Caltech Chemical Ionization Mass Spectrometer (CIMS) Measurements

INTEX-NA Data Review
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Instrument Block Diagram

Not to scale

Personal computer running real-time OS for all instrument control and data collection.
CIMS on DC-8
Measurements

- $\text{HNO}_3$ (0.5 s every 5 s)
- $\text{H}_2\text{O}_2$ (0.5 s every 5 s)
- Peroxyacetic Acid (PAA, $\text{CH}_3\text{C}(\text{O})\text{OOH}$)  
  - (0.5 s every 10 s)
- HCN (Flight #10 onwards)  
  - (0.5 s every 10 s)
Calibration

- Online HNO$_3$ calibration from perm tube held at constant temp.
- Online H$_2$O$_2$ calibration from urea-hydrogen peroxide held at constant temperature.
- Calibrations performed every hour.
Data Reduction

Concentration =
cts_signal_ion / cts_reagent_ion / F([H₂O]) * cal_factor

DLH-H₂O was used for ambient water concentrations.
H₂O₂ Measurements

• Compare well with URI HPLC/Fluorescence measurements
• There is an interference at high SO₂ and high H₂O, this only affects a small fraction of measurements.
CIT/URI $\text{H}_2\text{O}_2$ Comparison

Median: 0.98  
Mean: 1.10
Altitude Profile $H_2O_2$
HNO$_3$ Measurements

- Compared with UNH well overall but with certain differences: Altitude trend, low altitude trend, biomass burning plumes.
HNO₃ Comparison
Fast HNO$_3$ and H$_2$O$_2$ Measurements

• Interesting data within cloud, and around cloud/clear interfaces.
HNO₃ Measurements in Clouds, INTEX-NA flight of 040720

UTC-Time (hrs)

CIMS HNO₃ (ppt)
UNH-MC HNO₃ (ppt)
LaRC 5-25 micron particle count (/cc*20)

Various—see legend
H$_2$O$_2$ Measurements in Clouds, INTEX-NA flight of 040720

Various—see legend

- CIMS H$_2$O$_2$ (ppt)
- LaRC 5-25 micron particle count (/cc*50)
- DC-8 altitude (ft/2)
PAA Measurements

• Measured significant amounts of this molecule throughout mission, though it’s abundance was quite variable in space and time.
Significant concentrations observed. Mean: 213 pptv Median: 188 pptv

Falls off weakly with altitude.

Highly variable in space and time.
Does PAA come from the thermal decomposition of PAN?
PAA Lifetime?

• Atmospheric lifetime??
  – Photolysis: 3-4 weeks → J = 5 \times 10^{-7} \text{s}^{-1}
    (Orlando, et. al., 2003)
  – Reaction rate with OH has NOT been measured!!
    • Estimated to be 1-7 \times 10^{-12} from the measured rates of OH with HOOH, and CH_3OOH.
    • This gives lifetime of 2-12 days.
HCN Measurements

• Fair agreement with PANAK-HCN.
• CIT has high uncertainty at high H₂O mixing ratios as product ion has a water dependent mass analog interference, as well as decreased sensitivity at high H₂O.
• Fast HCN measurements may help understand complex air masses which may be a mixture of biomass burning and anthropogenic pollution.
HCN comparison versus altitude:

Median: 0.88
Mean: 0.98
HCN altitude profile:
Median: 279 pptv
Mean: 302 pptv
Areas of interest

• Understanding atmospheric importance of PAA: sources, sinks, and lifetime.
  – Utilize model to help constrain these
• Measurements of HNO$_3$ and H$_2$O$_2$ in clouds and around cloud/clear interfaces.
• Use of fast HCN measurements to help constrain ‘complicated’ air masses.