# Real-time Mobile Measurement of Aerosol Functional Groups in the Mid-infrared Using an Ultra-long Path, Multi-pass Cell

Nikira Labs Inc.
Science Made Simple

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## Motivation

Atmospheric particulate matter (PM) in urban environments is a key concern for two primary reasons. First, high PM load is associated with a wide range of negative health impacts including cancer, respiratory issues, and cardiovascular disease. Second, PM impacts climate and surrounding ecosystems by changing albedo and seeding local and downwind precipitation patterns.

PM is simplistically characterized by particle counts in size ranges (e.g., PM2.5), however, for complex urban aerosols, which often have large organic content, this metric is insufficient to identify and mitigate sources. For this reason, identification of molecular classes present within PM can aid source apportionment, proper understanding of oxidative potential, and the relation of these properties to epidemiological health impacts. Additionally, because PM sources are often localized and disproportionately impact disadvantaged communities, improvements in PM characterization that can finely resolve source types in both spatial and temporal dimension are critical to reducing exposure. Finally, wildfire smoke increasingly impacts health as fires encroach on the wildland urban interface, the severity of which is affected by the PM oxidative state.

## Technology

Nikira Labs has developed a sensor that measures the mid-infrared (MIR) optical absorption spectrum of aerosols. The instrument utilizes Nikira's non-paraxial multipass cell (**NP-MPC**) to achieve optical path lengths in excess of 400 m. The NP-MPC was coupled to a broadly tunable MIR laser to measure aerosol functional groups over the very large spectroscopic range of 7.6-10.4 µm. Further, the high signal to noise ratio made possible by the long path length and high transmission of Nikira's NP-MPC allows the prototype sensor to measuring aerosol absorption spectra at 1 Hz making it suitable for mobile measurements or stationary field measurements with a much higher temporal resolution than is currently possible with conventional filter based, FTIR techniques.

### Non-Paraxial Multi-pass cell

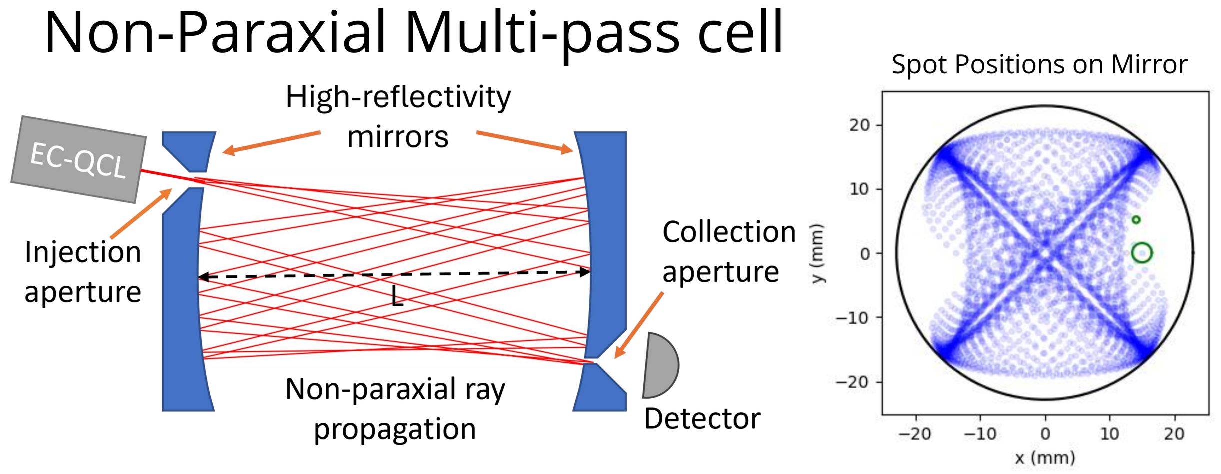


**Figure 1. (left)** Schematic diagram of the Non-Paraxial Multi-pass Cell (NP-MPC). The light source is injected through a hole in the first mirror at a steep angle and collected through another hole in the opposing mirror. **(right)** This plot shows the landing locations of the intracavity reflected rays. The position of the injection/collection holes are shown as green circles. The first ray is introduced through the larger injection hole. The steep angle and specific cavity configuration induces pattern precession that allows full use of the mirror surface with many thousands of intracavity reflections.

### Zero Referencing

The presence of gas phase absorptions makes the identification and analysis of aerosol absorptions difficult or impossible with most long path instruments (e.g., long-path FTIR). Nikira's instrument features a novel, patent pending referencing mechanism to minimize the impacts of ubiquitous gas phase absorptions, such that the analysis can focus on extracting aerosol chemical bond properties.

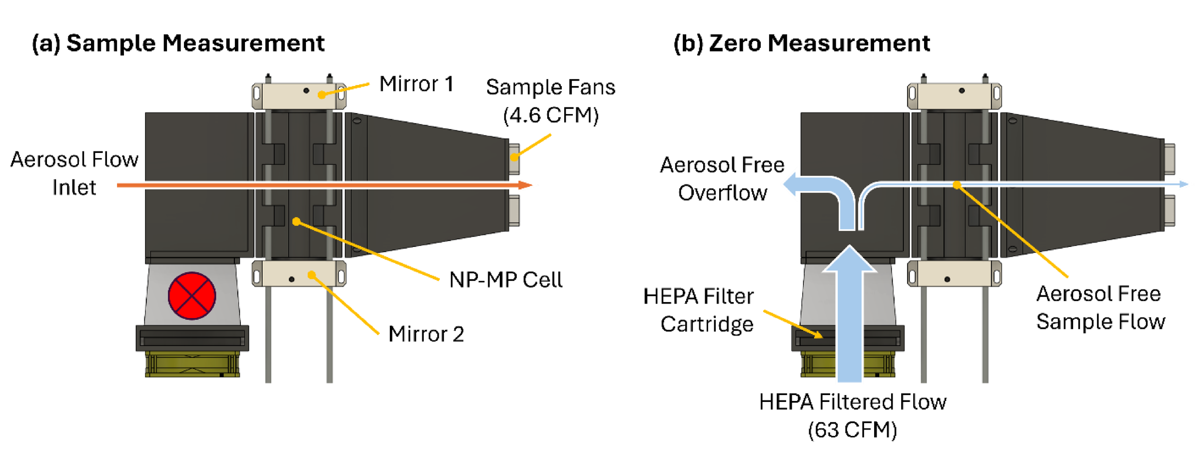


**Figure 2.** Nikira's patent pending aerosol zero referencing method to remove the contribution from gas phase absorbers. **(a)** During sampling, fans draw unconditioned air directly through the sample cell. **(b)** During zero referencing, HEPA filtered air overflows the inlet to provide an aerosol free air sample that retains the gas phase absorbers.

## NP-MP Cell Prototype

Nikira has developed detailed simulation tools and several fabrication methods to reliably predict cavity configurations that will have an ultra-long path and to align those NP-MP cavities in the lab. Critical to this alignment process is an accurate measure of path length. Because the NP-MPC has paths of hundreds of meters, the time delay of the optical pulse through the cavity is directly measurable and can be used to determine path length.

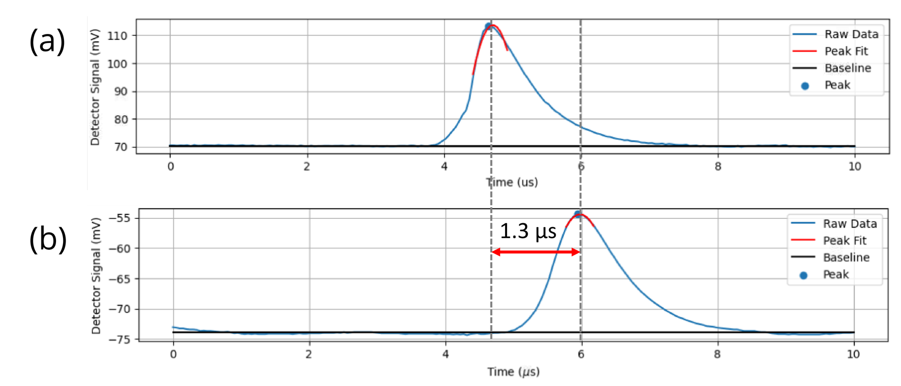


**Figure 3.** (a) Measured detector signal from a single pass laser pulse occurs at 4.7 µs. (b) Measured detector signal from an ultra-long path NP-MPC pulse is delayed by 1.3 µs, which is equivalent to a path length of 390 m.

The pulse delay can be used to evaluate the cavity performance vs. injection angle and select an optimal alignment.

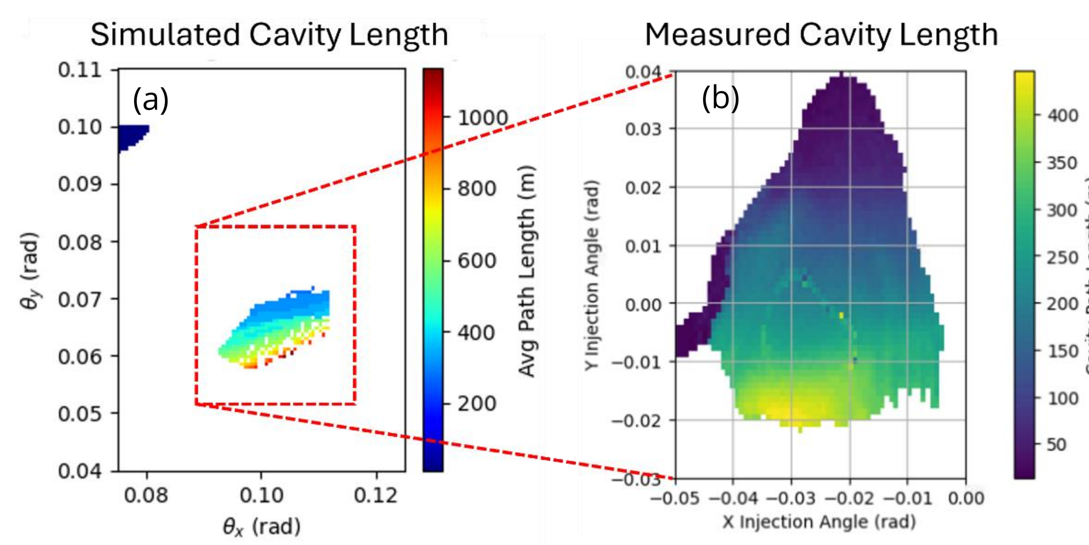


**Figure 4. (a)** Simulated NP-MPC path length vs. injection angle showing a large island of stability. **(b)** The experimentally measured path length for the same cavity configuration with measured path lengths of greater than 400 m. Note the very large angles involved – these angles are easy to achieve and can be stably held by standard optical systems which makes the alignment very robust to environmental perturbation.

### Breadboard Prototype

Nikira has fabricated a breadboard prototype for lab and field testing. It includes an open duct that draws un-conditioned sample air through the cell at ~6 CFM to achieve the very fast time response needed for mobile measurements.

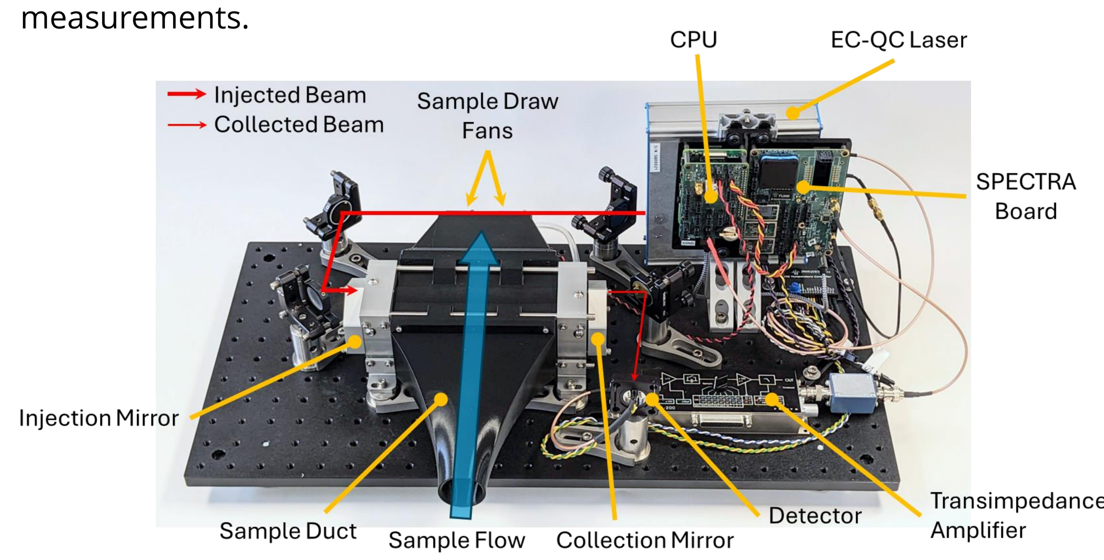


**Figure 5.** Image of the breadboard prototype. The system uses Nikira's custom electronics suite along with several off the shelf parts.

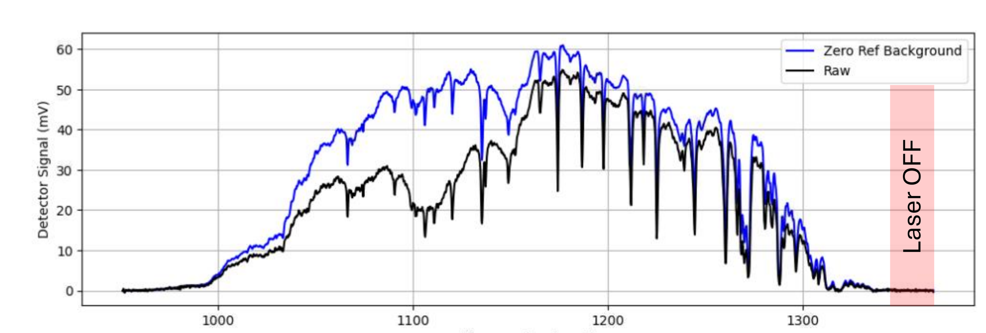


**Figure 6.** An example, raw measurement of aerosol absorption. The transmitted power measured when zero referencing is shown in blue. The black trace shows the transmitted power detected when ~200 µg/m³ of ammonium sulfate aerosol are introduced into the cavity. The detector baseline is determined when the laser is off (red).

## Lab Aerosol Measurements

Nikira has extensively tested the mid-infrared aerosol (MIRA) system on laboratory generated aerosols. These aerosol sample streams were generated with nebulizers, fluidized beds (for non-soluble aerosols) and biomass burning and introduced into Nikira's aerosol chamber for sampling by the MIRA instrument. Nikira has measured propylene glycol, ammonium sulfate, aluminum sulfate, magnesium sulfate and smoke from incense and several local tree species.

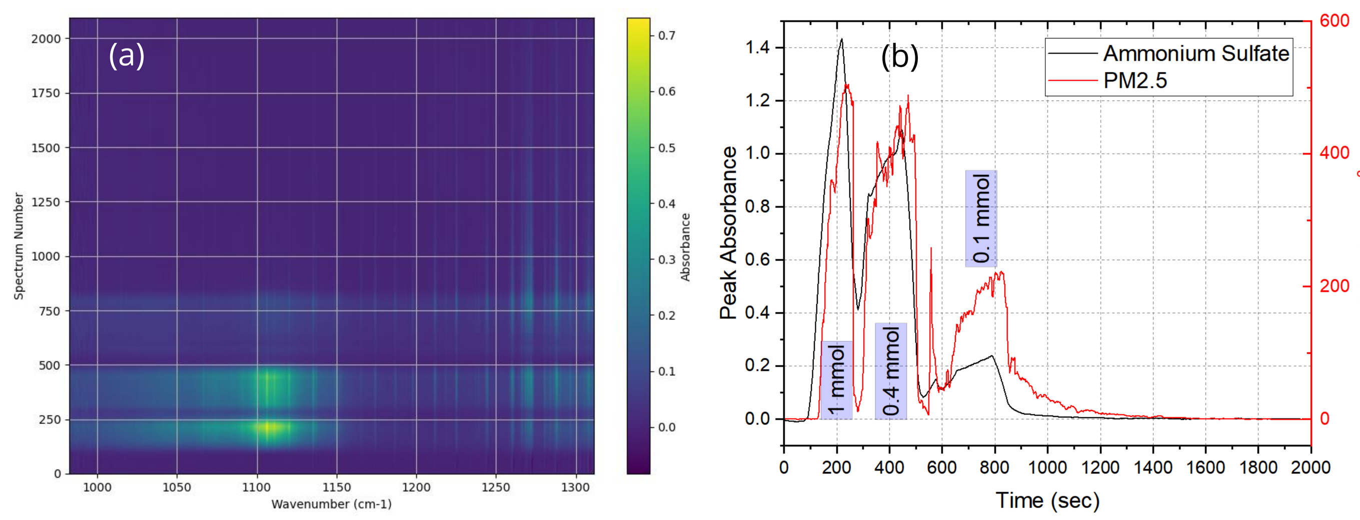


**Figure 7.** Ammonium sulfate aerosol generated by nebulizer. **(a)** measured spectra vs time (vertical axis). Sample number is equivalent to seconds. **(b)** The measured peak absorption vs. PM2.5. The nebulizer consumes 400 µL/min of solution and was configured with a carrier flow of 1 SLPM of zero air. The ammonium sulfate solution was initially 1 mmol, then reduced to 0.4 mmol and 0.1 mmol in steps. This configuration produced 200 – 500 µg/m³ of aerosol in the chamber.

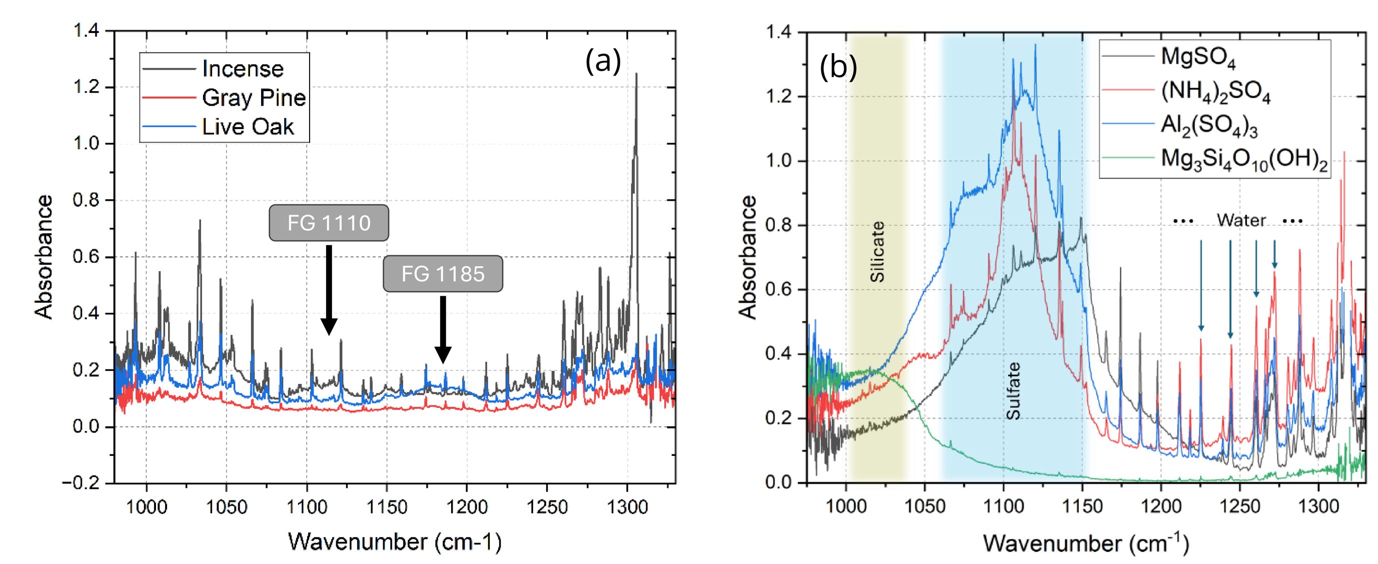


**Figure 8.** Measured aerosol spectra for various types. **(a)** Biomass burning aerosols. Note the very different structure from different smoke types. **(b)** Mineral and sulfate aerosols. The functional groups around the primary sulfate absorption provide easy differentiation between aerosol types. Water absorption is present due to its use as a carrier for the nebulizer.

### Functional Group Fitting

The functional groups present in the measured aerosol absorption spectra can be extracted by fitting the various functional group absorption peaks with a combination of Gaussian peaks[1]. The capability to also measure and quantify gas phase species with ppb resolution is a unique tool that can be used to study wildfire smoke with high spatial resolution.

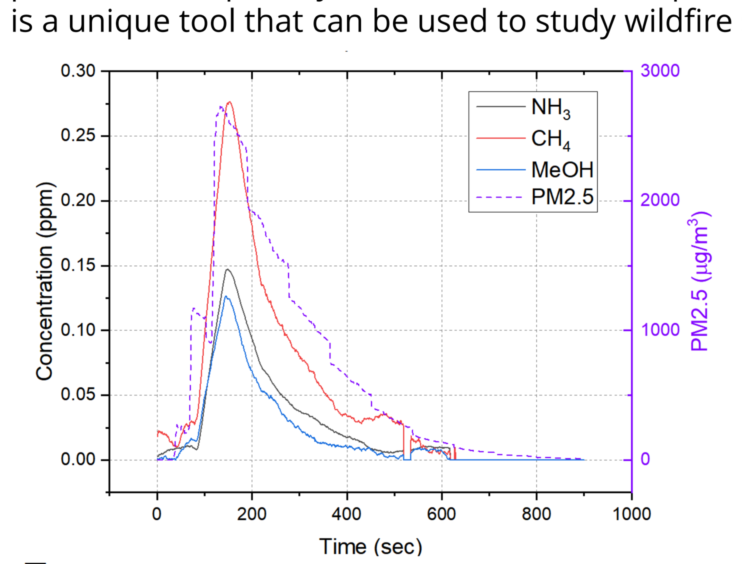


**Figure 9.** Gas phase species from Live Oak Leaf Smoke. In these measurements, the reference zero air is pulled from outside the aerosol chamber so that the gas phase combustion byproducts are included in the measured spectra. These gas phase absorptions are then included in the fit to provide additional information about the measured spectrum. $NH_3$, $CH_4$ and methanol are all present in easily detectable concentrations. The independently measured PM2.5 is shown in purple and shows a matching trend.

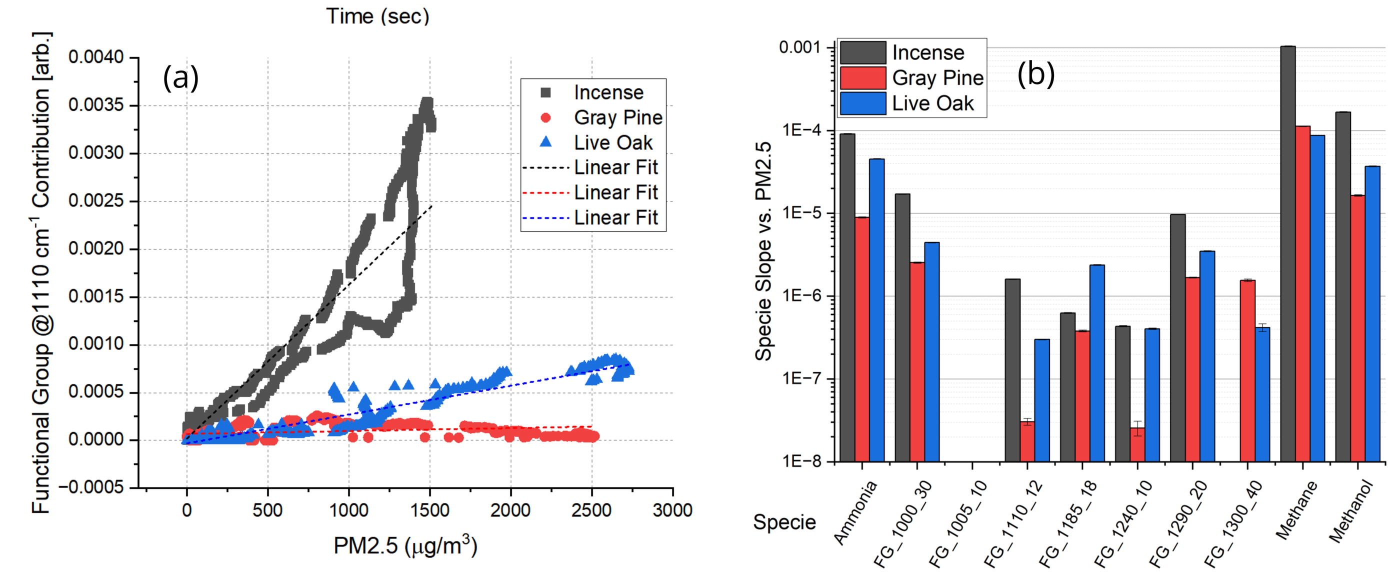


**Figure 10. (a)** The generation rate of functional groups vs. PM2.5 are very different for different biomass burning aerosols and can be used to fingerprint sources. Fitting functional group amplitude vs PM2.5 yields a characteristic slope. **(b)** Comparison of functional group slopes for three biomass burning aerosol types. Each identified functional group is indicated by FG, the center wavenumber and the gaussian width.

## Mobile Measurements

Nikira has demonstrated the MIRA system's ability to make mobile aerosol measurements from several aerosol source types.

The first deployment measured wildfire smoke from the Coffeepot fire during the summer of 2024. This fire was located in the Sierra Nevada mountains of southern California and burned approximately 14,000 acres of short grass, chaparral and timber. During the burn, stagnant overnight conditions lead to smoke settling into low lying valleys with concurrent clearing of particulate matter from higher altitudes.

This altitude stratification allowed Nikira to easily transit into and out of the smoke plume by driving to higher altitudes.

In addition to broad aerosol absorption associate with AQI, we also observed substantial methanol concentrations correlated with smoke density[2].

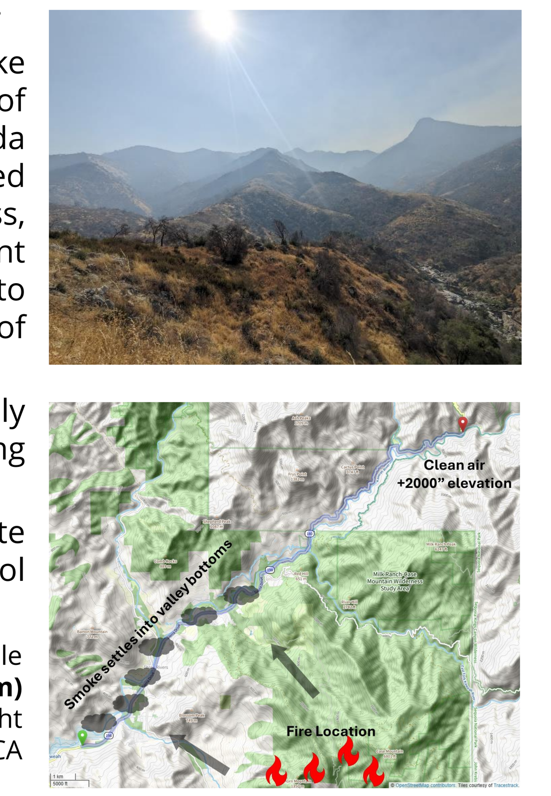


**Figure 11. (top)** Photo showing the air quality at a middle altitude where the AQI was approximately 120. **(bottom)** Diagram showing the fire location and direction of overnight smoke settling. The mobile survey path from Three Rivers, CA to Sequoia National Park is also shown.

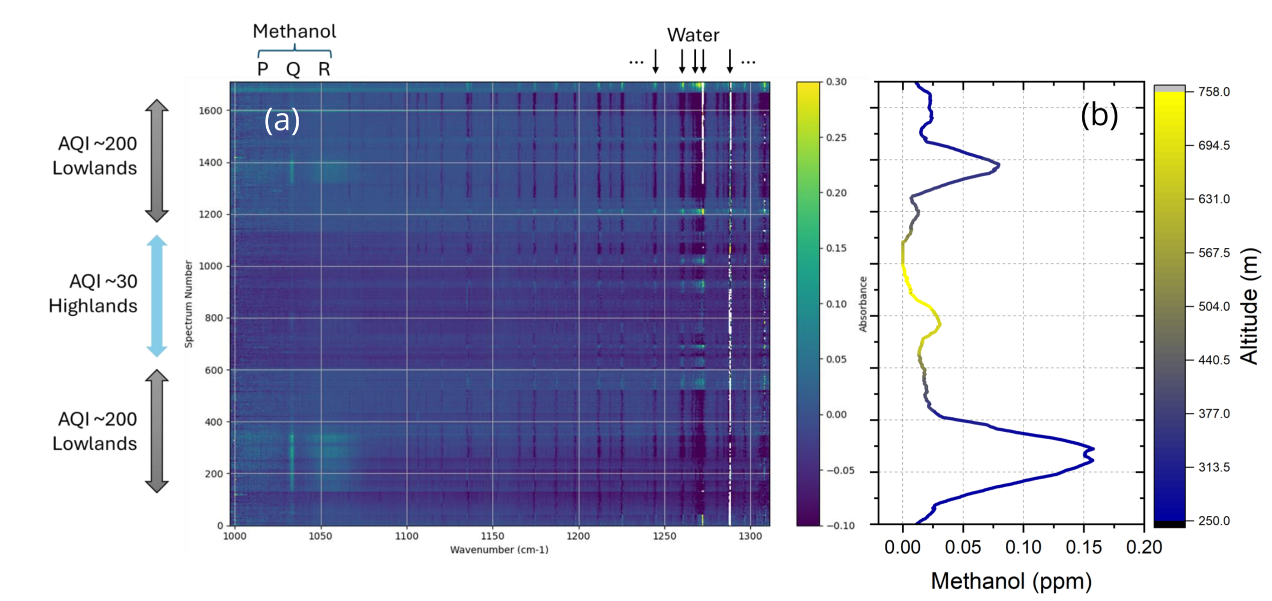


**Figure 12.** Absorption spectra of smoke aerosols from the 2024 Coffeepot fire. **(a)** Spectra measured vs time (sample number is equivalent to seconds). The broad band absorption decreases when transiting to cleaner highland air. Methanol and water lines are labeled. **(b)** The methanol concentration extracted from fitting the spectra is correlated with the low AQI, smoky air.

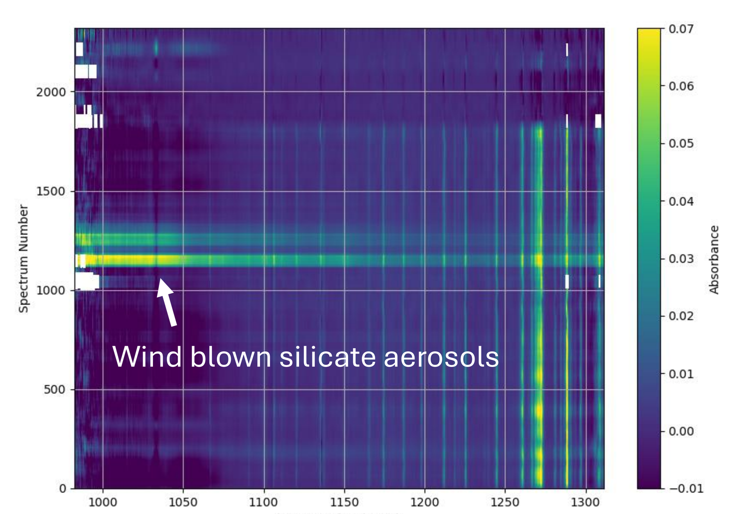


**Figure 13.** Absorption spectra measured at a cement distribution plant. The two prominent horizontal bands are measured cement (silicate) aerosol pollution from wind blown events. MIRA is exceptionally sensitive to silicates ad these PM2.5 concentrations have a mass load of only ~10 µg/m³.

The prominent vertical lines are water absorption caused by zero referencing taken in a slightly dryer location.

## Conclusions

- Nikira Labs has developed a new non-paraxial multi-pass cell (**NP-MPC**) technology with **>400 m path length** and **robust alignments**
- NP-MP cells can measure aerosols from a mobile platform at mass loads of <100 µg/m³
- Measurement of several aerosol types were demonstrated with Nikira's aerosol chamber
- Real-time, mobile measurements of wildfire smoke and cement plant pollution were demonstrated

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[1] Reggente, Matteo, Ann M. Dillner, and Satoshi Takahama. "Analysis of functional groups in atmospheric aerosols by infrared spectroscopy: systematic intercomparison of calibration methods for US measurement network samples." *Atmospheric Measurement Techniques* 12.4 (2019): 2287-2312.
[2] Paton-Walsh, Clare, et al. "Measurement of methanol emissions from Australian wildfires by ground-based solar Fourier transform spectroscopy." *Geophysical Research Letters* 35.8 (2008).