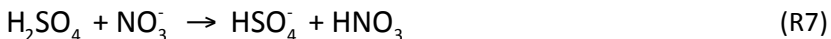


Measurements of HO_x and Other Species during FRAPPE

The University of Colorado four-channel chemical ionization mass spectrometer (CIMS) system is staged on the NSF/NCAR C-130 aircraft platform. One channel is used to measure OH, H₂SO₄, and the sum of sCIs, and another channel used to measure HO₂ and HO₂+RO₂. The remaining two channels will not be used. The measurement of H₂SO₄ is based on the chemical ionization via reaction with negatively-charged nitrate ions.



In reality, the reagent ions are a mixture of bare ions and those clustered with one or two nitric acid molecules. This is not a problem since the kinetics for all three are very similar. The nitrate ions are produced in a flow annular to the sample flow by exposing a part-per-million (ppmv) mixture of HNO₃ in air to a radioactive Americium-241 source. The ions are directed into the sample flow using electrostatic lenses. After reaction, the ions are directed through a dry nitrogen buffer into a pinhole entrance into the mass spectrometer chamber. Clusters are dissociated by gentle acceleration with electrostatic lenses at a moderate pressure (about 100 mtorr). The ions are directed with an octopole ion guide through a 1 mtorr pressure region into the quadrupole filter region at 10⁻⁵ torr when the ions are separated by their mass-to-charge (m/z) ratios. The mass separated ions are counted by a channel electron multiplier configured in the pulse counting mode.

Hydroxyl radicals are measured (e.g. Mauldin et al., 1998) using an inlet that slows the ambient flow (about 150 m/s) to about 10 m/s. The flow is sampled and mixed with a small amount of sulfur-34 labeled SO₂. The reaction of hydroxyl radicals with the labeled SO₂ produces labeled H₂SO₄. The labeled sulfuric acid product is measured the same as ambient sulfuric acid, but at an m/z value of 99 rather than 97. The OH background is measured by injection of propane to the front reagent injectors (it is present continually at the rear reagent injectors), which serves to remove ambient OH, but allows non-propane reacting species to survive. An electronic background is also measured by reversing the quadrupole filter polarity as a system check. It is typically less than 1 count per second (cps). Since sCIs do not apparently react at an appreciable rate with propane, they appear in the OH background. For those situations when the OH background has no artifacts (e.g. the artifact found when NO is very high and OH is produced from HO₂ plus NO within the instrument inlet), it may be interpreted as the sum of the concentrations of the sCIs. The OH, H₂SO₄, sCI sampling system is shown in Figure 1. Calibration is accomplished in

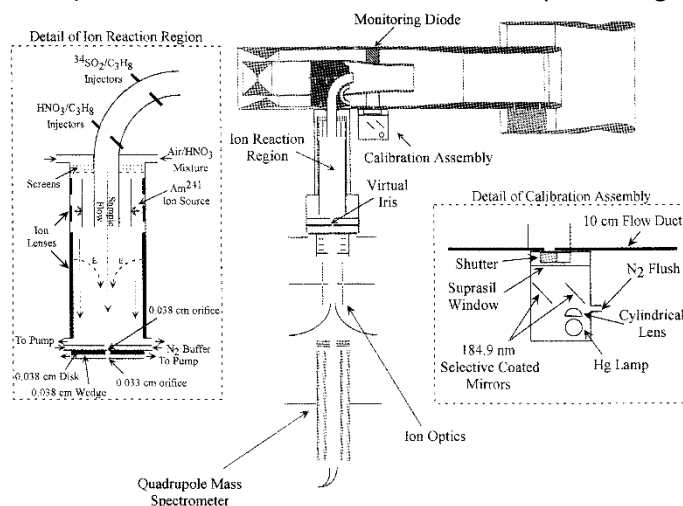


Figure 1. Components of OH measurement channel.

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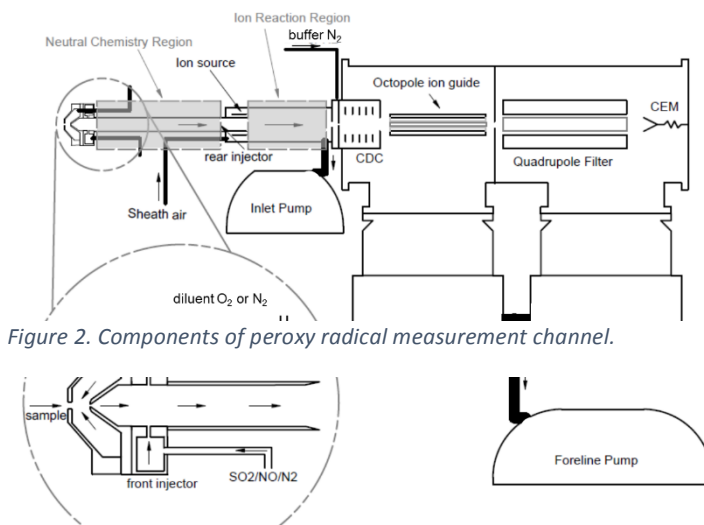


Figure 2. Components of peroxy radical measurement channel.

flight by the 184.9 nm photolysis of water vapor.

Peroxy radicals are measured similarly (e.g. Hornbrook et al., 2011). In the proposed instrumentation, the inlet samples the ambient flow in a perpendicular direction through a pinhole into 150 torr region. The ambient air is diluted with either nitrogen or oxygen which facilitates measurement of either HO₂ or HO₂ plus RO₂. Then the reagent gases NO and SO₂ (unlabeled) are added which leads to production of unlabeled sulfuric acid with some amplification. The background is measured by changing the addition of SO₂ to the rear injector, in which case ambient peroxy radicals are converted to nitrous acid (HONO). The sulfuric acid product of the chemistry is ionized and counted as with the OH channel. Calibration is accomplished on the ground also using the 184.9 nm photolysis of water vapor. The system is shown in Figure 2.

The parameters of these measurements (averaging times, detection limits, precision, etc.) are summarized in Table 1.

Parameter	OH	H ₂ SO ₄	sCl _s	HO ₂	HO ₂ +RO ₂
Sample Frequency	30 s	15 s	30 s	60 s	60 s
Averaging Period	8 s	5 s	8 s	8 s	8 s
Precision	1 x 10 ⁵ cm ⁻³	1 x 10 ⁵ cm ⁻³	1 x 10 ⁵ cm ⁻³	1 pptv	1 pptv
Accuracy (2σ)	40%	40%	50%	35%	35%
Detection Limit	3 x 10 ⁵ cm ⁻³	3 x 10 ⁵ cm ⁻³	3 x 10 ⁵ cm ⁻³	2 pptv	2 pptv

Table 1. Parameters of measurements.

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Hornbrook, R. S., J.H. Crawford, G.D. Edwards, O. Goyea, R.L. Mauldin, J.S. Olson, and C.A. Cantrell, Measurements of tropospheric HO₂ and RO₂ by oxygen dilution modulation and chemical ionization mass spectrometry, *Atm. Meas. Tech.*, 4, 735-756, 2011.