Aircraft-based Measurements of HO_2 and HO_2+RO_2 during MIRAGE-Mex

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Platform: C-130
Instrument: SICIMS in Four-Channel MS System
Quantities: 1 minute average HO_2 and HO_2+RO_2 concentrations
Group: NCAR/ACD/POP

We will deploy an instrument to quantify the concentrations of HO_2 and HO_2+RO_2 using chemical conversion with selected ion chemical ionization mass spectroscopy. It is based on the addition of NO and SO_2 to ambient air in the upper part of a medium pressure inlet (200 mbar) which leads to conversion of peroxy radicals to sulfuric acid (H_2SO_4). Nitrate ions (NO_3^-) are produced in the lower part of the inlet by the interaction of gas phase nitric acid (HNO_3) with alpha particles produced from Americium-241. The reaction between NO_3^- and H_2SO_4 leads to HSO_4^- ions. The reagent and product ions enter the vacuum system, which has ion optics and differential pumping followed by mass separation using a quadrupole filter and detection with a channel electron multiplier. The ion count ratios for mass 97 (corresponding to HSO_4^-) to mass 62 (corresponding to NO_3^-) are proportional to the peroxy radical concentrations entering the inlet. The proportionality coefficient is determined through ground-based and in-flight calibrations, through generating radicals via the UV photolysis of water vapor.

HO_2 is measured separately from HO_2+RO_2 by adjusting the [NO]/[O_2] ratio. This has been done in the past by changing the NO concentration. We have developed a new and improved method based on oxygen or nitrogen dilution. This will allow the switch between the two modes of operation to be made much more rapidly, leading to nearly simultaneous measurements of HO_2 and HO_2+RO_2.

We are also developing a new transfer standard for calibration that will allow all of the hydrogen radical measurements to be brought onto the same basis (in addition to the individual instrument calibrations).

The PeRCIMS instrument will make use of one channel of our group's four-channel mass spectrometer system (other channels for OH/H_2SO_4/MSA, NH_3, and HNO_3).

These measurements will address several MIRAGE-Mex scientific objectives, including helping to assess the geographical extent of influence of the MC outflow, an assessment of the oxidizing capacity and ozone tendency of the MC outflow, a connection to the assessment of the persistence of hydrocarbon oxidation products and how they influence the radical budgets, and connection to the reactive nitrogen budget particularly as it pertains to ozone production and the formation of organic and organic peroxy nitrates. We also will look at the influence of aerosols and clouds on peroxy radical levels in an attempt to quantify the role of multiphase processes (adsorption, reactive uptake, etc.).