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APPLICATION NOTE 2

Partitioning the Optical Extinction due to Gases and Aerosols that Determine Visibility

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Introduction

Visibility has become a key component of air quality and is regulated in many areas by laws such as the EPA Clean Air Act and Regional Haze Rule. As a result, monitoring networks, like the Interagency Monitoring of Protected Visual Environments (IMPROVE) network, have been established to measure visibility in regulated areas. Typically, visibility is calculated by estimating the optical absorption and scattering of both gases and aerosols. In this scheme, filter-based sampling is coupled with relative humidity measurements to estimate the optical extinction due to aerosols, the Rayleigh scattering of air is calculated from ambient temperature and pressure, and the optical absorption of air is calculated from nitrogen dioxide (NO_2) concentration (if available)[1].

In this brief application note, we demonstrate how the Nikira Labs OEA-532 Optical Extinction Analyzer can be used to determine and partition the optical extinction due to aerosols and gases.

Experimental Setup

Two OEA-532 analyzers (OEA #1 and OEA #2) were placed adjacent to one another in an urban environment. The OEA utilizes cavity ringdown spectroscopy to measure the optical loss difference between a cavity completely filled with purge gas and a cavity partially filled with purge gas and partially filled with ambient, aerosol-laden air. The former is measured by closing the cavity and allowing for the mirror purge gas to completely displace the sample inside the cavity. The latter is measured by opening the cavity and allowing for a portion of the cavity to be exposed to ambient, aerosol-laden air (open-path sampling). The difference between the open and closed readings is thus the increase in optical loss (optical extinction) due to adding ambient

[1] Pitchford, M., Malm, W., Schichtel, B., Kumar, N., Lowenthal, D. and Hand, J., 2007. Revised algorithm for estimating light extinction from IMPROVE particle speciation data. *Journal of the Air & Waste Management Association*, *57*(11), pp.1326-1336.

air and aerosols (Figure 1). If filtered, ambient air is used as the purge gas (typical configuration), the difference between the open and closed values is just the optical extinction due to ambient aerosols (given in Mm^{-1} and due to both aerosol scattering and absorption).

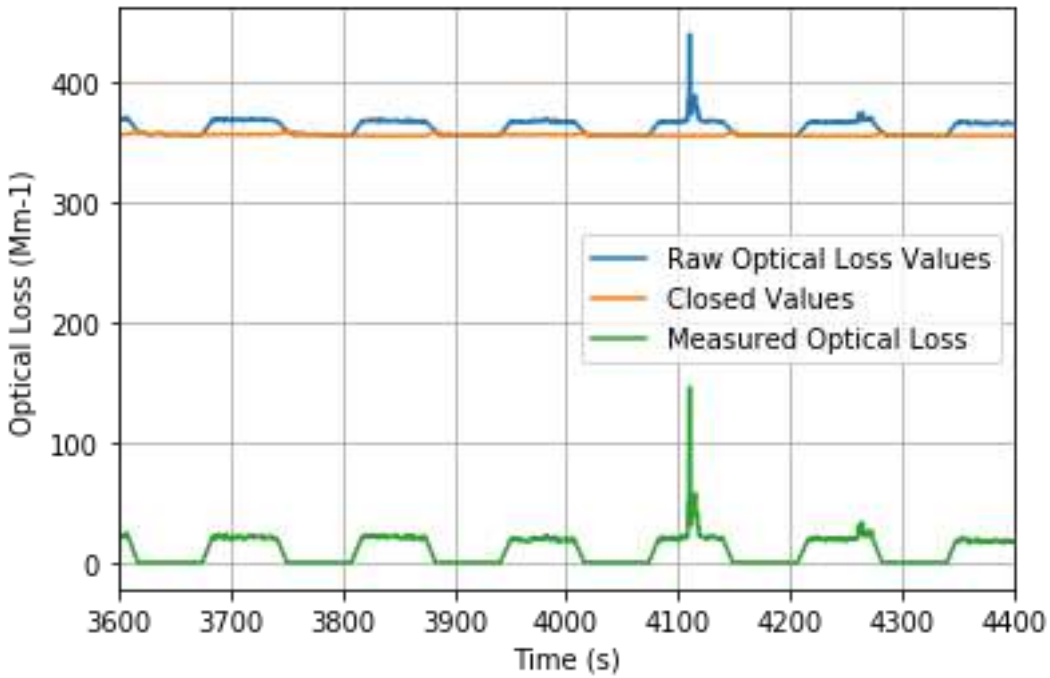

Figure 1: **The OEA alternates between measurements of purge gas (closed values) and ambient air. The closed values (orange) are then subtracted from the raw, measured optical loss values (blue) to determine the measured optical loss due to the ambient air sample (green)**

OEA #2 was operated in this typical configuration (filtered ambient air purge) continuously for 16 hours, and the optical extinction due to aerosols was determined in 2-minute averaging periods (1 Hz data averaged for 120 seconds). For OEA #1, the purge gas was switched between filtered ambient air, helium, and filtered ambient air passed through Drierite. The resulting measurements are shown in Figure 2.

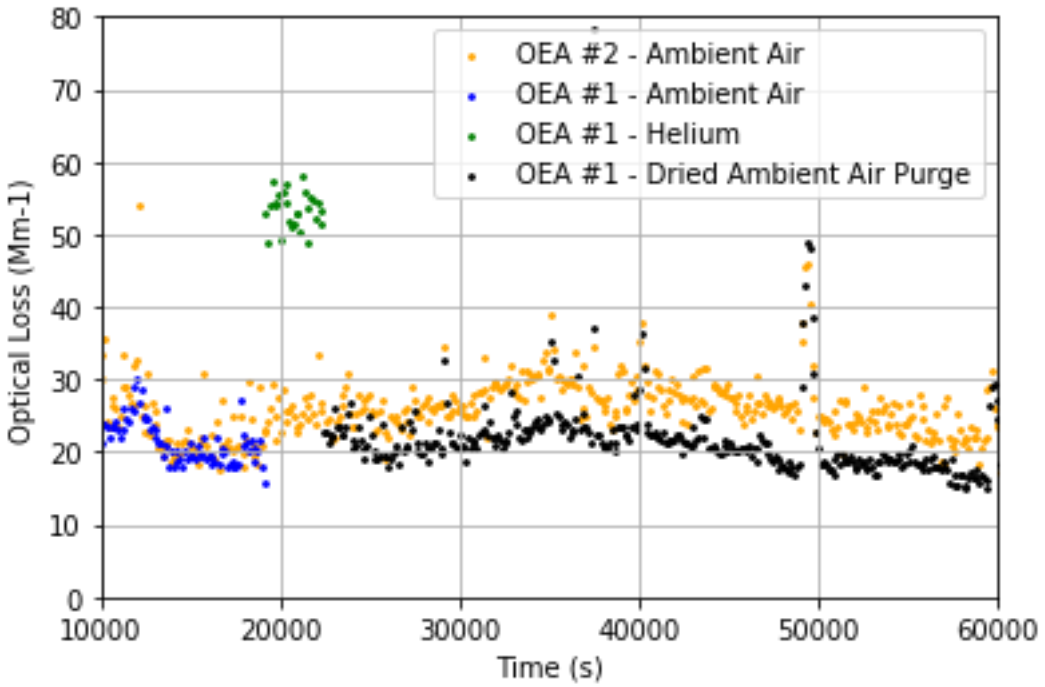

Figure 2: **OEA #2 continuously measured the optical loss difference between filtered ambient air and unfiltered ambient air to determine the optical extinction due to aerosols. By varying the purge gas on OEA #1, the optical loss could be further partitioned into gas-phase and aerosol components.**

Note that, when both instruments are purged using filtered ambient air, the measured optical extinction is 20 – 30 Mm^{-1} and the two analyzers agree to within 1 – 2 Mm^{-1}. This value is consistent with very clear conditions and maximal visibility readings from local weather stations. When the purge gas in OEA #1 is switched to helium (negligible optical extinction at 532 nm), the measured optical extinction increases to ~55 Mm^{-1}. Thus ~55 Mm^{-1} of optical loss is due to scattering and absorption by ambient air and aerosols. Given that the ~25 Mm^{-1} of optical loss is due to the aerosols (OEA #2 reading), the other 30 Mm^{-1} must be due to scattering and absorption in the ambient air. Given that the Rayleigh scattering of dry air is ~12 Mm^{-1}, the remaining 18 Mm^{-1} is due to the absorption (and scattering) of other air constituents. We attribute most of this optical extinction to light absorption by NO_2. Using the published value for the NO_2 absorption cross section at 532 nm[2], the optical loss due to NO_2 is 0.39 Mm^{-1}/ppb. Thus, for a typical urban, roadside NO_2 concentration of 30 – 40 ppb, the optical extinction due to NO_2 alone is approximately 12 – 16 Mm^{-1}. Note that, by passing the ambient air through Drierite prior to filtration, the measured optical loss difference is only ~5 Mm^{-1}. This is likely due to some NO_2 loss in the Drierite cartridge with a small contribution due to water vapor removal (~ 1 Mm^{-1} in accordance with HITRAN simulations).

[2] Osthoff, H.D., Brown, S.S., Ryerson, T.B., Fortin, T.J., Lerner, B.M., Williams, E.J., Pettersson, A., Baynard, T., Dubé, W.P., Ciciora, S.J. and Ravishankara, A.R., 2006. Measurement of atmospheric NO2 by pulsed cavity ring-down spectroscopy. *Journal of Geophysical Research: Atmospheres*, *111*(D12).

Further Work

This work can be extended and modified in a variety of ways, including:

- Using a single OEA and switching its purge inlet between ambient air and helium
- Switching between filtered ambient air and filtered ambient air with NO_2 removal to quantify NO_2