July 22, 1999

Dr. Jeremy M. Hales
NARSTO Management Coordinator
60 Eagle Reach
Pasco, WA 99301

Dear Dr. Hales:

This letter is in response to an article in the Winter/Spring, 1999, issue of *NARSTO News* regarding urban ambient ozone measurements ("One Step Forward and...: Some Cautionary Notes on Urban Ozone Measurements"). The article contains several quotations from a critical review paper entitled, "Methods for Gas-Phase Measurements of Ozone, Ozone Precursors and Aerosol Precursors" by David D. Parrish and Fred C. Fehsenfeld, and expresses concerns about the integrity of ambient ozone measurements using the UV absorption monitoring method. The potential measurement errors cited were calibration uncertainties, ambient interferences, and anomalous operating conditions.

We are concerned that the article may have given an overly pessimistic impression of the integrity of the Nation's ambient ozone measurements obtained using the UV monitoring method. This method is, by far, the most commonly used method in the States' ozone compliance monitoring networks. However, we are confident, based on data quality assessment systems reports, that the vast majority of the ozone monitoring data collected nationwide are of high quality and suitable for attainment/non-attainment determinations. At the same time, we acknowledge that there are some measurement uncertainties and anomalies associated with the UV ozone method (as mentioned below), as there are with other methods for measuring air quality, and we continually strive to reduce these uncertainties. Further studies are being undertaken to better characterize the nature, frequency, and impact of any potential measurement uncertainties encountered with the UV method for ozone. It is currently thought that the magnitude of these uncertainties is low and their impact minimal. Nevertheless, any updated quality assurance guidance determined to be appropriate, based upon the results of these studies, will be provided to assist monitoring agencies minimize potential measurement errors.

Calibration Uncertainties

Parrish and Fehsenfeld note that the UV absorption measurement technique is "...a particularly efficient technique for ambient monitoring of O_3..." then cite its further advantage as an "absolute measurement" and indicate that it is "curious" that EPA procedures specify independent calibration for UV ozone monitors[1]. They suggest that independent calibration (i.e. conventional calibration using a primary ozone UV photometric standard or an independently certified ozone transfer standard) is

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[1] "This particular language from the *NARSTO News* quotation is absent or changed in the November 20, 1998 version of the document obtained recently from the NARSTO web site, but the implication is similar.

"inadequate" and "...can at worst perpetuate serious measurement problems since the ozone standard itself is merely a similar UV absorption measurement system coupled to an ozone generator."[1]

EPA formally recognized the value of the UV absorption measurement technique as an "absolute" measurement for ozone in 1979 when a calibration procedure based on the UV measurement technique was promulgated as part of the federal reference method for ozone monitoring (40 CFR Part 50, Appendix D) and became, in effect, a *primary standard* for ambient ozone measurement. However, EPA did *not* specify the UV technique as the measurement principle for ozone reference methods, for a very significant reason. That reason is that other common gases absorb UV light at the same wavelength band used to measure ozone and can interfere with the ozone measurement. When one or more of these other gases is present, as is quite possible in ambient air, the UV measurement is no longer "absolute." These interferences are minimized in ambient air measurements by a differential process that uses a gas scrubber to create a reference gas sample from which the ozone is removed but other potentially interfering gasses remain. But the performance of this scrubber can be less than perfect. Also, UV ozone analyzers in every-day use are subject to other operational problems, including buildup of dirt in inlet lines, inlet filters, the solenoid valve, and the optic components[2], and scrubber deterioration or malfunction. Thus there is a substantial difference between using the UV absorption technique for calibration and using it for routine ambient air monitoring. The UV technique clearly makes a good calibration standard, when interfering gases can be avoided, no scrubber is used, and instrument components are not exposed to atmospheric contaminants. But using UV analyzers for routine monitoring without independent calibration is considerably more problematic.

Parrish and Fehsenfeld go on to suggest that (in lieu of conventional, independent calibration) the span adjustment of a UV analyzer should be maintained at its standard setting (*i.e.* the theoretical value based on the absorption coefficient of ozone), and the instrument's measurements should be frequently compared with another ozone analyzer that is in good repair, using ambient air. We believe that independent calibration of the UV analyzers is better for several reasons. First, independent calibration can compensate, at least to some extent, for some of the problems mentioned in the previous paragraph, such as some possible diminution of ozone in inlet lines and particulate filters as they become dirty in normal use and for when these components are, from time to time, cleaned or replaced. Second, the "reference" instrument that would be used for comparison with the primary monitoring instrument would likely be another UV type instrument, since chemiluminescence type instruments are now all but unavailable. Thus the "reference" instrument would likely be subject to the same interferences as the primary instrument and possibly some of the other problems as well, unless it was frequently cleaned and scrupulously maintained. Therefore, it may not be as reliable or credible as a "reference" measurement as we would like. Third, the comparison of the two instruments would likely often occur over a rather limited range of fairly low ozone concentrations. Such comparisons may be affected by otherwise minor zero offset errors and, while useful for assessment of precision, in general provide a rather limited quantitative assessment of analyzer accuracy, particularly for the higher ozone concentrations which are critical in attainment/non-attainment determinations. Longer-term collocated instrument comparisons to gain a wider range of ambient concentrations would profoundly raise costs to monitoring agencies and would gain only a modest advantage in assessing data quality. Of course, collocation of ozone analyzers is often useful for purposes other than calibration verification.

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[2] Dirt on cell interior surfaces and optical windows and mirrors should be compensated by the differential measurement process, but field reports indicate significant effects under some circumstances that may be reduced by cleaning.

Independent calibration of ozone analyzers with certified ozone standards is certainly not infallible. But we believe conventional, independent calibration of UV ozone analyzers is advantageous for a variety of reasons. For example, independent calibration...

- Is a conventional, familiar concept that is widely used for most measuring instruments,
- Is consistent with calibration of other ambient gaseous pollutant analyzers, using certified concentration standards,
- Is uniformly applicable to any type of ozone analyzer, not just the UV-absorption type,
- Allows all measurements to be *independently* related to common, NIST-traceable ozone standards,
- Avoids uncertainties from UV-method ambient air interferences and routine operational degradation,
- Provides an accurate and precise calibration over the full measurement scale range, and
- Provides credible and readily quantitative assessment (audit) of analyzer accuracy.

EPA provides a network of NIST-traceable ozone standard reference photometers by which ozone calibration standards can be verified or certified. We are convinced that conventional calibration of UV ozone analyzers with certified ozone standards leads to very accurately calibrated ozone monitoring instruments at reasonable cost, provides readily documented and highly credible quantitative audit assessments of ozone monitoring data quality, and, we believe, is substantially superior to the verification assessment technique alternatively proposed by Parrish and Fehsenfeld. We do agree with them that adjustment of the span setting of UV-type ozone instruments for calibration should be limited to small adjustments, as any large difference from the natural or theoretical setting should be taken as an indication of some problem in either the instrument or the calibration equipment. We have made that recommendation for decades, and it appears in many UV monitoring instrument manuals.

Interferences

As noted above, UV ozone analyzers depend upon a scrubber to provide a reference air sample from which ambient ozone is removed but other potential interfering gasses in the ambient air sample remain to minimize measurement interferences. This scheme is generally quite successful, but not perfect—particularly for gasses such as mercury and some aromatic hydrocarbon compounds that have large absorption coefficients relative to ozone (at 254 nm wavelength). Humidity does not appear to cause a direct interference but may affect susceptibility to other interferences. Unusually high concentrations of particulate matter can also cause interference, since PM may not pass through the scrubber undiminished.

These positive interferences have been known all along and are believed to be a generally insignificant problem at most ozone monitoring sites, particularly when the scrubber is replaced periodically according to the manufacturer recommendations. Parrish and Fehsenfeld state that "even though significant evidence of interferences in the UV absorption technique has been reported, such interferences are not always observed, even in urban plumes." They go on to cite a 1998 report by Ryerson et al. describing simultaneous measurements of ozone by UV and chemiluminescence instruments in an aircraft and indicate that "...excellent correlations were found between the measurements of the two instruments..." and "there was never any indication (<1%) that the UV instrument measured systematically higher in the urban plume."

Nevertheless, EPA has always cautioned against siting a UV-type ozone analyzer in an area where interferences could be problematic, such as in the vicinity of potentially high mercury concentrations, asphalt plants or large asphalt-paved surfaces, gasoline stations or transfer facilities, heavy automobile traffic, etc. Years ago, UV ozone monitoring sites could be checked for the presence of such interferences quite easily by collocating a chemiluminescence ozone analyzer with the UV analyzer for some period of time and comparing the measurements. Now, with chemiluminescence ozone analyzers becoming increasingly difficult to obtain, this means of checking for interferences—as well as an alternative to a UV-type analyzer to use at an interference-plagued site—may be no longer available. We thus share some concern with Parrish and Fehsenfeld on this issue, but we believe that careful siting of UV ozone analyzers will minimize this problem.

Anomalous Operating Conditions

As noted above, the accuracy of UV ozone measurements critically depends on the performance of the chemical scrubber, which must remove all ozone from a representative air sample without altering the concentration of any potentially interfering substances. Accumulating evidence from several state monitoring agencies indicates occasional measurement anomalies in UV analyzers, with a return to apparently normal measurement performance at other times. These anomalies may result in either positive or negative error and are generally associated with periods of high ambient temperatures, high humidity, and possibly other associated atmospheric conditions. Unfortunately, these conditions are also typical during periods when ozone concentrations peak and measurement accuracy is crucial. Further, these anomalies are often not detected by conventional ozone span checks or audits.

We are also concerned about this potential problem, but so far it has proved elusive and difficult to (1) reproduce in the laboratory, (2) determine the specific conditions under which it occurs or may occur, (3) predict the monitoring sites where it may occur, (4) define its specific manifestations, and (5) establish differences in susceptibility, if any, among different models of UV analyzers. Laboratory studies of this phenomenon have been inconclusive, and field studies are very expensive and difficult to carry out when resources are limited. Recent work by Joel Maddy of West Virginia appears to confirm our suspicions that the effect may be related to temporary partial failure of the scrubber, but that it also involves temporary effects in the optical cells, mirrors, and other internal surfaces. He has developed a test which appears to be able to identify UV analyzers that are most susceptible to anomalous measurements. His work further suggests that use of a heated silver wool scrubber (as opposed to other types), along with use of Teflon-coated stainless steel (rather then glass or quartz) absorption cells, will greatly reduce a UV analyzer's susceptibility to this effect. However, he acknowledges that these suggestions are based on empirical observations and not on an understanding of the mechanism that gives rise to the anomalies.

We are currently addressing this problem on three fronts. First, we are attempting to assess the extent and severity of these measurement anomalies by surveying monitoring agencies and monitoring agency associations. Second, we are collaborating with the American Petroleum Institute and state and local agencies by providing contract funding to conduct studies to better document the performance differences among various configurations of UV ozone analyzers. And third, we will evaluate Mr. Maddy's test for analyzer susceptibility and the use of the heated silver wool scrubbers in minimizing the impact of anomalous analyzer performance and, if warranted, implement or promote their use among monitoring agencies. We intend to provide any updated quality assurance guidance resulting from these activities to help monitoring agencies minimize any potential measurement errors from them.

Conclusion

We hope that this additional information might provide some further perspective. We remain confident that the vast majority of ozone monitoring data collected nationwide is of high quality. And we agree with the need Parrish and Fehsenfeld identified for additional field intercomparisons of the UV technique with other ozone measurement techniques, particularly during conditions typical of ozone exceedences, to better define the scope and impact of any potential UV ozone measurement uncertainties. We hope to be able to pursue such studies, but current resources for this activity appear to be insufficient. We will continue to pursue other means of investigating these potential uncertainties.

Sincerely,

Frank F. McElroy

Frank F. McElroy (MD-46)

David Gemmill

David B. Gemmill (MD-46)
Atmospheric Methods & Monitoring Branch
Human Exposure & Atmospheric Sciences Division

cc: Ms. Susan S. G. Wierman
Executive Director, MARAMA
711 West 40th Street, Suite 318
Baltimore, MD 21211-2109

Dr. Richard D. Scheffe, Group Leader, (MD-14)
Monitoring and Quality Assurance Group
Office of Air Quality Planning & Standards