



2023 O₃ TAD and Cross-Section Requirement Updates

**PQAO Training –
February 27-28, 2024**
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EPA Region 9

Introductions and Overview

Amy Seeds – EPA Region 9
Monitoring and Analysis
Section (MAS)

Kai Crombie – EPA Region 9
Quality Assurance Branch
(QAB)

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Part 1:
Ozone (O₃) Technical
Assistance Document (TAD)
Updates

Part 2:
Ozone Absorption Cross-
Section Value Requirement
Update

O₃ TAD General Organization

- Section 1 – Introduction
- Section 2 – EPA's O₃ Traceability Scheme
- Section 3 – Types of O₃ Devices
- Section 4 – Verification and Reverification Requirements for O₃ Transfer Standards
- Section 5 – Verification and Reverification Procedure for O₃ Transfer Standards
- Section 6 – Operational Considerations of O₃ Transfer Standards

O₃ TAD General Organization

Continued...

- Appendix A – Equations and Example Calculations
- Appendix B – Example Acceptance Testing Data Sheet
- Appendix C – Utilizing the National Institute of Standards and Technology (NIST) 7 Essential Elements of Traceability
- Appendix D – Rationale and Testing Methodology for O₃ Verification and Reverification Acceptance Criteria
- Appendix E – Qualification Testing

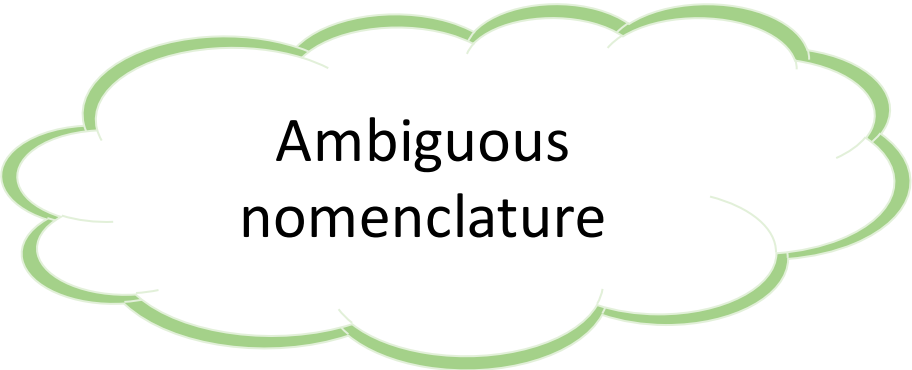
Section 1 - Introduction

2013 Version (EPA – 454/B-13-004)	2023 Version (EPA-454/B-22-003)
Transfer standard (TS) nomenclature was ambiguous to application and distance from Level 1	Transfer standard (TS) nomenclature is clarified and based on application and distance from Level 1
Reverification frequency was based on distance from standard reference photometer (SRP)	Reverification is based on application
Relative Standard Deviation was used as a measure of TS verification AND reverification cycles stability	Standard Deviation is used for <u>verification</u> cycles stability. Change from previous regression slope and intercept are used for <u>reverification</u> stability.
6 cycles were required for verifications and cycles had to be on different days	3 stable cycles are required for verification and can be conducted on same day
Allowed generator-only devices to be used as O ₃ TS	Does NOT allow use of generator-only devices as O ₃ TS
Level 4 TS were allowed	Level 4 TS are strongly discouraged and are allowed only if additional requirements are met
Did not include best practices	Includes hands-on operational best practices for working with O ₃ TS

Section 2 – EPA’s Traceability Scheme

2013 TAD

2023 TAD



Ambiguous
nomenclature



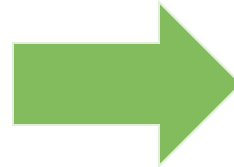
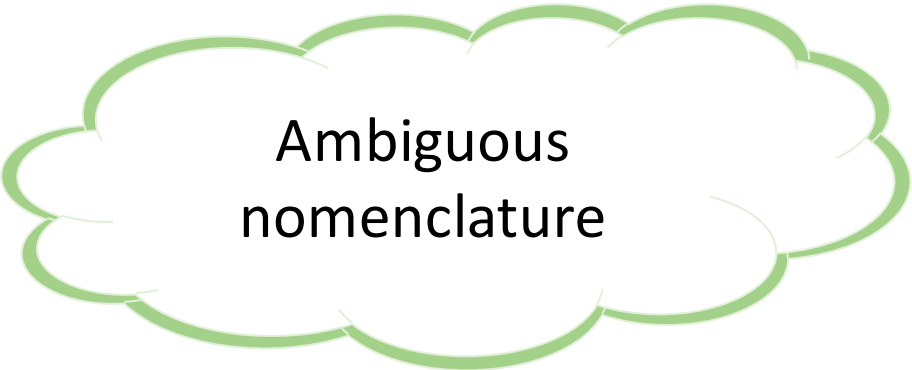
Reverification depended
on distance from SRP

Section 2 – EPA’s Traceability Scheme

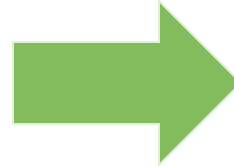
2013 TAD

2023 TAD

Ambiguous
nomenclature



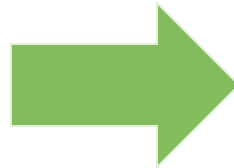
Reverification depended
on distance from SRP



Section 2 – EPA’s Traceability Scheme

2013 TAD

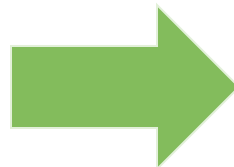
Ambiguous
nomenclature



2023 TAD

Clarification based
on application (bench/field)

Reverification depended
on distance from SRP



Reverification depends
on application (bench/field)

Section 2 – Standards Definition

Transfer Standard Levels

Defined by distance from SRP

- Level 1 = SRP
- Level 2 = compared to SRP
- Level 3 = compared to Level 2

Bench Standard

- Stationary Standards
- Traditional “primary standard”

Field Standard

- Moves from site to site
- Traditional “field standard”

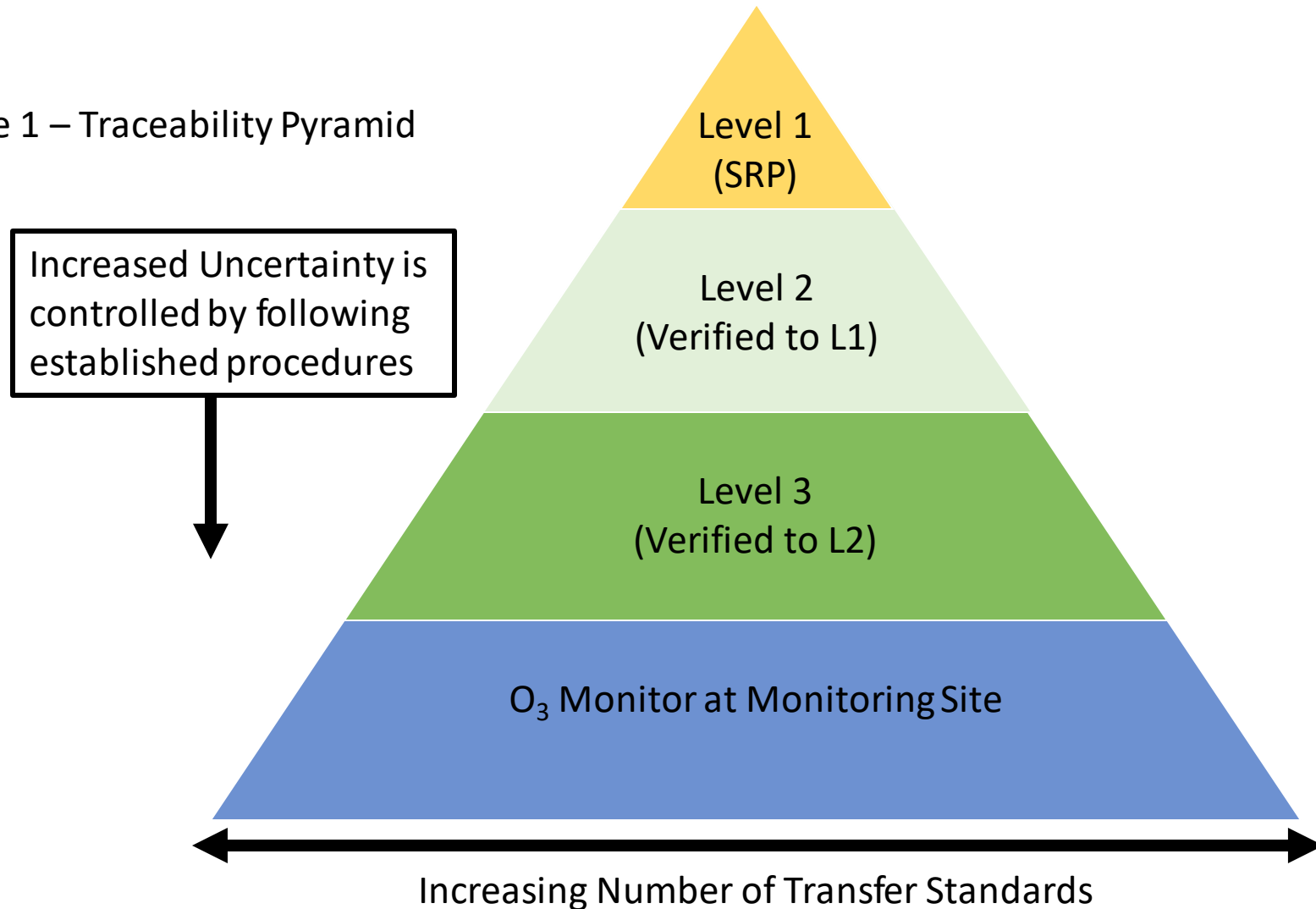


NIST SRP pictured above

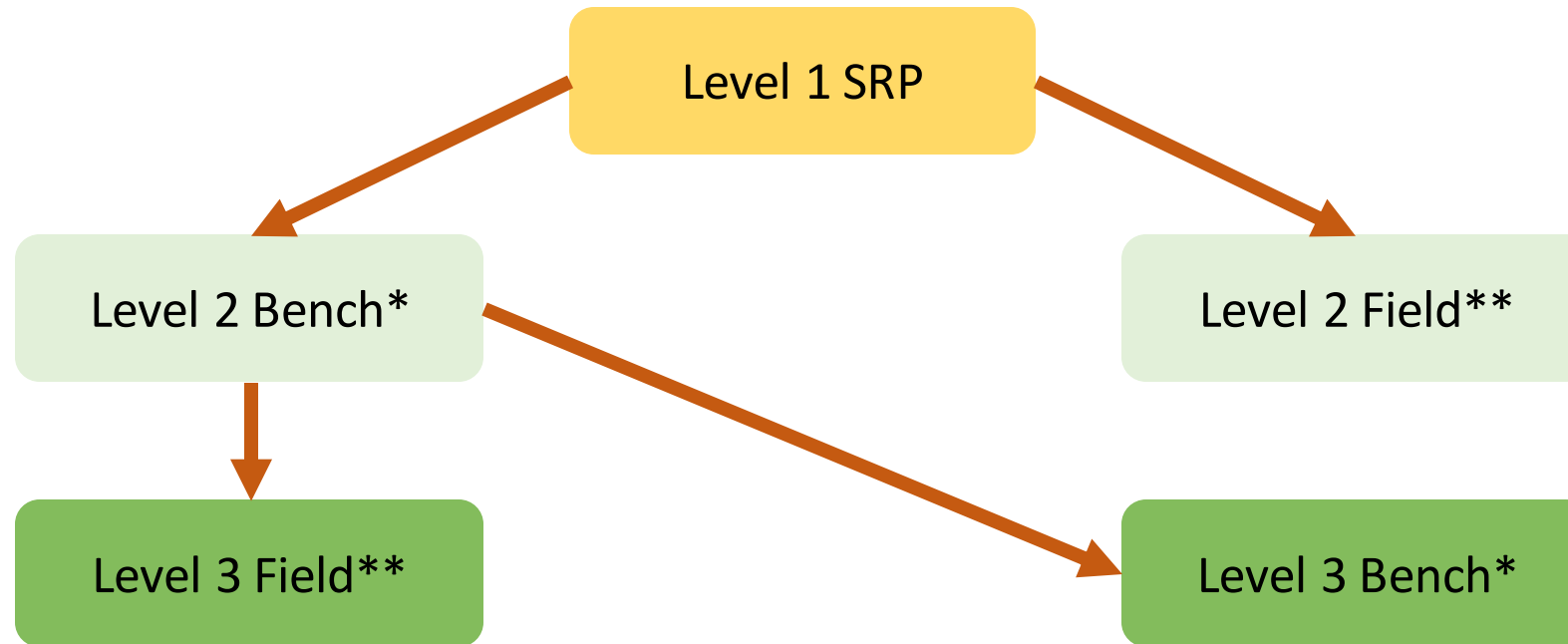
<https://www.nist.gov/programs-projects/nist-standard-reference-photometer-ozone-measurement-traceability>

Section 2 – EPA’s Traceability Scheme

Figure 1 – Traceability Pyramid



Section 2 – Verification Rules and Frequency



* Indicates verification annually

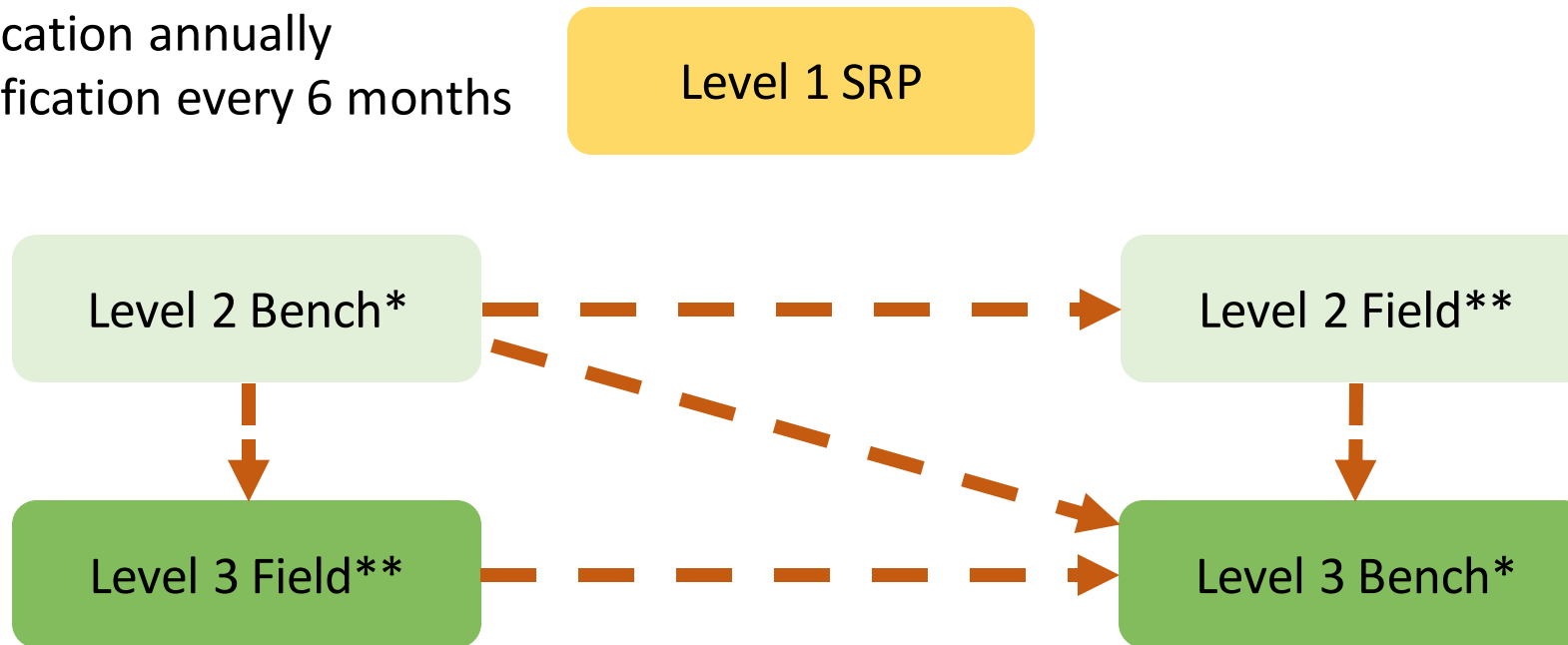
** Indicates verification every 6 months

Verification timeframe begins on the day the verification is completed. Not the day the standard is put into service. (Section 2.6)

Section 2 – Reverification Rules and Frequency

* Indicates verification annually

** Indicates verification every 6 months

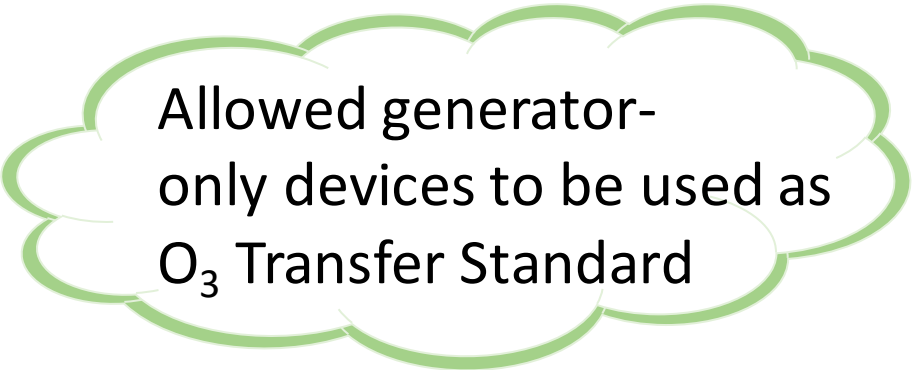


A TS may not be used after the reverification frequency time-period has been exceeded. However, it may not require a new verification (all 3 cycles). See Section 2.7

Section 3 – Types of O₃ Transfer Standards

2013 TAD

2023 TAD

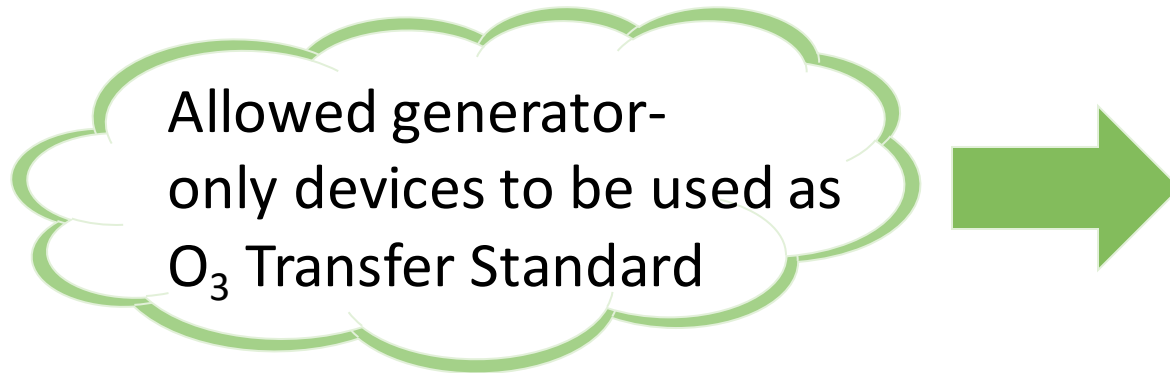


Allowed generator-
only devices to be used as
O₃ Transfer Standard

Section 3 – Types of O₃ Transfer Standards

2013 TAD

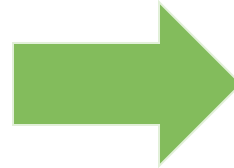
2023 TAD



Section 3 – Types of O₃ Transfer Standards

2013 TAD

Allowed generator-only devices to be used as O₃ Transfer Standard



2023 TAD

Does not allow generator-only devices to be used as O₃ Transfer Standard

Section 4 – Verification and Reverification Requirements for O₃ Transfer Standards

2013 TAD

Levels had different acceptance criteria

Level 4 Transfer Standards were allowed

6 cycles were required for verifications and had to be on different days

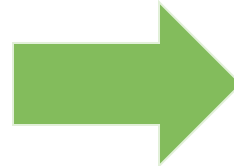
2023 TAD

Section 4 – Verification and Reverification Requirements for O₃ Transfer Standards

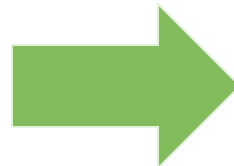
2013 TAD

2023 TAD

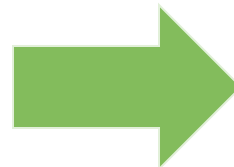
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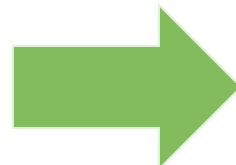
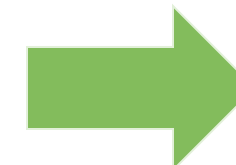
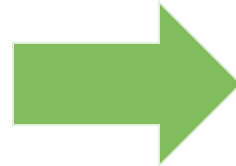
Section 4 – Verification and Reverification Requirements for O₃ Transfer Standards

2013 TAD

Levels had different acceptance criteria

Level 4 Transfer Standards were allowed

6 cycles were required for verifications and had to be on different days



2023 TAD

Levels 2 and 3 have the same acceptance criteria

Level 4 TS are strongly discouraged and are only allowed if additional criteria are met

3 cycles are required for verification and can be performed on the same day

Section 4.2.2 – Acceptance Testing Requirements

- Acceptance testing is required as part of normal practice for verification/reverification
 - Must be completed...
 - after a new TS is received from the manufacturer
 - Prior to verification or reverification of a TS
 - When a TS is shipped
 - When a device requires repair
- Example form in Appendix B

Section 4 – Acceptance Criteria

- Same acceptance criteria for levels 2 and 3
 - Verification (Equations = Appendix A)
 - Each point difference must be $< \pm 3.1\%$ (Equation 1) or ± 1.5 ppb for concentration points below 50 ppb (Equation 2).
 - All 3 regression slopes must be 1.00 ± 0.03 (Equation 4)
 - All 3 regression intercepts must be 0 ± 3 ppb (Equation 4)
 - SD of the 3 slopes must be < 0.0075 (Equation 8)
 - SD of the 3 intercepts must be < 1.00 ppb (Equation 9)

*Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone,
Technical Assistance Document (January 2023)*

Section 4 – Acceptance Criteria

- Reverification (Equations = Appendix A)
 - Use the data collected during the reverification cycle to calculate the following:
 - Percent difference (*% Diff*) in measured concentration, calculated at each tested concentration point > 50 ppb and must be within $\pm 3.1\%$ (Equation 1)
 - Absolute difference (*AbsDiff*) in measured concentration, calculated at each tested concentration point ≤ 50 ppb must be within ± 1.5 ppb (Equation 2)
 - The calculated value of the regression slope (m) must fall within 1.00 ± 0.03 (i.e., within $\pm 3\%$ of 1.00) (Equation 4)
 - m must **ALSO** fall within ± 0.015 of the calculated mean slope (\bar{m}) from the most recent successful verification test (Equation 6)
 - The calculated value of the regression intercept (b) must fall within 0.00 ± 0.03 ppb (Equation 4)
 - b must **ALSO** fall within ± 1.5 ppb of calculated mean intercept (\bar{b}) from the most recent successful verification test (Equation 7)

O₃ TAD Implementation

November 15, 2023 – November 15, 2025

- TAD was published on November 15, 2023
- “implementation will occur over a phase in period of not more than 2 years from the time this document becomes final” ¹

¹ *Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone, Technical Assistance Document (January 2023)*

Part 2

Ozone Absorption Cross-Section Value Requirement Update

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

Absorption cross-section (absorption coefficient, α) -

used to determine atmospheric O₃ concentrations based on the amount of light absorbed at an ultraviolet (UV) wavelength of 253.65 nm

$$\text{Transmittance} = \frac{I}{I_0} = e^{-\alpha cl} \quad (1)^2$$

$$[\text{O}_3]_{\text{OUT}} = \left(\frac{-1}{\alpha l} \ln \frac{I}{I_0} \right) \left(\frac{T}{273} \right) \left(\frac{760}{P} \right) \times \frac{10^6}{L} \quad (4)^2$$

Where:

$[\text{O}_3]_{\text{OUT}}$ = O₃ conc., ppm

l = optical path length, cm

P = sample pressure, torr

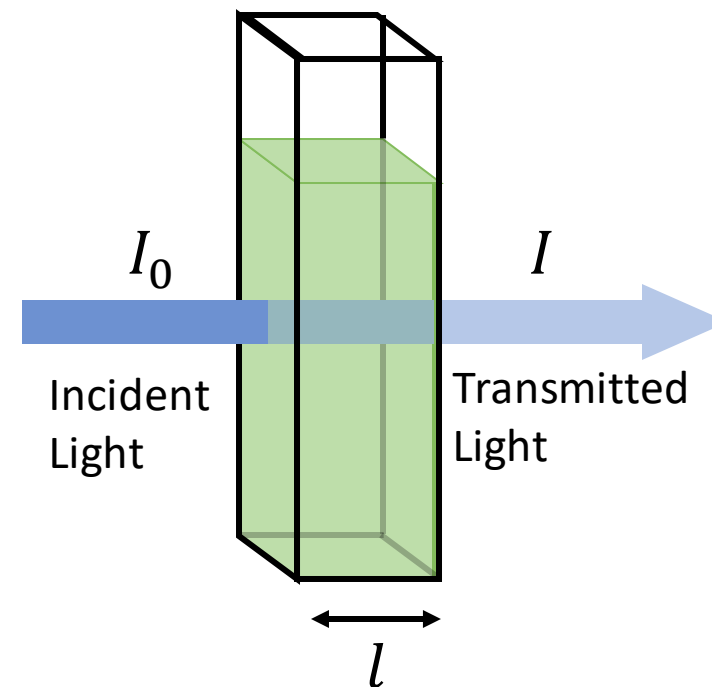
α = absorption coefficient

T = sample temp, K

L = O₃ loss correction

of O₃ @ STP, atm⁻¹ cm⁻¹

factor



² Appendix D to Part 50—Reference Measurement Principle and Calibration Procedure for the Measurement of Ozone in the Atmosphere (Chemiluminescence Method), 4.1 Principle

Cross-Section Value Requirement Update

- Updated value represents a more accurate and precise value
- It improves the accuracy of UV O₃ analyzers and SRPs
- Consensus value is 1.23% lower and uncertainty 4.25x smaller
- On October 12, 2023, the EPA revised 40 CFR Part 50 App D - Reference Measurement Principle and Calibration Procedure for the Measurement of Ozone in the Atmosphere (Chemiluminescence Method)
- Federal Register Notice posted on [EPA AMTIC website](#)

308 $atm^{-1}cm^{-1}$

“current” or “old” value

Uncertainty of 4 $atm^{-1}cm^{-1}$
(1.4%)

Reference Measurement Principle and Calibration Procedure for the Measurement of Ozone in the Atmosphere (Chemiluminescence Method), Federal Register Volume 88, Issue 196 (October 12, 2023)

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- Federal Register Notice posted on [EPA AMTIC website](#)
- **The update will be achieved through software/firmware modification and will NOT require any hardware changes**

Reference Measurement Principle and Calibration Procedure for the Measurement of Ozone in the Atmosphere (Chemiluminescence Method), Federal Register Volume 88, Issue 196 (October 12, 2023)

$308 \text{ atm}^{-1} \text{ cm}^{-1}$

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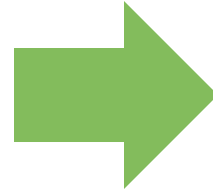
$304.39 \text{ atm}^{-1} \text{ cm}^{-1}$

“updated” value

Uncertainty of $0.94 \text{ atm}^{-1} \text{ cm}^{-1}$
(0.31%)

Managing and Implementing the Update

$308 \text{ atm}^{-1} \text{ cm}^{-1}$
“current” or “old”
value

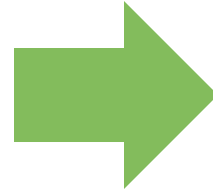


$304.39 \text{ atm}^{-1} \text{ cm}^{-1}$
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Managing and Implementing the Update

$308 \text{ atm}^{-1} \text{ cm}^{-1}$
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$304.39 \text{ atm}^{-1} \text{ cm}^{-1}$
“updated” value

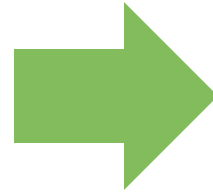
Until Jan. 1, 2025, the
**previous ozone absorption
cross-section value** ($308 \pm
4 \text{ atm}^{-1} \text{ cm}^{-1}$) will be used

January 1, 2025

January 1, 2026

Managing and Implementing the Update

$308 \text{ atm}^{-1} \text{ cm}^{-1}$
“current” or “old”
value



$304.39 \text{ atm}^{-1} \text{ cm}^{-1}$
“updated” value

Until Jan. 1, 2025, the
**previous ozone absorption
cross-section value** ($308 \pm 4 \text{ atm}^{-1} \text{ cm}^{-1}$) will be used

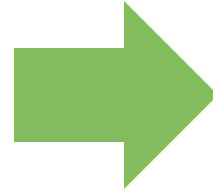
Between Jan. 1, 2025, and
Jan. 1, 2026, **BOTH**
cross-section values
may be used

January 1, 2025

January 1, 2026

Managing and Implementing the Update

$308 \text{ atm}^{-1} \text{ cm}^{-1}$
“current” or “old”
value



$304.39 \text{ atm}^{-1} \text{ cm}^{-1}$
“updated” value

Until Jan. 1, 2025, the **previous ozone absorption cross-section value** ($308 \pm 4 \text{ atm}^{-1} \text{ cm}^{-1}$) will be used

Between Jan. 1, 2025, and Jan. 1, 2026, **BOTH** cross-section values may be used

After Jan. 1, 2026, **ONLY** the “updated” ozone absorption cross-section value ($304.39 \pm 0.94 \text{ atm}^{-1} \text{ cm}^{-1}$) may be used

January 1, 2025

January 1, 2026

Questions?

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