Implementation of a New Absorption Cross-Section Value for Surface Ozone Measurements

National Ambient Air Monitoring Conference

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Outline

- What is the ultraviolet (UV) ozone absorption cross-section?
- How did the update to the cross-section come about?
- International Task Group activities
- Regulations and standards currently being updated
- Revised Reference Measurement Principle and Calibration Procedure in Code of Federal Regulations (CFR) 40 Part 50 Appendix D
- Implementation of the updated cross-section in the United States
- Potential impacts on the monitoring data

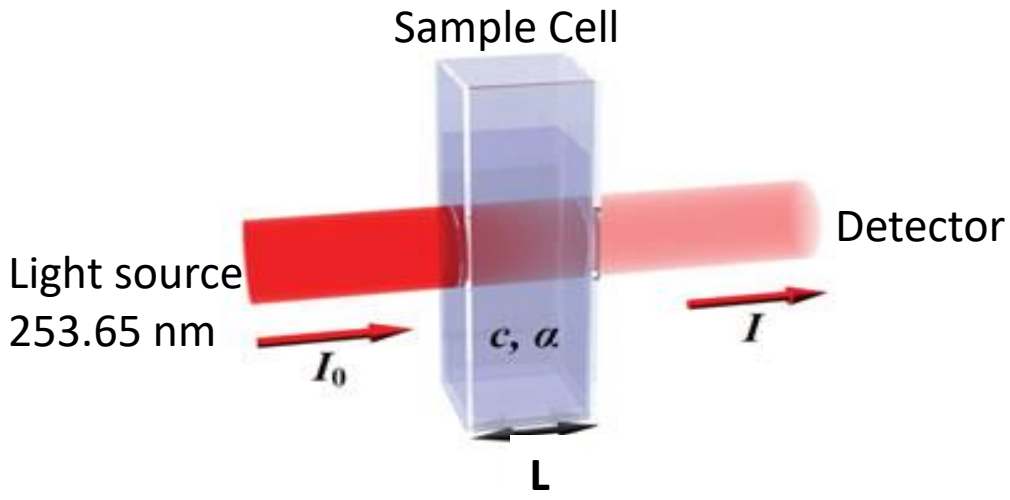
What is the Absorption Cross-Section for Surface Ozone Measurements?

- 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:

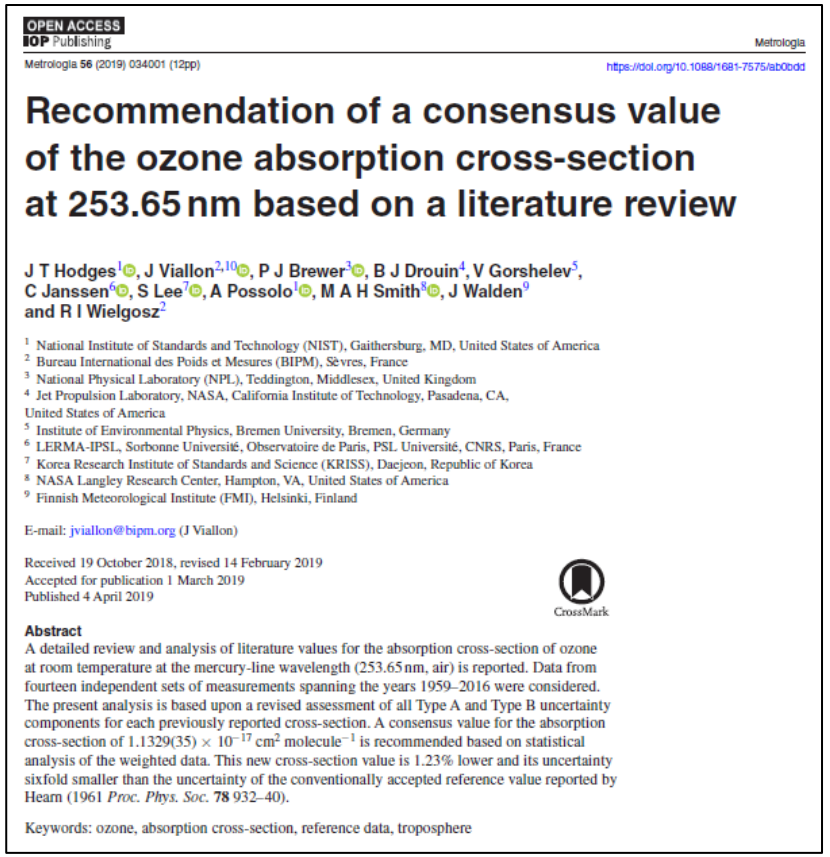
- ✓ the absorption coefficient (α) of O_3 at 253.65 nm
- ✓ the optical path length (L) through the sample
- ✓ the transmittance (I_o/I) of the sample at a nominal wavelength of 253.65 nm, and
- ✓ the sample temperature (T) and pressure (P)

Beer-Lambert Law



How Did this Update Come About?

- The current cross-section value was measured by Hearn in 1961 and incorporated into the Standard Reference Photometer (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 $1.1329 \pm 0.0035 \times 10^{-17}$ cm^2 and is 1.23% lower with an uncertainty six times smaller than the Hearn value
- The new value is an advancement in science and measurement technology that represents a more accurate and precise value than the current value



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Recommendation of a consensus value of the ozone absorption cross-section at 253.65 nm based on a literature review

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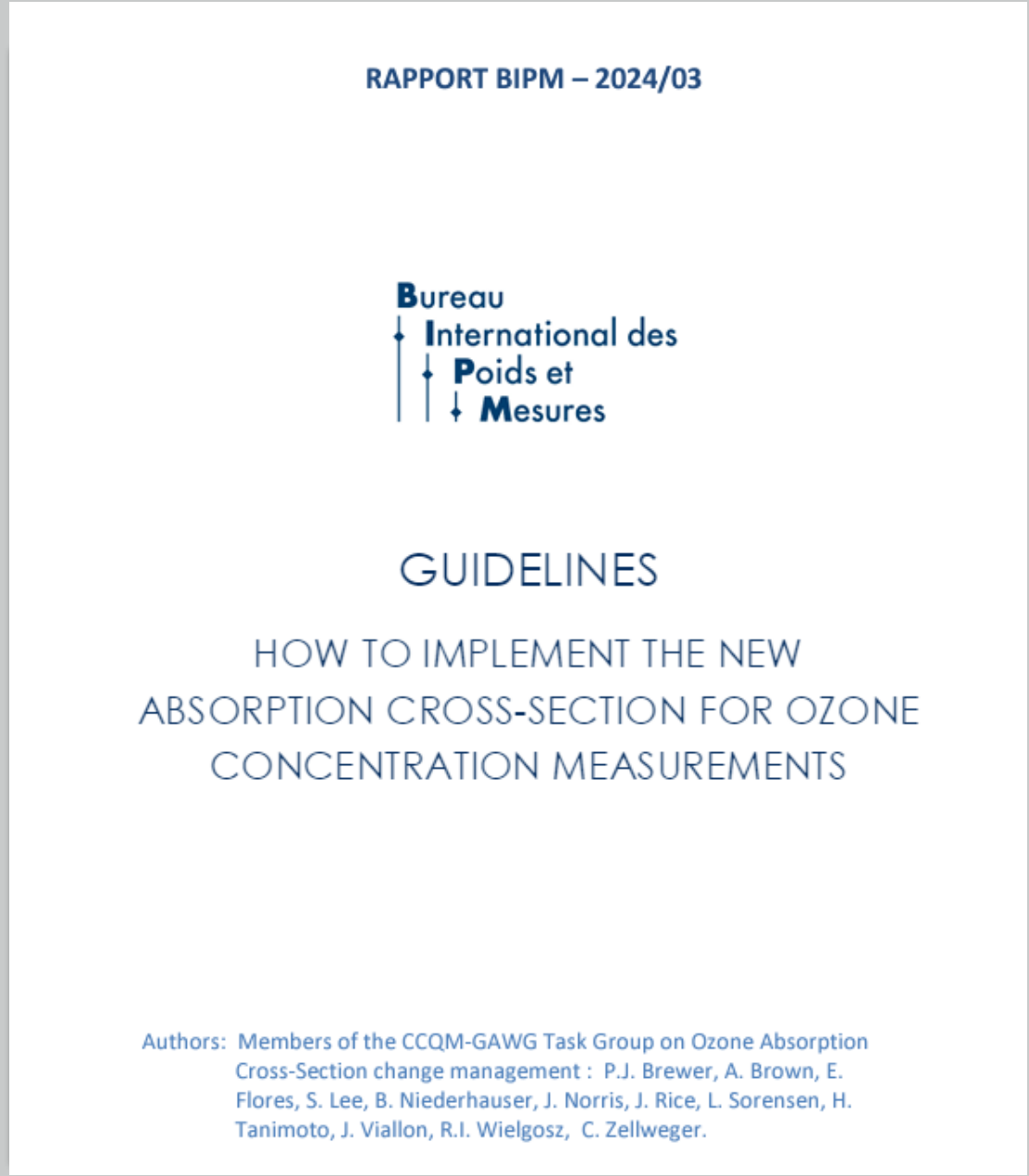
Abstract
A detailed review and analysis of literature values for the absorption cross-section of ozone at room temperature at the mercury-line wavelength (253.65 nm, air) is reported. Data from fourteen independent sets of measurements spanning the years 1959–2016 were considered. The present analysis is based upon a revised assessment of all Type A and Type B uncertainty components for each previously reported cross-section. A consensus value for the absorption cross-section of $1.1329(35) \times 10^{-17}$ cm^2 $molecule^{-1}$ is recommended based on statistical analysis of the weighted data. This new cross-section value is 1.23% lower and its uncertainty sixfold smaller than the uncertainty of the conventionally accepted reference value reported by Hearn (1961 *Proc. Phys. Soc.* **78** 932–40).

Keywords: ozone, absorption cross-section, reference data, troposphere

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

International Task Group Activities

- BIPM (International Bureau of Weights and Measures) organized an overall Task Group and 6 Task Teams to focus on various aspects of the cross-section update:
    - Website developed to communicate the why, what, when, how of the change: https://www.bipm.org/en/ozone.
    - Guidelines developed to provide general recommendations to countries on how to implement.
    - Tracking the update of various standards and regulations.


RAPPORT BIPM – 2024/03

Bureau International des Poids et Mesures

GUIDELINES

HOW TO IMPLEMENT THE NEW ABSORPTION CROSS-SECTION FOR OZONE CONCENTRATION MEASUREMENTS

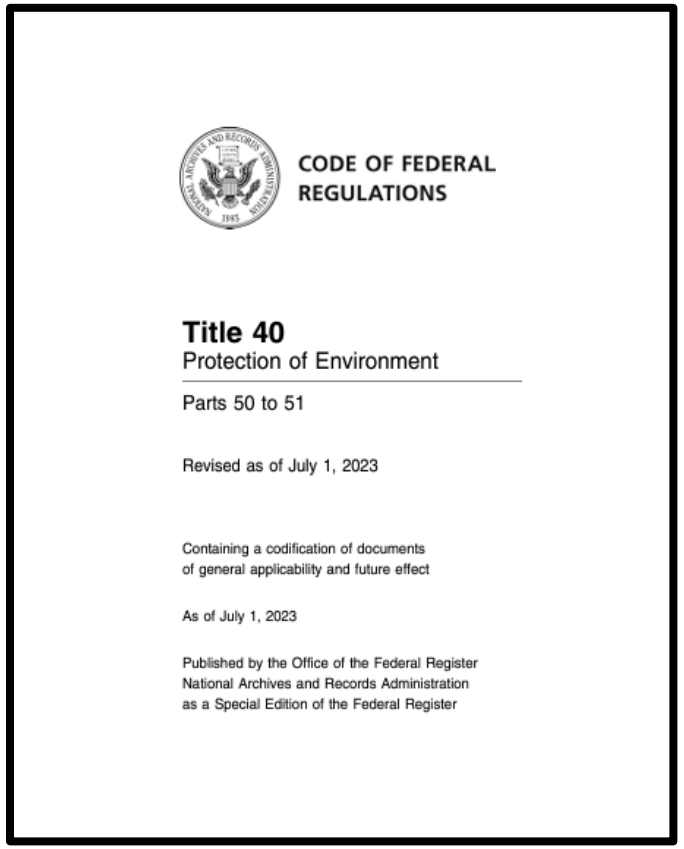
Authors: Members of the CCQM-GAWG Task Group on Ozone Absorption Cross-Section change management : P.J. Brewer, A. Brown, E. Flores, S. Lee, B. Niederhauser, J. Norris, J. Rice, L. Sorensen, H. Tanimoto, J. Viallon, R.I. Wielgosz, C. Zellweger.

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
- ☑ ASTM International D5110 – 98 (2017) and D5156 – 02 (2016)
- ☑ Japanese Industrial Standard Committee (JIS) B7957: 2006
- ☑ Australian Standard, AS 3580.6.1
- ☐ European Committee for Standardization (CEN) 14625:2012 (awaiting publication)
- ☐ China National Environmental Monitoring Center SAC HJ 590:2010 (deliberations continue)

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

- Final rule published on October 12, 2023 (88 FR 70595)
- Changed cross section value (α) in two places
  - Sections 4.1 Calibration Principle and 4.5 Calibration Procedure
    - **Old** α = absorption coefficient of O_3 at 254 nm = **308** ± **4** atm^{-1} cm^{-1} at 0 C and 760 torr
    - **New** α = absorption coefficient of O_3 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
  - Added Hodges et. al., 2019
  - Updated revision dates for the Ozone TAD and QA Handbook Volume II


CODE OF FEDERAL REGULATIONS

Title 40
Protection of Environment

Parts 50 to 51

Revised as of July 1, 2023

Containing a codification of documents of general applicability and future effect

As of July 1, 2023

Published by the Office of the Federal Register National Archives and Records Administration as a Special Edition of the Federal Register

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

2024	2025	2026
Hearn.1961	Either	CCQM.O3.2019
308* $atm^{-1}cm^{-1}$		304.39 $atm^{-1}cm^{-1}$

40 CFR Part 50, Appendix D, 2.0 Measurement Principle: … The new value "will be implemented January 1, 2025, with an additional year to complete implementation (January 1, 2026). Until January 1, 2025, the previous ozone absorption cross-section value, 308 ± 4 $atm^{-1}cm^{-1}$, will be used. After January 1, 2025, both cross-section values, 304.39 ± 0.94 $atm^{-1}cm^{-1}$ and 308 ± 4 $atm^{-1}cm^{-1}$, may be used. After January 1, 2026, only the cross-section value of 304.39 ± 0.94 $atm^{-1}cm^{-1}$may be used."

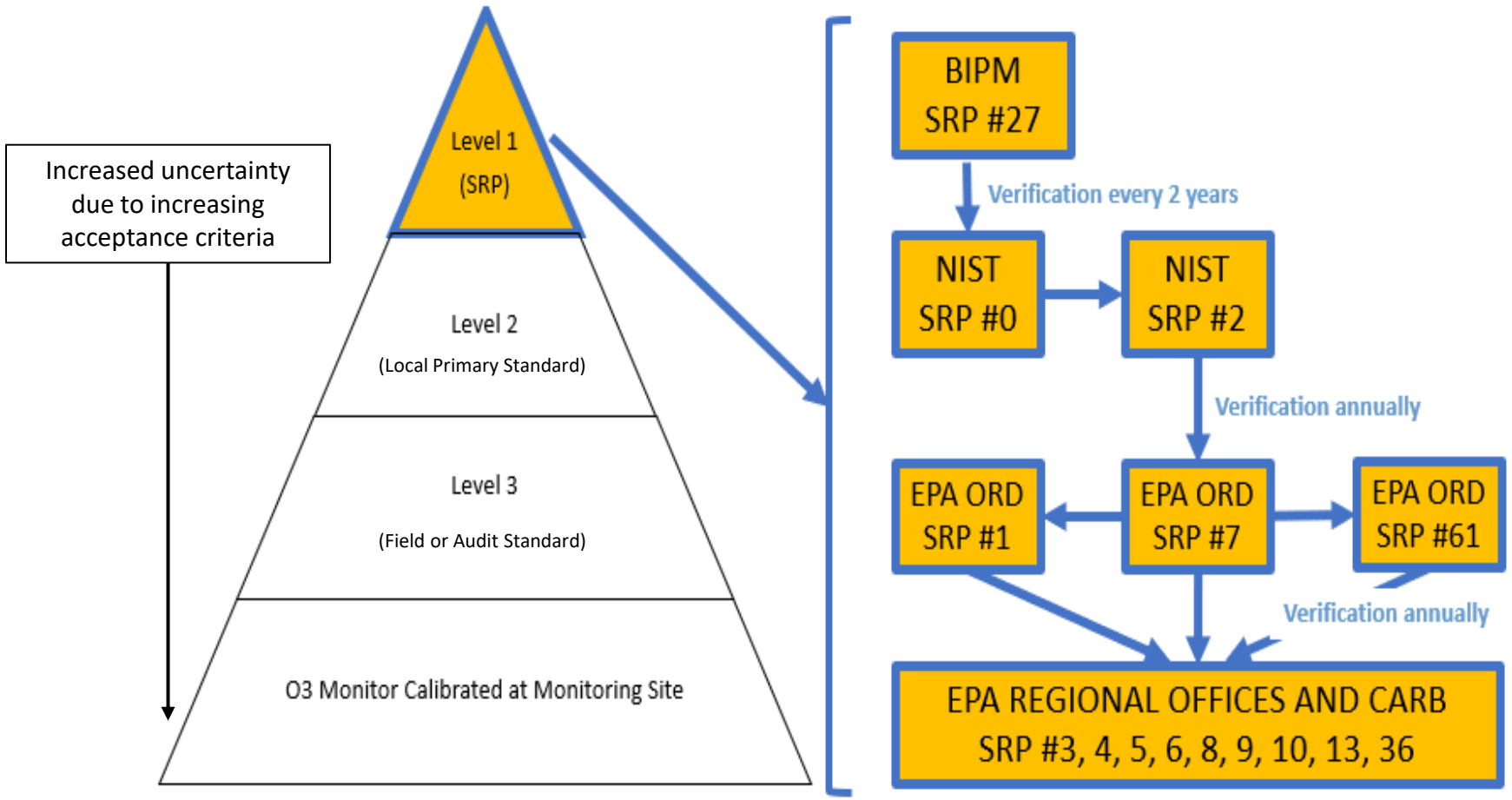
*Note, Standard Reference Photometers have been using 308.32 $atm^{-1}cm^{-1}$

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

<u>SRPs are the starting point for implementing the new cross-section value</u> because they use the value in the ozone determination



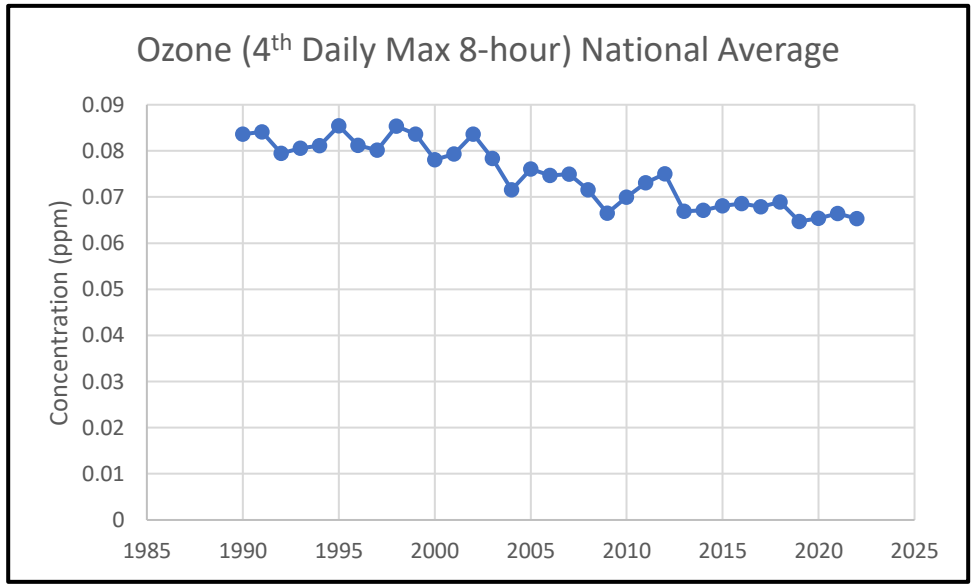
EPA's Implementation Plan

- OAQPS is currently working on a technical memo/note to document the plan for implementation of the revised cross-section within the United States:
  - Starting point is Standard Reference Photometers (SRPs) to start using the new cross-section.
  - Transfer standards will be adjusted/calibrated against SRPs that use the new cross-sections.
  - Change will be propagated throughout the traceability chain to the ozone monitors via transfer standards and calibration/adjustment.
  - No hardware changes required.
  - Starting Jan 1, 2025, use of AQS qualifier on hourly ozone data to indicate which cross-section the data are traceable to.

- Targeting final technical memo/note in Fall 2024.

Potential Impacts on the Ozone Monitoring Data

- Updated Ozone Absorption Cross-Section value is 1.29% lower than the current value used in SRPs.
- There are multiple factors that contribute to variability in ozone monitoring data:
  - 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
  - Ozone analyzer measurement precision, which is ± 0.001 ppm or ± 1 ppb
  - 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
- Could result in increases in measured ozone concentrations but given the existing sources of potential variability in monitoring data, unlikely that there will be any consistent, measurable, and predictable effect on reported data.

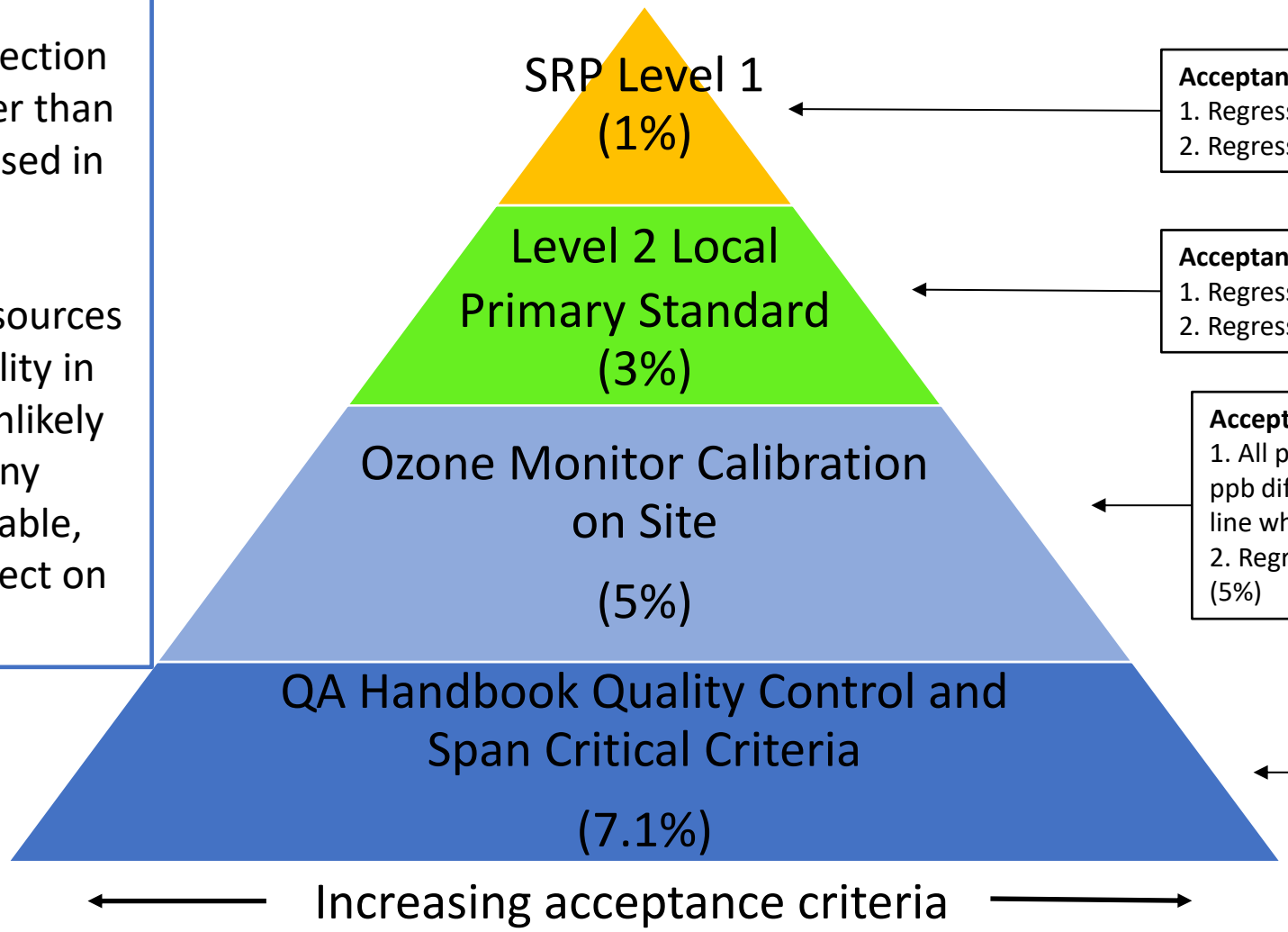


https://www.epa.gov/air-trends

Traceability, Calibration, Verification, QC

Updated Ozone Absorption Cross-Section value is 1.29% lower than the current value used in SRPs.

Given the existing sources of potential variability in monitoring data, unlikely that there will be any consistent, measurable, and predictable effect on reported data.



Acceptance Criteria for Level 1 (SRP):
1. Regression Slope = 1.00 ± 0.01 (1%)
2. Regression Intercept = 0 ± 1 ppb

Acceptance Criteria for Level 2:
1. Regression Slope = 1.00 ± 0.03 (3%)
2. Regression Intercept = 0 ± 3 ppb

Acceptance Criteria for Monitor:
1. All points < ± 2.1% or ≤ ± 1.5 ppb difference of best-fit straight line whichever is greater
2. Regression Slope of 1 ± 0.05 (5%)

QA Critical Criteria for Monitor:
1. One point QC check < ± 7.1% difference or ≤ ±1.5 ppb whichever is greater
2. Zero drift < ± 3.1 ppb (24 hour)
3. Span check drift < ± 7.1%

Ozone Cross-Section Value

- 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 coordinating the universal implementation of the updated value worldwide and tracking progress.
- The absorption cross-section value in 40 CFR part 50 Appendix D was updated through rulemaking which included a phased implementation to be complete by January 1, 2026.
- The updated value is 1.29% lower than currently used in SRPs, and the potential impact of the cross-section update on ozone monitoring data affected by various factors (e.g, monitor precision, calibration acceptance criteria, data handling rules, etc.).

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