

# **O3 Monitor Issues & Implications for Proposed Revised O3 NAAQS**

**Ozone Transport Commission**

**OTC Committee Meeting**

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# O<sub>3</sub> Measurement Developments and Recommendations

- A **re-measured 254 nm O<sub>3</sub>** cross-section, 1.8% lower than now used in NIST standard reference photometers (SRP), **increases ambient ozone levels by 1.35 ppb at the 75 ppb NAAQS**. This revision also **improves SRP agreement with independent non-UV-photometry based methods such as nitric oxide-gas phase titration (NO-GPT)**.
- Given this agreement and SRP's **failure to meet EPA's proposed UV calibration path length uncertainty specifications ( $\leq 0.5\%$ )** for calibrating FEM/FRM monitors, EPA should develop a **new, primary, gravimetric NO standard reference material (SRM)-based GPT ozone reference method**.

# A New BIPM 254 nm Ozone Absorption Cross Section?

- “If this new value was to be used in SRPs, it **would mean an average increase of the measured ozone concentration of 1.8 %**. This is consistent with the results obtained for gas phase **titration** in the international comparison CCQMP28 during which the bias between both methods was observed.”
- “The newly reported value should be used in future to obtain the most accurate measurements of ozone concentration, which are in closer agreement with non-UV-photometry based methods such as the gas phase titration of ozone with nitrogen monoxide.”

**Viallon et al. *Atmos Meas Tech* 8: 1245-57 (2015)**

# SRP Path Length Uncertainty

- “It should be noted that quantification of any bias due to divergence of the light beam down the cells was not determined. Although believed to be a small effect, added research is planned to determine the magnitude of this bias. Until this can be quantified, **an uncertainty of 0.52 cm has been added to the path-length uncertainty** and included in the overall NIST SRP uncertainty budget.”
- “A typical set of new **absorption cells have an average optical length of  $89.660 \pm 0.004$  cm.**”
- Percent path length uncertainty =  $100 \times (0.52/89.66) = 0.58\%$

**Norris et al. *JAWMA* 63: 565-74 (2013)**

# EPA-proposed NO-CL O<sub>3</sub> FRM Calibration Specification

Appendix D to Part 50 - 4.3.1 *UV photometer*. “...Because the low-pressure mercury lamp radiates several wavelengths, **the photometer must incorporate suitable means to assure that no O<sub>3</sub> is generated in the cell by the lamp** and that at least 99.5% of the radiation sensed by the detector is 254 nm radiation. (This can be readily achieved by prudent selection of optical filter and detector response characteristics.) **The length of the light path through the absorption cell must be known with an accuracy of at least 99.5%...**”

**79 FR 75398 - Proposed revised 40 CFR Part 50, Appendix D, 4.3.1**

# Recommendations

1. EPA should revise its proposed NO-CL FRM UV monitor calibration specifications **to accommodate current SRP capabilities.**
2. EPA should develop **a new gravimetric primary O<sub>3</sub> reference standard** based on NIST NO/N<sub>2</sub> SRMs and GPT, **measured by infrared QC laser detection rather than UV photometry.** [see Chu et al. *IEEE Trans Instrum Meas* 56: 305-308 (2007)].
3. The **existing SRPs** should be calibrated by the new primary O<sub>3</sub> reference standard and **continue in use as a secondary transfer standard network supporting routine field monitor calibrations.**