Cross-Section Changes for Ozone

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EPA's Office of Air Quality Planning and Standards
29th Annual Inter-tribal Environmental Council's (ITEC) Conference
August 13th, 2025

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Background on the O_3 Absorption Cross Section Change

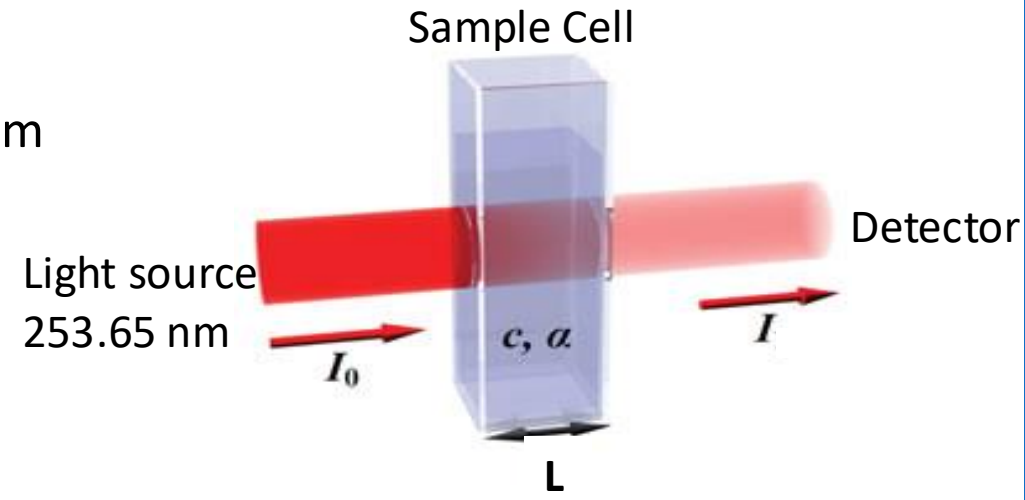
What is the Ozone Absorption Cross-Section?

- 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:

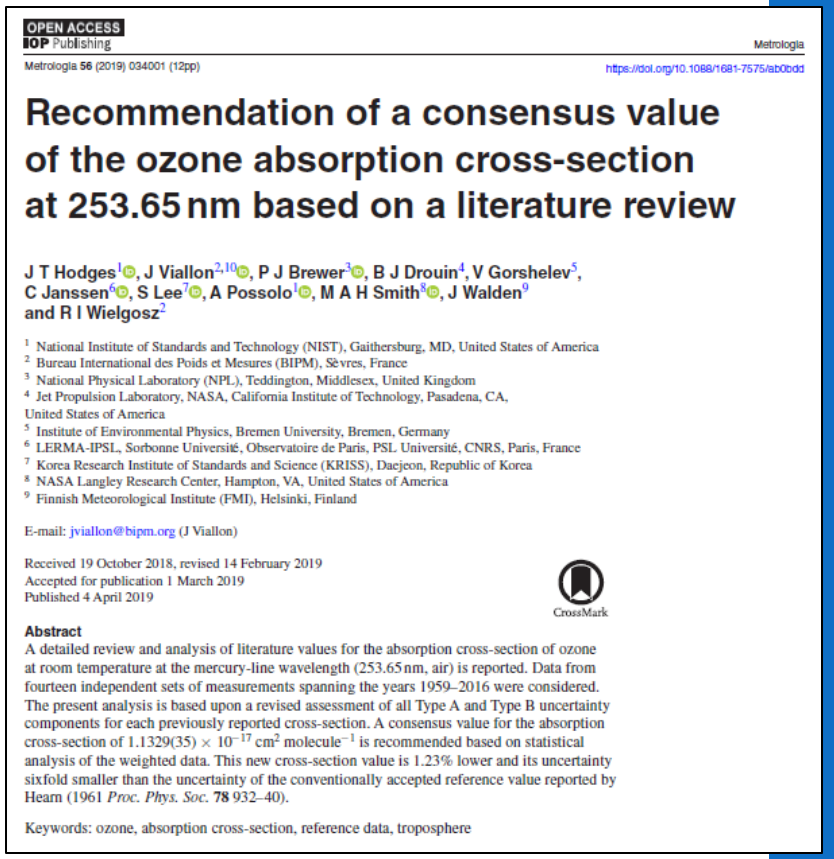
- ✓ the absorption coefficient (α) of O_3 at 253.65 nm
- ✓ the optical path length (L) through the sample
- ✓ the transmittance (I_o/I) of the sample at a nominal wavelength of 253.65 nm, and
- ✓ the sample temperature (T) and pressure (P)

Beer-Lambert Law



How Did this Update Come About?

- Before 2025, most ozone measurements used a cross-section value that 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 (CCQM.O3.2019) is $1.1329 \pm 0.0035 \times 10^{-17}$ cm^2 and is 1.23% lower with lower uncertainty 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
- Countries around the world have adopted the CCQM.O3.2019 value



OPEN ACCESS
IOP Publishing
Metrologia

Metrologia 56 (2019) 034001 (12pp)
https://doi.org/10.1088/1681-7575/ab0bdd

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

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Received 19 October 2018, revised 14 February 2019
Accepted for publication 1 March 2019
Published 4 April 2019

CrossMark

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).

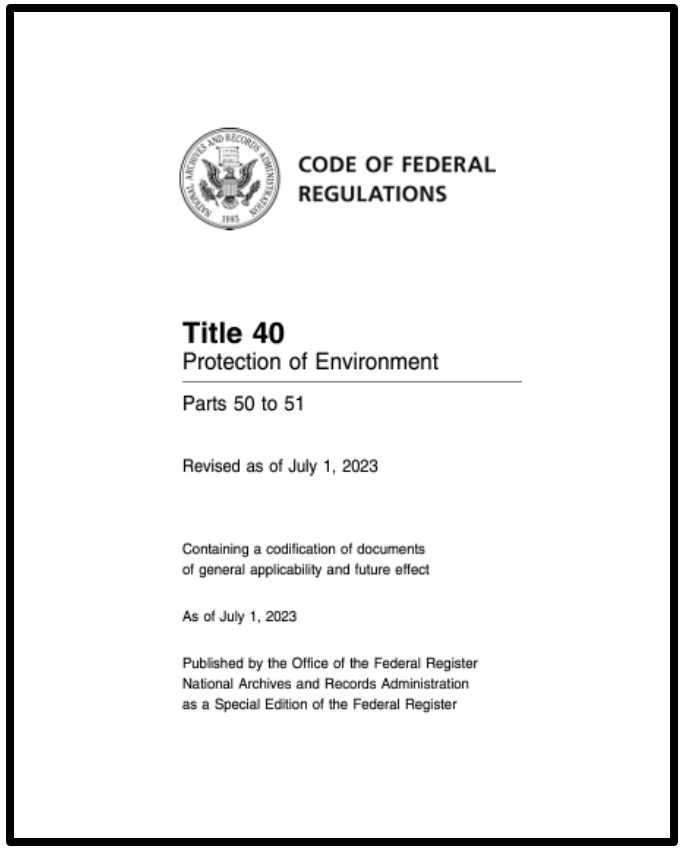
Keywords: ozone, absorption cross-section, reference data, troposphere

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

Implementation Plan for the U.S.

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); corrected on January 16, 2025 (90 FR 4649)
- 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

Hearn.1961

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

2025/2026

Transition

Period

by the end of 2026

CCQM.O3.2019

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

40 CFR Part 50, Appendix D, 2.0 Measurement Principle: … The new value "will begin use in all U.S. Standard Reference Photometers (SRPs) on January 1, 2025. It is expected that implementation across all other ozone transfer standards and ozone monitors in the field will be completed by December 31, 2026."

*Note, Standard Reference Photometers have been using 308.32 $atm^{-1}cm^{-1}$; CCQM value is 1.29% lower.

Summary of the Ozone Cross-Section Implementation Memo

Final memo was distributed on 2024-11-13. Available on AMTIC here.

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.
   - SRP operators do not need to wait for their SRP to be verified with CCQM.O3.2019 before beginning to conduct Level 2 verifications using CCQM.O3.2019.
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.

Data Qualifying in AQS

AQS Qualifying Requirement

- Per the Implementation Memo, "*starting January 1, 2025, monitoring agencies should begin flagging hourly ozone data with "XS" AQS qualifier if traceable to the Hearn.1961 value*".

Qualifier Code	Qualifier Description	Qualifier Type	Qaulifier Type Code	Still Active	Legacy Code
XS	Traceable to a Standard Reference Photometer (SRP) with the Hearn (1961) 308.32 atm-1 cm-1 Ozone Cross-Section Value.	Quality Assurance Qualifier	QA	YES	

- Qualify all O_3 data w/ "XS" while traceable to Hearn. Once traceable to CCQM, stop qualifying.
- XS should only be used on O_3 data and not reported for any other parameter (including oxides of nitrogen).
  - AQS will not allow XS to be used for NO, NO_2, NOx, NOy, and NOy-NO.
  - Other parameters will allow the flag but should not be used.

AQS Qualifying Status

Region 6 ITEC Member Tribe's Ozone Monitor Qualifying Status						
PQAO Code	**PQAO**	**AQS ID**	**First XS Flag**	**Last XS Flag**	**First Non-XS Flag**	**Last Non-XS Flag**
905	Cherokee Nation, Oklahoma	40-001-9009	2025-01-01	2025-03-31	NA	NA
		40-097-9014	2025-01-01	2025-03-31	NA	NA
		40-135-9021	2025-01-01	2025-03-31	NA	NA
907	Choctaw Nation of Oklahoma	40-023-2017	NA	NA	NA	NA
920	Quapaw Tribe of Indians, OK	40-115-9004	NA	NA	2025-03-01	2025-03-31

- Table summarizes ITEC O_3 monitor *XS* usage in CY2025.
- Data from AQS query on 2025-08-13.

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		40-135-9021	2025-01-01	2025-03-31	NA	NA
907	Choctaw Nation of Oklahoma	40-023-2017	NA	NA	NA	NA
920	Quapaw Tribe of Indians, OK	40-115-9004	NA	NA	2025-03-01	2025-03-31

Three PQAOs and five sites with ozone monitors.

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		40-135-9021	2025-01-01	2025-03-31	NA	NA
907	Choctaw Nation of Oklahoma	40-023-2017	NA	NA	NA	NA
920	Quapaw Tribe of Indians, OK	40-115-9004	NA	NA	2025-03-01	2025-03-31

One monitor is inactive (no data reported to AQS).

AQS Qualifying Status

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907	Choctaw Nation of Oklahoma	40-023-2017	NA	NA	NA	NA
920	Quapaw Tribe of Indians, OK	40-115-9004	NA	NA	2025-03-01	2025-03-31

Three sites with all hourly data qualified with XS.

AQS Qualifying Status

Region 6 ITEC Member Tribe's Ozone Monitor Qualifying Status						
PQAO Code	PQAO	AQS ID	First XS Flag	Last XS Flag	First Non-XS Flag	Last Non-XS Flag
905	Cherokee Nation, Oklahoma	40-001-9009	2025-01-01	2025-03-31	NA	NA
		40-097-9014	2025-01-01	2025-03-31	NA	NA
		40-135-9021	2025-01-01	2025-03-31	NA	NA
907	Choctaw Nation of Oklahoma	40-023-2017	NA	NA	NA	NA
920	Quapaw Tribe of Indians, OK	40-115-9004	NA	NA	2025-03-01	2025-03-31

- One site has not qualified any O_3 data with XS.
- Does not necessarily indicate an issue (if monitor adjusted to CCQM prior to start of O_3 monitoring season).

Conducting APEs during the Transition

Annual Performance Evaluation (APE) Background

- Requirements detailed in 40 CFR Part 58 Appendix A Section 3.1.2.
- Must be conducted on each primary monitor once a year.
- Procedure:
  - Challenge station analyzer w/ audit gas at minimally three concentration levels.
  - Report audit and analyzer concentrations to AQS.
- Percent differences in concentrations are used to assess quality of monitoring data.

Cross-Section Transition's Impact on APEs

- You *may* conduct APEs during the two-year transition period (2025-26) in which the audit standard and site analyzer are traceable to different cross-section values.
- In this scenario, EPA recommends that the audit standard concentration is recalculated prior to comparing concentrations and uploading results to AQS.

Recommended Recalculation Procedure

1. If the audit standard is traceable to the CCQM and site analyzer is traceable to the Hearn, recalculate the audit standard concentration via:

$$Audit_{recalc} = \frac{Audit_{orig}}{1.0129}$$

1.0129 is the ratio of the Hearn value (308.32 atm^{-1} cm^{-1}) to CCQM value (304.39 atm^{-1} cm^{-1})

2. If the audit standard is traceable to the Hearn and site analyzer is traceable to the CCQM, recalculate the audit standard concentration via:

$$Audit_{recalc} = Audit_{orig} \times 1.0129$$

3. If both devices are traceable to the CCQM or both are traceable to the Hearn, no recalculation is needed.

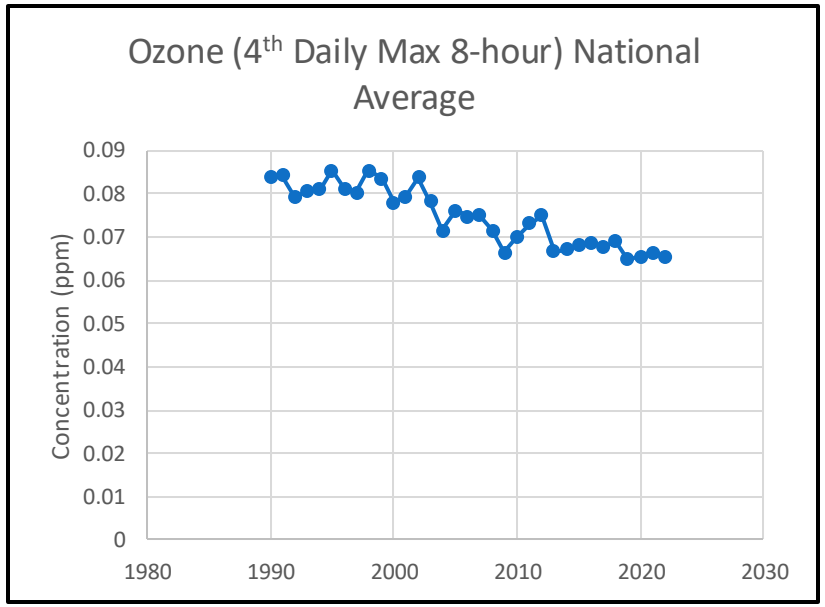
Summary

- EPA adopted the consensus-based ozone cross-section into ozone monitoring regulations in 2023.
  - The updated value (known as the CCQM value) is 1.29% lower than the prior value (the Hearn value) in the ozone monitoring calibration system.
- We are currently in the implementation period for the updated cross-section value, with complete implementation required by December 31, 2026.
  - The implementation memo contains details about the process.
  - SRPs are currently using the updated value in verifications of level 2 standards.
- During the implementation phase:
  - Please use the XS qualifier on hourly O_3 data uploaded to AQS if the given monitor is not yet traceable to the updated cross-section value.
  - During APEs, recalculate audit concentrations only if the audit standard and station analyzer are traceable to different cross-sections.
- If you have questions, please contact your EPA Regional Office, Brannon Seay (seay.brannon@epa.gov), or Melinda Beaver (beaver.melinda@epa.gov).

Extra Slides

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.