Measurements by the Caltech CIMS aboard the NCAR C-130 during MIRAGE and IMPEX

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Introduction

The Caltech chemical ionization mass spectrometer flew aboard the NCAR C-130 aircraft during MILAGRO and IMPEX which took place from March through May of 2006. MILAGRO focused measuring the impact of Mexico City pollution outflow on the local, regional and global scales, while the focus of IMPEX was with the long range transport and aging of pollution, specifically looking at the export of Asian pollution to the North America.

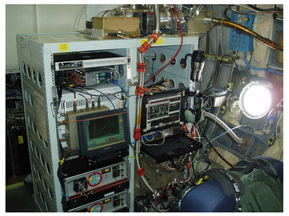


Figure 1: Caltech CIMS aboard NCAR C-130.

The CIMS measures atmospheric trace gasses (acids and hydroperoxides) by forming specific product ions through with a reagent ion directly in ambient air of the following reactions [Crounse, et al, 2006]:

A) $CF_3O^- + HA \rightarrow HF \cdot A^- + CF_2O$ (very acidic)
B) $CF_3O^- + HA + M \rightarrow CF_3O^- \cdot HA + M$ (less acidic)

The product ions seperated with a quadrupole and detected with a channelelectron detector operated in pulse counting mode.

During MIRAGE and IMPEX we flew two instruments: a single quadrupole instrument and triple quadrupole instrument. While the triple quadrupole has reduced sensitivity, it does allow seperation of mass analog product ions when operated in MS/MS mode. This afforded the first atmospheric CIMS measurements methyl hydrogen peroxide during IMPEX.

CIMS measurements for the following trace gases have been reported to the NASA archive:

- ✔ HNO_3
- ✔ H_2O_2
- ✔ peroxyacetic acid (PAA)
- ✔ methyl hydrogen peroxide (MHP)*
- ✔ SO_2
- ✔ formic acid
- ✔ acetic acid
- ✔ propanoic acid
- ✔ HCN

Measurements

With additional work the following CIMS measurements may be reported at a later time:

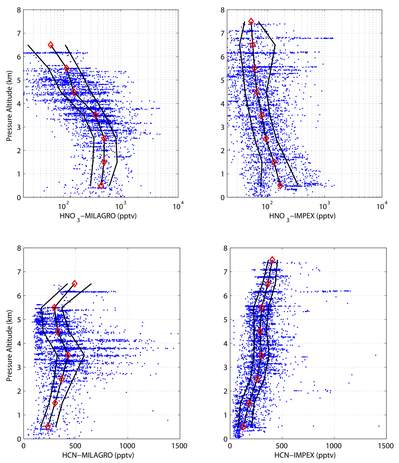
- ? peroxynitric acid (PNA)
- ? peroxynitrous acid (HONO)
- ? hydroxy acetone
- ? hydroxy methyl hydrogen peroxide (HMHP)

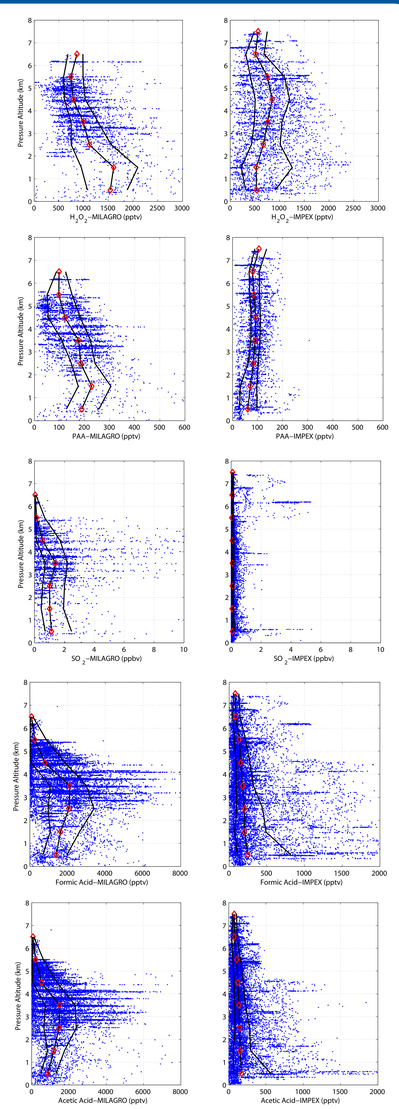
Instrument issues:

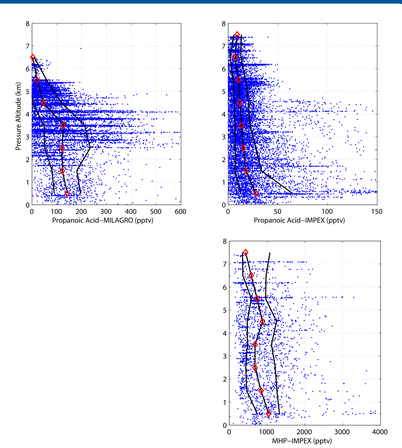
- No 'fast' water measurement on C-130. Knowing [H_2O] is crucial for determining sensitivity.
- Instrument backgrounds still limit the precision of several measurements, including SO_2 and the organic acids.
- Triple quadrupole instrument suffers from low sensitivity (factor of 4-10 less then single quad).

Data:

The following figures show column measurements for vaious species measured by the Caltech CIMS. Left-hand panels are the MIRAGE data, and right hand panels are the IMPEX data. The blue points are the original data, the red diamonds are the median values for 1 km bins, and the black lines are the upper and lower quartile medians.

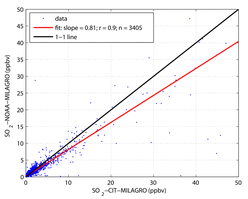


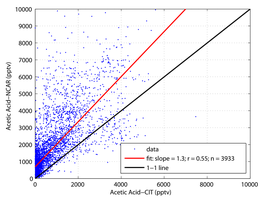




Intercomparisons

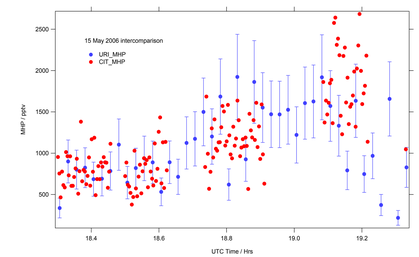
SO_2: NOAA instrument and CIMS instrument both on C-130 for MIRAGE campaign. Only data less than 50 ppbv was used for comparison.



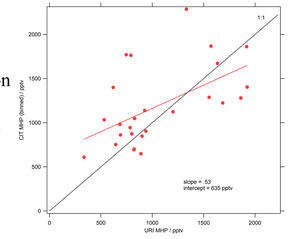


Acetic Acid: The NCAR PTRMS and the CIMS both measured acetic acid aboard the C-130. While some time alignment issues still exist, correction thereof will not bring these two measurements into agreement.

MHP: Intercomparison between URI instrument on the NASA-DC8, and CIMS instrument on the C-130, which took place May 15, 2006.



1-1 comparison for timeline shown above. Linear regression gives a slope of 0.5, but the data is quite noisey, and there is not much dynamic range.



Conclusions

While there is always room for improvement, the CIMS technique is a sensitive and fast technique for measuring a wide suite of interesting atmospheric trace gasses. We are continuing to improve the sensitivity of the triple quadrupole instrument, and improving the backgrounds for both instruments.

Acknowledgements

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