

Comment on Monitored Compliance with Ozone Standards CASAC Reconsideration of the 2008 Ozone National Ambient Air Quality Standards Teleconference February 18, 2011

Summary Comment

CASAC should reconsider and recommend changing the 1 ppb compliance requirement of the 2008 O₃ Standard to 1 pphm to match the current measurement precision of ozone monitors.

Introduction In the early 1980's the automated Ultraviolet (UV) Photometric method for measuring tropospheric ozone was hailed by the ambient monitoring community as a major innovation because it did not require the use of consumable reagents. However, even before the first UV-based monitor received "equivalency" status in June, 1977 comparison of its performance to the existing ethylene chemiluminescence (CL) "reference method" indicated a positive bias in the UV technique¹.

Researchers and ambient monitoring specialists have since cataloged a variety of interferences and anomalous behaviors associated with UV monitors. Interferences include particles², mercury³, and aromatic hydrocarbon derivatives^{4,5}. Anomalous behaviors include oscillation of monitor output tied to instrument shelter temperature swings⁶ and baseline shifts associated with calibration using dry air⁷. Interferences in the UV method are noteworthy because (1) they are frequently positive and (2) virtually all State and Local monitoring agency sites in the United States now employ UV monitors. The anomalous behavior of UV monitors is troubling due to the difficulty in detecting such behaviors within hourly averages.

Effects of Humidity on Monitor Bias

Evidence has accumulated that changes in the water content of sample or calibration air entering a UV monitor^{6,7} create short-term instability. These findings, in turn, led to methods identifying O₃ scrubbers in UV monitors that were prone to anomalous behavior⁸ and possible alternative scrubber configurations⁹. An alternate calibration scheme using humidified air was also proposed but not adopted by EPA.

More recent research⁷ has identified mechanisms responsible for moisture-based instability in UV monitors, especially those equipped with manganese dioxide (MnO₂) scrubbers. This research has provided mitigating solutions to Nafion moisture equilibration in UV O₃ that have achieved "equivalent" status¹⁰.

Given the historic problems associated with changing humidity and dry calibration, regulators should consider implementing this new technology.

Monitor Calibration/Drift/Noise/Sensitivity

The biases and errors inherent to current monitoring networks have been recognized by researchers¹¹.

Calibration of the U.S. ozone monitoring network involves transferring the authority of a limited number of “Standard Reference Photometers” through a chain of calibration devices operated by State and Local agencies to field-based monitors. At each stage of this transfer imprecision increases and is generally thought to accumulate to 2.25-5.0% of the value reported.

Equipment manufacturers recognize that component aging, temperature/line voltage variations and changes in air flow controllers accumulate as “span drift” which ranges from 0.5%/day to 0.5%/month. EPA also requires manufacturers to specify the sensitivity of their monitors, denoted as the “Lower Detection Limit” (LDL). For current monitors this level is ~ 1 ppb; however, the LDL is specified as being twice the “zero noise” and zero noise is measured in zero air the absence of ozone.

At the level of the reconsidered primary ozone standard (0.060-0.070ppm) the uncertainty due to calibration alone would be 1.4 - 1.6 ppb. Short-term drift adds 0.8 - 2.5 ppb and results in an uncertainty of 2.2 - 4.1 ppb due to these effects alone. This estimate agrees well with an examination of systematic bias in ozone measurements made by EPA¹². However, the calibration and precision-check performance results are performed with ozone in dry zero air and thus are far removed from compliance measurements occurring in wet, interference-laden ambient air. The resulting interferences and anomalous behaviors noted above could easily compound this imprecision. Current monitors cannot be assumed to reliably report concentrations to three decimal places as required by the 2008 O3 standards.

Conclusions

The vast majority of field studies which utilized collocated UV and CL monitors have shown bias in the UV method and most of those biases are positive. The MnO₂ ozone “scrubber” in UV O3 instruments has been identified as the source of bias and imprecision and monitor performance is heavily impacted by moisture content of the sample air. Calibrations at ambient moisture levels would be helpful however a “wet” calibration method has not been adopted. Regulators should consider implementing Nafion humidity equilibration to mitigate this problem and dry calibration issues. Regulators should also consider developing a procedure similar to the Method Detection Level employed in the Photochemical Assessment Monitoring Stations (PAMS) program for O3 instrument LDL determinations. Until O3 monitoring network precision improves, CASAC should recommend relaxing the current 1 ppb resolution requirement of compliance monitoring to 1 pphm (10 ppb).

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