

FASTPEX - An Airborne Chemical Ionization Mass Spectrometer for Fast Measurement of Peroxyacetylnitrates.

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OBJECTIVES

A Chemical Ionization Ion Trap Mass Spectrometer for the detection of PANs (peroxyacetyl nitrates) with high temporal resolution will be developed for the new research aircraft HALO. PANs are important compounds of the reactive nitrogen family (NO_x). A number of different PAN homologous have been observed in the atmosphere. The most abundant is peroxyacetyl nitrate (PAN, CH₃-C(O)OO-NO₂) with atmospheric mixing ratios in polluted urban areas between a few pmol/mol and several tens of nmol/mol. Some of the less abundant PAN compounds include PPN (peroxypropionyl nitrate, C₂H₅-C(O)OO-NO₂) & MPAN (peroxymethacryloyl nitrate, CH₂=C(CH₃)C(O)OO-NO₂).



IMPORTANCE FOR ATMOSPHERIC CHEMISTRY

- PANs are not emitted directly into the atmosphere but are produced in situ by the photochemical oxidation of various volatile organic compounds (VOC) in the presence of NO_x.

- PANs are important reservoir gases for NO_x (=NO+NO₂) and, through long-range transport and subsequent release of NO_x, may control the photochemical production of ozone in much of the remote marine troposphere [1].

- The relative abundance of the different PAN compounds reflects the mix of hydrocarbons involved in the photochemistry.

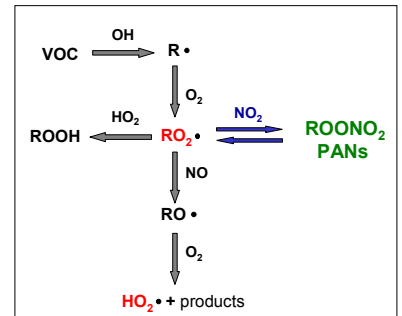
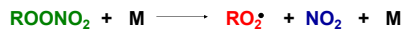


Fig. 1: VOC oxidation scheme.

INSTRUMENTAL SET-UP OF FASTPEX

The detection of PANs involves three steps:

Step 1: Thermal dissociation in the heated inlet (170 °C)



Step 2: Ionization of the source gas methyl iodide:



Step 3: Ion-molecule reaction (IMR)



The produced ions of the form RO⁺ are unique for each parent PAN species and can be detected by CIMS:

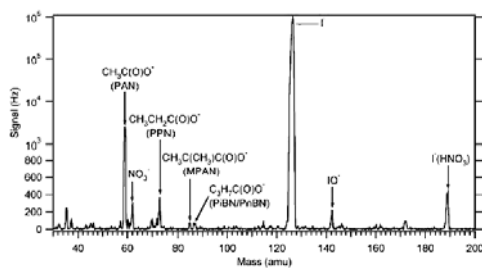


Fig. 2: Example Mass spectrum of atmospheric PANs [2].

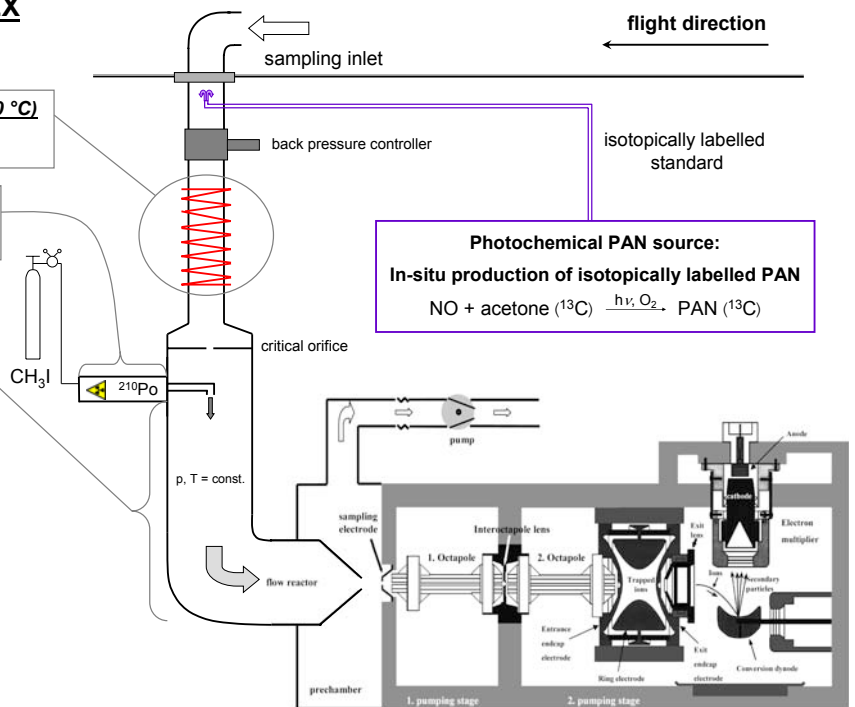


Fig. 3: Schematic of the FASTPEX instrumental set-up.

FIRST DEPLOYMENTS OF FASTPEX

The first operation of the FASTPEX instrument will be on the DLR research aircraft Falcon in June 2008 during the POLARCAT (Polar study using aircraft, remote sensing, surface measurements and modelling of climate, chemistry, aerosols and transport) campaign. POLARCAT is an International Polar Year core project with an overall goal to study the climatic impact of poleward long-range transport of aerosols and trace gases. FASTPEX will help to quantify the influence of PANs as a reservoir gas for the long-range transport of nitrogen oxides, in particular of air masses originating from boreal forest fires in North America.

It is also planned to use FASTPEX during OMO (Oxidation Mechanism Observations), one of the first demonstration missions of the new German research aircraft HALO (Fig. 4). OMO will study oxidation mechanisms and radical chemistry in the free troposphere over Europe in Summer 2009. The OMO instrument payload is designed to investigate different oxidation pathways of natural and anthropogenic emissions and the formation of gaseous and particulate products over Europe, hence, FASTPEX is one of the key instruments of the OMO mission.



Fig. 4: Research aircraft HALO (High Altitude and Long Range)

REFERENCES:

- [1] Singh, H. B. et al., Global distribution of peroxyacetyl nitrate, Nature, 321, 588-591, 1986.
- [2] Slusher, D. L. et al., A thermal dissociation-chemical ionization mass spectrometry (TD-CIMS) technique for the simultaneous measurement of peroxyacetyl nitrates and dinitrogen pentoxide, J. Geophys. Res., 109, D19315, 2004.