Ammonia Measurements From the NSF/NCAR C-130 Research Aircraft Using a TILDAS Spectrometer with Active Passivation During the WE-CAN Field Campaign

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Introduction

The Western Wildfire Experiment for Cloud Chemistry Aerosol Absorption and Nitrogen (WECAN) is an aircraft campaign focused on measuring the emissions of wildfire smoke in the western U.S. WE-CAN deployed an extensive suite of instrumentation on the NSF/NCAR C-130, and the aircraft was based in Boise, ID for two months during summer 2018. Ammonia (NH3) is a key molecule to measure in order to understand nitrogen chemistry in wildfires. NH3 was measured on the aircraft using a quantum cascade tunable infrared laser direct absorption spectrometer from Aerodyne Research (QC-TILDAS) optimized for use on the C-130. The large dipole moment of NH3 is a basis for its notorious ability to interact with polar molecules on sampling surfaces. This ‘stickiness’ increases instrument time response and can compromise fast-in situ measurements. To mitigate this ‘stickiness’, several methods were implemented during WECAN to improve or maintain a sufficient time response. These included: 1) using a treated aircraft inlet block and an inertial inlet, 2) coating with high sample flow rate (>10 sccm) and 3) employing active continuous passivation of sampling surfaces with 1H,1H-perfluoroctylamine. This molecule is a strong perfluorinated base that prevents adsorption of water and other basic species allowing NH3 to easily flow through the inlet to the TILDAS detector. Here, we report on how those techniques were integrated into the instrument system and their benefits with respect to in-situ sampling of NH3 during WE-CAN. NH3 measured with and without passivant addition are compared and contrasted.

Instrument configuration for flight

The detector is a QC-TILDAS trace gas monitor from Aerodyne Research Inc. This instrument employs direct absorption spectroscopy in the infrared (~967 cm⁻¹) to measure NH3. The optical path length of the spectrometer is 76 m. The optical cell is typically held at a constant pressure of 40 Torr and a constant temperature of 300 K.

Inertial Inlet allows for filter-less separation of aerosols from the sample stream

Thermal decomposition of ammonium species (e.g. NH4NO3) could result in a measurable gas phase NH3 signal. Inertial inlet can efficiently separate particles with sizes greater than 300 nm without a filter. Particulate species involving NH4+ typically range from 100 μm and 1 μm in size. Thus, we expect these particles to be sufficiently filtered by the inertial inlet.

Active Continuous Passivation with a Strong Base Improves Time Response

This is a picture of the installed impinger on the aircraft

1H,1H-Perfluoroctylamine is injected directly into the sample stream as close as possible to the inlet tip. The amine group sticks to water and other basic species adsorbed to sampling surfaces and presents a nonpolar tail to other molecules (like NH3) in the ambient sample stream. The passivating coating prevents further adsorption of water and NH3, and thus allows NH3 in an ambient air sample to pass through without sticking.

A double exponential decay function of the form, \(NH_3(t) = y_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}\), is used to quantify instrument time response. This equation represents the NH3 mixing ratio (in ppb) as a function of time (in seconds) and contains two time constants (\(\tau_1\) and \(\tau_2\)) that represent the two contributing factors to the time response. \(\tau_1\) is typically smaller and represents the gas exchange rate through the instrument flow path. \(\tau_2\) is typically larger and is related to the sticking of NH3 on sampling surfaces.

Time response profiles are created at 10 Hz data collection rate by turning the calibration gas off while overblowing the inlet tip with NH3-free air. As shown below, when samples are relatively clean, passivant only results in a small improvement in time response.

Instrumental Coefficient Values

<table>
<thead>
<tr>
<th>Sample With Passivant</th>
<th>Sample Without Passivant</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>0.460</td>
</tr>
<tr>
<td>A1</td>
<td>104.0</td>
</tr>
<tr>
<td>A2</td>
<td>0.662</td>
</tr>
<tr>
<td>(\tau_0)</td>
<td>8.17</td>
</tr>
<tr>
<td>B0</td>
<td>41.28</td>
</tr>
<tr>
<td>D0</td>
<td>0.0728</td>
</tr>
<tr>
<td>(\tau_2)</td>
<td>41.82</td>
</tr>
</tbody>
</table>

In-flight Precision and Detection Limit

Calculated precision and detection limit for 1Hz and 10Hz acquisition

1 Hz Precision: 0.0594 ppb

1 Hz Detection Limit: 0.178 ppb

10 Hz Precision: 0.440 ppb

10 Hz Detection Limit: 1.32 ppb

Passivation ensures collection of high-quality, fast-response NH3 data in flight

Concentrated animal feeding operations (CAFOs) are a large source of NH3 in the Colorado Front Range. Missed approaches at Greeley Regional Airport during WE-CAN test flights provided an opportunity to sample large and rapid changes in NH3 mixing ratios when operating the instrument with passivant (“pass”) and without passivant (“no pass”).

The time series from these missed approaches shows that passivant addition is less important for clean instruments (e.g., TF01 in 2018). In contrast, passivant addition makes a dramatic difference when added to a contaminated instrument system (e.g., very little NH3 was observed during the missed approach on TF03 in 2017 when no passivant was added).

Therefore, passivant addition is a unique technique for ensuring fast time response of mission critical instrumentation, especially when instrument sampling surfaces cannot be cleaned before flight.

In the case of the contaminated instrument system that could not be cleaned in time before flight, high accuracy and rapid response measurements of NH3 could still be collected by adding passivant (e.g., TF03 in 2017, when passivant is re-added to the instrument system).

References


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