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**Battelle**

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

Test/QA Plan for Verification of  
Chemiluminescent Ozone Analyzer

US EPA ARCHIVE DOCUMENT



# **TEST/QA PLAN**

**for**

## **Verification of Chemiluminescent Ozone Analyzer**

**June 6, 2007**

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## TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
SECTION A PROJECT MANAGEMENT .....	7
A1 Verification Test Organization .....	7
A2 Background .....	13
A3 Verification Test Description and Schedule .....	14
A4 Quality Objectives .....	17
A5 Special Training/Certification .....	17
A6 Documentation and Records .....	18
SECTION B MEASUREMENT AND DATA ACQUISITION .....	19
B1 Experimental Design .....	19
B2 Reference Sample Collection .....	27
B3 Sample Handling and Custody Requirements .....	27
B4 Laboratory Reference Methods .....	27
B5 Quality Control Requirements .....	28
B6 Instrument/Equipment Testing, Inspection, and Maintenance .....	28
B7 Instrument Calibration and Frequency .....	29
B8 Inspection/Acceptance of Supplies and Consumables .....	29
B9 Non-Direct Measurements .....	30
B10 Data Management .....	30
SECTION C ASSESSMENT AND OVERSIGHT .....	32
C1 Assessments and Response Actions .....	32
C2 Reports to Management .....	34
SECTION D DATA VALIDATION AND USABILITY .....	35
D1 Data Review, Validation, and Verification Requirements .....	35
D2 Validation and Verification Methods .....	35
SECTION E REFERENCES .....	37

List of Figures

Page

Figure 1. Organization Chart for the Verification Test..... 8

List of Tables

Table 1. Planned Verification Schedule..... 16  
Table 2. Ozone Analyzers..... 21  
Table 3. Interference Testing..... 22  
Table 4. Photochemical Testing..... 23  
Table 5. Summary of Data Recording Process ..... 31

## ACRONYMS AND ABBREVIATIONS

API	American Petroleum Institute
AMS	Advanced Monitoring Systems
$r^2$	Coefficient of determination
COA	Chemiluminescent ozone analyzer
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
FEM	Federal equivalent method
GC	Gas chromatograph
LRB	Laboratory record book
MSD	Mass selective detector
$m^3$	Meters cubed
mg	Milligrams
ppb	Parts per billion
%R	percent recovery
PE	Performance evaluation
QA	Quality assurance
QC	Quality control
QMP	Quality management plan
RH	Relative humidity
TSA	Technical systems audit
T	Temperature
UV	Ultraviolet
VOC	Volatile organic compounds

**ETV Advanced Monitoring Systems Center**

**Test/QA Plan**

**for**

**Verification of  
Chemiluminescent Ozone Analyzer**

**June 6, 2007**

**VENDOR ACCEPTANCE:**

Name \_\_\_\_\_

Company \_\_\_\_\_

Date \_\_\_\_\_

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## SECTION A PROJECT MANAGEMENT

### A1 VERIFICATION TEST ORGANIZATION

The verification test will be conducted under the auspices of the U.S. Environmental Protection Agency (EPA) through the Environmental Technology Verification (ETV) Program. It will be performed by Battelle, which is managing the ETV Advanced Monitoring Systems (AMS) Center through a cooperative agreement with EPA. The scope of the AMS Center covers verification of monitoring technologies for contaminants and natural species in air, water, and soil. The performance of the COA will be judged against a Federal Equivalent Method (FEM) ultraviolet (UV) continuous monitor for ozone. Specifically, the FEM used for this test will be method EQOA-0880-047.

The day to day operations of this verification test will be coordinated and supervised by Battelle personnel, with the participation of the vendor who will be having the performance of their COA verified. Testing will be conducted at Battelle in Columbus, Ohio. The vendor will provide Battelle with their COA and will train the Battelle staff in the operation of the COA. Battelle staff will operate the technology during verification testing.

The organization chart in Figure 1 identifies the responsibilities of the organizations and individuals associated with the verification test. Roles and responsibilities are defined further below. Quality Assurance (QA) oversight will be provided by the Battelle Quality Manager and also by the EPA AMS Center Quality Manager, at her discretion. The organization chart in Figure 1 identifies the responsibilities of the organizations and individuals primarily associated with the verification test. Roles and responsibilities are defined further below.

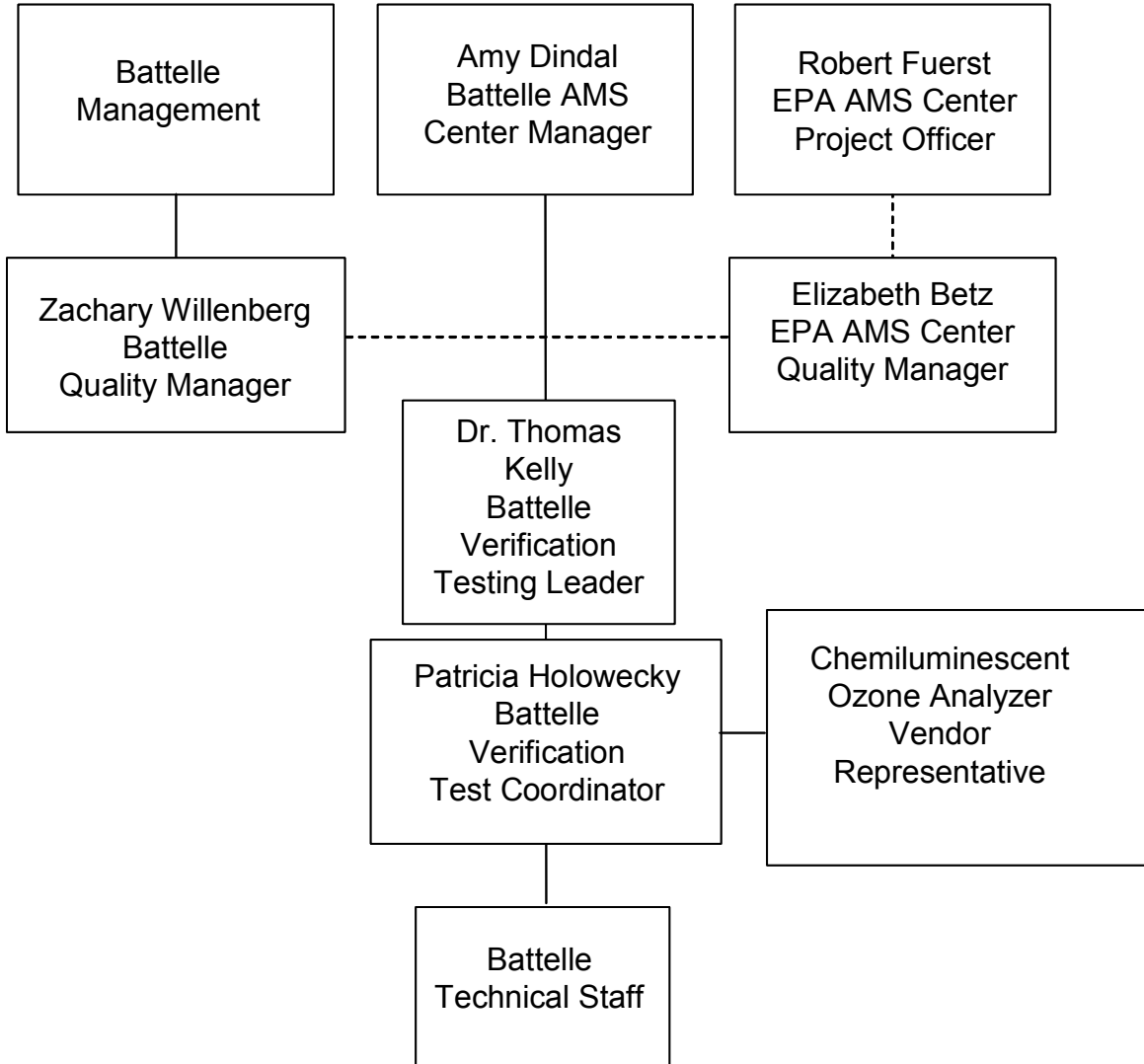


Figure 1. Organization Chart for the Verification Test

## A1.1 Battelle

Ms. Patricia Holowecky is the AMS Center's Verification Test Coordinator for this test. In this role, Ms. Holowecky will have overall responsibility for ensuring that the technical, schedule, and cost goals established for the verification test are met. Specifically, Ms. Holowecky 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 a team of qualified technical staff to conduct the verification test.
- Establish a budget for the verification test and manage staff to ensure the budget is not exceeded.
- Direct the team in performing the verification test in accordance with this test/QA plan.
- Hold a kick-off meeting approximately one week prior to the start of the verification test to review the critical logistical, technical, and administrative aspects of the verification test. Responsibility for each aspect of the verification test will be confirmed.
- Ensure that all quality procedures specified in this test/QA plan and in the AMS Center Quality Management Plan1 (QMP) are followed.
- Serve as the primary point of contact for vendor representatives.
- Ensure that confidentiality of sensitive vendor information is maintained.
- Assist vendors as needed during verification testing.
- Become familiar with the operation and maintenance of the COA through instruction by the vendor, if needed.
- Respond to any issues raised in assessment reports, audits, or from test staff observations, and institute corrective action as necessary.

- Coordinate distribution of the final test/QA plan, verification reports, and verification statements.

Dr. Thomas Kelly will serve as Verification Testing Leader. Dr. Kelly will:

- Support Ms. Holowecky in preparing the test/QA plan and designing the test.
- Review the draft and final test/QA plan.
- Attend the verification test kick-off meeting.
- Ensure that confidentiality of sensitive vendor information is maintained.
- Support Ms. Holowecky in responding to any issues raised in assessment reports and audits.
- Review the draft and final verification reports and verification statements.

Ms. Amy Dindal is Battelle's Manager for the AMS Center. As such, Ms. Dindal will oversee the various stages of verification testing. Ms. Dindal will:

- Review the draft and final test/QA plan.
- Attend the verification test kick-off meeting.
- Review the draft and final verification reports and verification statements.
- Ensure that necessary Battelle resources, including staff and facilities, are committed to the verification test.
- Maintain communication with EPA's technical and quality managers.
- Issue a stop work order if Battelle or EPA QA staff discover adverse findings that will compromise test results.

Technical staff from Battelle will support Ms. Holowecky in planning and conducting the verification test. The responsibilities of the technical staff will be to:

- Assist in planning for the test, and making arrangements for the receipt of and training on the COA.

- Attend the verification test kick-off meeting.
- Assist vendor staff as needed during technology receipt and training.
- Conduct verification testing using the vendor's COA technology.
- Conduct reference measurements during the testing.
- Perform statistical calculations specified in this test/QA plan on the technology data as needed.
- Provide results of statistical calculations and associated discussion for the verification reports as needed.
- Support Ms. Holowecky in responding to any issues raised in assessment reports and audits related to statistics and data reduction as needed.

Mr. Zachary Willenberg is Battelle's Quality Manager for the AMS Center.

Mr. Willenberg will:

- Review the draft and final test/QA plan.
- Attend the verification test kick-off meeting.
- Conduct a technical systems audit at least once during the verification test, or designate other QA staff to conduct the audit.
- Audit at least 10% of the verification data or designate other QA staff to conduct the data audit.
- Prepare and distribute an assessment report for each audit.
- Verify implementation of any necessary corrective action.
- Request that Battelle's AMS Center Manager issue a stop work order if audits indicate that data quality is being compromised.
- Provide a summary of the QA/quality control (QC) activities and results for the verification reports.
- Review the draft and final verification reports and verification statements.

## A1.2 COA Vendor

The responsibilities of the COA vendor are as follows:

- Review and provide comments on the draft test/QA plan.
- Accept (by signature of a company representative) the final test/QA plan prior to test initiation.
- Provide two units of their technology for evaluation during the verification test.
- Provide all other equipment/supplies/reagents/consumables needed to operate their technology for the duration of the verification test.
- Supply training on the use of the technology, and provide written consent and instructions for test staff to carry out verification testing, including written instructions for routine operation of their technology.
- Provide maintenance and repair support for their technology, on-site if necessary, throughout the duration of the verification test.
- Review and provide comments on the draft verification report and statement for their respective technology.

## A1.3 EPA

EPA's responsibilities in the AMS Center are based on the requirements stated in the "Environmental Technology Verification Program Quality Management Plan" (EPA ETV QMP).<sup>2</sup> The roles of specific EPA staff are as follows:

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

- Review the draft test/QA plan.
- Perform at her option one external technical systems audit during the verification test.
- Notify the EPA AMS Center Project Officer of the need for a stop work order if the external audit indicates that data quality is being compromised.

- Prepare and distribute an assessment report summarizing results of the external audit.
- Review the draft verification reports and verification statements.

Mr. Robert Fuerst is EPA's Project Officer for the AMS Center. Mr. Fuerst will:

- Review the draft test/QA plan.
- Approve the final test/QA plan.
- Review the draft verification reports and verification statements.
- Oversee the EPA review process for the test/QA plan, verification reports, and verification statements.
- Coordinate the submission of verification reports and verification statements for final EPA approval.

## **A2 BACKGROUND**

The ETV Program's AMS Center conducts third-party performance testing of commercially available technologies that detect or monitor natural species or contaminants in air, water, and soil. The purpose of ETV is to provide objective and quality assured performance data on environmental technologies, so that users, developers, regulators, and consultants can make informed decisions about purchasing and applying these technologies. Stakeholder committees of buyers and users of such technologies recommend technology categories, and technologies within those categories, as priorities for testing. Verification reports from previous tests are available at <http://www.epa.gov/etv/verifications/verification-index.html>.

The purpose of this test/QA plan is to specify procedures for a verification test applicable to commercial COA's such as the OPTEC 3.02 P-A COA.<sup>3</sup> The purpose of the verification test is to compare the response of the OPTEC COA to the response of a federally designated FEM UV method for ozone (specifically for this test the FEM will be method EQOA-0880-047). In performing the verification test, Battelle will follow the technical and QA procedures specified in this test/QA plan and will comply with the data quality requirements in the AMS Center QMP.<sup>1</sup>

## **A3 VERIFICATION TEST DESCRIPTION AND SCHEDULE**

### **A3.1 Summary of Technology Category**

Ozone is a pervasive pollutant that is formed by photochemical processes involving sunlight, nitrogen oxides and volatile organic compounds (VOC) in air. The U.S. Clean Air Act and its Amendments established air quality standards for ozone, and pollution control strategies require state and local authorities to regulate for compliance with the standards. Because of the costs associated with emission control programs and penalties for those organizations that are not in compliance, it is essential that the ozone measurements that determine compliance with the standards be performed accurately.

One of the methods currently utilized for ambient ozone monitoring is UV photometry, which makes use of the ozone molecule's strong absorption band in the ultraviolet region of the spectrum, with a maximum coinciding with the strong mercury emission line at 254 nanometers (nm). Measurements made with a low-pressure mercury light source and an optical cell of relatively short pathlength (typically 0.1 to 1 m) can achieve ozone detection limits of 5 parts per billion (ppb) or better. Commercial instruments that employ UV photometry measure the transmission of UV radiation through an air sample and compare the intensity with that obtained along the same pathlength through air containing no ozone. Ideally the ozone-free reference signal should be measured using ambient air containing all of the constituents of the sample air except ozone. This is because other atmospheric species that absorb 254 nm radiation will reduce the light intensity and will bias the ozone measurement unless they are present at the same concentrations in the sample and reference air. In practice, a scrubber (typically MnO<sub>2</sub>) has been used to selectively remove ozone from the air. However, any atmospheric constituent that absorbs 254 nm radiation and is removed by the scrubber represents a potential interference to the ozone measurements. Several commercial ozone monitors using UV absorption have been designated by EPA as FEMs; the monitor used specifically for this test will be method EQOA-0880-047.



Concerns have been raised over potential interference to the UV photometry method caused by aromatic hydrocarbons and their atmospheric reaction products,<sup>4,5,6,7</sup> mercury vapor,<sup>8</sup> sulfur dioxide,<sup>9</sup> and water vapor.<sup>8,10,11,12</sup> Wilson and Birks<sup>13</sup> have proposed a mechanism that explains the water vapor interference observed with UV absorption ozone monitors on hot humid days. They report that the scrubber can act as a reservoir for water vapor, and the water vapor films formed on cell walls can influence the transmission of reflected UV light through the measurement cell, thus affecting the ozone measurement signal. To control the water vapor interference, a Nafion tube that equilibrates humidity in the scrubbed and unscrubbed air samples is reported to resolve this problem.

The growing evidence for ozone measurement bias with the widely used MnO<sub>2</sub> scrubber has led to renewed interest in another technology that intends to resolve or minimize these interference problems. For example, the 3.02 P-A COA from OPTEC Inc. is claimed to be free from water vapor interference up to 98% relative humidity, as long as condensation does not occur.<sup>3</sup> The 3.02 P-A COA detects ozone by means of its reaction with a solid reagent surface to produce light (chemiluminescence),<sup>14,15,16</sup> which is then detected by a photomultiplier tube. The ETV test as described in this test/QA plan will explore the effectiveness of COAs and quantify their response relative to the response of FEM instrumentation (used specifically as FEM EQOA-0880-047) under various environmental interferent conditions.

### **A3.2 Verification Schedule**

Table 1 shows the planned schedule of activities for the verification testing and data analysis and reporting. As shown in Table 1, the laboratory activities are planned to begin in May 2007 with installation of the COA. Testing is expected to begin in June, and the period of testing will be approximately 2 weeks. A separate ETV verification report will then be drafted for each COA, and the report will be reviewed by the technology vendor and subsequently by

**Table 1. Planned Verification Schedule**

Month (2007)	Verification Activity	
	Testing	Data Analysis and Reporting
May	Analyzer training by vendor Set up/install COA	Begin preparation of ETV report template
June	Calibration of COA Humidity effect testing Interference testing Ambient outdoor measurements	Compile data from humidity effects Compile data from interferent challenges Analyze ambient outdoor data Review and summarize operator observations
July	Shutdown of test setup Return of COAs to vendors	Finalize data from all interferents Finalize data from ambient measurements Complete common sections of reports Complete report sections on interferent challenges and operator observations Internal review of draft reports Vendor review of draft reports
August		Revision of draft reports Peer review of draft reports
September		Revision of draft reports Submission of final reports for EPA approval

peer reviewers. The test/QA plan and final reports will be submitted to EPA for final signature, and these documents will be made publicly available on both the EPA/ETV and the Battelle AMS Center websites.

### A3.3 Test Facility

Laboratory analyses will be conducted in Battelle laboratories in Columbus, Ohio.

In performing this verification test, Battelle will follow the procedures specified in this test/QA plan and will comply with quality requirements in the AMS Center QMP.<sup>1</sup> The laboratory that will be used contains a 17.3 m<sup>3</sup> environmental chamber. This facility is equipped for safe handling of chemicals and will be used to maintain controlled testing atmospheres.

#### **A4 QUALITY OBJECTIVES**

This verification test is designed to evaluate the performance of the COAs for determining ozone in air. This evaluation will include a comparison of the COA results to the EPA designated FEM (EQOA-0880-047). These methods are both continuous real-time ozone analyzers. The calibration of the FEM analyzer will be based on delivery of ozone from an EnviroNics Model 6400 ozone generator that has itself been calibrated against a Dasibi Model 1008-PC UV calibration photometer. The addition of a Nafion dryer to one of the COAs will also be used during testing to determine the analyzers response to humidity effects. This comparison will be made between the COAs.

The validity of calibration of the FEM analyzer will be checked by a Performance Evaluation (PE) audit, performed by direct comparison of the Dasibi 1008 readings to those of a UV transfer standard photometer operated by the Ohio EPA. That PE audit is described in section C.1.1.

QA/QC requirements will be augmented by a Technical Systems Audit (TSA) and a data quality audit. These additional QA procedures will be carried out by Battelle. The planned audit procedures are described in Section C1. The EPA Quality Manager also may conduct an independent TSA, at her discretion.

#### **A5 SPECIAL TRAINING/CERTIFICATION**

Documentation of training related to technology testing, field testing, data analysis, and reporting is maintained for all Battelle technical staff in training files at their respective locations. The Battelle Quality Manager may verify the presence of appropriate training records prior to the start of testing. Battelle technical staff will have a minimum of a bachelor's degree in science/engineering or have equivalent work experience.

## **A6 DOCUMENTATION AND RECORDS**

The records for this verification test will be contained in the test/QA plan, chain-of-custody forms, laboratory record books (LRB), data collection forms, electronic files (both raw data and spreadsheets), the final verification report and assessment reports. All of these records will be maintained in the Verification Test Coordinator's office during the test and will be transferred to permanent storage at Battelle's Records Management Office at the conclusion of the verification test except for assessment reports which are permanently stored with the Battelle Quality Manager. All Battelle LRBs are stored indefinitely, either by the Verification Test Coordinator or Battelle's Records Management Office. EPA will be notified before disposal of any files. Section B10 further details the data recording practices and responsibilities.

All written records must be in ink. Any corrections to notebook entries, or changes in recorded data, must be made with a single line through the original entry. The correction is then to be entered, initialed, and dated by the person making the correction. In all cases, strict confidentiality of data from the vendor's technology will be maintained. Separate files (including manual records, printouts, and/or electronic data files) will be kept for the vendor's technology.

## SECTION B MEASUREMENT AND DATA ACQUISITION

### B1 EXPERIMENTAL DESIGN

This test/QA plan addresses the verification of the COA for ozone by evaluating various performance parameters created in an environmental testing chamber, and in monitoring of ozone in ambient air. The accuracy, linearity, comparability, and interference effects of water vapor, aromatic compounds, mercury, and products of atmospheric photochemistry will be evaluated. Completeness of the data and operational factors will also be assessed. Specifically the COA will be evaluated for the following performance parameters:

- Accuracy
- Linearity
- Interference Effects
- Comparability
- Data Completeness
- Operational factors such as ease of use, maintenance and data output needs, power and other consumables use, reliability, and operational costs.

Accuracy and linearity will be determined for the COA by determining the degree of agreement with ozone calibration standards made in zero air at various ozone concentrations. Comparability will be assessed by comparison of the COA response to the Thermo Environmental UV Model 49C FEM.

Interference effects will be determined by challenging the COA with various levels of relative humidity (RH), substituted aromatic compounds, mercury, and products of photochemistry. Data completeness will be assessed as the percentage of maximum data return that is achieved by the COA over the test period. Operational factors will be evaluated by means of

operator observations, and records of needed maintenance, vendor activities, and expendables used. This test/QA plan provides the verification procedures for the COA.

### **B1.1 Test Procedures**

The following sections describe the test procedures that will be used to evaluate each of the performance parameters listed above. Test atmospheres will be generated in a 17.3 m<sup>3</sup> environmental chamber. The ozone analyzers undergoing testing will be connected to the chamber via a common manifold and will sample through a Teflon filter (nominal 5 um pore size). Laboratory temperature (T) near the monitors will also be measured. The analyzers that will be used as part of the verification test are listed in Table 2, together with their Federal designation (if any), the source of the analyzer, the type of ozone scrubber, and any special notes regarding the testing. Two COAs will be tested, one operated with and one without a Nafion drier to control the humidity (and potentially select polar organic component levels) of the sample air.

The T, RH, and particle concentration of the air in the chamber will be monitored during each test, using standard T and RH sensors and a Climet particle counter, respectively. During tests in which organic species are injected into the chamber, the VOC content of the chamber will be monitored with a total hydrocarbon monitor (flame ionization, VIG Corp.), and an integrated sample will be collected and analyzed by a gas chromatograph with mass selective detector (GC/MSD) to confirm the concentration of the organic species. For selected tests, gaseous elemental mercury will also be added to the chamber using a high emission rate permeation tube following procedures employed successfully in the chamber during past projects. An integrated sample will be collected and analyzed as described in Section B.1.1.2 to confirm the concentration of elemental mercury in the chamber.

**Table 2. Ozone Analyzers**

Analyzer	Federal Status	Ozone Scrubber	Notes
Thermo Environmental UV Model 49C	FEM	MnO <sub>2</sub> unheated	Monitor absorbance tube T
OPTEC 3.02 P-A solid-phase chemiluminescence	--	NA	--
OPTEC 3.02 P-A solid-phase chemiluminescence	--	NA	Use Nafion drier to reduce RH of sampled air

The signals from the test analyzers and other ancillary equipment, such as T and RH monitors and the total hydrocarbon monitor, will be recorded at least every minute using a Campbell Scientific data acquisition system. The zero signals of the ozone monitors will be set to 10% of full scale in order to observe any negative shifts in signal during the tests.

*B.1.1.1 Accuracy and Linearity*

After the COA has been calibrated, the accuracy and linearity of the COA will be determined by challenges with ozone over a range of concentrations from 0 to 300 ppb, generated by using an EnviroNics Model 6400 ozone generator (transfer standard) that has itself been calibrated against a Dasibi 1008 UV calibration photometer. The ozone will be added in stepwise concentrations at both low (approximately 5%) and high (70 to 80%) relative humidity.

*B.1.1.2 Interference Effects*

Interference effects in ozone-free air will be determined by the zero response of the COA with both low and high humidity when challenged with chemical interferences. The interference effects and the response of the COA will be assessed in Tests 1 and 2 as shown in Table 3. In these tests, the COA will be challenged with a mixture of four interferents. The interferents are listed in Table 3 and will be added to the environmental chamber at their respective designated concentrations. The first interferent will be supplied to the chamber and the response of the COA monitored. After the analyzer responses stabilize, the next interferent will then be added into the chamber, and the process of injecting the interferent and recording response will be

**Table 3. Interference Testing**

Test	RH	Interferent	Concentration
1	5%	Naphthalene	10 ppb
	5%	o-nitrophenol	10 ppb
	5%	p-tolualdehyde	10 ppb
	5%	Mercury	50 ng/m <sup>3</sup>
2	70 to 80%	Naphthalene	10 ppb
	70 to 80%	o-nitrophenol	10 ppb
	70 to 80%	p-tolualdehyde	10 ppb
	70 to 80%	Mercury	50 ng/m <sup>3</sup>

repeated until all four interferents have been added. After each injection of an interferent, an integrated sample will be taken in the environmental chamber to confirm the injected concentration. The challenges to the COA will occur in Test 1 at low (~5%) and in Test 2 at high (70 to 80%) RH. In between the tests, the environmental chamber will be purged overnight and the COA will be backflushed in order to clear the analyzer of any potential carryover of interferences.

The response of the COA to photochemical reaction products, present in air along with ozone, will be tested in Tests 3 and 4 (Table 4). Both tests will be conducted in a series of steps, starting with monitoring of clean dry air, then of humidified clean air, and then proceeding to monitoring of that air, spiked with a 17-component hydrocarbon mixture and NO<sub>2</sub>. Finally, Tests 3 and 4 will each include the irradiation of the chamber and the monitoring of the COA response until the ozone photochemical maximum has been passed. The difference between Tests 3 and 4 will be the four times higher hydrocarbon concentrations and NO<sub>2</sub> used in Test 4. Those higher concentrations are designed to represent an extreme air pollution episode. In between the tests, the environmental chamber will be purged overnight and the COA will be backflushed in order to clear the analyzer of any potential concern of remaining interferences.



**Table 4. Photochemical Testing**

Test	Step	Concentration
3	Monitor dry zero air	0 to 5 % RH
	Monitor humidified air	70 to 80% RH
	Add 17-component urban hydrocarbon mixture	500 ppbC
	Add NO <sub>2</sub>	50 ppb
	Irradiate chamber contents	NA
4	Monitor dry zero air	0 to 5 % RH
	Monitor humidified air	70 to 80% RH
	Add 17-component urban hydrocarbon mixture	2000 ppbC
	Add NO <sub>2</sub>	200 ppb
	Irradiate chamber contents	NA

NA = not applicable

*B1.1.3 Comparability*

Comparability will be evaluated by comparing the responses of the COA to the responses of the Thermo Environmental UV Model 49C FEM with the various challenges. All the analyzers listed in Table 2 will undergo sampling of the same procedures created in the environmental chamber. These procedures include the response to humidity effects at low and high humidity levels and the challenge of ozone concentrations ranging from zero to 300 ppb. Each analyzer will also be tested with the same interferences. For the purposes of this test/QA plan, two COAs connected to a common manifold will sample from the environmental chamber, one with a Nafion Dryer and one without. The effect of the addition of a Nafion drier to one of the COAs will be evaluated by comparing the resulting response between the two COAs.

The comparability of the COA response to ambient air will also be evaluated by comparing the analyzer response to the Thermo Environmental UV Model 49C analyzer during ambient air monitoring, which will be carried out over four successive days at Battelle. The COA will be compared to the UV analyzer by calculating the relative percent difference of the response of the COA to the response of the UV analyzer. The analyzers will continuously monitor for 96 hours and the hourly averages will be calculated for use in this determination.

#### *B.1.1.4 Data Completeness*

No additional test procedures will be carried out specifically to address data completeness. This parameter will be assessed based on the overall data return achieved by the COA.

#### *B.1.1.5 Operational Factors*

Operational factors such as maintenance needs, data output, consumables used, ease of use, etc., will be evaluated based on observations recorded by Battelle staff. A separate laboratory record book will be maintained and will be used to enter daily observations on these factors. Examples of information to be recorded in the record books include the daily status of diagnostic indicators for the COA; use or replacement of any consumables; the effort or cost associated with maintenance or repair; vendor effort (e.g., time on site) for repair or maintenance; the duration and causes of the COA down time or data acquisition failure; the sustainability of the analyzer (e.g. power consumed, wastes generated, disposal costs required); and operator observations about ease of use of the COA. These observations will be summarized to aid in describing COA performance in the verification report on each COA.

### **B1.2 Statistical Analysis**

The statistical methods and calculations used for evaluating quantitative performance parameters are described in the following sections. In all cases, COA readings in mg/m<sup>3</sup> will be converted to ppb, using measured T and barometric data, before comparisons to standard ozone concentrations and FEM data.

#### *B.1.2.1 Accuracy*

The accuracy of the COA with respect to the ozone transfer standard will be assessed as a percentage recovery (%R), using Equation 1:

$$\%R = \left[ 1 + \left( \frac{Y - X}{X} \right) \right] \times 100 \quad (1)$$

Where Y is the COA reading and X is the delivered ozone transfer standard concentration. The average, minimum, and maximum %R values will be reported for each series of multi level ozone challenges.

#### *B1.2.2 Linearity*

Linearity will be assessed by a linear regression analysis using the ozone concentration delivered from the transfer standard as the independent variable and the results from the COA being tested as the dependent variable. Linearity will be expressed in terms of slope, intercept, and coefficient of determination ( $r^2$ ).

#### *B1.2.3 Interference Effects*

The interference effects of the COA will be calculated in terms of the ratio of the response of the COA when challenged with the interferent, to the actual concentration of the interferent. For example, if 100 ppb of an interferent results in a 1 ppb change in the response of the analyzer, the interference effect will be reported as 1% (i.e., 1 ppb/100 ppb). Interference effects will be reported separately for each interferent. The actual interferent concentration determined by analysis will be used in the calculation, not the nominal concentration shown in Table 3.

#### *B1.2.4 Comparability*

Comparability between the COA results and the FEM analyzer results will be assessed by linear regressions using the FEM readings as the independent variable and results from the COA as the dependent variable. Linearity will be expressed in terms of slope, intercept, and  $r^2$ . This calculation will be done separately for each test described in Table 4, and separately with the FEM data from those tests. This calculation will also be done using the FEM data from the period of ambient air monitoring. Comparability calculations on the chamber tests will be based on minute-by-minute average data, whereas this calculation on the ambient data will be based on the hourly average values.

Comparability will also be calculated between the COA operated with a Nafion drier and the one operated without such a drier. This calculation will be done using the data from the photochemical ozone chamber tests (Table 4) and the period of ambient air monitoring.

#### *B.1.2.5 Data Completeness*

Data Completeness will be calculated as the percentage of the total possible data return over the entire set of tests that is achieved by the COA. This calculation will use the total hours of data recorded from the COA divided by the total hours of data in the entire set of tests. No distinction will be made in this calculation between data recorded during different test activities. The causes of any substantial incompleteness of data return will be established from operator observations, and noted in the discussion of data completeness results.

### **B1.3 Reporting**

The statistical comparisons described above will be conducted separately for each COA being tested, and information on the operational parameters will be compiled and reported. The data for each COA will be kept separate from data for all other COA's, and no intercomparison of the data from different vendors' analyzers will be performed at any time. A verification report will be prepared for the COA tested, that presents the test procedures and test data, as well as the results of the statistical evaluation of those data.

Operational aspects of the COA will be recorded by testing staff at the time of observation during the environmental chamber tests and field testing, and summarized in the verification report. For example, descriptions of the data-acquisition procedures, use of vendor-supplied proprietary software, consumables used, repairs and maintenance needed, and the nature of any problems will be presented in the report. The verification report will briefly describe the ETV program, the AMS Center, the test equipment and test conditions, and the procedures used in verification testing. The results of the verification test will be stated quantitatively, without comparison to any other COA's tested, or comment on the acceptability of the technology's

performance. The draft verification report will first be subjected to review by the technology vendor, then revised and subjected to a review by EPA, and/or other peer reviewers. The EPA comments and the peer review comments will be addressed in further revisions of the report, and the comments and responses will be tabulated to document the peer review process. The reporting and review process will be conducted according to the requirements of the AMS Center QMP.

## **B2 REFERENCE SAMPLE COLLECTION**

Sample collection does not apply in this verification, because ozone cannot readily be collected in sampling devices. In lieu of the collection of reference samples the COA will be challenged with ozone using an Environics Model 6400 ozone generator (transfer standard) that has itself been calibrated against a Dasibi 1008 UV calibration photometer. In addition, COA response to photochemical ozone mixtures and ambient air will be compared with the corresponding response of the FEM as designated by their respective analyzers. In addition, independent audits of sampling procedures will be performed by Battelle as part of the Technical Systems Audit procedure (Section C1.1).

## **B3 SAMPLE HANDLING AND CUSTODY REQUIREMENTS**

No reference samples will be collected in this test. However, samples will be collected for confirmation of the chamber concentrations of the interferent compounds. Such samples will be collected by, and remain in the custody of, the Battelle analyst who performs the confirming analysis.

## **B4 LABORATORY REFERENCE METHODS**

The reference method used for ozone determination in this test is an EPA designated UV absorption FEM (EQOA-0880-047) that is a continuous real-time ozone analyzer. The FEM

analyzer will be operated by Battelle staff according to the manufacturers' instructions, including those for warm-up and stabilization time before testing.

The FEM will be calibrated at the start of each day of testing using the ozone transfer standard described in Sections B1.1.4 and B2. This transfer standard itself will be calibrated against the Dasibi 1008 UV calibration photometer at the start of the series of chamber tests.

Laboratory measurements to confirm the interferent compound (i.e., naphthalene, o-nitrophenol, p-tolualdehyde) concentrations will be made using GC/MSD, with samples collected from the test chamber using commercially prepared sorbent traps. Prior to any chamber tests the sorbent method will be validated by tests of sorbent trap recovery and transfer of the interferent compounds to the GC/MSD. The GC/MSD response will be calibrated using standards prepared in Battelle's laboratories from the pure compounds. A linear regression of peak area versus compound mass will be established as the calibration curve, and used to calculate the actual chamber interferent concentrations. Similar procedures will be used for mercury determination by sampling on a gold trap and analysis in Battelle's laboratories by cold vapor atomic fluorescence on a Tekran series 2600 instrument.

## **B5 QUALITY CONTROL REQUIREMENTS**

Quality of the reference ozone measurements will be assured by calibration of the FEM analyzer at the start of each day of testing, using the ozone transfer standard. The calibration slope must equal  $1 \pm 0.01$  and the  $r^2$  greater than 0.95 in order for the reference measurement to meet QC requirements. Blank samples will be generated by challenging the ozone analyzers through the chamber sampling manifold with zero gas. If measurements fall outside of the required tolerances, the QC procedures will be repeated.

## **B6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE**

The Thermo Environmental FEM used for the reference sampling and analysis will be tested, inspected, and maintained as per the manufacturers operating instructions, so as to meet

the performance requirements established in the ozone reference method for ozone measurements. The GC/MSD and mercury fluorescence instrument used for the reference sampling and analysis will be tested, inspected, and maintained as per the standard operating procedures of Battelle. Battelle staff will operate and maintain the COA undergoing testing, those activities will be done as directed by the vendor. Otherwise, repair and maintenance of the COA will be the responsibility of the technology vendor. Other equipment such as T and RH instruments will be obtained from the Battelle Instrument Services Laboratory and will have been calibrated within the past year.

#### **B7 INSTRUMENT CALIBRATION AND FREQUENCY**

Prior to the start of the environmental chamber tests a multipoint calibration will be performed on the FEM using an Environics Model 6400 ozone generator (transfer standard) that has itself been calibrated against a Dasibi 1008 UV calibration photometer. The ozone calibration standards will be generated in dry zero air. On each day of testing the ozone monitors will be challenged through the chamber sampling manifold with zero gas and a single point ozone span, both using dry zero air. In addition, the COA will be calibrated before the start of each test, using its internal ozone source. The GC/MSD and mercury fluorescence instrument will be calibrated prior to analyses and a minimum of a one point calibration will be performed on consecutive analyses days.

#### **B8 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES**

All materials, supplies, and consumables will be ordered by the Verification Test Coordinator or designee. Where possible, Battelle will rely on sources of materials and consumables that have been used previously as part of ETV verification testing without problems. Battelle will also rely on previous experience or recommendations from EPA advisors or the COA vendor.

## **B9 NON-DIRECT MEASUREMENTS**

Data published previously in the scientific literature will not be used during this verification test.

## **B10 DATA MANAGEMENT**

Various types of data will be acquired and recorded electronically or manually by Battelle during this verification test. Table 5 summarizes the types of data to be recorded. All maintenance activities, repairs, calibrations, and operator observations relevant to the operation of the COA will be documented by Battelle staff in laboratory record books. A separate record book will be provided for each COA. Results from the COA and the FEM reference methods will be recorded in electronic format. All Battelle LRBs, record books and files are stored indefinitely, either by the Verification Test Coordinator or Battelle's Records Management Office. EPA will be notified before disposal of any files.

Records generated by any Battelle staff during the verification test will be reviewed by a Battelle staff member within two weeks of generation, before the records are used to calculate, evaluate, or report verification results. This review will be performed by a Battelle technical staff member involved in the verification test, but not the staff member who originally received or generated the record. The review will be documented by the person performing the review by adding his/her initials and date to the hard copy of the record being reviewed. In addition, any calculations performed by Battelle staff will be spot-checked by another Battelle technical staff member to ensure that calculations are performed correctly. Calculations to be checked include any statistical calculations described in this test/QA plan. The data obtained from this verification test will be compiled and reported independently for each COA tested.



**Table 5. Summary of Data Recording Process**

<b>Data to Be Recorded</b>	<b>Where Recorded</b>	<b>How Often Recorded</b>	<b>Disposition of Data</b>
Dates, times, and details of test events, COA maintenance, down time, etc.	ETV test notebooks	Start/end of test procedure, and at each change of a test parameter or change of COA status	Used to organize/check test results; manually incorporated in data spreadsheets as necessary
COA calibration information	ETV test notebooks, or electronically	At COA calibration or re-calibration	Incorporated in verification report as necessary
COA ozone readings	Recorded electronically for each analyzer	Recorded continuously throughout testing process	Converted to spreadsheet for statistical analysis and comparisons
Reference method procedures, calibrations, QA, etc.	Laboratory record books, or data recording forms	At each calibration, QA check, or change in method status	Retained as documentation of reference method performance
Reference method ozone results	Recorded electronically from each reference method	Recorded continuously throughout testing process	Converted to spreadsheets for statistical analysis and comparisons
Results of analyses for interferences in chamber tests	Electronically by GC/MSD instrument; summarized in analysts laboratory record book	At every sample analysis	Converted to spreadsheet for calculation of interference effects

Among the QA activities conducted by Battelle QA staff will be an audit of data quality. This audit will consist of a review by the Battelle Quality Manager of at least 10% of the test data. During the course of any such audit, the Battelle Quality Manager will inform the technical staff of any findings and any immediate corrective action that should be taken. If serious data quality problems exist, the Battelle Quality Manager will notify the AMS Center Manager, who 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. The Battelle Quality Manager will ensure that follow-up corrective action has been taken.

## **SECTION C**

### **ASSESSMENT AND OVERSIGHT**

#### **C1 ASSESSMENTS AND RESPONSE ACTIONS**

Every effort will be made in this verification test to anticipate and resolve potential problems before the quality of performance is compromised. One of the major objectives of this test/QA plan is to establish mechanisms necessary to ensure this. The procedures described in this test/QA plan, which is peer reviewed by a panel of outside experts, implemented by the technical staff and monitored by the Verification Test Coordinator, will give information on data quality on a day-to-day basis. The responsibility for interpreting the results of these checks and resolving any potential problems resides with the Verification Test Coordinator. Technical staff have the responsibility to identify problems that could affect data quality or the ability to use the data. Any problems that are identified will be reported to the Verification Test Coordinator, who will work with the Battelle Quality Manager to resolve any issues. Action will be taken to control the problem, identify a solution to the problem, and minimize losses and correct data, where possible. Independent of any EPA QA activities, Battelle will be responsible for ensuring that the following audits are conducted as part of this verification test.

##### **C1.1 Performance Evaluation Audit**

A Performance Evaluation (PE) audit will be conducted to establish the traceability of the ozone measurements made in this verification test. An ozone transfer standard photometer provided by Ohio EPA, care of Mr. Christopher Galilei, will be used to compare to the measurements made by the Dasibi 1008 calibration photometer. Ozone will be generated by an Environics Model 6400 ozone generator and a series of simultaneous measurements made by the transfer standard and Dasibi photometer over the range of zero to at least 300 ppb ozone will be compared. The ozone transfer standard is traceable to the primary ozone standard reference

photometer located at the EPA Region 5, Chicago, Illinois. Documentation of that traceability will be obtained and kept in the test records. If the readings of the Dasibi instrument are not the same as the readings of the ozone transfer standard, the data generated throughout this verification test will be corrected to comply with the values generated from the transfer standard. This audit will be performed once during the verification test

### **C1.2 Technical Systems Audit**

The Battelle Quality Manager will perform a technical systems audit (TSA) at least once during this verification test. The purpose of this audit is to ensure that the verification test is being performed in accordance with the AMS Center QMP,<sup>1</sup> this test/QA plan, using the EPA designated reference method, and any Standard Operating Procedures (SOPs) used by Battelle. In the TSA, the Battelle Quality Manager or a designee may review the reference methods used, compare actual test procedures to those specified or referenced in this plan, and review data acquisition and handling procedures. The Battelle Quality Manager will tour the environmental chamber laboratory, observe the ozone monitoring and review test chamber procedures, and review COA-specific record books. He will also check calibration certifications for test measurement devices. A TSA report will be prepared, including a statement of findings and the actions taken to address any adverse findings. The EPA AMS Center Quality Manager will receive a copy of Battelle's TSA report. At EPA's discretion, EPA QA staff may also conduct an independent on-site TSA during the verification test. The TSA findings will be communicated to technical staff at the time of the audit and documented in a TSA report.

### **C1.3 Data Quality Audit**

The Battelle Quality Manager will audit at least 10% of the verification data acquired in the verification test. The Battelle Quality Manager will trace the data from initial acquisition,

through reduction and statistical comparisons, to final reporting. All calculations performed on the data undergoing the audit will be checked.

#### **C1.4 QA/QC Reporting**

Each assessment and audit will be documented in accordance with Sections 3.3.4 and 3.3.5 of the AMS Center QMP.<sup>1</sup> The results of the technical systems audit will be submitted to EPA. Assessment reports will include the following:

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

#### **C2 REPORTS TO MANAGEMENT**

The Battelle 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 will notify the AMS Center Manager, who 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. The Battelle Quality Manager will ensure that follow-up corrective action has been taken. The test/QA plan and final report will be reviewed by EPA AMS Center QA staff and EPA AMS Center program management staff. Upon final review and approval, both documents will then be posted on both the EPA/ETV and the Battelle AMS Center websites.

## **SECTION D**

### **DATA VALIDATION AND USABILITY**

#### **D1 DATA REVIEW, VALIDATION, AND VERIFICATION REQUIREMENTS**

The key data review requirements for the verification test are stated in Section B10 of this test/QA plan. The QA audits described within Section C of this document, including the audit of data quality, are designed to assure the quality of the data. Data will be verified for completeness, correctness, and compliance with the procedures as written in this test/QA plan.

#### **D2 VALIDATION AND VERIFICATION METHODS**

Section C of this test/QA plan provides a description of the validation safeguards employed for this verification test. Data validation and verification efforts include the use of the EPA designated FEM and ozone calibration equipment, and the performance of TSA, PE, and data audits as described in Section C. An audit of data quality will be conducted by the Battelle Quality Assurance Manager to ensure that data review and validation procedures were completed, and to assure the overall quality of the data. Any findings will be communicated to technical staff at the time of the audit and documented in a report.

#### **D3 RECONCILIATION WITH USER REQUIREMENTS**

The purpose of the verification test is to compare the response of the OPTEC COA to the response of a federally designated FEM UV method for ozone (specifically method EQOA-0880-047). The data obtained should include thorough documentation of the performance of each COA. The data review and validation procedures described in the previous sections will assure that data meet these requirements and are accurately presented in the evaluation reports generated from this test.

This test/QA plan and the resulting ETV verification report(s) will be subjected to review by the COA vendor, EPA, and expert peer reviewers. These reviews will assure that this test/QA plan and the resulting report(s) meet the needs of potential users and permittees of COAs. The final report(s) will be submitted to EPA in Word and Adobe PDF format, both 508 compliant, and subsequently posted on the on the EPA/ETV and the Battelle AMS websites.

## SECTION E

### REFERENCES

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