February 2008

Environmental Technology Verification Report

JSC OPTEC 3.02 P-A
CHEMILUMINESCENT OZONE ANALYZER

Prepared by
Battelle

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EPA **U.S. Environmental Protection Agency**

ETV ETV ETV

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ETV Advanced Monitoring Systems Center

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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 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. ETV consists of five environmental technology centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

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. Under a cooperative agreement, Battelle has received EPA funding 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/centers/center1.html.

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. We particularly thank Will Ollison of the American Petroleum Institute, Rudy Eden of the South Coast Air Quality Management District, and Dennis Mikel of U.S. EPA's Office of Air Quality Planning and Standards for their reviews of this verification report.

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List of Abbreviations and Acronyms

AMS	Advanced Monitoring Systems
°C	Degrees Celsius
COA	Chemiluminescent Ozone Analyzer
cm^3	Cubic centimeter
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
FEM	Federal Equivalent Method
GC	Gas chromatograph
MSD	Mass selective detector
m^3	Cubic meter
$\mu g/m^3$	Microgram per cubic meter
µm	Micrometer
nm	Nanometer
NO_2	Nitrogen dioxide
O_3	Ozone
OEPA	Ohio Environmental Protection Agency
ppbC	Parts per billion carbon
ppbv	Parts per billion by volume
ppmv	Parts per million by volume
pptv	Parts per trillion by volume
%R	Percent recovery
RPD	Relative percent difference
%RR	Percent relative response
PE	Performance evaluation
QA	Quality assurance
QC	Quality control
QMP	Quality Management Plan
r^2	Coefficient of determination
RH	Relative Humidity
TSA	Technical systems audit
UV	Ultraviolet
VOC	Volatile organic compounds
V	Volt

Chapter 1
Background

The U.S. EPA's Environmental Technology Verification (ETV) Program verifies the performance of innovative technologies that have the potential to improve protection of human health and the environment. ETV accelerates the entrance of new environmental technologies into the domestic and international marketplaces. Verified technologies are included for all environmental media–air, water, and land.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; 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 (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The U.S. EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center verifies the performance of commercial-ready technologies that monitor contaminants and natural species in air, water, and soil. The center tests both field-portable and stationary monitors, as well as innovative technologies that can be used to describe the environment (site characterization). The AMS Center recently evaluated the performance of the JSC Optec Inc. 3.02 P-A chemiluminescent ozone analyzer (COA), a continuous monitor for determining ozone (O_3) in air.

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 JSC Optec 3.02 P-A (referred to in this report as the 3.02 P-A). The following general description of the 3.02 P-A is adapted from information provided by the vendor, and was not verified in this test.

The 3.02 P-A COA combines a novel solid phase chemilumi-nescence approach with easy to use menu-driven software with diagnostic functions, and is intended to provide flexibility and reliability in measurement. It is designed to measure ozone concentrations in ambient air.

The Model 3.02P-A is designed to have the following features:
- Automatic continuous measurements
- Automatic internal calibration
- High sensitivity
- Fast response time
- Linearity
- Menu driven software
- Digital display
- Data output

The 3.02 P-A detects ambient ozone by means of its chemical reaction with a solid-phase reactant of proprietary composition, resulting in the emission of light with peak intensity near

560 nm wavelength. The emitted light is detected by a photomultiplier tube, and converted to a digital signal that is linearly proportional to the gaseous ozone concentration. An internal pump draws sample air through two alternating flow paths: in the measurement path sample air passes directly into contact with the solid-phase reactant, whereas in the zeroing path ozone in the sample air is removed by a selective scrubber element before the air contacts the reactant. The 3.02 P-A thus measures ozone by comparison of the signals from these two paths. An internal ozone generator (ultraviolet (UV) lamp), located in the zeroing path downstream of the selective scrubber element, provides a calibration mixture to the 3.02 P-A at 10-minute intervals, and the internal software automatically adjusts instrument response with each calibration. The measured ozone concentration is displayed on the front panel of the 3.02 P-A and can be transmitted via analog outputs. The estimated price of the base model analyzer is $5,000.

Chapter 3
Test Design and Procedures

3.1 Introduction

This verification test was conducted according to procedures specified in the peer-reviewed *Test/QA Plan for Verification of Chemiluminescent Ozone Analyzer*,(1) and was carried out at Battelle laboratories in Columbus, Ohio from June 12 to June 28, 2007.

The objective of this verification test was to evaluate the performance of the Optec 3.02 P-A, in part by comparing it to the response of the UV-absorption Federal Equivalent Method (FEM) for ozone. FEMs are established by EPA to assure high quality in ambient air monitoring data. The UV-absorption FEM for ozone is the method used for virtually all ambient ozone monitoring in the U.S. The specific commercial FEM monitor used in this test was the Thermo Environmental Model 49C (method EQOA-0880-047).(2)

The COA was verified by evaluating the following parameters:

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

Accuracy was determined by assessing the percent recovery of the 3.02 P-A with respect to different levels of ozone challenges. Linearity was assessed by a linear regression analysis using the ozone challenge concentration as the independent variable and the results from the 3.02 P-A as the dependent variable. The interference effects were calculated in terms of the ratio of the response when challenged with the interferent, to the actual concentration of the interferent. Comparability was assessed by comparing the 3.02 P-A response to that of the FEM in selected tests. Data completeness was assessed as the percentage of maximum data return achieved by the 3.02 P-A over the test period. Operational factors were evaluated by means of observations during testing and records of needed maintenance, vendor activities, and expendables use.

3.2 Test Procedures

Prior to testing Battelle staff were trained in operation of the 3.02 P-A by the vendor. This training included studying the instrument manual, which had been translated into English from the original Russian.(3)

All test procedures were conducted using two units of the 3.02 P-A. One unit was operated exactly as recommended by the manufacturer. Results from that unit are the primary focus of this verification. In addition, a second unit was operated with a Nafion humidifier tube (obtained from 2B Technologies, Inc.) connected to the analyzer's air inlet. This Nafion tube is designed to equilibrate the humidity of the incoming sample stream with that of the room air in the test laboratory (i.e., about 50% relative humidity (RH)). However the Nafion modification was not optimized to the 3.02 P-A unit so complete equilibration of humidity was probably not achieved at the sample flow rate of the 3.02 P-A (i.e., 1.8 L/min). Thus the RH of the sample air entering the first 3.02 P-A unit varied with test conditions, as described below, whereas that for the second unit was equilibrated towards 50% RH. The Nafion tube was used to assess the impact of humidity and humidity control on the 3.02 P-A response. The 3.02 P-A specifications accept a humidity range for continuous operation of 15 to 95% RH. However, EPA data quality protocols for routine ambient monitoring generally require clean dry air for calibrations and daily zero and span checks. The Nafion attachment provides a means to mitigate the effects of humidity extremes. As a result, testing with the unmodified 3.02 P-A unit at low relative humidity and with the second unit modified by addition of the Nafion attachment provided information relevant to routine use of the 3.02 P-A.

Following are the test procedures used to evaluate the 3.02 P-A.

3.2.1 Accuracy

The accuracy of the 3.02 P-A was evaluated by two approaches. One approach determined the degree of agreement with ozone standards produced at 100 to 300 parts per billion by volume (ppbv) in dry zero air by an Environics Model 6400 ozone generator that was quantified by a Dasibi 1008 UV photometer, itself validated by a performance audit, as described in section 4.2.1. The delivered concentrations of ozone, once shown to be stable by the Dasibi 1008 UV photometer, were monitored by the 3.02 P-A unit for 3 to 5 minutes. The 3.02 P-A reading was recorded, and the Environics generator was then adjusted to the next desired concentration.

The second approach used to evaluate accuracy compared the 3.02 P-A and FEM responses to ozone generated in dry and humidified zero air in Battelle's 17.3 m^3 environmental chamber. Ozone was added stepwise to clean air in the test chamber at both low (< 5%) and high (approximately 70 to 80%) RH. The response of the 3.02 P-A to various ozone concentrations was compared to the corresponding response of the FEM.

3.2.2 Linearity

Linearity was also evaluated from the chamber test data used to assess accuracy. Linearity was determined by linear regression of the response of the 3.02 P-A against the simultaneous FEM responses.

3.2.3 Interference Effects

Interference effects were evaluated by three approaches in Battelle's 17.3 m^3 environmental test chamber. The first tests were conducted on June 13 and 14 to determine the response of the 3.02 P-A to ozone added stepwise to clean air in the test chamber at both low (< 5%) and high (approximately 70 to 80%) RH. Those tests, which were also used to assess 3.02 P-A accuracy and linearity relative to the FEM (Sections 3.2.1 and 3.2.2), indicated whether humidity affected 3.02 P-A response.

The second approach evaluated 3.02 P-A interference effects in ozone-free air at both low and high humidity, by adding stepwise chemicals found in primary source emissions or produced by urban photochemistry that have been found to be potential interferents in ozone monitoring. The interference effects and the response of the 3.02 P-A were assessed during Tests 1 and 2 as shown in Table 3-1, on June 20 and 22, respectively. In these tests, the 3.02 P-A was challenged with a mixture of four interferents added sequentially to the environmental chamber to produce their respective designated concentrations shown in Table 3-1. Once the first interferent was supplied to the chamber, the instruments were allowed to monitor for several minutes before moving on to the next interferent injection. Once all four interferents had been added, an integrated sample was taken in the environmental chamber to determine the actual interferent concentrations. The interferent concentrations used in these tests were at elevated levels that might plausibly exist in the atmosphere near roadways or other sources, or during stagnant meteorological conditions.

Table 3-1. Interference Testing Conditions

Test	RH	Interferent	Target Concentration	Actual Concentration
1	< 5%	Naphthalene	10 ppbv	10.9 ppbv
	< 5%	o-nitrophenol	10 ppbv	6.1 ppbv
	< 5%	p-tolualdehyde	10 ppbv	7.3 ppbv
	< 5%	Mercury	50 ng/m^3	630 ng/m^{3a} (78.7 pptv)^b
2	70 to 80%	Naphthalene	10 ppbv	11.0 ppbv
	70 to 80%	o-nitrophenol	10 ppbv	9.9 ppbv
	70 to 80%	p-tolualdehyde	10 ppbv	14.9 ppbv
	70 to 80%	Mercury	50 ng/m^3	54 ng/m^3 (6.8 pptv)^b

a. Mercury was injected into the environmental chamber at a higher concentration than originally planned in this test procedure.

b. pptv = parts per trillion by volume (=1x10-12 v/v)

The third approach assessed the response of the 3.02 P-A to ozone precursors and photochemical reactants during photochemical chamber Tests 3 and 4 (Table 3-2) on June 27 and 28, respectively. Both of these tests were 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 then with NO_2. The response of the 3.02 P-A up to that point was used to assess the interferent effects of these ozone precursors. After the hydrocarbons and NO_2 were delivered to the chamber, irradiation of the chamber took place until the maximum ozone concentration (approximately 130 ppbv for Test 3 and approximately 80 ppbv for Test 4) had been passed. The difference between Tests 3 and 4 was the four-fold higher hydrocarbon and NO_2 concentrations used in Test 4. The hydrocarbon levels targeted in these tests (500 and 2,000 ppbC) were chosen to reflect moderate photochemical periods when ozone standards are likely to be met, and severe photochemical periods when such standards are likely to be exceeded, respectively.

Table 3-2. Photochemical Chamber Testing Conditions

Test	Step	Target Concentration	Actual Concentration
3	Monitor dry zero air	< 5% RH	< 5% RH
	Monitor humidified air	≈ 80% RH	82% RH
	Add 17-component urban hydrocarbon mixture	500 ppbC	670 ppbC (167 ppbv)
	Add NO_2	50 ppbv	55 ppbv
	Irradiate chamber contents	NA	NA
4	Monitor dry zero air	< 5% RH	< 5% RH
	Monitor humidified air	≈ 80% RH	85% RH
	Add 17-component urban hydrocarbon mixture	2000 ppbC	2370 ppbC (593 ppbv)
	Add NO_2	200 ppbv	200 ppbv
	Irradiate chamber contents	NA	NA

NA = not applicable

Particle number concentrations in the photochemical tests ranged up to approximately 8 x 10^5 per cubic centimeter (cm^3) almost entirely in the 0.3 to 0.5 µm size range, and those particles were almost completely removed by the filter on the inlet manifold from which the 3.02 P-A units and the FEM drew their sample air.

3.2.4 Comparability

Comparability was evaluated by comparing the responses of the 3.02 P-A to the simultaneous response of the Thermo Environmental UV Model 49C FEM in the photochemical chamber tests and in ambient air monitoring. The comparability of the 3.02 P-A and FEM response in ambient air was evaluated during ambient air monitoring over a period of 110 hours June 22-27, 2007. During this period the 3.02 P-A units and FEM all remained inside the test laboratory, but sampled ambient air outside the laboratory window through a common inlet attached to the sampling manifold. Calibration checks were performed periodically during the test, and hourly average ozone values were recorded.

3.2.5 Data Completeness

No additional test procedures were carried out specifically to address data completeness. This parameter was assessed based on the overall data return relative to the total amount of data return possible for the technology being tested.

3.2.6 Operational Factors

Operational factors such as maintenance needs, data output, consumables used, and ease of use were evaluated based on observations by Battelle. A laboratory record book was used to enter daily observations on these factors. Examples of relevant information include the daily status of diagnostic indicators for the 3.02 P-A, 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 any 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 3.02 P-A.

3.3 Reference Methods

Reference methods for ozone consisted of a commercial photometer, the calibration of which is traceable to the primary reference photometer at EPA Region 5 in Chicago (as described in Section 4.2), and the Model 49C FEM. The UV-absorption method is used for virtually all ambient ozone monitoring in the U.S., and the Model 49C is a commonly used instrument established as an FEM for ozone.

During the interference and photochemical tests, integrated samples were taken of the injected contaminants and laboratory measurements were used to confirm the interferent compound concentrations added to the environmental chamber. Samples of naphthalene, o-nitrophenol, and p-tolualdehyde were collected from the chamber using commercially prepared sorbent traps, and their chamber concentrations were confirmed by gas chromatography with mass selective detection (GC/MSD). Mercury was confirmed by cold vapor atomic fluorescence using a Tekran Series 2600 instrument. A total hydrocarbon monitor (flame ionization, VIG Corp), was used during the photochemical tests to measure the volatile organic compounds (VOC) content.

3.4 Verification Schedule

The 3.02 P-A was verified between June 12 and June 28, 2007. Table 3-3 shows the dates of activities relevant to the 3.02 P-A verification.

Table 3-3. Test Activities During the Optec 3.02 P-A Verification Test

Date	Test Activity
May 7	Optec 3.02 P-A arrive at Battelle
May 22	Installation of 3.02 P-A into test set up
June 12	Transfer Standard Performance Audit
June 13	Ozone Challenge High Humidity
June 14	Ozone Challenge Low Humidity
June 20	Interferent Test Low Humidity
June 22	Interferent Test High Humidity
June 22-27	Ambient Monitoring
June 27	Photochemical Test High Concentration
June 28	Photochemical Test Low Concentration
June 28	End Testing

Chapter 4
Quality Assurance/Quality Control

QA/QC procedures were performed in accordance with the quality management plan (QMP) for the AMS Center[(4)] and the test/QA plan for this verification test.[(1)] QA/QC procedures and results are described below.

4.1 Equipment Calibrations

Prior to the start of the environmental chamber tests a multipoint calibration was performed on the FEM using the Environics Model 6400 ozone generator and Dasibi 1008 UV photometer. The ozone calibration standards were generated in dry zero air. The FEM was also calibrated in the same manner at the start of each day before the start of any tests.

The 3.02 P-A units were calibrated automatically at 10-minute intervals throughout the entire test, using their internal ozone sources. This internal calibration was the basis for all 3.02 P-A readings.

The GC/MSD and mercury fluorescence instruments were calibrated prior to analyses and a minimum of a one point calibration was performed on each analysis day.

4.2 Audits

Three types of audits were performed during the verification test: a performance evaluation (PE) audit of the ozone standard used in testing, a technical systems audit (TSA) of the verification test procedures, and a data quality audit. Audit procedures are described further below.

4.2.1 Performance Evaluation Audit

A PE audit was conducted on June 12, 2007 to establish the traceability of the Battelle-owned Dasibi 1008 UV photometer relative to the standard photometer owned by the Ohio Environmental Protection Agency (OEPA), which was also a Dasibi 1008 UV photometer, and which is traceable to the primary ozone standard reference photometer located at EPA Region 5, Chicago, Illinois. In the PE audit, simultaneous measurements were made from a range of zero to 400 ppbv with the Battelle-owned and OEPA photometers using Battelle's Environics Model 6400 ozone generator as the ozone source. The results of the audit are provided in Figure 4-1, in the form of a linear regression of the Battelle photometer response against the OEPA photometer response corrected to match the EPA Region 5 reference photometer. Figure 4-1 shows close agreement of the results, with the linear regression showing Battelle O_3= 0.9923 (EPA Region 5 O_3) -0.7628 ppbv, with a coefficient of determination (r^2) of 1.0. Ozone concentrations delivered in testing were determined using Battelle's photometer, and corrected to the EPA Region 5 standard using this equation.

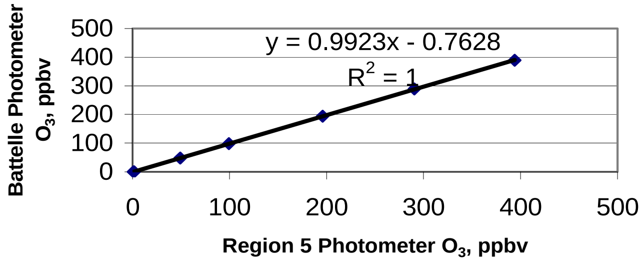

Figure 4-1. Performance Audit of Battelle's Dasibi 1008 UV Photometer.

4.2.2 Technical Systems Audit

A TSA was conducted by Battelle's AMS Center Quality Manager during testing on June 22, 2007. Observations and findings from this audit were documented and submitted to the Battelle Verification Test Coordinator for response. No major findings were noted. All minor findings were documented, and all required corrective actions were taken. The records concerning the TSA are permanently stored with the Battelle Quality Manager. EPA's ETV QA Officer also conducted a TSA on June 14, 2007. No adverse findings were reported from that audit.

4.2.3 Audit of Data Quality

Battelle's Quality Manager traced the test data from the initial acquisition, through reduction and statistical analysis, to final reporting to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked during the technical review process.

4.3 QA/QC Reporting

Each audit was documented in accordance with Sections 3.3.4 and 3.3.5 of the QMP for the ETV AMS Center.(4) Once the audit report was prepared, the Battelle Verification Test Coordinator ensured that a response was provided for each adverse finding or potential problem and implemented any necessary follow-up corrective action. The Battelle Quality Manager ensured that follow-up corrective action was taken. The results of the TSA were sent to the EPA.

4.4 Data Review

Records generated in the verification test received a one-over-one review before these records were used to calculate, evaluate, or report verification results. Data were reviewed by a Battelle technical staff member involved in the verification test. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed.

Chapter 5
Statistical Methods

The statistical methods in this chapter were used to verify the performance parameters listed in Section 3.1.

5.1 Accuracy

The accuracy of the 3.02 P-A, with respect to either delivered ozone standard concentrations or simultaneous FEM readings, was assessed as a percentage recovery (%R), using Equation 1:

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

Where Y is the 3.02 P-A reading and X is the delivered ozone standard concentration, or the FEM reading in simultaneous monitoring with the FEM and the 3.02 P-A. The average, and range (minimum, and maximum) %R values are reported for each assessment of accuracy.

5.2 Linearity

Linearity was assessed using the same 3.02 P-A and FEM data used to assess accuracy, by a linear regression of the FEM ozone concentration (independent variable) and the 3.02 P-A reading (dependent variable). Linearity was expressed in terms of slope, intercept, and r^2.

5.3 Interference Effects

The interference effects of the 3.02 P-A were illustrated by comparison of the response of the 3.02 P-A when challenged with each chemical interferent. The interference effects were considered separately for each of the three sets of interferent tests. Quantitative interference effects were calculated as a percent relative response (%RR) to the interferent for the two tests in which chemical interferents were added to the test chamber, i.e.:

$$\%\mathrm{RR} = \left(\frac{\text{ppbv O}_3\text{ response}}{\text{ppbv interferent}}\right) \times 100 \tag{2}$$

5.4 Comparability

Comparability between the 3.02 P-A results and the FEM analyzer results was illustrated by graphing the data for visual comparison and assessed by linear regressions using the FEM readings as the independent variable and results from the 3.02 P-A as the dependent variable. Linearity was expressed in terms of slope, intercept, and r^2. This calculation was done for the photochemical ozone chamber tests described in Table 3-2, and for the period of ambient air monitoring. Thus comparability was assessed using complex pollutant mixtures, either prepared in the test chamber or naturally present in ambient air. The data from these tests are not the same as those used to assess accuracy or linearity (Sections 5.1 and 5.2). Comparability calculations on the photochemical chamber tests were based on minute-by-minute average data, whereas these calculations on the ambient data were based on the hourly average values. Comparability was calculated in this way for each of the 3.02 P-A units, relative to the FEM.

Comparability of the 3.02 P-A to the FEM in the photochemical tests and ambient monitoring was also calculated in terms of relative percent difference (RPD), where

$$\text{RPD} = \left(\frac{(3.02\ \text{P - A}_{\text{avg}}) - \text{FEM}_{\text{avg}}}{\text{FEM}_{\text{avg}}} \right) \times 100 \tag{3}$$

and 3.02 P-A_{avg} and FEM_{avg} represent corresponding readings from the two types of monitors, i.e., short-term averages in the photochemical tests and hourly averages in the ambient monitoring. The RPD is reported at the mean, maximum, and minimum value of the FEM readings within each data set. This calculation of RPD was conducted only for the 3.02 P-A unit operated normally (i.e., without the added Nafion tube).

5.5 Data Completeness

Data completeness was calculated as the percentage of the total possible data return that was achieved by the 3.02 P-A over the entire testing period. This calculation used the total hours of data recorded divided by the total hours of data in the entire testing period. Testing began on June 12 and ended on June 28, 2007, and both 3.02 P-A units operated continuously throughout this time, though test procedures did not occupy that entire time. For this calculation, no distinction was made between data recorded during calibration or zeroing, or in performance of linearity, interference effects, photochemical testing, or ambient monitoring. The causes of any substantial incompleteness of data were established from operator observations or vendor records.

Chapter 6
Test Results

The results of the verification test of the Optec 3.02 P-A are presented in this section. As noted in Section 4.2.1, a correction factor based on the results of the performance evaluation audit and the equation in Figure 4-1 was applied to all reference ozone data before the following data comparisons were made. Results are presented in this chapter for both units of the 3.02 P-A. It must be stressed that the Nafion humidification tube was not optimized for use with the 3.02 P-A, but was used on one unit solely to explore whether humidity and humidity control affected 3.02 P-A response. In all cases results for the 3.02 P-A unit operated normally (i.e., without a Nafion tube) are the primary result, and are distinguished from the results of the unit operated with an added Nafion humidification tube.

6.1 Accuracy

The accuracy of the 3.02 P-A with respect to the ozone standard concentrations was calculated using Equation 1 in Chapter 5. Table 6-1 lists the 3.02 P-A results when multi-level ozone challenges were delivered to the analyzers in clean dry air from the Environics 6400. The average, maximum, and minimum values of percentage recovery are listed. These data were obtained from all 3.02 P-A readings in the daily checks performed each day of testing. The actual ozone output of the Environics 6400 is shown in the first column of Table 6-1, as determined during the PE audit (Section 4.2.1) at nominal ozone settings of 300, 250, 200, and 100 ppbv respectively.

Table 6-1. Percent Recoveries Relative to Ozone Standard Concentrations

Concentration ppbv	N Readings	3.02 P-A	Average %R	Minimum %R	Maximum %R
289	98	Optec wout[a]	88.3	88.5	88.2
		Optec w/Naf[b]	84.3	65.1	89.5
242	51	Optec wout	85.9	53.2	94.5
		Optec w/Naf	89.2	80.1	106.6
194	169	Optec wout	85.4	79.0	92.7
		Optec w/Naf	69.8	61.8	86.7
98	10	Optec wout	107.7	105.8	108.6
		Optec w/Naf	81.0	80.5	81.4

a. Optec 3.02 P-A operated without Nafion tube.

b. Optec 3.02 P-A operated with Nafion tube.

Table 6-1 shows that the average %R value for the Optec 3.02 P-A analyzer operated normally (i.e., without the additional Nafion humidity equilibration tube) was about 85 to 88 %, except for the few readings at a delivered concentration of 98 ppbv, for which %R was over 100%. The average %R values for the 3.02 P-A with the Nafion tube ranged more widely, from about 70 to 89%. Note that the ozone standards delivered from the Environics 6400 were in dry zero air (RH of 5% or less), and that this RH is below the recommended lower RH limit (15% RH) for continuous operation of the Optec 3.02 P-A analyzer. In this case the addition of the Nafion humidity equilibration system did not appreciably improve the performance of the 3.02 P-A with ozone in dry air; however, the Nafion system was designed for sample flows about 1 liter per minute and humidity equilibration of the Optec 3.02 P-A was probably incomplete at the sample flow rate of approximately 1.8 liter per minute.

Accuracy of the 3.02 P-A was also evaluated by comparison to FEM readings obtained simultaneously in monitoring of ozone in dry and humid zero air. The calculation of accuracy was done using Equation 1 in Chapter 5. Tables 6-2 and 6-3 show those accuracy results in terms of the average, maximum, and minimum %R for the ozone chamber tests conducted on June 13 and 14, 2007, at high and low RH, respectively. For these tests ozone was added to the chamber by brief injections from a high concentration source, and the ozone concentration was determined by the average response of the FEM over a series of 10 stable data points. The simultaneous 3.02 P-A readings were similarly determined as the average of 10 successive stable readings.

Table 6-2. Percent Recoveries of Ozone from High Humidity (70 to 80% RH) Chamber Tests on June 13, 2007

Concentration (ppbv)	3.02 P-A	Average %R	Minimum %R	Maximum %R
257	Optec wout[a]	93.9	92.7	95.0
	Optec w/Naf[b]	94.9	93.7	96.1
223	Optec wout	95.2	93.5	97.0
	Optec w/Naf	99.1	92.8	101.5
172	Optec wout	94.0	92.8	96.2
	Optec w/Naf	96.7	95.0	97.3
108	Optec wout	93.2	92.6	94.3
	Optec w/Naf	110.3	107.3	113.3
51	Optec wout	109.9	108.5	111.5
	Optec w/Naf	105.4	103.9	107.2

a. Optec 3.02 P-A operated without Nafion tube.
b. Optec 3.02 P-A operated with Nafion tube.

Table 6-3. Percent Recoveries of Ozone from Low Humidity (<5% RH) Chamber Tests on June 14, 2007

Concentration (ppbv)	3.02 P-A	Average %R	Minimum %R	Maximum %R
260	Optec wout[a]	84.9	84.1	85.7
	Optec w/Naf[b]	70.2	69.5	71.1
206	Optec wout	83.8	83.3	84.1
	Optec w/Naf	74.5	72.7	81.2
163	Optec wout	83.6	83.4	83.9
	Optec w/Naf	73.1	72.3	73.9
119	Optec wout	83.4	83.2	83.7
	Optec w/Naf	73.9	73.3	74.2
69	Optec wout	88.3	87.4	90.2
	Optec w/Naf	78.1	76.5	87.5

a. Optec 3.02 P-A operated without Nafion tube.
b. Optec 3.02 P-A operated with Nafion tube.

Table 6-2 shows that the average %R value for the 3.02 P-A without the Nafion tube was about 93 to 95%, when sampling ozone in humid air from the test chamber, except for a %R value of about 110% at the lowest ozone concentration The corresponding %R for the 3.02 P-A with the Nafion tube was 95 to 99% at the higher ozone levels, with values of 105 to 110% at the lowest two ozone concentrations.

Table 6-3 shows that the average %R value for the 3.02 P-A without the Nafion tube was about 83 to 88%, when sampling ozone in dry air from the test chamber. The corresponding %R for the 3.02 P-A with the Nafion tube was lower, at 70 to 78%.

These results show that the 3.02 P-A exhibited higher %R values with ozone in humid air than in dry air, which is consistent with the recommendation by Optec that the analyzer not operate continuously on air of RH less than about 15%. Values of %R near 100% were observed both with and without the added Nafion tube when sampling humid air, whereas %R values were much lower both with and without the Nafion when sampling dry air. These results suggest that the addition of the Nafion tube does not improve the %R results for the 3.02 P-A. It is noteworthy that in routine ambient monitoring at standard compliance network sites, it is mandatory to produce ozone calibration mixtures in clean dry air.

6.2 Linearity

The linearity of the 3.02 P-A was evaluated using the data from the chamber ozone tests at both low (< 5%) and high (70-80%) RH. Figure 6-1 shows the results from the high humidity chamber test on June 13, 2007. The responses of the 3.02 P-A with and without the Nafion tube are shown in relation to the delivered ozone as determined by the FEM. Shown in the figure are the slope, intercept, and r^2 of the linear fit for each 3.02 P-A unit.

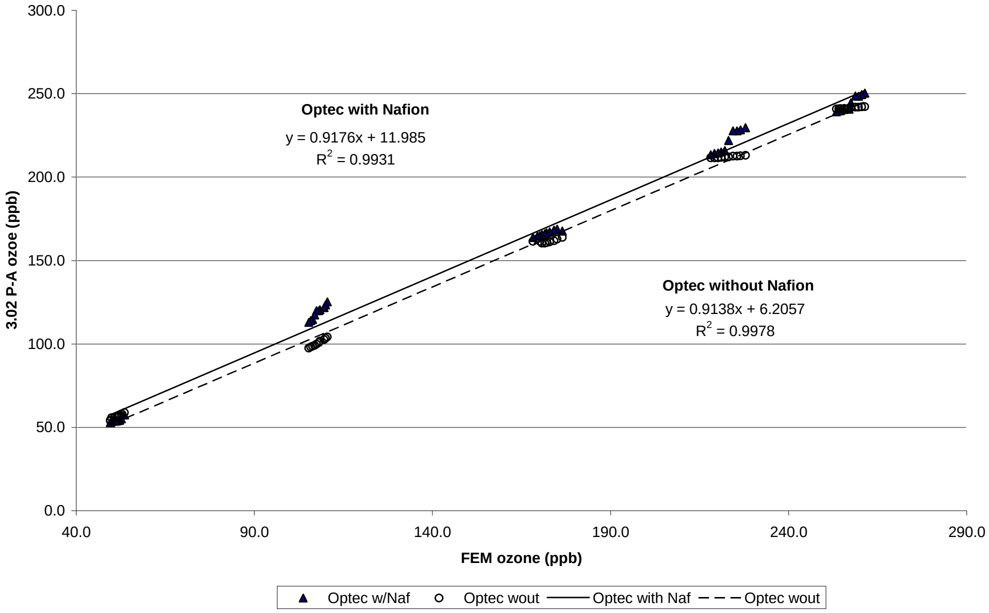

Figure 6-1. Linearity of 3.02 P-A Response to Ozone in Chamber at High Humidity.

Figure 6-2 shows the results from the low humidity chamber test on June 14, 2007. The responses of the 3.02 P-A with and without the Nafion tube are shown in relation to the delivered ozone as determined by the FEM. Shown in the figure are the slope, intercept and r^2 of the linear fit for each 3.02 P-A unit.

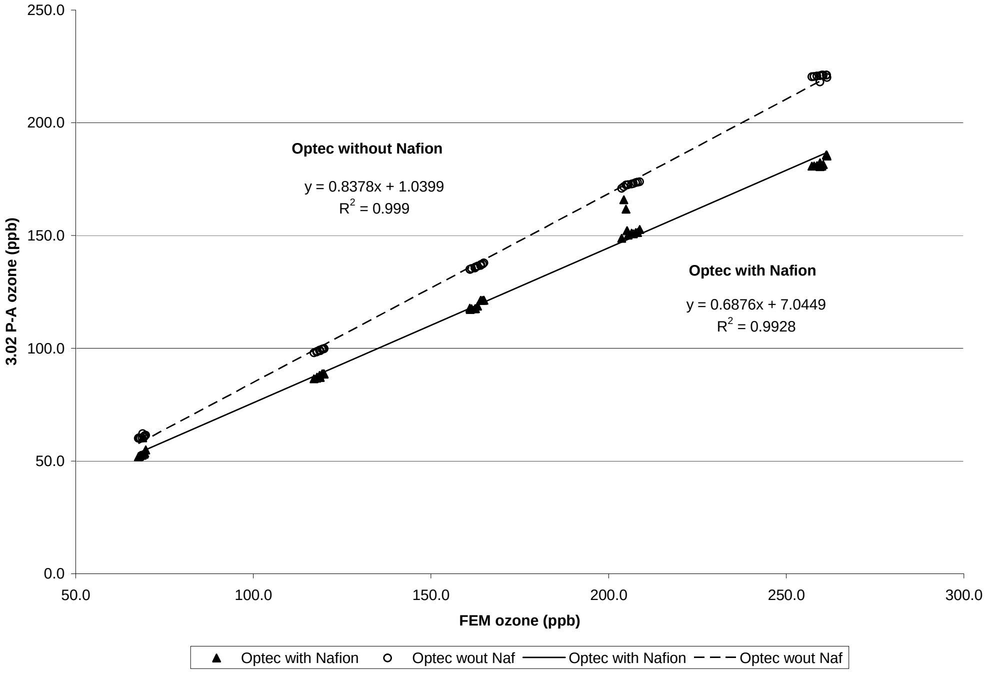

Figure 6-2. Linearity of 3.02 P-A Response to Ozone in Chamber at Low Humidity.

The linearity results in Figures 6-1 and 6-2 demonstrate linear response by both 3.02 P-A units, but confirm the results shown for %R in Section 6.1, in that the linear regression slopes are much closer to 1.0 when sampling humid air than when sampling dry air. The degradation of performance caused by the added Nafion tube when sampling dry air is evident in Figure 6-2, as it was in Table 6-3 (Section 6.1).

6.3 Interference Effects

The effect of humidity as an interferent is shown in the preceding sections 6.1 and 6.2. Low humidity (< 5% RH) clearly degrades the performance of the 3.02 P-A. As noted above, this RH level is below that recommended by the vendor for continuous operation of the 3.02 P-A.

The responses of the two 3.02 P-A units to the interferents in Test 1 are illustrated in Figure 6-3. This test was conducted on June 20, 2007 with low humidity (< 5%) in the chamber. The interferents are noted as to the time they were injected into the chamber.

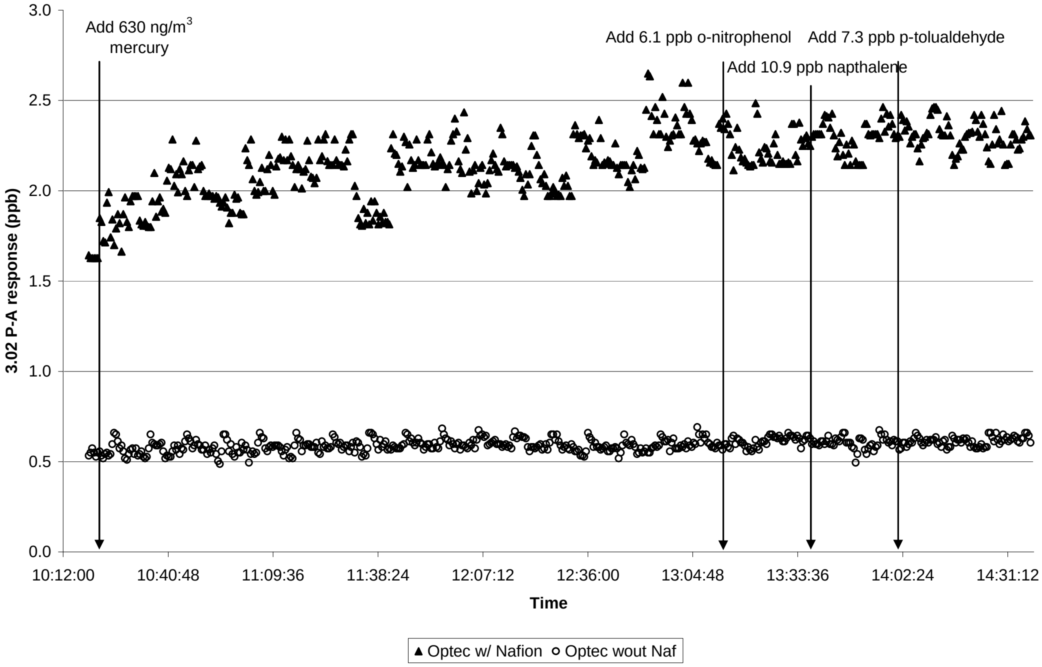

Figure 6-3. 3.02 P-A Response to Interferents in Chamber at Low Humidity.

Figure 6-3 shows that the zero air ozone readings of the 3.02 P-A unit operated normally (without the added Nafion tube) were about 0.6 ppbv, and showed no significant changes associated with the successive additions of the four potential interferents. The readings of the 3.02 P-A operated with the added Nafion were higher (about 2.3 ppbv), but also showed no trends associated with the additions of the interferents. Thus the %RR values for the 3.02 P-A for these four interferents in dry air were all zero.

Figure 6-4 illustrates the responses of the two 3.02 P-A units to the interferents injected into the chamber in Test 2, conducted on June 22 with high (70-80 %) RH in the chamber. Figure 6-4 shows that the zero air readings of the 3.02 P-A unit without the Nafion tube were about 0.6 to 0.7 ppbv, whereas those of the unit with the Nafion tube were slightly higher and more variable, ranging from 0.5 to 1.2 ppbv. Readings affected by the analyzer's automatic calibration at 10-minute intervals are evident in the data for the 3.02 P-A operated without the Nafion. Although there is scatter in the data, there is no clear trend associated with the addition of the potential interferents. Thus the %RR values for the 3.02 P-A for these four interferents in humidified air were all zero.

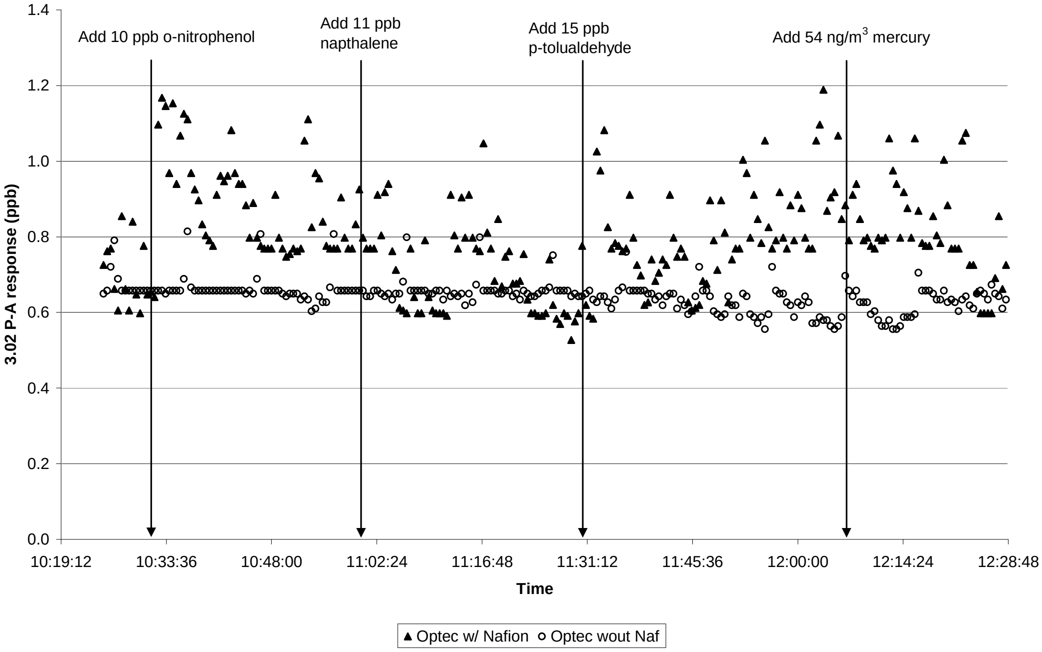

Figure 6-4. 3.02 P-A Response to Interferents in Chamber at High Humidity.

Two photochemical tests were conducted with the addition of a 17 component hydrocarbon mixture (both gas and liquid components) and NO_2. These tests were performed at a humidity of approximately 80%. Figure 6-5 shows the response of the two 3.02 P-A units over time while these ozone precursors were injected into the environmental chamber on June 27, 2007 (before the chamber lights were turned on to begin ozone production). The hydrocarbon concentration injected into the chamber was approximately 2,370 ppbC (593 ppbv) and the NO_2 concentration was 200 ppbv.

Figure 6-5 shows that in this test the readings of the 3.02 P-A operated with no Nafion tube were about 0.6 ppbv, and those of the other unit were about 3.5 to 4.5 ppbv. Slight shifts of the readings can be seen, associated with the analyzers' autocalibration at 10-minute intervals, and the readings of the 3.02 P-A operated with the Nafion tube exhibit some drift. However, there is no clear effect on the readings associated with the introduction of any of the ozone precursors. The 3.02 P-A unit operated normally (i.e., without the Nafion tube) showed no more than 0.1 ppbv variation in readings throughout the precursor injections.

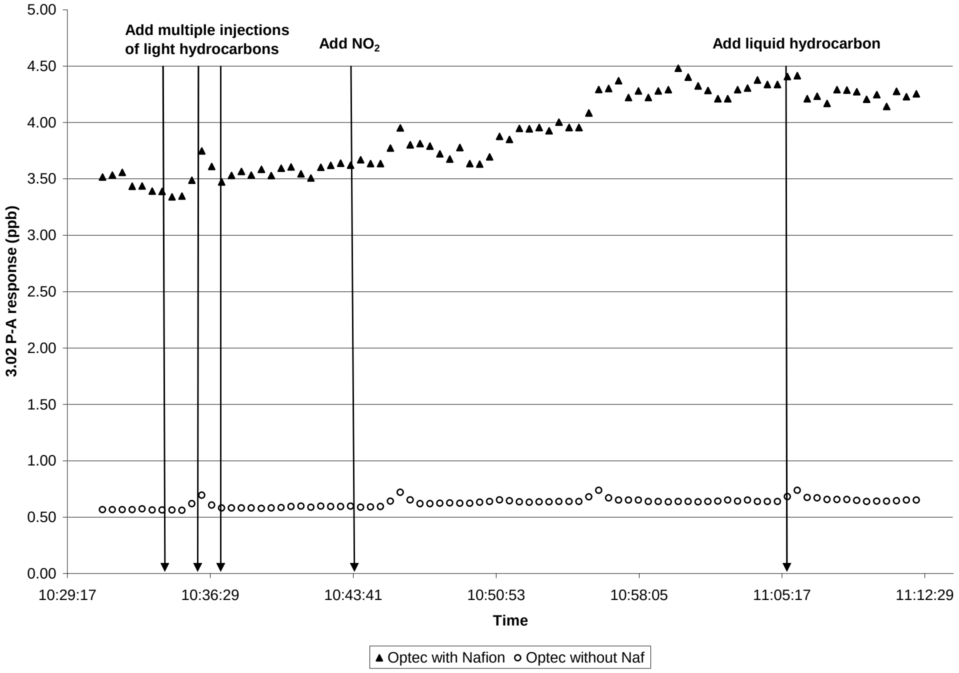

Figure 6-5. Photochemical Interferent Test with High Precursor Concentrations.

Figure 6-6 illustrates the response of the two 3.02 P-A units over time while the interferents were injected into the environmental chamber on June 28, 2007. The hydrocarbon concentration injected into the chamber was approximately 670 ppbC (167 ppbv) and the NO_2 concentration was 55 ppbv. Also shown in Figure 6-6 is a similar result to that of Figure 6-5, in that the readings of the two 3.02 P-A units are unaffected by the addition of the ozone precursors. Thus the %RR values for these ozone precursors with the 3.02 P-A appear to be zero.

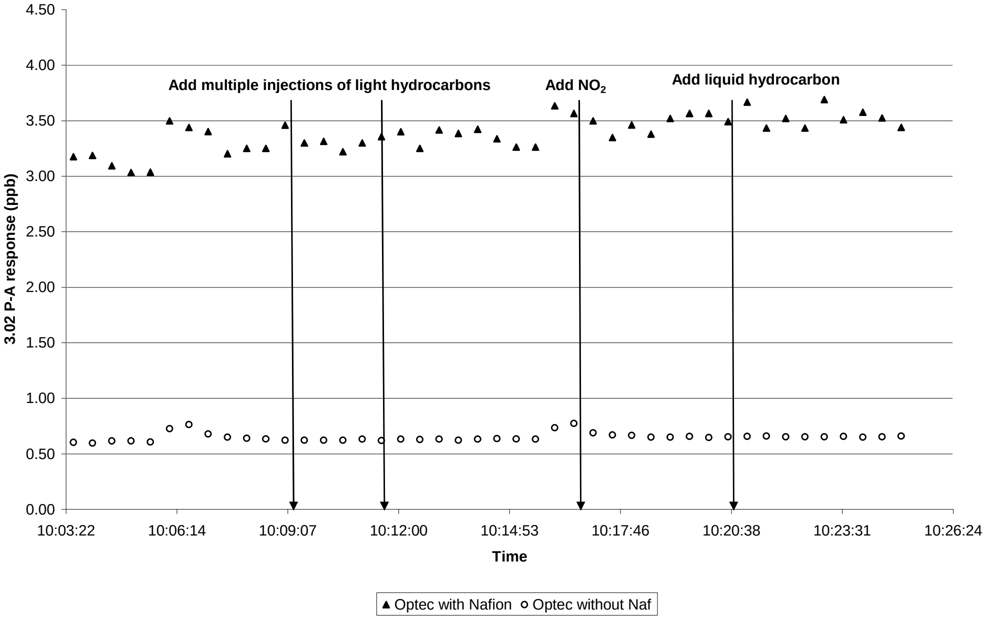

Figure 6-6. Photochemical Interferent Test with Low Precursor Concentrations.

6.4 Comparability

Linear regression was used to compare the response of the two 3.02 P-A units to that of the FEM during the photochemical tests and ambient monitoring. Figure 6-7 shows the readings of the 3.02 P-A both with and without the Nafion tube in comparison to the response of the FEM during the photochemical ozone test with high precursor concentrations. Figure 6-7 covers the time following the injection of precursors into the environmental chamber while ozone was being produced. The injections included approximately 2,370 ppbC (593 ppbv) of hydrocarbons and 200 ppbv NO_2.

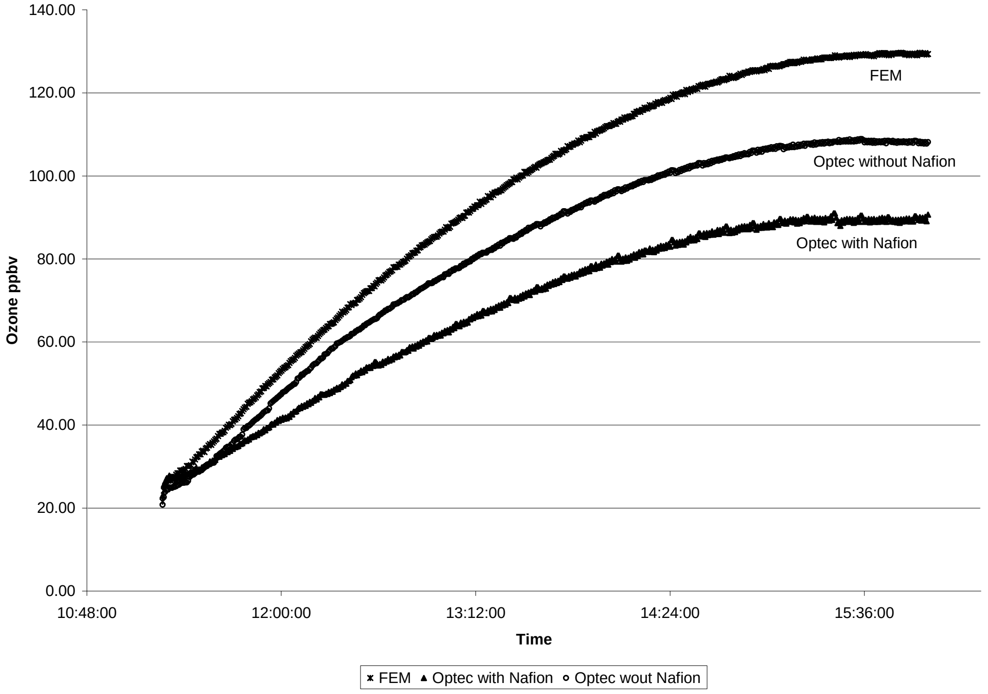

Figure 6-7. 3.02 P-A Response to Ozone During Photochemical Test with High Precursor Concentrations.

Figure 6-8 shows the linear regression results for this photochemical chamber test. Shown in the figure are the slope, intercept, and r^2 of 3.02 P-A response relative to FEM response. Figure 6-8 shows that both 3.02 P-A units provided response that was linearly correlated with that of the FEM in this photochemical test (e.g., both r^2 values exceeded 0.998), but with slopes that were substantially lower than 1.0. The 3.02 P-A operated normally (i.e., without the added Nafion tube) had a slope of 0.81 relative to the FEM, whereas the unit operated with the Nafion had a slope of only 0.63. In this test the chamber RH was near 80%, so the relatively low regression slopes cannot be attributed to the effect of lower humidity reported in previous sections.

In this test the RPD of the 3.02 P-A (operated without the Nafion tube) was -14.2%, -16.0%, and -3.5% relative to the FEM at the mean, maximum, and minimum ozone concentrations, respectively.

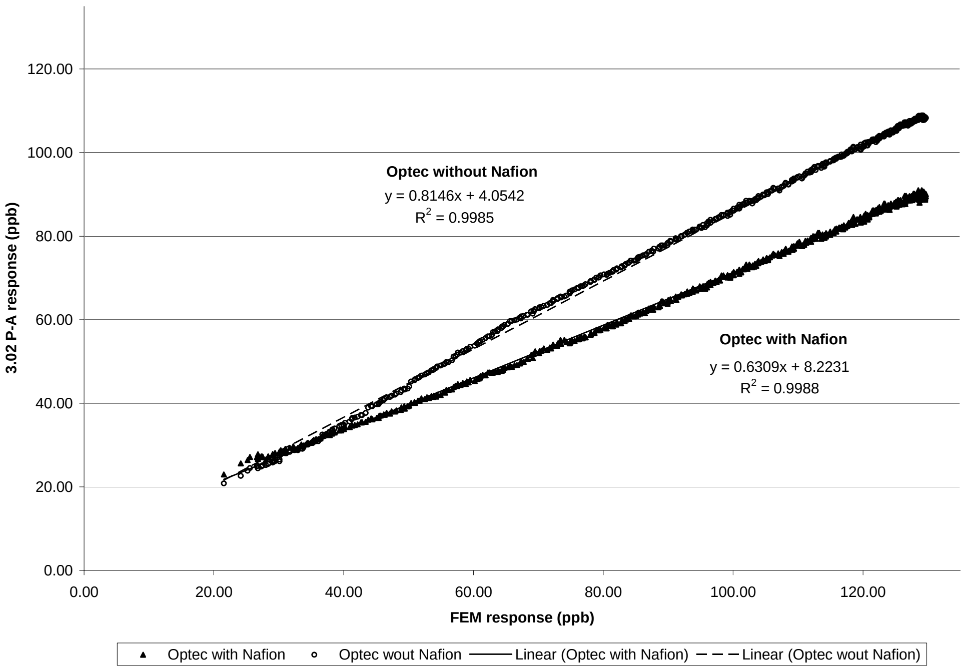

Figure 6-8. Photochemical Ozone Comparison with High Precursor Concentrations.

Figure 6-9 shows the readings of the two 3.02 P-A units in comparison to the response of the FEM in the photochemical test with lower precursor concentrations. The data depicted are from the time following the injection of precursors into the environmental chamber while ozone was being produced. The injections were of approximately 670 ppbC (167 ppbv) of hydrocarbons and 55 ppbv of NO_2. Occasional offsets are evident in the two 3.02 P-A traces, due to the automated internal calibrations performed by these units.

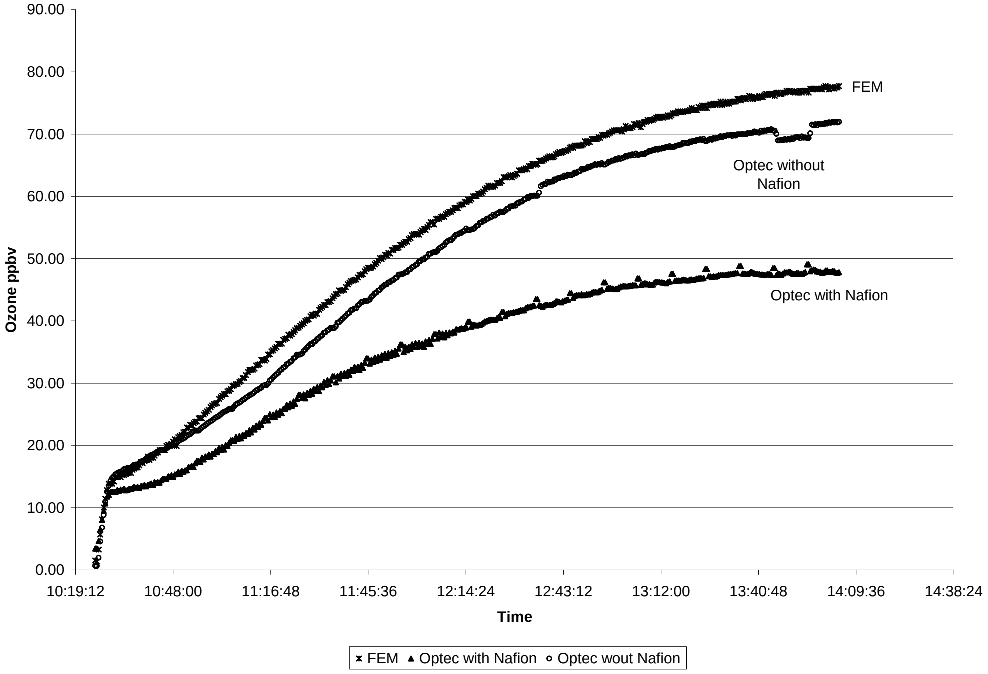

Figure 6-9. 3.02 P-A Response to Ozone During Photochemical Test with Low Precursor Concentrations.

Figure 6-10 shows the linear regression results from this photochemical chamber test. Shown in the figure are the slope, intercept, and r^2 of 3.02 P-A response relative to FEM response. Figure 6-10 shows that both 3.02 P-A units provided response that was linearly correlated with that of the FEM in this photochemical test (e.g., both r^2 values exceeded 0.99). In this test the slope of the regression for the 3.02 P-A operated without the Nafion tube was 0.94, close to the optimum value of 1.0. However the 3.02 P-A unit operated with the Nafion tube had a regression slope of only 0.58 relative to the FEM readings. These results indicate that at less severe hydrocarbon and NO_2 levels, the 3.02 P-A readings matched those of the FEM relatively closely, but that the addition of the Nafion tube degraded the performance of the 3.02 P-A.

In this test the RPD of the 3.02 P-A (operated without the Nafion tube) was -8.0%, -7.4%, and 0.2% relative to the FEM at the mean, maximum, and minimum ozone concentrations, respectively.

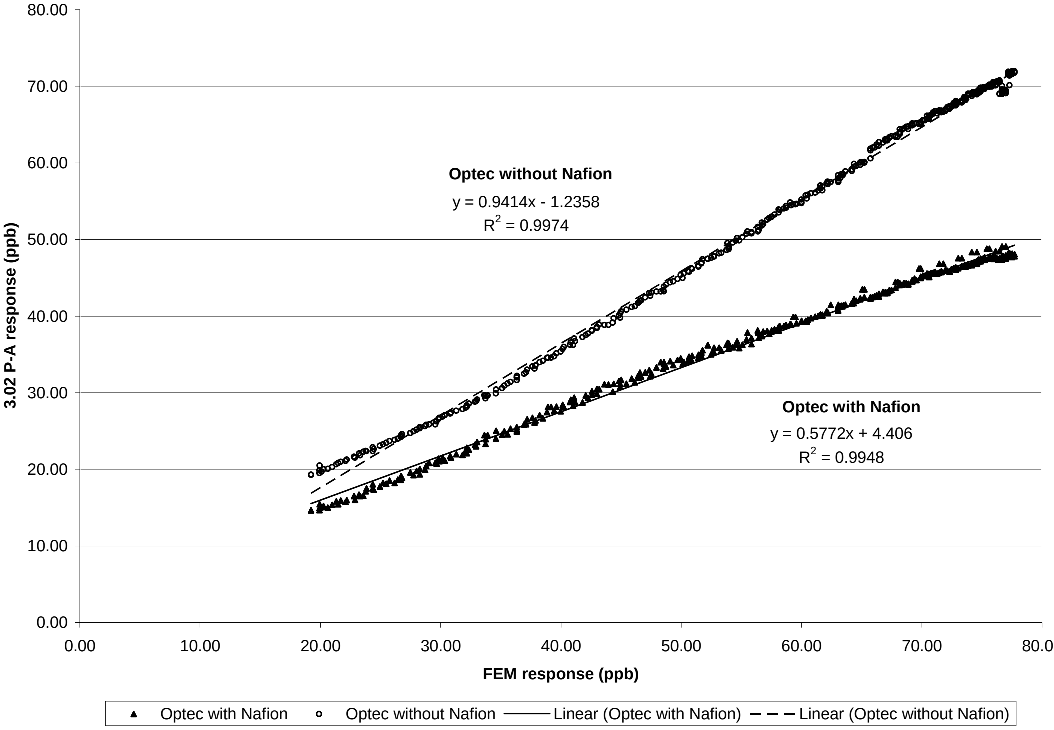

Figure 6-10 Photochemical Ozone Comparison with Low Precursor Concentrations.

Figure 6-11 shows the response of the two 3.02 P-A units and the FEM during the ambient monitoring period of about four and one-half days. The hourly averages are shown. Close correspondence is seen of the temporal pattern of readings from the three monitors. In addition, the readings from the 3.02 P-A operated normally closely match those of the FEM in most of the period, at ozone levels from less than 10 to nearly 80 ppbv. The readings from the 3.02 P-A with the added Nafion tube do not track those of the FEM as closely.

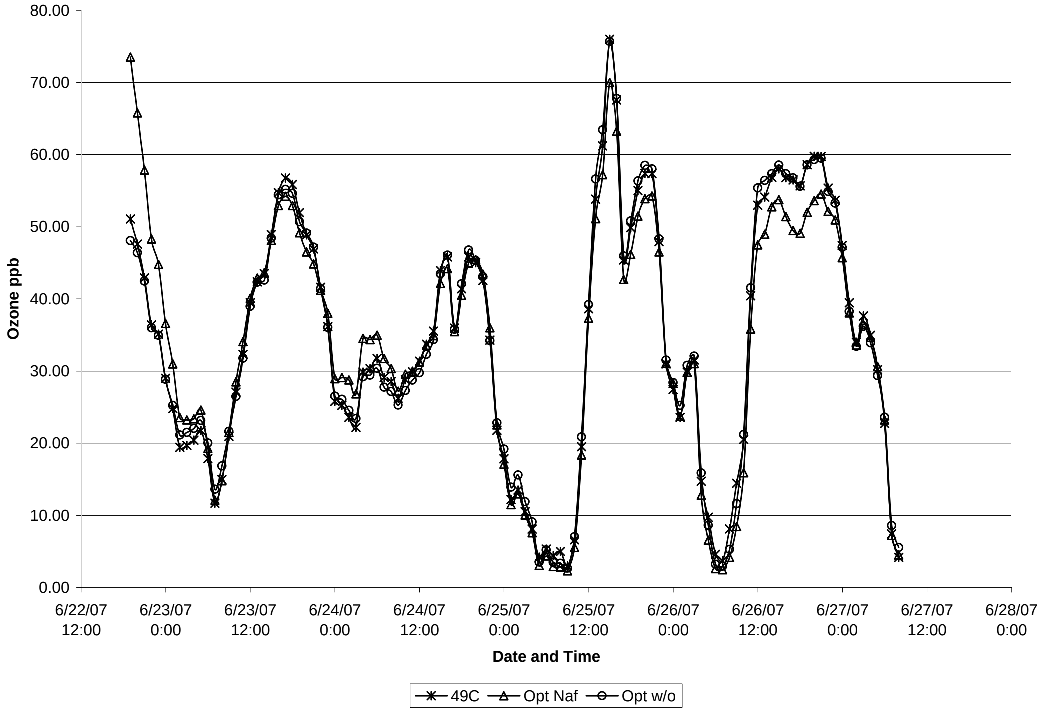

Figure 6-11. 3.02 P-A and FEM Ambient Monitoring Results.

The results of the linear regression of ambient monitoring data are shown in Figure 6-12, where the response of each 3.02 P-A unit is compared to the response of the FEM. Shown in the figure are the slope, intercept, and r^2 of the linear regression for each 3.02 P-A unit.

Figure 6-12 shows that the regression of data from the 3.02 P-A operated normally against the FEM data gives a slope of 0.998, an intercept of 0.19 ppbv, and an r^2 value of 0.9954. These results indicate an extremely close correspondence of the 3.02 P-A data to the FEM data in the ambient monitoring period. The data from the 3.02 P-A operated with the added Nafion tube do not agree as well with the FEM data, exhibiting a slope of 0.949, an intercept of 1.6 ppbv, and an r^2 of 0.93. Several data points diverge markedly from the regression line for this unit.

In ambient monitoring the RPD of the 3.02 P-A (operated without the Nafion tube) was 0.3%, -0.4%, and -10.7% relative to the FEM at the mean, maximum, and minimum ozone concentrations, respectively.

The agreement of the Optec 3.02 P-A with the FEM was closer in the ambient monitoring than in either photochemical chamber test; this difference was particularly pronounced for the unit operating with the added Nafion tube. Although detailed air quality measurements were not made in the ambient monitoring period, it is likely that the ambient levels of co-pollutants were lower in ambient air than in either of the photochemical chamber tests. Thus the ambient results continue the trend of better agreement between the FEM and 3.02 P-A with lower concentrations of ozone precursors.

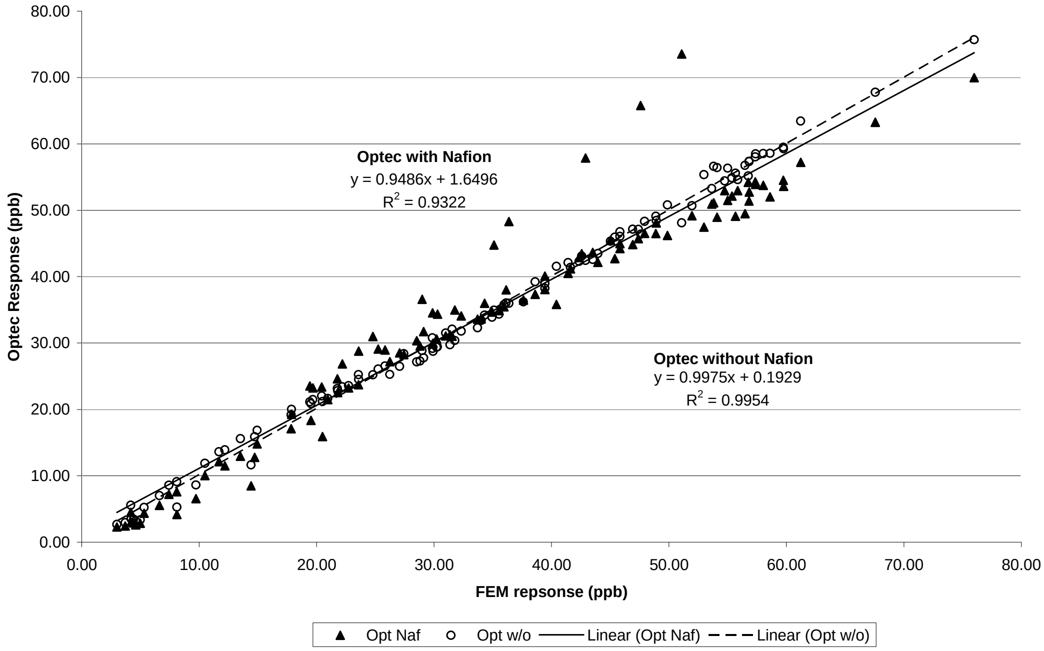

Figure 6-12. Linear Regression of 3.02 P-A and FEM Data During Ambient Monitoring.

6.5 Data Completeness

The total duration of the verification test was from June 12 to June 28, 2007, a period of 16 days, and the two Optec units each operated without problems for that entire period. Testing only occurred on 6 of those days. Each 3.02 P-A unit was operational for a total of 6.07 days or 100% of the testing time. Table 6-4 shows a breakdown of the operating activities of the 3.02 P-A units over those test days.

Table 6-4 shows that the 6.07 days of testing of the 3.02 P-A consisted of an approximate total of 0.27 days of calibration, zeroing, and other programmed QC procedures; 4.6 days conducting the ambient air monitoring; and a combined total of 1.2 days of chamber testing. Although the combined total of hours of testing was 6.07 days, the 3.02 P-A units were running continuously throughout June 12 to June 28.

Table 6-4. Optec 3.02 P-A Testing Activities June 12 to 28, 2007

Activity	Number of Measurement Intervals[a]	Days	Percent of Time
Ambient Air Monitoring	6,668	4.6	75.8%
Chamber Testing	1,687	1.2	19.7%
Calibration/Zeroing/Other Checks	393	0.27	4.5%
Totals	8,748	6.07	100%

a: Each measurement was a one-minute average.

6.6 Operational Factors

The Optec 3.02 P-A used only electrical power with no other consumables. The 3.02 P-A required 220 V power so a converter to 120 V was used for testing.

Once the 3.02 P-A was turned on, it took approximately 1 hour for the 3.02 P-A to warm up and stabilize. The 3.02 P-A has a nominal monitoring range up to 250 ppbv. When the analyzer detects ozone above 250 ppbv a repeated alarm is sounded indicating that the analyzer is over its programmed detection range. During testing, there were occasions when ozone greater than 250 ppbv was delivered to the 3.02 P-A, however the alarm would often not sound until the sampled ozone concentration reached a range of 270 to 300 ppbv.

The 3.02 P-A is programmed to internally calibrate and self adjust every 10 minutes. The outcome of the internal calibration was often apparent in the data, when the values would noticeably shift every 10 minutes. The ozone reading was displayed on the panel of the 3.02 P-A in parts per million by volume (ppmv). However, the electronic data output is programmed to report readings in micrograms per cubic meter ($\mu g/m^3$) at 21 degrees Celsius (^oC). The electronic data used for reporting were corrected to ppbv units after testing using the actual laboratory temperature and pressure.

No repair was needed during the test and the need for vendor assistance was minimal in the operation of the 3.02 P-A. The instrument manual was provided by the vendor, translated from the original Russian to English. Although the 3.02 P-A is easy to operate, the translation of the manual from Russian to English was difficult to understand in some areas. Overall the 3.02 P-A operated as expected and required no maintenance during testing. The estimated price of the base model analyzer is $5,000.

Chapter 7
Performance Summary

The performance of the Optec 3.02 P-A ozone analyzer was verified by a series of tests that included comparison to the EPA-established UV-absorption FEM for ozone. The particular FEM instrument used as the reference analyzer was a Thermo Environmental Model 49C (FEM EQOA-0880-047).

The Optec 3.02 P-A ozone analyzer averaged a %R of 85.4 to 107.7% over a concentration range of 98 to 289 ppbv when ozone was delivered to the analyzer in dry air from the Environics Model 6400. When ozone was added to clean air in the test chamber in stepwise concentrations of 51 to 257 ppbv at high humidity (≈ 80% RH), the average %R was 93.2 to 110% relative to the response of the FEM. In dry test conditions (< 5% RH) at concentrations of 69 to 260 ppbv, the average %R of the 3.02 P-A was 83.4 to 88.3% relative to the response of the FEM. Thus the %R of the 3.02 P-A during the high humidity ozone test was higher than its %R during the low humidity chamber test.

The linearity of the 3.02 P-A under humidified (≈80% RH) chamber test conditions showed a slope of 0.914, an intercept of 6.2 ppbv, and an r^2 value of 0.998 over a concentration range of 51 to 257 ppbv. The linearity of the 3.02 P-A in low humidity (<5% RH) chamber conditions showed a slope of 0.838, an intercept of 1.0 ppbv, and an r^2 value of 0.999 over a concentration range of 69 to 260 ppbv.

The interferents tested in the environmental chamber caused no response to the 3.02 P-A. The analyzer readings remained stable and under 1 ppbv when the organic and mercury vapor interferents were added to the chamber and also when the 17-component hydrocarbon mixture and NO_2 were added.

The comparison between the 3.02 P-A and FEM during the photochemical test with high precursor concentrations showed a slope of 0.815, an intercept of 4.1 ppbv, and an r^2 value of 0.999 over an ozone concentration range of 20 to 130 ppbv. The photochemical test with lower precursor concentrations showed a slope of 0.941, an intercept of -1.2 ppbv, and an r^2 value of 0.997 over an ozone concentration range of 20 to 80 ppbv. The ambient monitoring comparison of the 3.02 P-A and FEM readings over the four day sampling period showed a slope of 0.998, an intercept of 0.19 ppbv, and an r^2 value of 0.995 over an ozone concentration range of 3 to 80 ppbv. The RPD of the 3.02 P-A relative to the FEM was -14.2%, -8.0%, and 0.3% at the average ozone concentration in the photochemical/high precursors, photochemical/low precursors, and ambient air comparisons, respectively.

The performance of a 3.02 P-A unit operated with an added Nafion humidity equilibration tube was reduced in nearly all performance measures, relative to that reported above for the 3.02 P-A unit operated normally. The responses of the 3.02 P-A unit with the Nafion tube were reduced in chamber tests in comparison with the FEM, and that unit agreed less well with the FEM during ambient monitoring.

Data completeness for the 3.02 P-A was 100%, based on its operation over a total of 6.07 test days during a 16 day operational period. Considering only those 6.07 days on which the 3.02 P-A was tested, there were 4.6 days of ambient monitoring, 0.27 days spent in calibration/ zeroing/other instrument checks, and 1.2 days total spent conducting measurements in the environmental chamber. Both 3.02 P-A units also operated without problems throughout the 16-day period in which those 6 test days occurred.

The Optec 3.02 P-A was operated on a 220 V to 120 V converter during testing. When the 3.02 P-A was turned on, it took approximately 1 hour for the 3.02 P-A to stabilize and it then remained functional throughout the entire test period. A repeated alarm sounded only when the 3.02 P-A was reading ozone concentrations over range. The analyzer calibrated itself internally every ten minutes. The ozone measurements were displayed on the front panel in ppmv. No repair was needed during the test and the need for vendor assistance was minimal. Manuals were provided and although translated from Russian to English, the manuals were somewhat difficult to understand.

The estimated price of the base model Optec 3.02 P-A analyzer is $5,000.

Chapter 8
References

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2. List of Designated Reference and Equivalent Methods, U.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Issue Date: November 13, 2007, available at http://www.epa.gov/ttn/amtic/criteria.html.

3. Operation Manual for the Optec 3.02 P-A Chemiluminescent Ozone Analyzer, Optec Ltd., St. Petersburg, Russia, 2005.

4. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center*, Version 6.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, November 2005.