PANs Observations from the NOAA R/V Ronald H. Brown

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The peroxycarboxylic nitric anhydrides (PANs) were measured onboard the Ronald H. Brown during the TexAQS II/GoMACCS project by thermal decomposition chemical ionization mass spectrometry (TD-CIMS) and by gas chromatography with electron capture detection (GC/ECD). The relative abundance of peroxyacetic nitric anhydride (PAN) and peroxypropionic (PPN), and relatively low or absent peroxymethacrylic nitric anhydride (MPAN) confirms the result from TexAQS 2000, that biogenic isoprene is not a big contributor to the VOC chemistry in the Houston-Galveston area. There were a number of observations of plumes containing unusually high PPN/PAN ratios or the presence of peroxyacrylic nitric anhydride (APAN) indicating the influence of local petrochemical VOC sources.

PANs: Peroxycarboxylic Nitric Anhydrides

General Structure ; $RC(O)OONO_2$

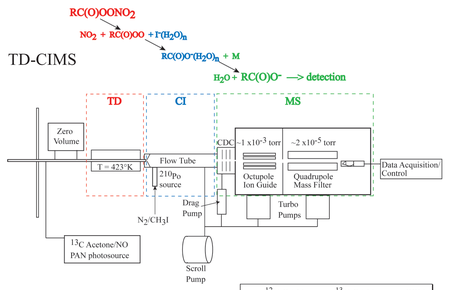
PAN = Peroxyacetic Nitric Anhydride; $CH_3C(O)OONO_2$
Anthropogenic VOCs, Isoprene

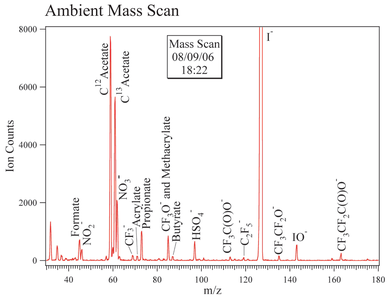
PPN = Peroxypropionic; $CH_3CH_2C(O)OONO_2$
Anthropogenic VOCs

MPAN = Peroxymethacrylic; $CH_2C(CH_3)C(O)OONO_2$
Isoprene

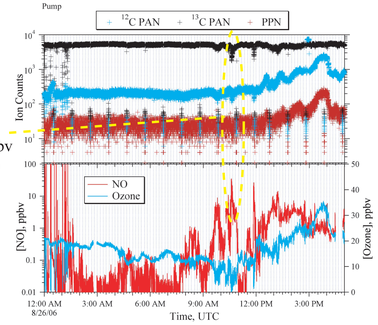
APAN = Peroxyacrylic; $CH_2CHC(O)OONO_2$
1,3-dienes, Acrolein

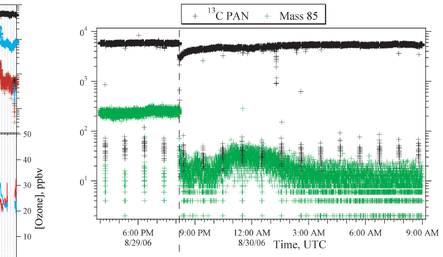
The mixture of PANs found in an airmass can tell us lot about the VOC-NOx photochemistry that has happened in that airmass. Since this is the same chmistry that forms O_3, it tells us what VOCs were involved in that process.





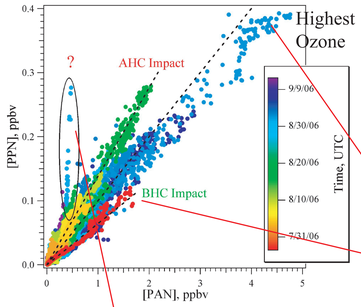
The CIMS can be impacted by plumes of high Nitric Oxide; for example, an NO mixing ratio of 35 ppbv caused x3 decrease in CIMS sensitivity. The ^{13}C-PAN ratio allows this effect to be corrected.

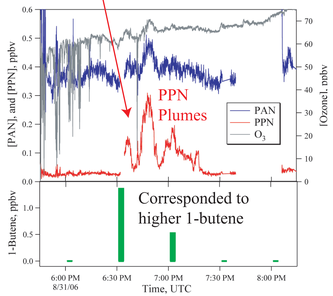


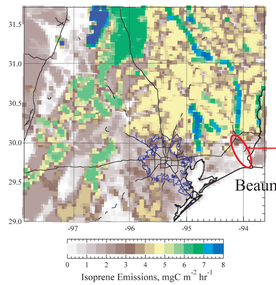


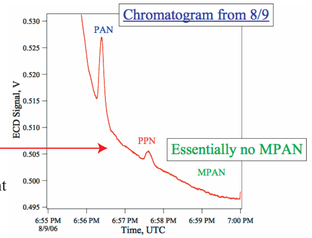
PFA inlet
CF_3O- Background

Kynar Inlet -{CH_2-CF_2}-
No m/z 85 Background





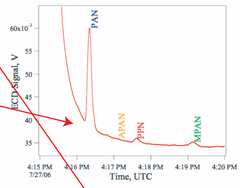


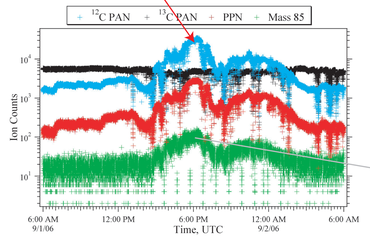


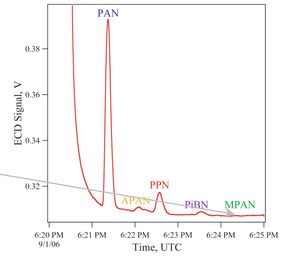
The transect into the Beaumont Area was an opportunity to get close to the higher isoprene emission areas, however, no MPAN was observed in those measurements, implying no significant isoprene impact while we were there.

The highest MPAN during the whole study was observed in Charleston S.C. at the start of the cruise.

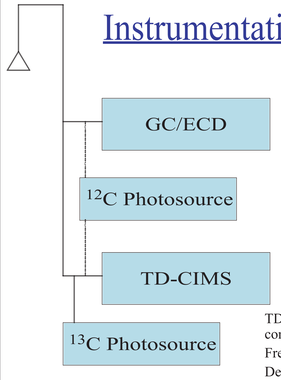
The highest O_3 event had some indication of a peak at m/z 85 however the GC showed this not to be MPAN. It was probably CPAN, {$CH_3CHCHC(O)OONO_2$}, a product of crotonaldehyde and 1,3-pentadiene.

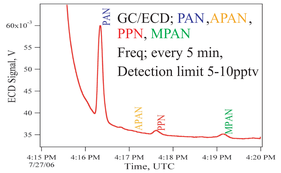


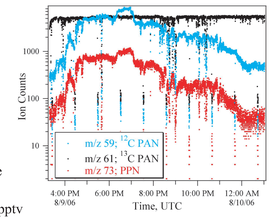




Instrumentation



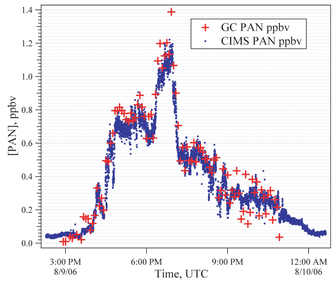


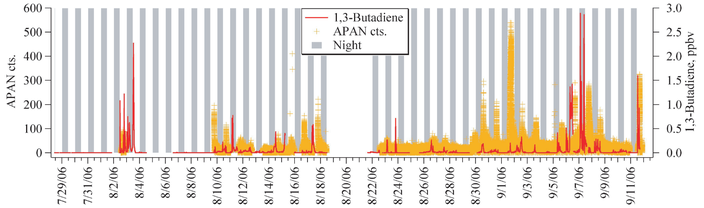


TD-CIMS; 43+ compounds possible
Freq; 1 Hz,
Detection limit, ~1 pptv

Comparison of the Two Methods

They agree within the combined uncertainties.





Sources of 1,3-butadiene drive the formation of APAN. However, the highest concentrations of 1,3, butadiene were observed as short-term plumes at night. APAN was only observed in significant quantities in the daytime as a result of photochemistry.

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Conclusions

The CIMS and GC techniques agree well for PAN (&PPN).

There is very little (if any) biogenic isoprene impact in the HGA (and Beaumont on 8/9), consistent with the 2000 findings.

Plumes of high PPN and APAN were observed at times, indicating local RVOC sources.

References

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