

US EPA ARCHIVE DOCUMENT

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION
PROGRAM



ETV Joint Verification Statement

TECHNOLOGY TYPE: CHEMILUMINESCENT OZONE ANALYZER

APPLICATION: MEASURING OZONE IN AMBIENT AIR

TECHNOLOGY NAME: 3.02 P-A

COMPANY: JSC OPTEC Ltd.

ADDRESS: 1985 West Henderson Road **PHONE:** (614) 477-1020
Columbus, Ohio 43220 **FAX:** (614) 486-2693

WEB SITE: www.optec-corp.com

E-MAIL: mkozliner@gmail.com

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

ETV works in partnership with recognized standards and testing organizations, with stakeholder groups (consisting of buyers, vendor organizations, and permittees), and with 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 Advanced Monitoring Systems (AMS) Center, one of five verification centers under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. The AMS Center evaluated the performance of a chemiluminescent ozone analyzer, a continuous monitor for determining ozone in air. This verification statement provides a summary of the test results for the JSC Optec Ltd. 3.02 P-A ozone analyzer.

VERIFICATION TEST DESCRIPTION

The objective of this verification test was to evaluate the 3.02 P-A performance for determining ozone in air in part by comparing it to the response of the ultraviolet (UV)-absorption Federal Equivalent Method (FEM) for ozone. The specific commercial FEM monitor used in this test was the Thermo Environmental Model 49 C (FEM EQOA-880-047). The verification test was conducted between June 13 and June 28, 2007 at Battelle laboratories located in Columbus, Ohio.

The response of the 3.02 P-A to ozone in ambient air and at low (< 5%) and high ($\approx 80\%$) relative humidity (RH) in clean air was used to evaluate for accuracy, linearity, interference effects, comparability to the FEM, data completeness, and operational factors. Two 3.02 P-A instruments were operated, one with no additional equipment and per the manufacturer's recommendations, and the other with a Nafion humidity equilibration tube added to the monitor's inlet. Results from the first unit are the primary results of this verification. The Nafion tube was added to the second unit to assess the impact of humidity and humidity control on the 3.02 P-A response. Both 3.02 P-A units relied entirely on their internal automated calibration systems, as specified by the vendor.

Accuracy was calculated from the response of the 3.02 P-A with respect to different levels of ozone challenges, established either by a known ozone source or by FEM response. Linearity was assessed by a linear regression analysis using the FEM reading as the independent variable and the response of the 3.02 P-A as the dependent variable. Interferences tested were naphthalene, o-nitrophenol, and p-tolualdehyde, each at approximately 6 to 15 parts per billion by volume (ppbv) in both dry and humidified air; mercury vapor at 630 nanograms per cubic meter (ng/m^3) in dry air and $54 \text{ ng}/\text{m}^3$ in humidified air; nitrogen dioxide (NO_2) at up to 200 ppbv in humidified air; and a 17-component mix of volatile organic compounds at up to 593 ppbv total concentration in humidified air. Interference effects were calculated in terms of the ratio of the 3.02 P-A response to the actual concentration of the interferent. Comparability was assessed by comparing the 3.02 P-A response to that of the FEM during generation of ozone in photochemical chamber tests at 80% RH, and in ambient ozone monitoring. 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.

QA oversight of verification testing was provided by Battelle and EPA. Battelle QA staff conducted a technical systems audit, a performance evaluation audit, and a data quality audit of 10% of the test data. EPA QA staff also conducted an on-site technical systems audit. This verification statement, the full report on which it is based, and the test/QA plan for this verification test are all available at www.epa.gov/etv/centers/center1.html.

TECHNOLOGY DESCRIPTION

The following description of the 3.02 P-A was provided by the vendor and does not represent verified information.

The 3.02 P-A chemiluminescent ozone analyzer combines a solid phase chemiluminescence approach with menu-driven software with diagnostic functions. It is designed to measure ozone concentrations in ambient air.

The Model 3.02 P-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
- Electronic 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 alternate 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 (UV lamp) 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.

VERIFICATION RESULTS

The addition of the Nafion humidity equilibration tube to the inlet of one unit of the 3.02 P-A reduced the performance of that unit in nearly all performance measures. The performance of the 3.02 P-A unit operated normally is summarized below.

Accuracy: The accuracy of the Optec 3.02 P-A ozone analyzer was assessed in terms of percent recovery (%R). The 3.02 P-A averaged a %R of 85.4 to 107.7% at concentrations of 98 to 289 parts ppbv when ozone was delivered to the analyzer in dry air directly from a calibration source. When ozone was added to clean air in the test chamber in stepwise concentrations of 51 to 257 ppbv at high humidity ($\approx 80\%$ RH), the average %R was 93.2 to 110%. In the corresponding chamber test at concentrations of 69 to 260 ppbv in dry test conditions ($< 5\%$ RH), the average %R of the 3.02 P-A was 83.4 to 88.3%.

Linearity: Linearity was evaluated in terms of slope, intercept, and coefficient of determination (r^2). The linearity of the 3.02 P-A under $\approx 80\%$ RH 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 $< 5\%$ RH 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.

Interference Effects: None of the interferents tested caused any response on the 3.02 P-A. As a result, all interferent response ratios were zero.

Comparability: Comparability was evaluated in terms of the slope, intercept, and r^2 of a linear regression of 3.02 P-A readings against FEM readings. The comparison between the 3.02 P-A and FEM during the photochemical ozone test with high precursor concentrations resulted in 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 same comparison in the photochemical test with lower precursor concentrations resulted in 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 comparison of the 3.02 P-A and FEM readings over the four day ambient monitoring

period resulted in 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 average relative percent difference of the 3.02 P-A with respect to the FEM in these three comparisons was -14.2%, -8.0%, and 0.3%, respectively.

Data Completeness: 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.

Operational Factors: 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 16-day test period. No repair was needed during the test and the need for vendor assistance was minimal. The analyzer calibrated itself internally every ten minutes. The ozone measurements were displayed on the front panel in parts per million. An operating manual was provided and although translated from Russian to English, the manual was somewhat difficult to understand. The monitor includes an audible alarm which sounds when ozone readings exceed the maximum full scale value (i.e., above about 250 ppbv).

Signed by Martin E. Toomajian 03/06/08
Martin E. Toomajian Date
Manager
Chemical, Environmental, and
Materials Operations
Battelle

Signed by Sally Gutierrez 04/15/08
Sally Gutierrez Date
Director
National Risk Management Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency

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