OFFICE OF AIR QUALITY PLANNING AND STANDARDS
RESEARCH TRIANGLE PARK, NC 27711

November 12, 2024

MEMORANDUM

SUBJECT: Ozone Absorption Cross-Section Implementation in the U.S. Ambient Air Monitoring Network

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TO: EPA Regional Office Ambient Air Monitoring Contacts

Background

In 1961, the ozone ultraviolet (UV) absorption cross-section was measured to be 1.1476 x10^{-17} cm^2 $molecule^{-1}$ or 308.3 $atmosphere\ (atm)^{-1}$ $centimeter\ (cm)^{-1}$ with a reported relative standard uncertainty of 1.4% (Hearn, 1961).[1] In the 1980s, the National Institute of Standards and Technology (NIST), in collaboration with the Environmental Protection Agency (EPA), developed the Standard Reference Photometer (SRP), which is the international standard for the measurement of ozone. The SRP is based on UV photometry and uses this cross-section value as the reference value for UV ozone measurements. Efforts to improve the accuracy of the ozone absorption cross-section have continued over several years and rigorous assessment of the bias and uncertainty in the value became a high priority.

The Consultive Committee for Metrology in Chemistry and Biology – Gas Analysis Working Group (CCQM-GAWG) of the Bureau of Weights and Measures in France (BIPM) convened a task group in 2016 to review all published measurements of the ozone cross-section since 1950. This task group was also charged with recommending a consensus-based cross-section value and associated uncertainty for adoption in measurements of ozone concentrations by standard UV photometric instruments, including the SRP (Hodges et al., 2019).[2]

After publication in Hodges et al., 2019, the CCQM-GAWG[3] convened an international group of stakeholders in October 2020 to discuss adopting and implementing a globally coordinated change in the cross-section value for surface ozone monitoring. This group, representing several international and national metrology institutes, NIST, and environmental agencies (including EPA), agreed to adopt and implement the new cross-section value as it represents a more accurate value with less uncertainty and is an advancement and improvement in the UV photometer measurement method.

After the October 2020 meeting, the CCQM-GAWG assembled a Task Group to work on various aspects of implementing the new cross-section for surface ozone measurements. As part of this Task Group's efforts, a general guideline document[4] on implementation was developed. To ensure consistency in reported values, an additional document (Rapport BIPM – 2022/02)[5] was prepared on the recommended numerical values and uncertainties of the ozone absorption cross section, with appropriate significant digits and rounding, expressed in the different units commonly found in standards was developed.

Rule Changes to 40 CFR Part 50, Appendix D

The "Reference Measurement Principle and Calibration Procedure for the Measurement of Ozone in the Atmosphere," 40 CFR Part 50, Appendix D, provides EPA's requirements for the UV-based ozone calibration procedure for SRPs. On October 12, 2023, the EPA published a final rule revising the absorption cross-section value (88FR 70595).[6] This final action updated the previous Hearn 1961 (Hearn.1961) absorption cross-section value (308 atm^{-1} cm^{-1}) to align with the BIPM CCQM-GAWG's international cross-section value of 304.39 atm^{-1} cm^{-1}, or CCQM.O3.2019. The updated value also reduces the uncertainty to 0.31% from 1.4%. The final rule was effective November 13, 2023.

U.S. Implementation Process

Beyond the international guideline developed by the BIPM CCQM-GAWG noted above, this memo provides the process needed to implement the cross-section across the U.S. traceability scheme. The procedures in this memo are only for implementation of the CCQM.O3.2019 cross-section and not a replacement for the normal procedures to be followed in the "Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone" Technical Assistance Document (TAD)[7], January 2023 (herein referred to as the TAD). The TAD is required to be implemented by November 2025, but earlier implementation is highly encouraged.

To establish and maintain traceability, the readings of an ozone analyzer are compared to an SRP through a hierarchy of standards. As the highest level of traceability, all SRPs are referred to as Level 1 standards. Figure 1 presents the U.S. traceability scheme. Traceability of NIST's Level 1 SRPs and EPA's Level 1 SRPs is achieved by demonstrating traceability to BIPM SRP #27 through the BIPM.QM-K1 ongoing comparison.[8] The BIPM.QM-K1 is the international comparison for ozone reference standards.

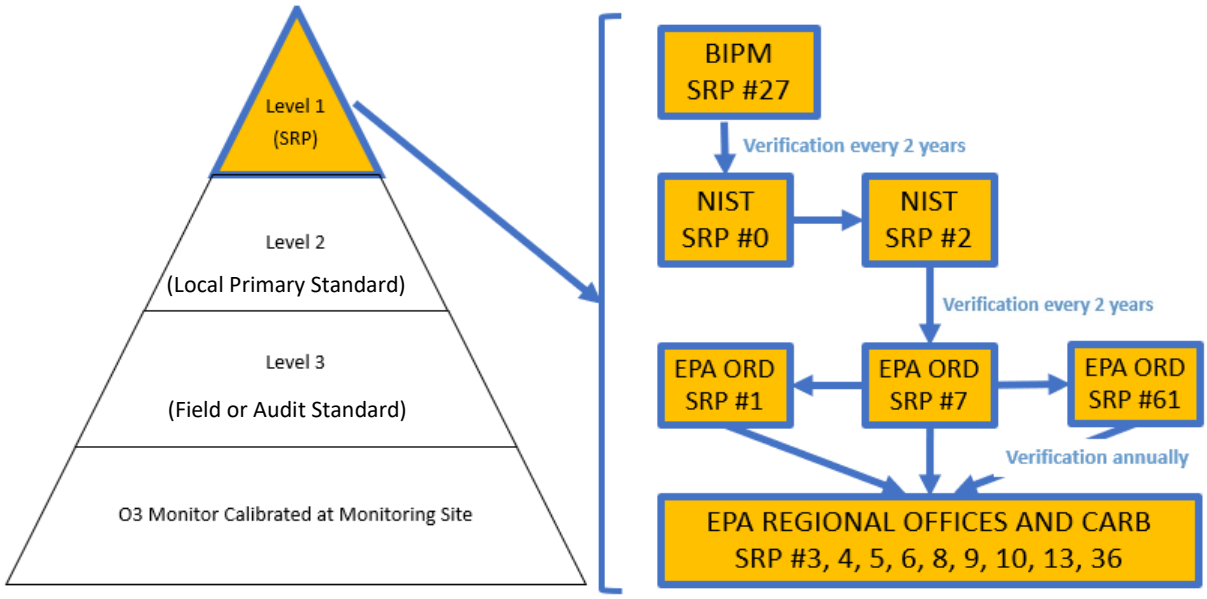

Figure 1. U.S. and International Standard Traceability Scheme

In summary, the overall U.S. implementation process for the CCQM.O3.2019 value consists of five key steps that are explained in detail in the following sections of this memo:

1) Update SRP software to a version that allows the SRP operator to begin using the CCQM.O3.2019 value by January 1, 2025.
2) The CCQM.O3.2019 value will be used in SRP Level 1 verifications starting late 2024 and will continue throughout 2025.
3) Level 2 transfer standards will be checked against the Hearn.1961 value, then adjusted to and verified against the CCQM.O3.2019 value by the end of 2025. Level 3 transfer standards will be adjusted to the CCQM.O3.2019 value, to be complete by the end of 2026.
4) Ozone monitors are expected to be calibrated to transfer standards using the CCQM.O3.2019 value by the end of 2026.
5) Starting January 1, 2025, monitoring agencies should begin flagging hourly ozone data with “XS” AQS qualifier if traceable to the Hearn.1961 value.

<u>SRP Software Update for the CCQM.O3.2019 Cross-Section</u>

EPA has 12 SRPs that support the U.S. monitoring network. Each EPA Regional office and the CARB SRP is verified or reverified annually back to an EPA ORD (or NIST) SRP (Figure 2).

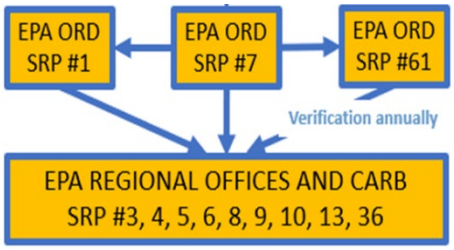

Figure 2. U.S. EPA Level 1 Standard Traceability Scheme

The first step in implementing the cross-section is to update all EPA SRP computers with new software (version 2021_04A or later) to incorporate both the CCQM.O3.2019 value of 304.39 atm^{-1} cm^{-1} and the Hearn.1961 value as selectable dropdown options for use. The current cross-section value in the SRP software is 308.32 atm^{-1} cm^{-1} which, when compared to the new value of 304.39 atm^{-1} cm^{-1}, is a 1.29% decrease. This decrease results in an increase in the calculated SRP ozone concentrations of 1.29%. However, there are several factors that make it unlikely that this change will have a measurable, predictable influence on ozone data measured at the monitor level. Early installation of the new software is critical to prepare for use on January 1, 2025. All SRPs must have the updated software installed and operational no later than December 31, 2024, and documentation of the software update must be submitted to EPA, OAQPS.

The absorption cross-section value stated in 40 CFR Part 50 Appendix D (304.39 ± 0.94 atm^{-1} cm^{-1}) will begin use in all U.S. SRPs on January 1, 2025. There will be an additional year to complete implementation across all Level 2 transfer standards (bench and field) by January 1, 2026. In the preamble to the final rule published in the Federal Register on October 12, 2023, EPA erroneously stated that the updated absorption cross-section value "will be implemented January 1, 2025, with an additional year for state, local, and tribal monitoring agencies to complete implementation, to January 1, 2026." 88 FR 70595, 70597. That is incorrect. Instead, as stated here, implementation across all Level 2 bench and field transfer standards will be completed by January 1, 2026. It is expected that all SLT transfer standards and ozone monitors in the field will be updated throughout the year until December 31, 2026. EPA is preparing to publish a correction notice making this change to the preamble language plus a corresponding clarification of the regulatory language at part 50, Appendix D, 2.2. 88 FR at 70598. Refer to the timeline in Appendix A.

SRP Level 1 Verification/Reverification Procedure

Verification is the initial process used to relate a candidate transfer standard output to a standard of higher authority. Reverification is verification of a transfer standard that occurs after a verification when all acceptance testing passes the prescribed frequency and criteria. Reverifications include fewer complete cycles of ozone concentrations and are quicker to conduct.

The EPA ORD SRP is verified against a NIST SRP every two years. Each of the 9 Regional office/CARB SRPs are verified or reverified against an SRP annually. Starting in late 2024, each SRP will be reverified/verified using the CCQM.O3.2019 cross-section value. SRP operators do not need to wait for a verification providing results for the CCQM.O3.2019 value before beginning to conduct Level 2 reverifications using CCQM.O3.2019. This is because the cross-section update does not change anything physical or mechanical within the SRP; it is only a multiplier, or constant, within the software. Therefore, this type of change does not require a reverification before implementation.

Transfer Standard Verification/Reverification and Adjustment Procedure

See the TAD for EPA's transfer standard traceability scheme, terminology, verification or reverification requirements, normal testing procedures, and qualification and acceptance testing requirements. SRPs will use the CCQM.O3.2019 value for verification of Level 2 transfer standards starting January 1, 2025. The transfer standards will first be checked against the SRP using the Hearn.1961 value to allow for bracketing the data. No adjustments or maintenance activities that could affect the operation of or

measurement by the transfer standard will be made prior to this check. After the check against the Hearn.1961, the transfer standard must be calibrated by adjusting the internal calibration factors (slope and intercept) and verified against the CCQM.O3.2019 value. Even if the transfer standard is within the acceptance criteria as compared to CCQM.O3.2019, the slope and intercept will be adjusted. All Level 2 transfer standards should be calibrated and adjusted to the CCQM.O3.2019 value by January 1, 2026.

New Level 2 transfer standards will be initially qualified/acceptance tested by monitoring agencies as described in the TAD. They are then subsequently verified against an SRP with the CCQM.O3.2019 value.

It is expected that Level 3 transfer standards (or any transfer standard that is verified against a Level 2 transfer standard) will be verified against the CCQM.O3.2019 value, by December 31, 2026. No final Hearn.1961 check is needed for Level 3 transfer standards due to the many other checks and balances in the O_3 traceability chain (precision checks, zero and span checks, annual performance evaluations and the national performance audit program) that should address potential transfer standard issues.

Ozone Monitor Calibration (Adjustment)

Once a transfer standard has been verified against the CCQM.O3.2019 value, and its internal calibration adjusted, it can then be used to calibrate (adjust) ozone monitors. All ozone FRMs/FEMs will be calibrated and adjusted in the same manner. It is expected that all ozone monitors should be adjusted to the CCQM.O3.2019 value by December 31, 2026. While this provides a two-year period in which the monitor adjustment may occur, agencies are encouraged to being using the CCQM.O3.2019 value as soon as possible.

Refer to Section 12.3 of the QA Handbook Volume II [6] for the ozone calibration procedure. To implement the CCQM.O3.2019 value at the monitor, a calibration (adjustment) will be done. Even if the monitor is within the calibration acceptance criteria as compared to the CCQM.O3.2019 transfer standard, the slope and intercept will be adjusted.

Before calibrating the monitor, confirm that it has passed the required one-point QC, zero drift, and span check criteria, as specified in the critical criteria section of the ozone validation template in Appendix D[7] of the QA Handbook Volume II, and no major maintenance or repair is required.

Newly purchased ozone monitors should continue to be initially set up and acceptance tested as outlined in the QA Handbook Volume II Section 11.1.1. In addition, they should be calibrated and verified according to Sections 12.2 and 12.3 of the QA Handbook Volume II to ensure the new analyzer is traceable to CCQM.O3.2019.

Tracking Implementation (Data Flagging)

The CCQM-GAWG Task Group's general guideline document on implementation includes a recommendation that ozone monitoring data include a flag indicating which absorption cross-section was used for the measurement. To address this recommendation, starting January 1, 2025, hourly data reported to AQS by monitors that have not yet been calibrated against the CCQM.O3.2019 value will be flagged with the newly created AQS information flag, "XS: Traceable to a Standard Reference Photometer (SRP) with the Hearn 308.32 atm^{-1} cm^{-1} Ozone Cross-Section Value." Monitoring agencies

will flag the hourly ozone values in AQS until the ozone data are collected with a monitor that is traceable to the new CCQM.O3.2019 value. At that time, flagging will stop, and subsequent data will be presumed to be generated with the new value. EPA Regional Office staff will review the monitoring agency flag use during regular data reviews, data certification, and audits.

For questions about this memo, please contact Melinda Beaver (beaver.melinda@epa.gov). For questions about the SRP Program, please contact Trisha Curran (curran.trisha@epa.gov).

References

[1] Hearn A. G. (1961). Absorption of ozone in ultra-violet and visible regions of spectrum, Proc. Phys. Soc. 78 932, DOI: 10.1088/0370-1328/78/5/340.

[2] Hodges, J.T., Viallon, J., Brewer, P.J., Drouin, B.J., Gorshelev, V., Janssen, C., Lee, S., Possolo, A., Smith, M.A.H., Walden, and Wielgosz, R.I. (2019). Recommendation of a consensus value of the ozone absorption cross-section at 253.65 nm based on a literature review, Metrologia, 56, 034001. https://doi.org/10.1088/1681-7575/ab0bdd.

[3] https://www.bipm.org/en/committees/cc/ccqm/wg/ccqm-gawg-ozone-tg

[4] Guidelines How to Implement the New Absorption Cross-Section for Ozone Concentration Measurements. Members of the CCQM-GAWG Task Group on Ozone Absorption Cross-Section change management: P.J. Brewer, A. Brown, E. Flores, S. Lee, B. Niederhauser, J. Norris, J. Rice, L. Sorensen, H. Tanimoto, J. Viallon, R.I. Wielgosz, C. Zellweger.

[5] Units and values for the ozone absorption cross section at 253.65 nm (air) with appropriate significant digits and rounding for use in documentary standards Authors: R. S. Davis, B. Niederhauser, J.T. Hodges, J. Viallon and R. I. Wielgosz, January 16, 2023.

[6] Federal Register / Vol. 88, No. 196 / Thursday, October 12, 2023 /Reference Measurement Principle and Calibration Procedure for the Measurement of Ozone in the Atmosphere (Chemiluminescence Method), Final Rule.

[7] Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone, January 2023, EPA-454/B-22-003.

[8] BIPM.QM.K-1 international comparison, https://www.bipm.org/en/gas-metrology/ozone/bipm.qm-k1.

Appendix A

CCQM.2019 Cross-section Implementation in U.S. Timeline