



Updating the Absorption Cross- Section for Surface Ozone Measurements

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Absorption Cross-Section Topics

- What is the ultraviolet (UV) ozone absorption cross-section?
- How did the update to the cross-section come about?
- Why update the value?
- Managing and implementing the update and the International Task Group
- Regulations and standards currently being updated
- Proposed changes to Reference Measurement Principle and Calibration Procedure in Code of Federal Regulations (CFR) 40 Part 50 Appendix D
- Affects on the monitoring data

What is the Absorption Cross-Section for Surface Ozone Measurements?

- The absorption cross-section (absorption coefficient, α) is a parameter used to determine atmospheric ozone concentrations based on the amount of light absorbed at an ultraviolet (UV) wavelength of 253.65 nm

Concentration (C) determination requires:

- ✓ the absorption coefficient (α) of O₃ at 253.65 nm
- ✓ the optical path length (L) through the sample
- ✓ the transmittance (I_o/I) of the sample at a nominal wavelength of 253.65 nm, and
- ✓ the sample temperature (T) and pressure (P)

How Did this Update Come About?

- The cross-section is used in UV ozone analyzers and Standard Reference Photometers (SRPs)
- The current cross-section value was measured by Hearn in 1961 and incorporated into the SRP when developed in the 1980s
- Results of several studies have called into question the cross-section value measured by Hearn
- A review of all measurements of the absorption cross section was carried out by an international group and a consensus value published in J.T. Hodges et. al., 2019
 - The consensus value is $1.1329 \pm 0.0035 \times 10^{-17} \text{ cm}^2$ and is 1.23% lower with an uncertainty six times smaller than the current value
 - The lower value may increase monitoring data by 1.23%

Hodges et al., 2019

<https://doi.org/10.1088/1681-7575/ab0bdd>

Why Update the Absorption Cross-Section Value?

- The new value is an advancement in science and measurement technology that represents a more accurate and precise value than the current value
- UV photometer measurements with the current value were shown to be 2-3% lower than Gas Phase Titration (GPT)¹ and the updated value brings them closer together
- The updated value improves the accuracy of UV ozone analyzers and the SRPs

¹ Viallon et al., 2006, "Ozone Cross-Section Measurement by Gas Phase Titration", Anal. Chem. 2016, 88, 10720–10727. DOI: [10.1021/acs.analchem.6b03299](https://doi.org/10.1021/acs.analchem.6b03299)

Managing and Implementing the Update

- Following a consensus recommendation of participants in an International Bureau of Weight and Measures (BIPM) workshop on “Accurate Monitoring of Surface Ozone”, October 2020, an [Intention to Change](#) document was published by BIPM on 12/4/2021
- **The target date for implementing the update is January 1, 2024**
- A task group has been organized to coordinate the universal implementation of the cross-section value for surface ozone measurements worldwide and consists of six international teams established to manage and track the change

The BIPM has established an International Task Group to manage the Cross-Section update

- 1 Publishing a timeline** for transitioning to the updated ozone cross section value
- 2 Identify regulations and standards** worldwide that require updating
- 3 Develop a communication plan** and website where information on the process can be disseminated
- 3 Establish and maintain a database of interested stakeholders** to provide updates on progress
- 4 Preparing publications** and contributing to peer-reviewed publications on the importance and challenges of
- 5 Develop guidance for users and manufacturers of instruments** in the field on how to deal with the change in cross section value
- 5 Develop guidance** to ensure manufacturers instruments are making measurements with new value correctly
- 6 Inform communities focusing on trend analysis** of ozone concentrations of potential step function effects in historic data

www.bipm.org/en/committees/cc/ccqm/wg/ccqm-gawg-ozone-tg

Regulations and Standards Being Updated

- **EPA 40 Code of Federal Regulations (CFR) part 50, Appendix D**
- International Organizations for Standardization (ISO) 13964:1998 and ISO 10313:1993
- European Committee for Standardization (CEN) 14625:2012
- ASTM International D5110 – 98 (2017) and D5156 – 02 (2016)
- Japanese Industrial Standard Committee (JIS) B7957: 2006
- Australian Standard, AS 3580.6.1
- China National Environmental Monitoring Center SAC HJ 590:2010

Reference Measurement Principle and Calibration Procedure for the Measurement of Ozone in the Atmosphere, 40 CFR part 50 Appendix D

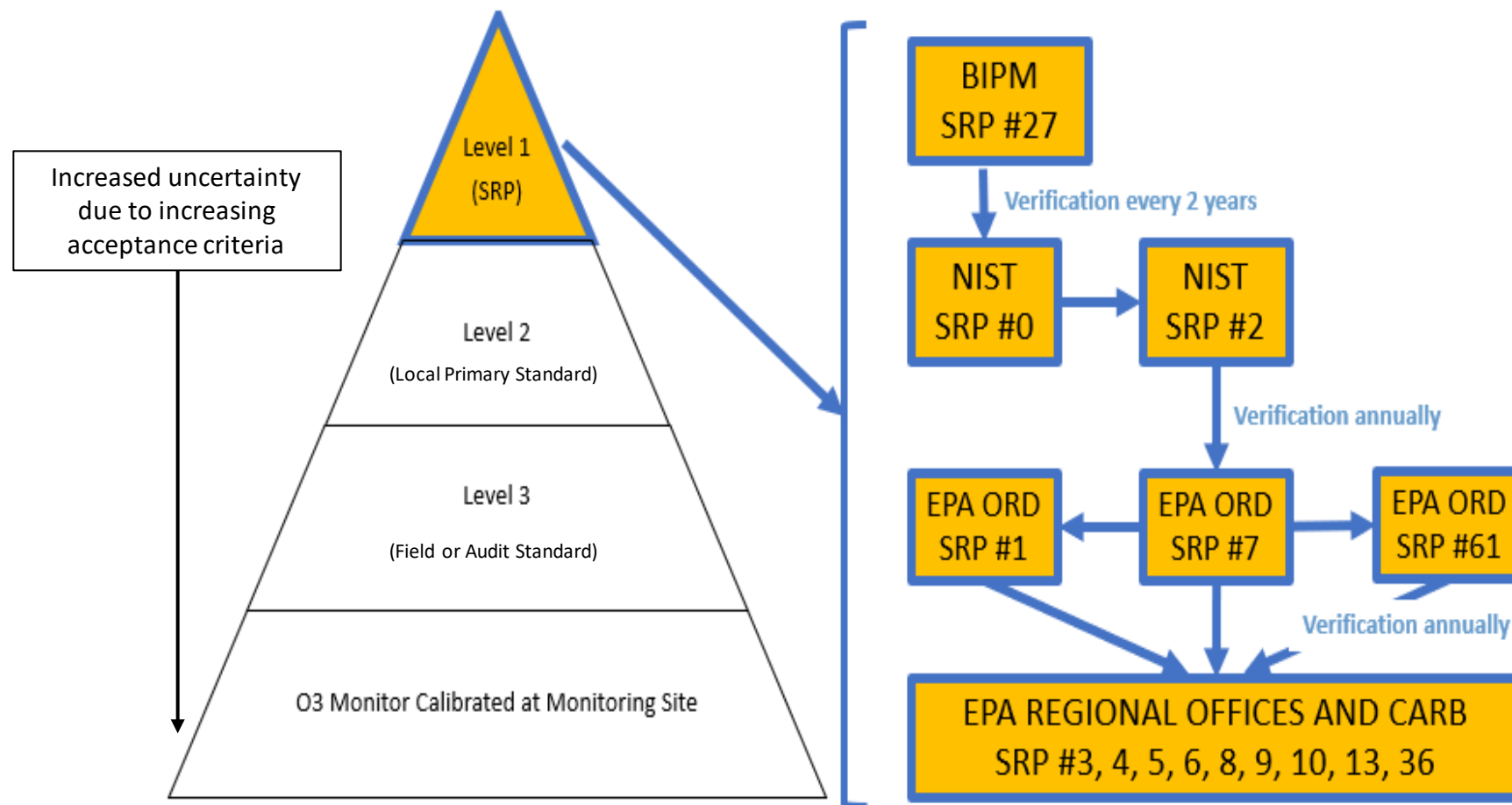
- Plan to have proposed rule out late 2022
- Changing cross section value (α) in two places
 - Sections 4.1 Principle and 4.5 Procedure
 - **Old** α = absorption coefficient of O₃ at 254 nm = **308 ± 4** atm⁻¹ cm⁻¹ at 0 C and 760 torr
 - **New** α = absorption coefficient of O₃ at 254 nm = **304.39** atm⁻¹ cm⁻¹ with an uncertainty of **0.94** atm⁻¹ cm⁻¹ at 0 C and 760 torr
- Minor changes to references
 - Adding Hodges et. al., 2019
 - Updating revision dates for the Ozone TAD and QA Handbook Volume II
- Goal: update to Appendix D by end of 2023

Standard Reference Photometers (SRPs)

The calibration reference for ground-level ozone measurements is based on UV photometry, SRPs acting as primary standards for national and international ozone-monitoring networks

There are more than 60 SRPs worldwide

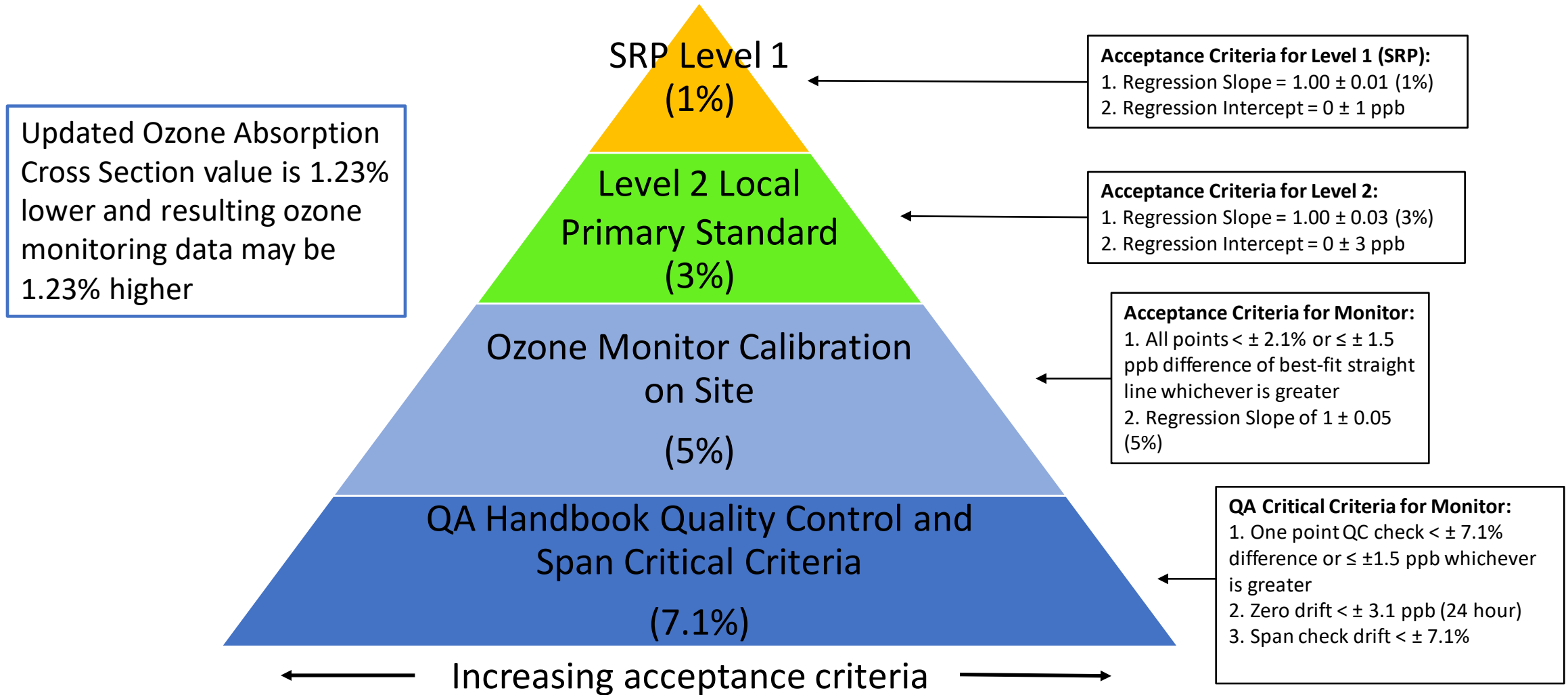
SRPs use the cross-section value as the reference for calculating ozone concentrations



Affects on the Monitoring Data It's Complicated!

- There are multiple factors that contribute to variability in monitoring data
 - Ozone analyzer measurement precision, which is ± 0.001 ppm or ± 1 ppb
 - Slope and intercept acceptance criteria for calibration and verification of SRPs
 - Slope and intercept acceptance criteria for bench/field standards used to calibrate ozone monitors in the field
 - Precision and bias criteria in EPA's [QA Handbook volume II](#)
 - Span checks, one point QC checks, zero drift
 - Data handling and design value computation procedures in 40 CFR part 50, [Appendix U](#), 3 levels of truncation
 - How calibrations and verifications are performed in the field and whether the analyzer response is adjusted

Traceability, Calibration, Verification, and QC



Cross-Section Value Summary

- A review of absorption cross-section measurements was carried out by an international group and a consensus value published in 2019
- The updated value is an advancement in science and measurement technology that represents the most accurate value of the ozone cross-section available
- A task group has been organized to coordinate the universal implementation of the updated value worldwide and track progress
- The target date for implementation is **January 1, 2024**
- The updated value is 1.23% lower and may increase monitoring data 1.23%
- The impact of the cross-section update on ozone monitoring data is complicated
- The absorption cross-section value in 40 CFR part 50 Appendix D will be updated through rulemaking and the proposed rule is planned to be out late 2022