Georgia Tech Chemical Ionization Mass Spectrometer (GT-CIMS)

Principal Investigator: L. Gregory Huey (greg.huey@eas.gatech.edu)

Co-Investigators: David Tanner (tanner@eas.gatech.edu), John Nowak (john.nowak@noaa.gov), and Andy Neuman (andy.neuman@noaa.gov)

Instrument

Two CIMS instrument will be deployed on the NASA DC-8 during the SEAC4RS mission. Each CIMS consists of a low pressure ion molecule reactor (IMR) coupled to a quadrupole mass filter by an actively pumped collisional dissociation chamber (CDC) and an octopole ion guide. One CIMS, devoted to measure sulfur dioxide, utilizes a 160 mm OD vacuum chamber evacuated by two turbopumps (250 l s⁻¹). The mass filter is a set of 19 mm dia. quadrupole rods housed in the vacuum chamber. The IMR is evacuated with a scroll pump (300 l min⁻¹) that also serves as the backing pump for the mass spectrometer. The other CIMS, devoted to measurement of PANS, utilizes a smaller vacuum chamber (100 mm OD), 9.5 mm quadrupole rods, and is evacuated with two small turbo pumps (70 l s⁻¹). The PAN IMR is evacuated with a small scroll pump (100 l min⁻¹). The CDC of each CIMS instruments is a short 80 mm diameter chamber that houses an octopole ion guide and is evacuated with a hybrid molecular drag pump.

Detected Species and Data

The first CIMS will be configured to detect sulfur dioxide (SO₂), pernitric acid (HO₂NO₂), and hydrochloric acid (HCl). These species will be detected by the following ion molecule reactions:

$$SF_5^- + SO_2 \rightarrow FSO_2^- + SF_4$$

 $SF_5^- + HO_2NO_2 \rightarrow (NO_4^-) \cdot HF + SF_4$
 $SF_5^- + HC1 \rightarrow (HF)C1^- + SF_4$

Detection limits for all species are expected to be of the order of 10 pptv for a one second integration period. Each species will be measured each second with a duty cycle of 20% except for SO₂ which will be measured with a duty cycle of 40%. The accuracy of the measurements are expected to range from 10% for SO₂ to 35% for HO₂NO₂.

The second CIMS will be configured to detect PANs by thermally decomposing these species into the corresponding acyl peroxy radical. The detection scheme for PAN $(CH_3C(O)O_2NO_2)$ is:

$$CH_3C(O)O_2NO_2$$
 + heat \rightarrow $CH_3C(O)O_2$ + NO_2
 Γ + $CH_3C(O)O_2$ \rightarrow $CH_3C(O)O_2$ + IO

The detection limit for PAN is expected to be of the order of 2 pptv for a one second integration period. PAN will be measured each second with a duty cycle of 50% and other compounds such as PPN and APAN will be measured with the remaining. The accuracy of the PAN measurements is of the order of 15%.

Configuration for SEAC4RS

The CIMS instruments will be mounted in a standard DC-8 high bay rack. The rack will house the CIMS, pumps, calibration sources, control and acquisition electronics, and an automated zeroing valve. Gas cylinders will be mounted external to the rack. Both instruments will be calibrated semi-continuously with isotopically labeled standards for PAN and SO₂. The background signals will be measured periodically by scrubbing the sampled air with activated carbon.

References:

Kim, S., L. G. Huey, R. E. Stickel, D. J. Tanner, J. H. Crawford, J. R. Olson, G. Chen, W. H. Brune, X. Ren, R. Lesher, P. J. Wooldridge, T. H. Bertram, A. Perring, R. C. Cohen, B. L. Lefer, R. E. Shetter, M. Avery, G. Diskin, and I. Sokolik (2007), Measurement of HO2NO2 in the free troposphere during the intercontinental chemical transport experiment - North America 2004, J. Geophys. Res.-Atmos., 112(D12).

Huey, L. G. (2007), Measurement of trace atmospheric species by chemical ionization mass spectrometry: Speciation of reactive nitrogen and future directions, *Mass Spectrom. Rev.*, 26(2), 166-184.

Slusher, D. L., L. G. Huey, D. J. Tanner, F. M. Flocke, and J. M. Roberts (2004), A thermal dissociation-chemical ionization mass spectrometry (TD-CIMS) technique for the simultaneous measurement of peroxyacyl nitrates and dinitrogen pentoxide, *J. Geophys. Res.-Atmos.*, 109(D19).