

Technical Note No. 070

Ozone UV Cross Section Update

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Summary:

In October of 2023 and January of 2025, the US EPA issued new guidance regarding the ozone absorption cross section at 253.65 nm. This technical note outlines some background on the ozone absorption cross section value and the reason for the change, technical details of the change, and what this means for users of 2B Technologies ozone monitors.

Tools/Materials Needed

None.

Introduction

The absorption cross section per molecule (σ) is a constant used in photometry to calculate the concentration of ozone from the measurement of the absorption of ultraviolet light. It is implemented according to Beer's law:

$$[O_3] = \frac{1}{\sigma L} ln \left(\frac{l}{l_0}\right) \tag{1}$$

where σ is the UV absorption cross section, *L* is the path length of the instrument's absorption cell, *I* is the light intensity after passing through sample air inside the cell, and *I*₀ is the incident light intensity, measured in photometry after passing through the cell in the absence of ozone. [1]

For several decades, the value of the ozone UV absorption cross section as measured by A. G. Hearn was the NIST and EPA accepted value equal to 1.146×10^{-17} cm² molecule⁻¹ (308.32 atm⁻¹cm⁻¹ at standard temperature and pressure) with an estimated uncertainty of 1.4% [2]. After Hearn's original published work, multiple gas phase titration (GPT) studies called this accepted value into question. In April of 2019 in cooperation with the National Institute of Standards and Technology (NIST) and the International Bureau of Weights and Measures (BIPM). Hodges et al. published a literature review recommending the updating of the accepted ozone crosssection value at 253.65 nm to 1.1329×10^{-17} cm² molecule⁻¹ (304.39 atm⁻¹cm⁻¹ at standard temperature and pressure) with an estimated uncertainty of 0.31% [3]. Further review in late 2020 by the BIPM's Consultive Committee for Metrology in Chemistry and Biology – Gas Analysis Working Group (CCQM-GAWG) eventually led to the publishing of new regulations regarding the ozone cross section in October of 2024, a memo by EPA in November of 2024, and a final correction to the implementation process in January of 2025. A goal of the EPA guidance is to update all standards by the end of 2025 and all monitors by the end of 2026 [4, 5, 6].



Implementation of the New Cross-Section Value at 2B Technologies

Following changes to EPA guidance in 2024, 2B Tech began the process of updating transfer standards according to EPA recommendations as set out in their 2024 memo. All ozone calibrations performed by 2B Technologies are traceable to a Thermo Model 49i Primary Standard, which is calibrated regularly by NIST. The Thermo 49i Primary Standard was verified against an ozone photometer using the Hearn 1961 value, before being adjusted to and verified against the CCQM.O3.2019 value as per EPA regulations and recommendations [4, 5, 6].

Due to the update in the cross-section value, instruments calibrated by 2B Technologies starting January of 2025 can be expected to measure ozone 1.29% higher than instruments calibrated prior, as all in-house standards have been updated following EPA guidance. While the EPA guidance allows for use of either cross section value in ozone monitoring equipment for the time being, EPA is changing to the new cross section value across all of their standard reference photometers (SRPs) in January of 2025, and expects implementation in all level 2 transfer standards by the end of 2025. [5, 6].

References:

- [1] Davis, RS., et al. 2022 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 *Rapport BIPM* – 2022/02
- [2] Hearn, AG., 1961 The absorption of ozone in the ultra-violet and visible regions of the spectrum *Proc. Phys. Soc.* <u>https://doi.org/10.1088/0370-1328/78/5/340</u>
- [3] Hodges JT., et al. 2019 Recommendation of a consensus value of the ozone absorption cross-section at 253.65 nm based on a literature review *Meterologia* <u>https://doi.org/10.1088/1681-7575/ab0bdd</u>
- [4] Environmental Protection Agency, 2023 Reference measurement principle and calibration procedure for the measurement of ozone in the atmosphere (chemiluminescence method), 88FR 70595 USEPA Federal Register, Vol. 88 No. 196, October 12, 2023 <u>https://www.epa.gov/system/files/documents/2023-10/federal-register-88fr70595.pdf</u>
- [5] Beaver, M., Curran, T. 2024 Ozone absorption cross-section implementation in the U.S. ambient air monitoring network United States Environmental Protection Agency Office of Air Quality Planning and Standards <u>https://www.epa.gov/system/files/documents/2024-</u> 11/o3xs-implementation-memo_2024november12_final.pdf
- [6] Environmental Protection Agency, 2025 Reference measurement principle and calibration procedure for the measurement of ozone in the atmosphere (chemiluminescence method); Correction, 90FR 4649 USEPA Federal Register, Vol. 90 No. 10, January 16, 2025 <u>https://www.govinfo.gov/content/pkg/FR-2025-01-16/pdf/2025-00946.pdf</u>