help to identify emission sources.

The system uses Window-based software, and the RAM 2000 components may be located in a facility control room and integrated with in-plant networks. The built-in analytical software includes multicomponent regression algorithms that automatically identify and quantify the individual components in a complex chemical mixture without operator intervention. Each chemical species concentration is displayed in a bar graph with individual user-set warning and trigger levels that are color coded for display and also may activate facility-desired responses or alarms. The software performs data quality checks on each data set. The software also computes concentration averages, in addition to keeping track of maximum values and the time of their occurrence.

# Chapter 3
# Test Design and Procedures

## 3.1 Introduction

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Optical Open-Path Monitors*.(1) The test was designed to challenge the RAM 2000 in a manner similar to that which would be experienced in field operations and was modeled after Compendium Method TO-16(2). The monitor was challenged using an optically transparent gas cell filled with known concentrations of a target gas. The gas cell was inserted into the optical path of the monitor during operation under field conditions, simulating a condition where the target gas would be present in the ambient air. The gas cell was used to challenge the monitor in a controlled and uniform manner.

The monitor was challenged with three target gases at known concentrations, and the measurement result was compared to the known concentration of the target gas. The gases and concentrations used for testing the RAM 2000 are shown in Table 3-1. The verification was conducted by measuring the gases in a fixed sequence over three days. The sequence of activities for testing the monitor for a single gas is shown in Table 3-2.

**Table 3-1. Target Gases and Concentrations for Testing the RAM 2000**

| Gas | Concentration Level | Target Gas Concentration (ppm*m) | Gas Cell Concentration[a] (ppm) |
|---|---|---|---|
| Ethylene | c1 | 5 | 34 |
| | c2 | 10 | 67 |
| | c3 | 25 | 168 |
| | c4 | 50 | 337 |
| Cyclohexane | c1 | 5 | 34 |
| | c2 | 10 | 67 |
| | c3 | 25 | 168 |
| | c4 | 50 | 337 |
| Tetrachloroethylene | c1 | 5 | 34 |
| | c2 | 10 | 67 |
| | c3 | 25 | 168 |
| | c4 | 50 | 337 |

[a] Length of gas cell = 14.8 cm.

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

| Meas. # | Gas Cell Conc. | Activity | Collected # of Spectra | Times (min) | | Path Length (m) | Verification Parameter Calculated |
|---|---|---|---|---|---|---|---|
| | | | | Integrate | Equilibrate | | |
| | $N_2$ | Change gas & stabilize | | | 10 | 200 | |
| 1 | $N_2$ | Collect spectra | 26 | 1 | | 200 | Accuracy, Concentration linearity, MDL |
| | c1[a] | Change gas & stabilize | | | 10 | 200 | |
| 2 | c1 | Collect spectra | 5 | 1 | | 200 | Accuracy, Concentration linearity |
| 3 | c1 | Collect spectra - ND 1 | 5 | 1 | | 200 | Source strength linearity |
| 4 | c1 | Collect spectra - ND 2 | 5 | 1 | | 200 | Source strength linearity |
| 5 | c1 | Collect spectra - ND 3 | 5 | 1 | | 200 | Source strength linearity |
| | $N_2$ | Change gas & stabilize | | | 10 | 200 | |
| 6 | $N_2$ | Collect spectra | 5 | 1 | | 200 | Accuracy, Concentration linearity |
| | c2 | Change gas & stabilize | | | 10 | 200 | |
| 7 | c2 | Collect spectra | 5 | 1 | | 200 | Accuracy, Concentration linearity, Interference Effect (Int.) |
| | $N_2$ | Change gas & stabilize | | | 10 | 200 | |
| 8 | $N_2$ | Collect spectra | 5 | 1 | | 200 | Accuracy, Concentration linearity |
| | c3 | Change gas & stabilize | | | 10 | 200 | |
| 9 | c3 | Collect spectra | 5 | 1 | | 200 | Accuracy, Concentration linearity |
| 10 | c3 | Collect spectra - ND 1 | 5 | 1 | | 200 | Source strength linearity |
| 11 | c3 | Collect spectra - ND 2 | 5 | 1 | | 200 | Source strength linearity |
| 12 | c3 | Collect spectra - ND 3 | 5 | 1 | | 200 | Source strength linearity |
| | $N_2$ | Change gas & stabilize | | | 10 | 200 | |
| 13 | $N_2$ | Collect spectra | 5 | 1 | | 200 | Accuracy, Concentration linearity |
| | c4 | Change gas & stabilize | | | 10 | 200 | |
| 14 | c4 | Collect spectra | 26 | 1 | | 200 | Accuracy, Concentration linearity, Precision |
| 14b | $N_2$ | Collect spectra | 5 | | | 200 | Accuracy, Concentration linearity |
| | $N_2$ | Change gas & stabilize | | | 10 | 200 | |
| 15 | $N_2$ | Collect spectra | 26 | 5 | | 200 | Concentration linearity, MDL |
| | | Change to Path length 2 | | | 20 | 910 | |
| 16 | $N_2$ | Collect spectra | 5 | 5 | | 910 | Int. |
| | c2 | Change gas & stabilize | | | 10 | 910 | |
| 17 | c2 | Collect spectra | 5 | 5 | | 910 | Int., Accuracy, Concentration linearity |
| | $N_2$ | Change gas & stabilize | | | 10 | 910 | |
| 18 | $N_2$ | Collect spectra | 5 | 5 | | 910 | Int., Accuracy, Concentration linearity |
| | | Change to Path length 3 | | | 20 | optimum[b] | |
| 19 | $N_2$ | Collect spectra | 5 | 1 | | optimum | Int., Accuracy, Concentration linearity |
| | c2 | Change gas & stabilize | | | 10 | optimum | |
| 20 | c2 | Collect spectra | 5 | 1 | | optimum | Int., Accuracy, Concentration linearity |
| | $N_2$ | Change gas & stabilize | | | 10 | optimum | |
| 21 | $N_2$ | Collect spectra | 26 | 1 | | optimum | Int., MDL |

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

[b] Vendor's optimum of 2 meters was selected.

## 3.2 Test Design

The verification test was performed between March 13 and 17, 2000, at the AIL outdoor test site at Deer Park in Long Island, New York. This location provided a sufficient path length and a direct line of sight to each of the positioned retroreflectors. The FTIR, including the power supply, autopositioner, and telescope, was located inside the second story of AIL's facility. The infrared beam exited the second story of the building through an opening in a Lexan window where it was directed at one of two retroreflectors located at a distance from the monitor. The first retroreflector was located 100 meters from the monitor near the top of an M68 antenna tower. The second retroreflector was located 455 meters from the monitor on an antenna tower, approximately 85 feet above the ground. Figure 3-1 shows the test site at the Deer Park facility. The facility was located near a waste treatment plant and near automotive and painting facilities that, depending upon the wind conditions, may have produced chemical effluents that affected the test.

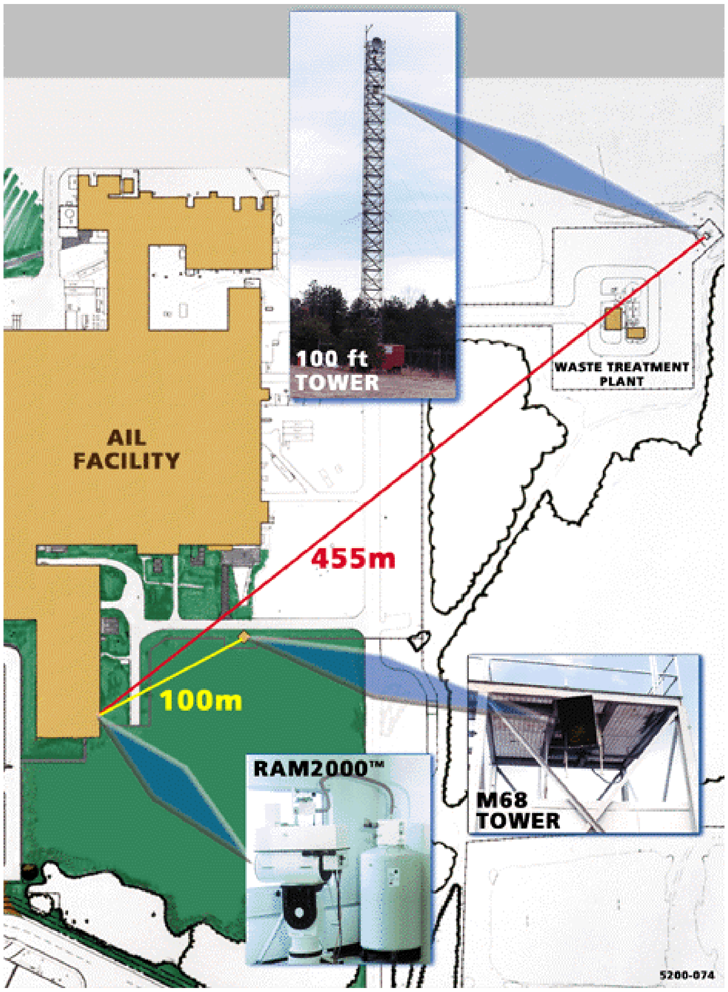

**Figure 3-1. Test Site at Deer Park Facility**

The RAM 2000 was challenged with the target gases shown in Table 3-1 at known concentrations, and the RAM 2000 measurement of light absorption by the monitor was compared to the known concentration of the target gas. For each target gas, the monitor was set up as if it were operating in the field, except that an optically transparent gas cell was placed in the light beam's path (see Figure 3-2). National Institute of Standards and Technology (NIST) traceable or commercially certified standard gases, a calibrated gas diluter, and a supply of certified high-purity dilution gas were used to supply the target gases to the gas cell.

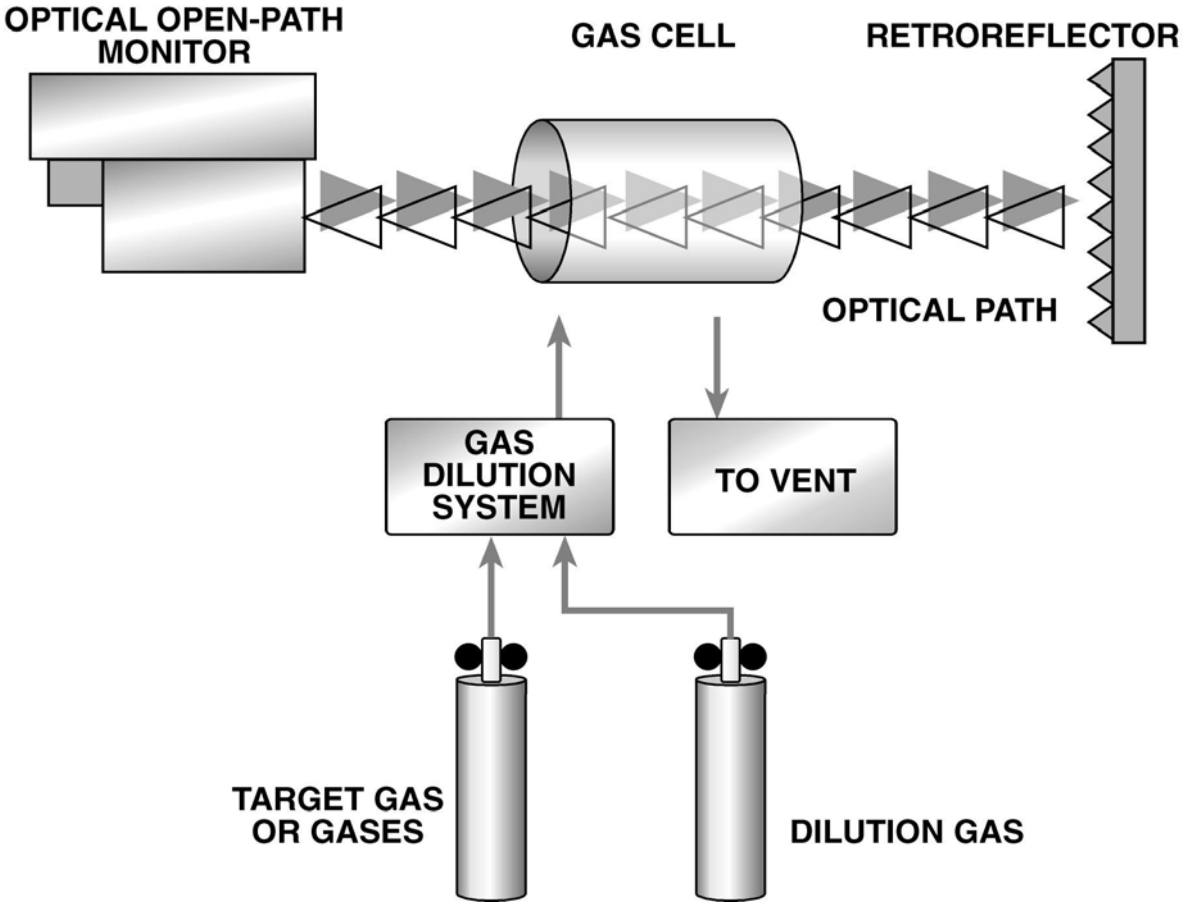

**Figure 3-2. Optical Open-Path Monitor Setup**

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

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

The test procedures shown in Table 3-2 were nested, in that each measurement was used to evaluate more than one of the above parameters. In Table 3-2, $N_2$ in the gas cell concentration column denotes a period of cell flushing with high-purity nitrogen. The denotations c1, c2, c3, and c4 refer to the concentrations shown in Table 3-1. The last column shows the parameters to be calculated with the data from that measurement.

## 3.3 Experimental Apparatus and Materials

### *3.3.1 Standard Gases*

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

### *3.3.2 Dilution Gas*

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

### *3.3.3 Gas Dilution System*

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

### *3.3.4 Gas Cell*

The gas calibration cell built into the RAM 2000 as a standard component was used as the gas cell for the verification test. The gas calibration cell of the RAM 2000 consists of a quartz cylindrical body 14.8 centimeters long with anti-reflection coated zinc selenide windows. Input and output quick-disconnect ports were used for flowing the test gases through the cell, as well as flushing the test gases out with nitrogen.

### *3.3.5 Temperature Sensor*

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

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

The RH sensor used to determine the ambient air humidity was an EG&G Dew Prime II RH/Dew Point monitor (Serial No. 018460) that used the chilled mirror principle. This sensor was operated in accordance with the manufacturer's instructions, which called for cleaning the mirror and rebalancing the optical path when necessary, as indicated by the diagnostic display of the monitor. The manufacturer's accuracy specification of this monitor was ± 5% RH.

### *3.3.7 Carbon Dioxide Monitor*

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

### *3.3.8 Target Gas Measurement*

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

## 3.4 Test Parameters

### *3.4.1 Minimum Detection Limit*

The MDL was calculated for each target gas by supplying pure nitrogen to the test cell in the optical path of the monitor and taking a series of 26 single-beam spectra using integration times of 1 and 5 minutes. The single-beam spectra were then used to create absorption spectra, using each single-beam spectrum as the background for the next spectrum. The absorption spectra were created by using the first and second single-beam spectra, the second and third, the third and fourth, etc. The resulting 25 absorption spectra were then analyzed for the target gas. This sequence of measurements was conducted at both integration times, twice at a 200-meter path length and once at a 2-meter path length. The MDL was defined as two times the standard deviation of the calculated concentrations.

### *3.4.2 Linearity*

Two types of linearity were investigated during this verification: source strength and concentration. The source strength linearity was investigated by challenging the monitor with ethylene concentrations of 5 and 25 ppm*m at a path length of 200 meters. In the field, light signal levels can be attenuated by mist, rain, snow, or dirty optical components. During each challenge, three aluminum wire screens of various meshes were placed in the beam path to determine how the monitor’s measurements were affected by an attenuated light signal. These screens were approximately 1 foot square and had a mesh spacing of approximately ¼, ½, and 1 inch.

Concentration linearity was investigated by challenging the monitor with each target gas at concentrations ranging between 5 ppm*m and 50 ppm*m while the path length and integration time were kept constant. At each concentration, the monitor response was recorded and its linearity evaluated by comparing the recorded response with the input target gas concentration.

### *3.4.3 Accuracy*

Accuracy of the monitor relative to the gas standards was verified by introducing known concentrations of the target gas into the cell. The gas cell was first flushed with at least five cell volumes of nitrogen, and a single-beam spectrum was recorded. The target gas was then introduced into the cell and, after flushing with at least five cell volumes, a second single-beam spectrum of the target gas was obtained. The cell was again flushed with at least five cell volumes of nitrogen, and a third spectrum was recorded. The three spectra were analyzed for the target gas, using the background selected by the vendor. The concentration of the target gas was the result of analyzing the second spectrum minus the average of the first and third (flushed cell) spectra.

The accuracy was evaluated at concentrations denoted as c1 through c4, using an integration time of 1 minute. The accuracy was then evaluated at concentration c2 using a 5-minute integration time, and then again at concentration c2 during the interference measurements (Table 3-2). The percent relative accuracy for an experimental condition is the absolute value of the difference between the average monitor response and the reference monitor response, divided by the reference monitor response, times 100 (see Section 5.3).

### *3.4.4 Precision*

The procedure for determining precision was very similar to the procedure for determining accuracy. The gas cell was flushed with at least five cell volumes of nitrogen. The target gas was then introduced into the cell and, after flushing with at least five cell volumes, 25 absorption spectra of the target gas were obtained. These spectra were analyzed for the target gas. The relative standard deviation (RSD) of this set of measurements was the precision at the target gas concentration. Precision was evaluated by this procedure at two different concentrations of each of the target gases (see Table 3-2). Additional precision information was obtained from the replicate analyses conducted in the interference test.

### *3.4.5 Interferences*

The effects of interfering gases were established by supplying the gas cell with a target gas and varying the distance (i.e., the path length) between the source and detector of the monitor. The purpose of the interference measurements was to determine the effects of the ambient atmospheric gases on accuracy and MDL of the RAM 2000. Using two different integration times, these tests were conducted to determine the effect of integration time on the monitor’s ability to perform measurements with interfering gases in the light path.

To determine the effect of the interferences, the path length was first changed from 200 meters to 910 meters; the gas cell was supplied with nitrogen; and, after flushing with at least five cell volumes, five single-beam spectra were recorded. Next, the target gas was introduced into the cell and, after similarly flushing the cell, five single-beam spectra were recorded. Finally, nitrogen was again introduced into the cell, and five spectra were recorded.

The path length was then set to 2 meters, which was the length that AIL chose as optimum, and the entire measurement procedure was repeated. Atmospheric concentrations of $H_2O$ and $CO_2$ were recorded at the beginning and end of these measurements. The extent of interference was assessed in terms of the monitor's sensitivity to these interferant gases in the optical path.

# Chapter 4
# Quality Assurance/Quality Control

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

## 4.1 Data Review and Validation

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

## 4.2 Changes from the Test/QA Plan

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

- The test/QA plan called for a one-over-one data review within two weeks of generating the data. While the entire data set was reviewed within this two-week period, documentation of this task was not completed. Although this task was documented after the two-week period, no reduction in the quality of the data occurred.
- The test plan called for Acid Rain CEM zero nitrogen to be used to flush the cell and as dilution gas. Instead, ultra-high-purity nitrogen was used.
- In the performance evaluation audit of the $CO_2$ monitor, two separate $CO_2$ gas standards from the same supplier were used, rather than two standards from different suppliers.

Deviation reports have been filed for each deviation.

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

- MDL was determined using twice the standard deviation, as described in Section 3.4.1. The test/QA plan inadvertently called for the MDL to be determined by two different methods. The correct method was chosen and used during the verification test.

- The Summa® canister analysis procedure was changed from that specified in the test/QA plan. The test/QA plan specified using Method 18 to determine the hydrocarbon emissions from combustion or other source facilities. This method broadly describes an analysis procedure, but does not specify how the analysis is to be done, and calls for the use of Tedlar bags rather than Summa® canisters. Instead of as described in the test/QA plan, the analysis was done according to Battelle's GC/FID/MS analysis procedure for canister samples.

- The long and the short path lengths in the test/QA plan, which were stated as 100 and 400 meters, were changed to meet the specific technology requirements of the monitor tested.

- The order of testing in the test/QA plan was changed. The test order was originally developed to maximize the efficiency of the test procedure. Several improvements were made to the test matrix to further improve its efficiency. For example, instead of conducting all of the measurements for one gas and then changing to the next gas, all of the short path measurements were conducted before moving to the long path. This was done because changing the path length was more time consuming than changing the target gas.

- One additional test was added to complete the data set collected. Originally, the test/QA plan lacked a nitrogen flush after measurement 14, under the same conditions as measurement 14. This additional measurement was added to the test matrix and denoted as measurement #14b (see Table 3-2).

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

- Although monitoring CO was part of the test/QA plan, it was decided that CO measurements would not add any useful information to the verification. No CO monitoring was done.

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

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

## 4.3 Calibration

### *4.3.1 Gas Dilution System*

Mass flow controllers in the Environics 2020 gas dilution system were calibrated prior to the start of the verification test by means of a soap bubble flow meter. Corrections were applied to the bubble meter data for pressure, temperature, and water content.

### *4.3.2 Temperature Sensor*

The thermocouple was calibrated by Battelle’s Instrument Laboratory by comparing it to a certified standard within the six months preceding the test.

### *4.3.3 RH Sensor*

The RH sensor used the manufacturer’s calibration.

### *4.3.4 Carbon Dioxide Monitor*

The NDIR $CO_2$ monitor was calibrated before testing using a commercially prepared, certified standard of $CO_2$ in air. That standard was an EPA Protocol Gas of 7.98% $CO_2$ in $N_2$, NIST traceable, with ± 1% analytical accuracy (Cylinder No. ALM 015985, Scott Specialty Gases).

### *4.3.5 Target Gas Measurement*

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

## 4.4 Data Collection

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

**Table 4-1. Summary of Data Recording Process for the RAM 2000 Verification Test**

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

## 4.5 Performance Systems Audits

### *4.5.1 Technical Systems Audit*

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

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

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

### *4.5.2 Performance Evaluation Audit*

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

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

| Measurement Audited | Audit Procedure | Expected Reading | Actual Reading | Difference |
|---|---|---|---|---|
| Temperature | Compare to independent temperature measurement (Hg thermometer) | 20.1°C | 21.0°C | 0.9°C |
| Relative humidity | Compare to independent RH measurement (wet/dry bulb device) | 22.5% RH | 22% RH | 2.3% |
| Carbon dioxide concentration | Compare measurement using another carbon dioxide standard from the same supplier | 975 ppm | 975 ppm | 0% |
| Ethylene | Compare to results of gas chromatographic analysis of canister sample | 34 ppm | 32 ppm | -6.3% |
| Cyclohexane | | 168 ppm | 160 ppm | -5.0% |
| Tetrachloroethylene | | 168 ppm | 169 ppm | 0.6% |
| Tetrachloroethylene | | 168 ppm | 164 ppm | -2.4% |

Each of the required procedures for the performance evaluation audit was conducted during the testing period in accordance with the direction specified in the test/QA plan, except for the deviation concerning the $CO_2$ performance evaluation listed in Section 4.2. The results from the performance evaluations are shown in Table 4-2. The temperature measurement agreed to within 0.9°C and the relative humidity agreed to within 2.3% relative (within 0.5% RH absolute difference). When the $CO_2$ gas standard comparison was conducted, the monitor reading agreed exactly with the PE test gas.

The target gas concentrations were audited by independent analysis of the test gas mixture supplied to the gas cell during verification testing. This procedure involved collecting a sample of the test gas mixture exiting the cell using a pre-cleaned and evacuated summa-polished sampling canister. This gas sample was analyzed for ethylene, cyclohexane, and tetrachloroethylene by a method based on EPA Method 18, using gas chromatography with flame ionization detection (GC/FID). Calibration of the FID response was based on the standards cited in

Section 4.3.5. The results of the performance audit for the target gas concentrations were within 10% of the expected concentrations, which met the test/QA plan criterion.

Field blank and background samples were also taken with Summa® canisters, with resulting analyses showing non-detects for the target gas concentrations.

### *4.5.3 Data Quality Audit*

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

# Chapter 5
# Statistical Methods

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

## 5.1 Minimum Detection Limit

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

$$MDL = 2\sigma_o$$

## 5.2 Linearity

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

$$y = mx + b$$

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

## 5.3 Accuracy

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

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

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

## 5.4 Precision

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

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

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

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

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

## 5.5 Interferences

The extent to which interferences affected MDL and accuracy was calculated in terms of sensitivity of the monitor to the interferant species, relative to its sensitivity to the target gas, at a fixed path length and integration time. The relative sensitivity is calculated as the ratio of the observed response of the monitor to the actual concentration of the interferant. For example, a monitor that indicates 26 ppm of cyclohexane in air with an interference concentration of 100 ppm of $CO_2$ indicates 30 ppm of cyclohexane when the $CO_2$ concentration is changed to 200 ppm. This would result in an interference effect of $(30\text{ ppm} - 26\text{ ppm})_{\text{cyclohexane}/}(200\text{ ppm} - 100\text{ ppm})_{CO2}$ = 0.04 or 4% relative sensitivity.

# Chapter 6
# Test Results

The results of the verification test of the RAM 2000 are presented in this section, based upon the statistical methods shown in Chapter 5. The monitor was challenged with ethylene, cyclohexane, and tetrachloroethylene over path lengths of 200 and 910 meters, which are typical path lengths for this monitor. These gases were chosen because they are analyzed using a different region of the infrared spectra and therefore challenge the monitor and its analysis software in different ways. Test parameters included MDL, linearity, accuracy, precision, and the effects of atmospheric interferants on concentration measurements.

## 6.1 Minimum Detection Limit

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

The results in Table 6-2 show that the RAM 2000 has an MDL of between 0.19 and 0.32 ppm*m for ethylene, 0.04 and 0.19 ppm*m for cyclohexane, and 0.08 and 0.19 ppm*m for tetrachloroethylene at the path lengths and integration times tested. Changing the path lengths between 2 and 200 meters and changing the integration times between 1 and 5 minutes had little consistent effect on the MDL. These MDL values were consistent with the values expected by the vendor.

## 6.2 Linearity

### *6.2.1 Source Strength Linearity*

Table 6-3 shows the results from this evaluation of source strength linearity. Figure 6-1 shows a plot of the effect that the light signal level has on the monitor's measurements. In Table 6-3, the relative signal power is the measure of light attenuation during that measurement. For example, a relative signal power of 0.89 means that the light level for that test is 89% of what the light level is during normal operating conditions. The ethylene concentration is the concentration of

**Table 6-1. MDL Data for the RAM 2000**

| | Ethylene | | | Cyclohexane | | | Tetrachloroethylene | | |
|---|---|---|---|---|---|---|---|---|---|
| | Path Length (m) | | | Path Length (m) | | | Path Length (m) | | |
| | 2 | 200 | 200 | 2 | 200 | 200 | 2 | 200 | 200 |
| | Integration Time (min) | | | Integration Time (min) | | | Integration Time (min) | | |
| Measurement Number | 1 | 1 | 5 | 1 | 1 | 5 | 1 | 1 | 5 |
| | Concentration (ppm*m) | | | | | | | | |
| 1 | 0.05 | -0.27 | 0.04 | -0.07 | -0.04 | -0.03 | 0.09 | 0.03 | -0.04 |
| 2 | 0.03 | 0.06 | -0.03 | 0.01 | 0.00 | 0.02 | -0.07 | -0.05 | 0.04 |
| 3 | 0.14 | -0.06 | 0.06 | 0.04 | 0.00 | 0.00 | -0.07 | 0.02 | 0.05 |
| 4 | -0.01 | 0.14 | -0.27 | 0.07 | -0.01 | 0.00 | 0.04 | -0.05 | 0.04 |
| 5 | -0.14 | -0.01 | 0.26 | -0.14 | 0.05 | 0.02 | 0.02 | 0.00 | 0.07 |
| 6 | 0.10 | -0.18 | -0.12 | 0.04 | -0.02 | 0.00 | -0.03 | 0.02 | -0.13 |
| 7 | -0.16 | 0.07 | -0.32 | -0.07 | -0.03 | 0.01 | -0.01 | 0.00 | 0.25 |
| 8 | 0.05 | 0.08 | 0.13 | 0.06 | -0.02 | 0.03 | -0.05 | 0.01 | -0.07 |
| 9 | -0.13 | -0.15 | -0.09 | -0.04 | 0.05 | 0.04 | 0.06 | 0.03 | -0.03 |
| 10 | 0.05 | 0.09 | -0.04 | 0.03 | -0.02 | 0.00 | -0.09 | -0.04 | 0.09 |
| 11 | 0.04 | -0.07 | 0.05 | 0.00 | -0.02 | -0.02 | 0.05 | 0.03 | 0.15 |
| 12 | -0.17 | -0.12 | 0.08 | 0.00 | 0.03 | 0.03 | 0.01 | 0.03 | 0.15 |
| 13 | -0.06 | 0.00 | -0.06 | 0.01 | 0.03 | 0.02 | -0.07 | -0.09 | -0.02 |
| 14 | 0.03 | 0.13 | -0.01 | -0.03 | -0.03 | -0.01 | 0.06 | 0.05 | -0.07 |
| 15 | -0.07 | -0.07 | 0.08 | -0.14 | 0.00 | 0.00 | -0.03 | 0.03 | 0.07 |
| 16 | -0.03 | -0.01 | -0.12 | 0.15 | 0.36 | -0.01 | -0.05 | -0.07 | -0.07 |
| 17 | -0.10 | 0.02 | 0.07 | -0.01 | 0.08 | -0.02 | 0.00 | 0.06 | -0.01 |
| 18 | -0.05 | -0.04 | -0.08 | 0.03 | -0.21 | 0.01 | -0.02 | -0.03 | -0.16 |
| 19 | 0.20 | -0.22 | -0.21 | -0.02 | -0.06 | -0.03 | -0.01 | -0.03 | -0.01 |
| 20 | -0.11 | 0.09 | 0.12 | 0.01 | -0.03 | -0.06 | 0.01 | 0.00 | -0.14 |
| 21 | 0.07 | 0.06 | -0.03 | 0.00 | -0.07 | -0.01 | -0.01 | 0.01 | -0.03 |
| 22 | -0.11 | -0.13 | 0.20 | 0.02 | 0.00 | -0.02 | 0.01 | 0.01 | -0.07 |
| 23 | -0.04 | 0.26 | 0.35 | -0.02 | 0.06 | 0.00 | 0.03 | 0.00 | -0.05 |
| 24 | 0.09 | -0.19 | 0.16 | 0.01 | -0.02 | -0.02 | -0.02 | 0.04 | 0.03 |
| 25 | -0.04 | 0.30 | 0.01 | -0.03 | -0.02 | 0.01 | -0.06 | -0.03 | 0.10 |

**Table 6-2. Minimum Detection Limits of the RAM 2000**

| Target Gas | Path Length (m) | Integration Time (min) | MDL (ppm*m) |
|---|---|---|---|
| Ethylene | 2 | 1 | 0.19 |
| Ethylene | 200 | 1 | 0.28 |
| Ethylene | 200 | 5 | 0.32 |
| Cyclohexane | 2 | 1 | 0.12 |
| Cyclohexane | 200 | 1 | 0.19 |
| Cyclohexane | 200 | 5 | 0.04 |
| Tetrachloroethylene | 2 | 1 | 0.09 |
| Tetrachloroethylene | 200 | 1 | 0.08 |
| Tetrachloroethylene | 200 | 5 | 0.19 |

**Table 6-3. Source Strength Linearity of the RAM 2000**

| Relative Signal Power | Ethylene Concentration (ppm*m) | Monitor Response (ppm*m) |
|---|---|---|
| 1.0 | 5 | 5.01 |
| 0.89 | 5 | 4.23 |
| 0.67 | 5 | 4.51 |
| 0.46 | 5 | 5.97 |
| 1.0 | 25 | 24.26 |
| 0.89 | 25 | 24.00 |
| 0.67 | 25 | 25.00 |
| 0.47 | 25 | 24.20 |

gas being delivered to the gas cell during the measurement, and the monitor response is the resulting reading from the RAM 2000. The source strength results show that there is little degradation in monitor performance during conditions of declining source strength. The monitor showed a maximum deviation from the target gas concentration of approximately 1.0 ppm*m at both 5 ppm*m and 25 ppm*m.

### *6.2.2 Concentration Linearity*

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

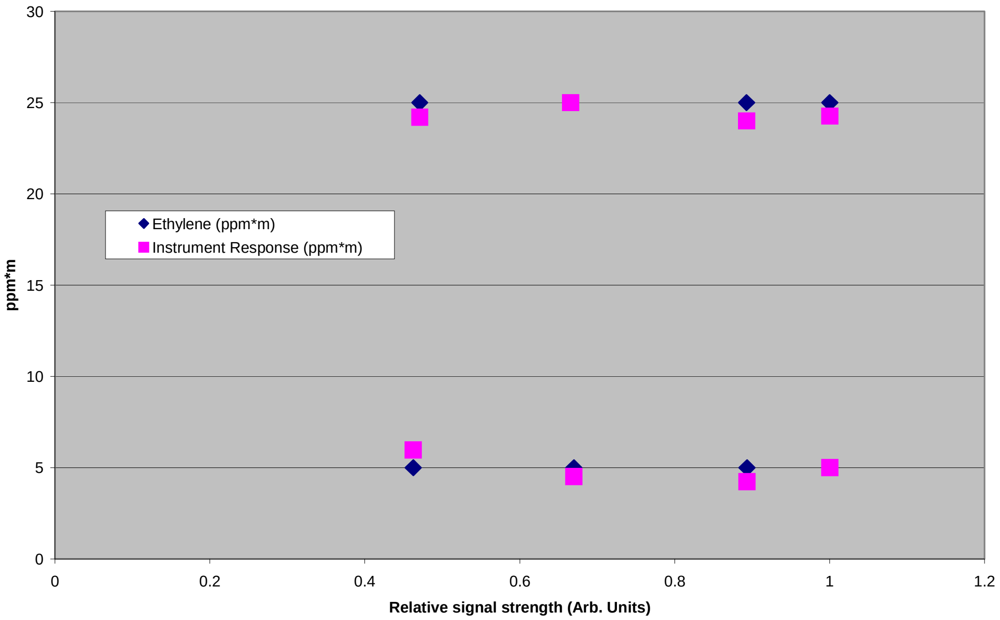

**Figure 6-1. Source Strength Linearity Plot for the RAM 2000**

**Table 6-4. Concentration Linearity Data for the RAM 2000**

| Target Gas Concentration (ppm*m) | Monitor Response | | |
|---|---|---|---|
| | Ethylene (ppm*m) | Cyclohexane (ppm*m) | Tetrachloroethylene (ppm*m) |
| 5 | 5.01 | 4.20 | 5.03 |
| 10 | 9.31 | 7.92 | 7.09 |
| 10 | 9.71 | 8.50 | 8.47 |
| 10 | 9.28 | 8.95 | 7.55 |
| 25 | 24.3 | 22.2 | 21.9 |
| 50 | 49.2 | 46.5 | 52.4 |

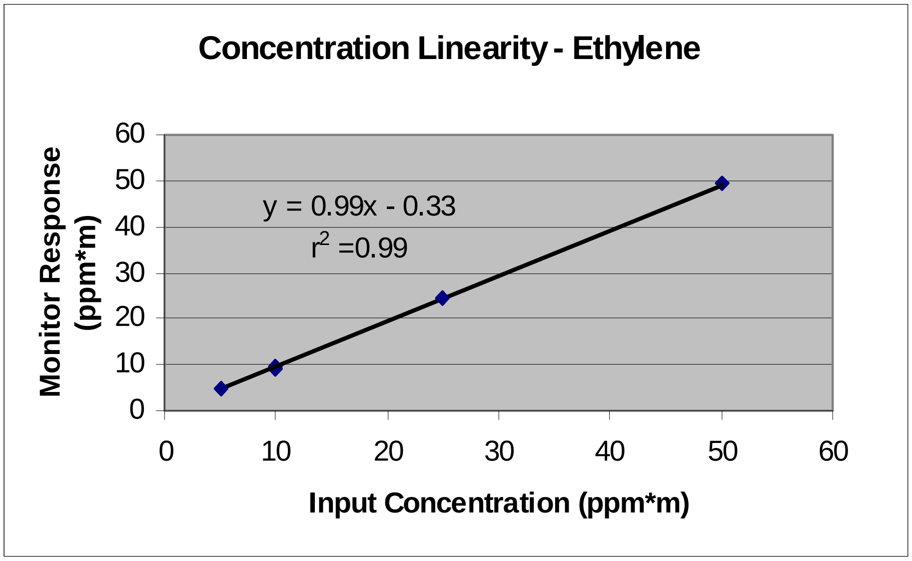

**Figure 6-2. Concentration Linearity Plot of the RAM 2000 Challenged with Ethylene**

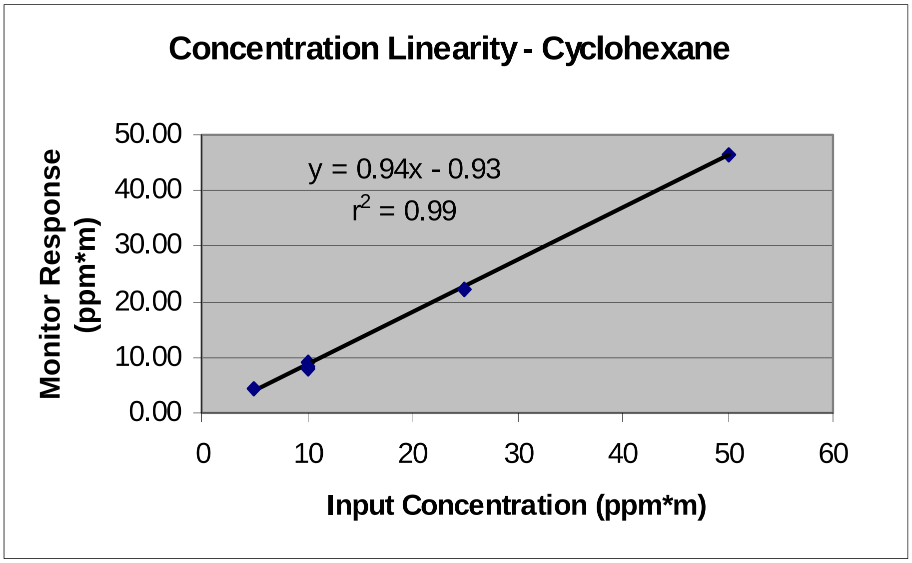

**Figure 6-3. Concentration Linearity Plot of the RAM 2000 Challenged with Cyclohexane**

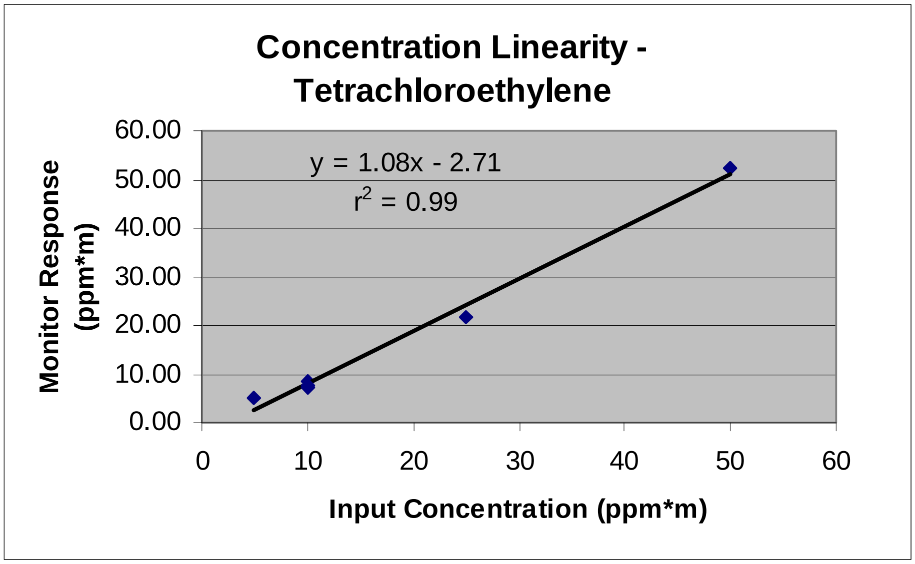

**Figure 6-4. Concentration Linearity Plot of the RAM 2000 Challenged with Tetrachloroethylene**

The concentration linearity results show that the monitor has a linear response over the range tested. The monitor response, as given by the slope of the linear regression line, varies from 0.94 for cyclohexane to 1.08 for tetrachloroethylene, with $r^2$ values of 0.99 for all three gases.

### 6.3 Accuracy

The accuracy of the RAM 2000 was evaluated at each target gas concentration introduced into the cell. These concentrations were introduced at the path lengths and integration times shown in Table 6-5, where the measurement data and relative accuracy results are shown. (Note that the same data were used for verification of concentration linearity and of relative accuracy, as shown by comparison of Tables 6-4 and 6-5.) The accuracy results compare the monitor response with the target gas concentration as delivered by the Environics 2020 gas dilution system.

These results show that the RAM 2000 had a relative accuracy of between 0.2 and 7.2% for ethylene, 7.0 and 21% for cyclohexane, and 0.7 and 29% for tetrachloroethylene. The monitor had the poorest accuracy in each case at the shortest path length of 2 meters, while the best accuracy occurred at 200 meters for each of the gases. There was no strong indication that consistently better accuracy was obtained at either higher or lower concentrations. Relative accuracy results are more variable for cyclohexane and for tetrachloroethylene than for ethylene.

Whenever the mixture of the test gas with nitrogen from target gas cylinders is changed, a suitable time interval is required for the mixture to displace whatever gas is presently in the gas calibration cell as well as the connecting apparatus. With some gases, the equilibration time may be lengthened by wall effects of the connecting tubes, valves, mixing chamber, and cell walls.

**Table 6-5. Results of Accuracy Tests for the RAM 2000**

| Gas | Target Gas Concentration (ppm*m) | Path Length (m) | Integration Time (min) | Monitor Response (ppm*m) | Relative Accuracy (%) |
|---|---|---|---|---|---|
| Ethylene | 5 | 200 | 1 | 5.01 | 0.2 |
| Ethylene | 10 | 2 | 1 | 9.31 | 6.9 |
| Ethylene | 10 | 200 | 1 | 9.71 | 2.9 |
| Ethylene | 10 | 910 | 5 | 9.28 | 7.2 |
| Ethylene | 25 | 200 | 1 | 24.3 | 3.0 |
| Ethylene | 50 | 200 | 1 | 49.2 | 1.6 |
| Cyclohexane | 5 | 200 | 1 | 4.20 | 16 |
| Cyclohexane | 10 | 2 | 1 | 7.92 | 21 |
| Cyclohexane | 10 | 200 | 1 | 8.50 | 15 |
| Cyclohexane | 10 | 910 | 5 | 8.95 | 12 |
| Cyclohexane | 25 | 200 | 1 | 22.2 | 11 |
| Cyclohexane | 50 | 200 | 1 | 46.5 | 7.0 |
| Tetrachloroethylene | 5 | 200 | 1 | 5.03 | 0.7 |
| Tetrachloroethylene | 10 | 2 | 1 | 7.09 | 29 |
| Tetrachloroethylene | 10 | 200 | 1 | 8.47 | 15 |
| Tetrachloroethylene | 10 | 910 | 5 | 7.55 | 25 |
| Tetrachloroethylene | 25 | 200 | 1 | 21.9 | 13 |
| Tetrachloroethylene | 50 | 200 | 1 | 52.4 | 4.9 |

Wall effect processes involving adhesion or passivation can make some gases take longer times to equilibrate during the flow process, particularly when a new gas is introduced for the first time. An example of this was discovered during the tests conducted the last day of testing when the third gas, tetrachloroethylene, was being tested. The initial tests with tetrachloroethylene were run with a flow of 5 ppp*m; however, the monitor reading after five or ten cell volumes were displaced was only 2.9 ppm*m. This would have resulted in a relative accuracy of only 58%. Testing then proceeded with the flow of tetrachloroethylene concentration increased to 10, then 25, and finally 50 ppm*m, with each increasing concentration achieving a better correspondence to the reference mixture. To see whether wall effect processes could be playing a role, we reduced the concentration of the flowing tetrachloroethylene to 5 ppm*m. The monitor reading dropped to 5.03 ppm*m, and this reading was included in Table 6-5. Unfortunately time had run out on the testing so neither the 10 ppm*m concentrations could be repeated nor could we investigate whether a similar effect had occurred with the second test gas, cyclohexane. As indicated in Table 6-5, the relative accuracy of cyclohexane also improved as the input concentration increased. An improvement in the test procedure to minimize wall effects would be to begin the testing of each gas with the highest concentration instead of the lowest. If this had taken place during this, the first open-path monitor test, the relative accuracies reported for cyclohexane and tetrachloroethylene at concentrations below 50 ppm*m may have been significantly improved, coming closer to the relative accuracies obtained at 50 ppm*m. The high relative percent accuracies quoted in Table 6-5 could therefore be considered questionable.

### 6.4 Precision

Precision data were collected during measurement #14 (see Table 3-2) using an integration time of 1 minute and a path length of 200 meters. The target gas was introduced into the gas cell at a concentration of 50 ppm*m, and 25 successive analyses were made for the target gas. The data from these measurements are found in Table 6-6, and the results are shown in Table 6-7.

These results show that the ethylene data had an RSD of 0.53%, cyclohexane data had an RSD of 0.51%, and tetrachloroethylene data had an RSD of 0.66%. The magnitude of these values shows that the monitor performed very consistently over the 25 minutes required for this measurement. In addition, the similarity of the RSD values to each other (a total spread of 0.15% in RSD values) shows that the monitor performs consistently while analyzing for the three target gases.

### 6.5 Interferences

Interference tests of the RAM 2000 evaluated the effects that the common atmospheric interferants water and carbon dioxide have on the monitor's ability to determine the concentration of the target gases, and on the MDL for the target gases. Tables 6-8 and 6-9 show the data used to determine the interference effect of water and carbon dioxide on the concentration and MDL determination, respectively.

Both water and carbon dioxide have absorption features in the same infrared region that the RAM 2000 uses to analyze for the target compounds. Because the concentration of these two potential interferants is usually much greater than the concentration of the compounds of interest, the presence of water and carbon dioxide can make analyzing for the target compounds difficult. FTIR monitors use various methods to deal with these interferants, and this test evaluated the effectiveness of the RAM 2000's methods.

As shown in Table 6-8, changing the total number of water and carbon dioxide molecules in the path length had little effect on the monitor's ability to accurately calculate the concentrations of the target gas. The measured concentrations were between 9.44 and 10.00 ppm*m for ethylene, between 7.95 and 9.34 ppm*m for cyclohexane, and between 7.18 and 8.55 ppm*m for tetrachloroethylene, while the water concentration in the path changed from approximately $1.2 \times 10^4$ to $7.7 \times 10^6$ ppm*m and the carbon dioxide concentration varied from approximately $1.1 \times 10^3$ to $5.5 \times 10^5$ ppm*m. Overall, no consistent effect was found of $CO_2$ and $H_2O$ levels on relative accuracy for the three gases.

**Table 6-6. Data from Precision Tests on the RAM 2000**

| | Target Gas | | |
|---|---|---|---|
| Analysis | Ethylene (ppm*m) | Cyclohexane (ppm*m) | Tetrachloroethylene (ppm*m) |
| 1 | 48.46 | 45.35 | 51.58 |
| 2 | 48.51 | 45.89 | 51.70 |
| 3 | 48.55 | 46.12 | 51.56 |
| 4 | 48.38 | 46.30 | 51.76 |
| 5 | 48.74 | 46.40 | 51.94 |
| 6 | 48.60 | 46.39 | 51.84 |
| 7 | 48.58 | 46.41 | 51.85 |
| 8 | 48.74 | 46.40 | 51.79 |
| 9 | 48.76 | 46.47 | 51.82 |
| 10 | 48.70 | 46.52 | 51.81 |
| 11 | 48.66 | 46.44 | 51.97 |
| 12 | 48.61 | 46.44 | 51.84 |
| 13 | 48.56 | 46.36 | 51.97 |
| 14 | 48.44 | 46.42 | 52.09 |
| 15 | 48.56 | 46.41 | 52.18 |
| 16 | 48.74 | 46.48 | 52.05 |
| 17 | 49.03 | 46.40 | 52.23 |
| 18 | 49.17 | 46.32 | 52.35 |
| 19 | 48.91 | 46.29 | 52.31 |
| 20 | 48.66 | 46.37 | 52.54 |
| 21 | 48.70 | 46.35 | 52.66 |
| 22 | 48.64 | 46.40 | 52.42 |
| 23 | 48.97 | 46.39 | 52.41 |
| 24 | 49.17 | 46.35 | 52.76 |
| 25 | 49.48 | 46.36 | 52.61 |

**Table 6-7. Results of Precision Tests on the RAM 2000[a]**

| Target Gas | Gas Concentration (ppm*m) | RAM 2000 Average (ppm*m) | Standard Deviation (ppm*m) | Relative Standard Deviation (%) |
|---|---|---|---|---|
| Ethylene | 50 | 48.7 | 0.26 | 0.53 |
| Cyclohexane | 50 | 46.3 | 0.24 | 0.51 |
| Tetrachloroethylene | 50 | 52.6 | 0.35 | 0.66 |

[a] Integration time = 1 minute; path length = 200 meters.

**Table 6-8. Concentration Data from Interference Tests on the RAM 2000**

| Target Gas[a] | Path Length (m) | Target Gas Concen-tration (ppm) | Concentration of $CO_2$ (ppm*m) | Concentration of $H_2O$ (ppm*m) | Monitor Response (ppm*m) | Relative Accuracy (%) |
|---|---|---|---|---|---|---|
| Ethylene | 2 | 10 | 1.1E+03 | 1.22E+04 | 9.58 | 4.2 |
| Ethylene | 200 | 10 | 9.5E+04 | 1.10E+06 | 10.0 | 0.0 |
| Ethylene | 910 | 10 | 4.78E+05 | 6.18E+06 | 9.44 | 5.6 |
| Cyclohexane | 2 | 10 | 1.40E+03 | 1.62E+04 | 7.95 | 21 |
| Cyclohexane | 200 | 10 | 1.15E+05 | 1.63E+06 | 8.37 | 16 |
| Cyclohexane | 910 | 10 | 5.23E+05 | 7.66E+06 | 9.34 | 6.6 |
| Tetrachloroethylene | 2 | 10 | 1.35E+03 | 1.57E+04 | 7.18 | 28 |
| Tetrachloroethylene | 200 | 10 | 1.15E+05 | 1.09E+06 | 8.55 | 15 |
| Tetrachloroethylene | 910 | 10 | 5.46E+05 | 5.006E+06 | 7.47 | 25 |

**Table 6-9. MDL Data from Interference Tests on the RAM 2000**

| Target Gas | Path Length (m) | Concentration of $CO_2$ (ppm*m) | Concentration of $H_2O$ (ppm*m) | MDL (ppm*m) |
|---|---|---|---|---|
| Ethylene | 2 | 1.05E+03 | 1.34E+04 | 0.19 |
| Ethylene | 200 | 1.20E+05 | 1.20E+06 | 0.28 |
| Cyclohexane | 2 | 1.40E+03 | 1.09E+04 | 0.12 |
| Cyclohexane | 200 | 1.15E+05 | 2.78E+06 | 0.19 |
| Tetrachloroethylene | 2 | 1.55E+03 | 1.64E+04 | 0.09 |
| Tetrachloroethylene | 200 | 1.15E+05 | 1.12E+06 | 0.08 |

As Table 6-9 shows, changing the total number of water and carbon dioxide molecules in the path length also had little effect on the monitor’s MDL for the target gas. The MDL varied from 0.19 to 0.28 ppm*m for ethylene, from 0.12 to 0.19 ppm*m for cyclohexane, and from 0.8 to 0.09 ppm*m for tetrachloroethylene, while the water concentration in the path changed from approximately $1.1\text{x}10^4$ to $2.8\text{x}10^6$ ppm*m and the carbon dioxide concentration varied from approximately $1.1\text{x}10^3$ to $1.2\text{x}10^5$ ppm*m. For both ethylene and cyclohexane, the MDL increased with increasing interferant concentration; but for tetrachloroethylene, the MDL actually decreased with the increase in the interferant concentration.

## 6.6 Other Factors

### *6.6.1 Costs*

The total retail cost of the RAM 2000, the autopositioner, and the retroreflectors, as tested, is approximately $198,000, according to AIL.

### 6.6.2 Data Completeness

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

# Chapter 7
# Performance Summary

The RAM 2000 detection limits for the three gases tested ranged between 0.19 and 0.32 ppm*m for ethylene, between 0.04 and 0.19 ppm*m for cyclohexane, and between 0.08 and 0.19 ppm*m for tetrachloroethylene. While the variation in detection limits could be due to the changes in path length (between 2 and 200 meters) and integration time (between 1 and 5 minutes), there was no consistent trend. That is, longer integration times did not, in general, lead to lower detection limits, nor did longer path lengths.

The tests of the effects of source strength on the measurement capability of the monitor for ethylene showed that there was little to no degradation of monitor performance over the range tested. The monitor showed a maximum deviation from the actual ethylene concentration of 1 ppm*m at both 5 ppm*m and 25 ppm*m. The concentration linearity results showed that the RAM 2000 had a regression slope of 0.99 and an $r^2$ value of 0.99 for ethylene; a regression slope of 0.94 and an $r^2$ value of 0.99 for cyclohexane; and a regression slope of 1.08 and an $r^2$ value of 0.99 for tetrachloroethylene, each over a range of 5 to 50 ppm*m.

The relative accuracy of the RAM 2000 was 1.6, 7.0, and 4.9% for 50 ppm*m of ethylene, cyclohexane, and tetrachloroethylene respectively. At lower concentrations of 5 to 25 ppm*m, the relative accuracy of the RAM 2000 ranged from 0.2 to 7.0% for ethylene. Non-equilibrium conditions probably caused the measured relative accuracies at lower concentrations of cyclohexane and tetrachloroethylene to reach 20.8 and 29% respectively. The monitor performed equally well at 1- and 5-minute integration times and at 200 and 910-meter path lengths.

Precision results showed that ethylene data had an RSD of 0.53%, cyclohexane data had an RSD of 0.51%, and tetrachloroethylene data had an RSD of 0.66%. This RSD was calculated at one experimental condition using a path length of 200 meters, an integration time of 1 minute, and a concentration of 50 ppm*m.

Analysis of the effects of the interferences of water and carbon dioxide on the measurement ability of the RAM 2000 showed that neither the accuracy nor the MDL were affected consistently by the changing concentrations of water and carbon dioxide in the atmosphere. Variations in MDL and relative accuracy were similar to those found during other measurements, made under normal operating conditions, and no consistent interference effect could be inferred.

# Chapter 8
# References

1. *Test/QA Plan for Verification of Optical Open-Path Monitors*, Battelle, Columbus, Ohio, October 28, 1999.

2. *Compendium Method TO-16 Long-Path Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases*, EPA-625/R-96/010b, U.S. Environmental Protection Agency, Cincinnati, Ohio, January 1997.

3. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Pilot*, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, September 1998.

# Appendix A
# Data Recording Sheet

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sample Gas:** | **Date:** | | | **Operator:** | | | | | | | | |
| | | | | **Reviewed by:** | | | | | | | | |
| Measurement # | | | | | | | | | | | | |
| Cell Temp (F) | | | | | | | | | | | | |
| Ambient $O_2$ Concentrations (ppb) | | | | | | | | | | | | |
| Ambient $CO_2$ Concentrations (ppb) | | | | | | | | | | | | |
| Ambient RH (%) | | | | | | | | | | | | |
| Ambient $O_3$ Concentrations (ppb) | | | | | | | | | | | | |
| Ambient Temp (F) | | | | | | | | | | | | |
| Integration Time | | | | | | | | | | | | |
| Path Length | | | | | | | | | | | | |
| Concentration in Cell | | | | | | | | | | | | |
| Cell Length | | | | | | | | | | | | |
| Time of Measurement | | | | | | | | | | | | |