5.2.3. PAN AND OTHER TRACE HYDROHALO-COMPOUNDS EXPERIMENT (PANTHER)

The next step in evolution for the HATS airborne gas chromatographs is the development of the PANTHER instrument. ACATS-IV and LACE instruments use packed columns and electron capture detectors. In addition to these technologies, PANTHER will incorporate cryogenic trapping to collect larger samples, capillary columns to increase separation and signal-to-noise, and a Hewlett Packard (HP, now Agilent Technologies) model 5973 quadrupole mass selective detector (MSD). These added technologies will enable PANTHER to make in situ measurements of the CFC replacement molecules, methyl halides, peroxyacetyl nitrate (PAN, $CH_3C(O)OONO_2$), and one of PAN's precursors, acetone.

Initial activities focused on proof of concept studies. Three basic concepts (chromatography, calibration, and data acquisition) had to be addressed before design and construction of the flight instrument could begin.

The first objective was to show that adequate chromatography could be achieved. Reliable chromatography of the CFC replacements and the methyl halides has already been demonstrated within the HATS group by the flask, ocean, and in situ projects. Chromatography for PAN and acetone are new concepts for the HATS group. This year, in collaboration with NOAA Aeronomy Laboratory, PAN was successfully separated from the air peak using a 5-m, 0.53-mm inside diameter, mega-bore column with a 1-µm thick RTX 200 coating, cooled to 15ºC. Output from this column was directed into the HP-G1533A anode-purged ECD and the MSD. A detection limit of better than 3 ppt was demonstrated for the ECD, and an impressive detection limit of better than 0.8 ppt was demonstrated for the MSD using the chemical ionization source, with a flow of 1 sccm CH_4. Peroxypropionyl nitrate (PPN, $CH_3CH_2C(O)$-$OONO_2$) was also detected.

A modest sensitivity to acetone was detected on the MSD; the ECD has no sensitivity to acetone. However, large (100 cm^3), cryo-focused samples are needed. A 30-m, 0.25-mm inside diameter HP-5MS capillary column was used with a 0.25-µm thick 5% PH ME siloxane film to separate acetone and many of the HCFCs from the air peak. Using an electron ionization source and running the quadrupole in single ion mode, tuned to mass/charge (m/z) ratios of 58 and 43, a detection limit of 1 ppt was obtained for acetone. A detection limit of 0.3 ppt for HCFC-141b at m/z of 81 was verified. No chromatographic interference was found when 50 ppm of O_3 was dynamically mixed with the inlet stream. For ease, this work was done with a liquid N_2 cryogen. Thermal electric coolers will be employed in the flight instrument.

Calibration of ACATS-IV and LACE systems was achieved by in situ analysis of gas mixtures stored in Aculife-treated aluminum cylinders. This method will not work for PAN because it cannot be reliably stored as a gas mixture. An in-flight PAN source will be required for calibration. The generation of PAN from a calibrated NO source dynamically diluted to the ppt level was studied. PAN was produced by photolyzing acetone at 285 nm in the presence of NO. Carbon monoxide was added to quench competing reactions.

The third proof of concept area was to resolve incompatibilities between the HP MSD instrument control, data acquisition involving Chemstation on a Windows NT operating system utilizing an HPIB bus, and the airborne HATS approach using DOS with a metrobite bus. The most recent GCs built within the HATS group are the CATS GCs with QNX. Substantial development of reliable GC control and data acquisition was invested in this operating system. QNX requires a relatively small memory overhead compared to the NT operating system and is less prone to system crashes prevalent with the Windows NT environment. Both HP-IB (IEEE) and RS-485 drivers for the QNX operating system exist. Using these drivers the HP MSD runs entirely from QNX. The new smart electrometers, gas-sample valves, and the stream-selection valve were moved off of the stack built by Tommy Thompson and onto RS-232 and RS-485 serial communication lines, reducing wiring and power requirements. This should result in an instrument that is lighter, easier to work with, and more dependable.

With these three issues resolved, the design and construction phase of the project will proceed in 2000. Validation flights onboard the ER-2, WB-57F, or both will take place in 2001.