Ozone and HO$_X$ Generation in Oxidation Flow Reactors

Researchers from Aerodyne Research Inc., University of Colorado at Boulder, and Pennsylvania State University Investigate the Effect of Varying λ = 185 and 254 nm Photon Flux Ratio on Radical Generation In Oxidation Flow Reactors

Edited from a write-up provided by Andrew Lambe of Aerodyne Research Inc.

The Problem: Oxidation flow reactors (OFRs) complement environmental smog chambers as a portable, low-cost technique for exposing atmospheric compounds to oxidants such as ozone (O_3), nitrate (NO_3) radicals, and hydroxyl (OH) radicals. OH is most commonly generated in OFRs via photolysis of externally added O_3 at λ=254 nm (OFR254) or combined photolysis of O_2 and H_2O at λ=185 nm plus photolysis of O_3 at λ=254 nm (OFR185) using low-pressure mercury (Hg) lamps. Whereas OFR254 radical generation is influenced by $[O_3]$, $[H_2O]$, and photon flux at λ=254 nm (I_{254}), OFR185 radical generation is influenced by $[O_2]$, $[H_2O]$, I_{185}, and I_{254}. Because the ratio of photon fluxes, $I_{185}{:}I_{254}$, is OFR-specific, OFR185 performance varies between different systems even when constant $[H_2O]$ and I_{254} are maintained. Thus, calibrations and models developed for one OFR185 system may not be applicable to another.

The Solution: To investigate these issues, we conducted a series of experiments in which $I_{185}{:}I_{254}$ emitted by Hg lamps installed in a Potential Aerosol Mass OFR (Aerodyne Research, Inc.) was systematically varied by fusing multiple segments of lamp quartz together that either transmitted or blocked λ=185 nm radiation (Figure 1). Lamp type A is an ozone-producing low-pressure Hg germicidal fluorescent lamp in which type 214 quartz that transmits λ=185 and 254 nm radiation is present along the entire 356 mm arc length. This lamp type is a standard component of the Aerodyne PAM OFR. The relative transmissivity of λ=185 nm radiation (T_{185}) in lamp type A is thus equal to 1. Lamp type B is equivalent to lamp type A with added segments of opaque heat shrink tubing applied to approximately 86 % of the arc length ($T_{185}{\approx}0.14$) to reduce I_{185} and I_{254} to levels below what is achievable using the ballast dimming voltage.

A different type of quartz is available (type 219) that blocks λ=185 nm and transmits λ=254 nm radiation (T_{185}=0). To cover the largest possible range of $I_{185}{:}I_{254}$, lamp types C, D, and E fused one segment each of quartz with T_{185}=0 and T_{185}=1 to provide reduced I_{185} relative to lamp type A while maintaining constant I_{254}. Finally, to evaluate the effect of lamp design at fixed T_{185} and I_{254}, lamp types F and G contain the same ratios of T_{185}=0 and T_{185}=1 quartz as types C and D, but with 5 and 13 total segments instead of 2 segments. These different designs isolate the effect of discretized λ=185 nm irradiation across the entire arc length of the lamp vs. having all λ=185 nm radiation
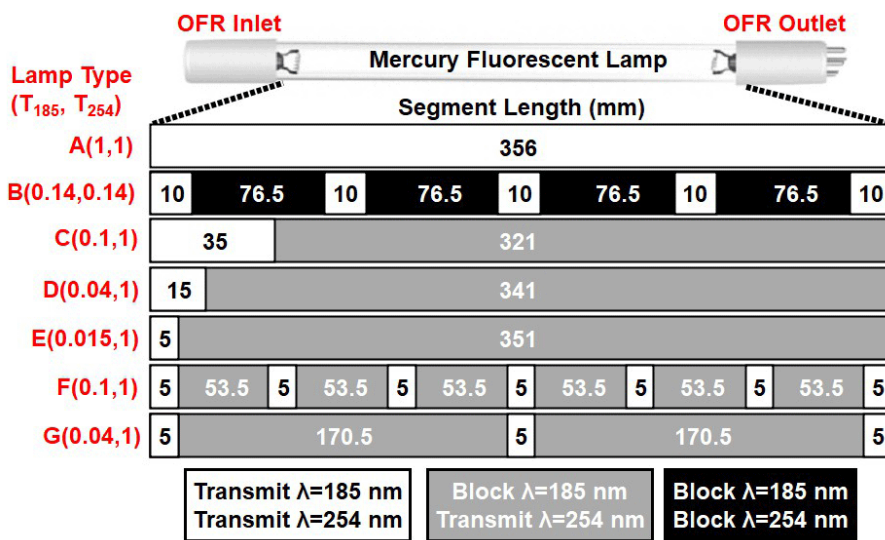
Figure 1. *Low-pressure Hg fluorescent lamp types used in this study. Each lamp type contains 356 mm of quartz material that either transmits both λ=185 and 254 nm radiation (white, T_{185}=1), blocks λ=185 nm and transmits λ=254 nm radiation (grey, T185=0), or blocks both λ=185 and 254 nm radiation (black, T185=0).*

near the entrance of the OFR. For each lamp type, a fluorescent dimming ballast was used to systematically vary the UV intensity in the reactor.

Radical generation was initiated from photolysis of H_2O and O_2 at $\lambda = 185$ nm and photolysis of O_3 at $\lambda = 254$ nm according to the reactions:

$$H_2O + h\nu_{185} \rightarrow H + OH$$
$$H + O_2 \rightarrow HO_2$$
$$O_2 + h\nu_{185} \rightarrow 2O(^3P)$$
$$O(^3P) + O_2 \rightarrow O_3$$
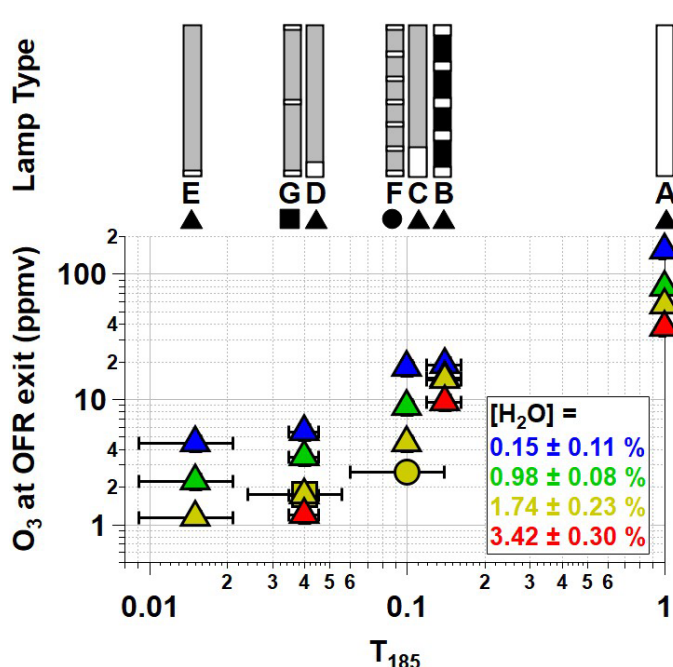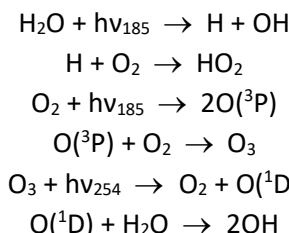$$O_3 + h\nu_{254} \rightarrow O_2 + O(^1D)$$
$$O(^1D) + H_2O \rightarrow 2OH$$

Figure 2. O_3 mixing ratio generated using OFR185 at $I_{254}=(3.5\pm0.7)\times10^{15}$ photons cm^{-2} s^{-1} (lamp types A and C–G) and $I_{254}=5.8\times10^{14}$ photons cm^{-2} s^{-1} (lamp type B) as a function of T_{185} and [H_2O]. Error bars represent $\pm1\sigma$ of replicate O_3 measurements and ±2 mm uncertainty in lengths of individual $T_{185}=0$ and 1 segments.

Across all experiments, [H_2O] ranged from 0.03 % (1 % RH at 25.3 °C) to 3.9 % (88 % RH at 30.9 °C). The integrated OH exposure (OH$_{exp}$), defined here as the product of the average OH concentration and the mean OFR residence time (τ_{OFR}), was characterized by measuring the decay of carbon monoxide and/or sulfur dioxide tracers. The O_3 mixing ratio at the exit of the OFR was measured with a UV ozone analyzer (106-M, 2B Technologies).

Results: Figure 2 shows [O_3] measured at the exit of the OFR as a function of T_{185} with each lamp type operated at maximum UV output. At fixed [H_2O], [O_3] increased as a function of T_{185} due to faster O_2 photolysis at $\lambda = 185$ nm. At fixed T_{185} and I_{254}, [O_3] decreased with increasing [H_2O] due to faster $O(^1D)+H_2O$ reaction rate following O_3 photolysis at $\lambda=254$ nm.

At [H_2O]=1.74 % and T_{185}=0.04 and 0.1, Fig. 2 shows that [O_3] generated using lamp types D and G was approximately 1.7 and 1.8 ppmv; here, lamp type D had one 15 mm quartz segment with T_{185}=1, whereas lamp type G had three 5 mm quartz segments with T_{185}=1. Thus, we hypothesize that the OFR-volume-averaged I_{185} is sufficient to describe associated HO$_x$ production for these cases.

Taken together, these measurements were used to develop a set of empirical OH$_{exp}$ estimation equations that parameterized OH$_{exp}$ as a function of OH reactivity, [H_2O], [O_3], τ_{OFR}, and I_{185}:I_{254}. This approach provides a simpler alternative than detailed photochemical models for experimental planning and analysis. Future work will investigate the sensitivity of NO$_x$-dependent, OH-initiated oxygenated volatile organic compound and secondary organic aerosol formation processes to I_{185}:I_{254}.

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https://acp.copernicus.org/articles/20/13417/2020/

The 2B Tech Instrument's Role: The Model 106-M was used to measure the ozone mixing ratio at the OFR exit produced by each of the different types of lamps. The instrument's wide measurement range of 0-1,000 ppm allowed for one instrument to be used to measure the vastly different ozone output from each of the lamps. The high accuracy of the Model 106-M enabled the researchers to be completely confident in reaching their conclusions about [O_3] either increasing or decreasing depending on which experimental variables were held constant.

The Model 106-M Ozone Monitor

The Bottom Line: If you have an industrial application that requires ozone measurements with high accuracy and precision, then the Model 106-M is right for you. With a measurement range of 0-1,000 ppm the instrument is widely used for university research studies, to measure ozone off-gas in water treatment plants, in food sanitation/cold storage applications, and in various other industrial processes. The instrument can either be provided in a benchtop enclosure for laboratory studies, in an Industrial/NEMA wall-mount enclosure for water treatment and other industrial applications, or as an OEM for integration into an existing system. All versions of the Model 106-M are provided with relays, have various data output options (RS232, USB, 0-2.5 V, 4-20 mA), and have the ability to provide ozone measurements with a fast response time (4 seconds). Please Contact 2B Technologies to discuss using the Model 106-M for your application.