Airborne gas chromatograph for in situ measurements of long-lived species in the upper troposphere and lower stratosphere

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Abstract. A new instrument, the Airborne Chromatograph for Atmospheric Trace Species IV (ACATS-IV), for measuring long-lived species in the upper troposphere and lower stratosphere is described. Using an advanced approach to gas chromatography and electron capture detection, the instrument can detect low levels of CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), CFC-113 (CCl_2F-$CClF_2$), methyl chloroform (CH_3CCl_3), carbon tetrachloride (CCl_4), nitrous oxide (N_2O), sulfur hexafluoride (SF_6), Halon-1211 ($CBrClF_2$), hydrogen (H_2), and methane (CH_4) acquired in ambient samples every 180 or 360 s. The instrument operates fully-automated onboard the NASA ER-2 high-altitude aircraft on flights lasting up to 8 hours or more in duration. Recent measurements include 24 successful flights covering a broad latitude range (70°S-61°N) during the Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) campaign in 1994.

Introduction

The Earth's atmosphere contains a variety of long-lived gaseous species that reflect emissions at the surface. Chlorofluorocarbons (CFCs), as well as other chlorine- and bromine-containing species, are emitted at the Earth's surface and carried to the stratosphere, where they are destroyed by photochemical processes, liberating chlorine (Cl) and bromine (Br) radicals [*Molina and Rowland*, 1974; *WMO*, 1995]. Recent ground-based measurements show that the growth rates of principal CFCs are declining as a result of the United Nations Montreal Protocol [*Elkins et al.*, 1993]. As greenhouse gases, the growth of CFCs, N_2O, and CH_4 emissions are included in scenarios used to evaluate global warming [*IPCC*, 1995]. In the stratosphere, N_2O and CH_4 are source gases for reactive nitrogen (NOy) [*Fahey et al.*, 1990] and water vapor (H_2O), respectively.

Defining the distribution and growth rates of these various long-lived species requires the use of instrumentation that has suitable precision and accuracy and can be adapted to appro-priate sampling platforms. Efforts in ground-based monitoring have shown continued success [*Fraser et al.*, 1994]. However, attempts to make in situ measurements in the stratosphere have proven to be more difficult as a result of the inherent restrictions of aircraft and balloon platforms. Precise measurements above the tropopause involve samples collected in cans or otherwise trapped onto absorbents and subsequently analyzed with laboratory instruments [*Heidt et al.*, 1989; *Goldan et al.*, 1980; *Schmidt et al.*, 1991]. Although an advantage of grab samples is that many species can be detected and quantified, disadvantages include potential changes in sample composition during storage and a limited number of samples per flight.

An alternative is the operation of an in situ gas chromatograph (GC). Airborne GCs have been used on medium-altitude aircraft for measurements of CFC-11, CFC-12, CCl_4, and N_2O [*Bamber et al.*, 1984; *Tyson et al.*, 1978] and for the measurement of peroxyacetyl nitrate and other hydrocarbon species [*Ridley et al.*, 1990; *Singh et al.*, 1990]. Measurements on high-altitude aircraft include those of CFC-11, CFC-12, and N_2O made with 12 min resolution on the NASA U-2 aircraft [*Vedder et al.*, 1983].

We describe a new airborne GC that operates onboard the NASA ER-2 high-altitude aircraft. The instrument expands and improves upon the design of the first ACATS GC that operated on the ER-2 aircraft as a one-channel electron capture detector (ECD) for CFC-11 and CFC-113 [*Woodbridge et al.*, 1995]. The new GC incorporates a number of features that are useful for other field applications where a high degree of precision and miniaturization of components are required.

Experimental

Sampling. ACATS-IV is located in the Q-bay of the ER-2 fuselage, forward of the NOAA NOy instrument. The basic rectangular enclosure measures 84 W $\times$ 49 H $\times$ 32 L cm (0.13 m^3) and weighs 52 kg (Figure 1). The enclosure includes all components except the gas cylinders and pump which amount to an additional 15 kg. The ACATS diaphragm pump is located inside the NOy instrument enclosure. A single motor (400 Hz, 1.6 Hp) operates the ACATS-IV pump and the vacuum pump for the NOy instrument. Power to ACATS-IV is supplied as 24 DC (300 W peak, ~160 W continuous) and 120 VAC (400 Hz, 680 W peak, ~420 W continuous) from the aircraft power system.

The pump pressurizes the sample loops with ambient air drawn through an L-shaped inlet line (6.4 mm outside diameter, o. d.) located on the lower Q-bay hatch. The pump is a dual-head diaphragm compression unit (KNF Neuberger Model N726.3-STR, Trenton, NJ) with Teflon and stainless steel surfaces. At inlet pressures between 50 and 1000 mbar, the pump maintains a continuous flow of ~200 STP cm^3 min^{-1} (sccm) through the sample loops.

Compressed gas cylinders are used to store both carrier gases (refilled every flight from bulk tanks) and the calibrated standard mixture (refilled every 3-4 flights). Three (standard and nitrogen, N_2) and 1-L (P-5, 5% CH_4 in argon, Ar) aluminum cylinders reinforced with Kevlar and fiberglass (Structural Composites Ind., Pomona, CA) allow a working pressure of 20 MPa (3000 psi) with minimum weight. The cylinders are mounted outside the main ACATS-IV enclosure in combination with gases used in the NOy instrument. The carrier gases are scrubbed through heated zirconium, hopcalite (MnO_2 and CuO), Sofnacat (Molecular Products, Thaxted, UK), and molecular sieve 13X traps. Because ACATS-IV consumes only small quantities of zero air (79% N_2, 21% O_2), this gas is provided by the NOy instrument. The addition of ~15 parts per million (ppm) of N_2O to the make-up inlet of the ECD on channel 4 enhances the response to H_2 and CH_4 [*Phillips et al.* 1979].

Instrumental Analysis. The instrument includes four separate gas chromatographic channels each requiring a gas sampling valve (GSV, Valco Instruments Co. Inc, Houston, TX), a GC column oven, and an ECD inside a hermetically sealed, thermostated oven (both ovens are 10 cm o.d. by 13 cm long and are thermostated to ±0.2°C, 1 s.d., of temperatures listed in Table 1). Individual channels can be configured by selecting different GC columns and sample loop volumes to measure the following combination of species (see Table 1 and Figures 1 and 2): On channel 1, trace species, CFC-11, CFC-113, CH_3CCl_3 and CCl_4 are separated from air; similarly, on channel 2, N_2O and SF_6; on channel 3, CFC-12 and Halon-1211; and on channel 4, H_2 and CH_4.

A sampling period of 180 or 360 s (the latter for channel 2) is made possible with the use of a 2-position, 12-port GSV and an appropriate choice of column materials and lengths, flows, and temperatures (Table 1). Each GSV can be configured in either the 12-port or 10-port mode. In the 12-port mode, the GSV injects air from the sample loop onto two separation columns (a pre-column and a main column coupled in series), diverts air away from the ECD, and backflushes the pre-column after trace gases of interest enter the main column. The 10-port mode is configured by connecting the outlet of the main column to the ECD and a tube between ports 8 and 9 in Figures 1b and 1c. This mode does not divert the air peak away from the ECD but allows backflushing (see Figure 2b and 2c).

The ECDs, GSVs, and stream selection valve (SSV, Valco) are all enclosed in separate housings that are thermostated and purged with a continuous flow of carrier gas with operational parameters listed in Figure 1 and Table 1. The purge flows reduce the impact of small leaks into the carrier and sample flows upstream of the ECD and allow pressurization to 975 mbar using an absolute backpressure relief valve (Tavco, Chatsworth, CA). All purge assemblies are supplied with N_2 at ~3-10 sccm, and the make-up line into each ECD has a carrier gas purge of ~3-5 sccm to protect the ECD in case the GSV accidentally shuts off the flow. Purge flows that remain constant even when the GC is without power contribute to rapid stabilization (5-10 min) when power is restored. The flow control module uses crimped capillary tubing for purge lines, a mass flow controller (Model FC-260, Tylan General, Torrance, CA) for the main columns, and a differential pressure flow controller (Porter Instruments, Inc., Hatfield, PA) for backflushing the pre-columns. As the ER-2 altitude increases, the pressure in the aircraft payload area is allowed to decrease to 300 mbar and then is maintained at that level. To eliminate any sensitivity to this pressure change, the exhaust lines of each ECD and sample loop are separately controlled to 975 ±0.5 mbar.

The ECDs for channels 2 and 3 are manufactured by Valco (Model 140BN) and for channels 1 and 4 by Shimadzu (Model GC-Mini-2, Tokyo, Japan). Under identical GC conditions, the substitution of the Valco radioactive ECD for the Shimadzu ECD results in a 2.3 (SF_6 at 3 parts per trillion, ppt) to 28 (CFC-11 at 150 ppt) times improvement in signal-to-noise (SNR) depending on the molecule and the mixing ratio range. Our electrometers are based on the original Shimadzu GC-Mini-2 design and are modified for frequency output. The Valco ECD is so sensitive that the electrometer was run at a standing current of about one tenth of that of the Shimadzu.

Control of the instrument modes and data acquisition is provided by a 80486-based computer (Ampro Computers, Inc., Sunnyvale, CA), interface board, and flash-RAM storage disk. The PC interface board accommodates custom boards for analog-to-digital and TTL control functions. Another custom board uses a dedicated microprocessor to measure the ECD frequency output with a resolution of 0.1 Hz for peaks ranging from 10 to 20000 Hz sampling at 8 times per second. The precision (1 s.d.) for each gas, including reproducibility and calibration curve errors, throughout an 8-hour flight is summarized in Table 2.

Standardization. The accuracy of mixing ratio values expressed as dry mole fraction is established with the use of calibrated gravimetric standard mixtures [*Elkins et al.*, 1993]. The bulk secondary standards used for this project were air samples from Niwot Ridge, CO (40.0°N, 105.5°W, 3013 m) in pressurized, (9 kL at STP) aluminum (Luxfer, Riverside, CA) gas cylinders treated with Aculife-IV (Scott Specialty Gases, Plumsteadville, PA) to improve stability of some species. The air in these tanks contained either mid-tropospheric or lower-stratospheric mixing ratios of each species, where the latter is obtained from the former by diluting with zero air (see Table 2). The resulting secondary standards are calibrated against gravimetric standards on a laboratory GC. Absolute error is estimated as the variation among individually prepared gravimetric standards noted in Table 2. After every injection of a sample from the calibration tank, four ambient air samples are analyzed and this calibration cycle is repeated throughout the flight, resulting in a calibration every 15 min on channels 1, 3, and 4, and every 30 min on channel 2.

By selecting the position of the SSV, the sample loops are provided with either ambient air, zero air, or a calibrated standard mixture. Zero air, sampled every 2 hours, provides an instrument blank as an aid in detecting and correcting for contamination. Although the sample loops were connected in series, no contamination or dilution of the sample from the carrier gases was observed in the zero air. Cycles that send calibration gas or zero air to the sample line through the pump are used to correct for contamination peaks (<5 ppt) coeluting with CFC-113, CH_3CCl_3, and CCl_4. A calibration curve is generated once in the first half of the flight by using one standard mixture and varying the pressure of the gas in the sample loop (R. Weiss, private communication, 1995) during four separate calibration injections (ranging from 80 to 110% of normal sample loop pressure). This pressure calibration curve was used as a measure of detector linearity during each flight. The flight curve compared within a few percent with our calibration curve generated using 5-8 secondary standards that were run on the ground spanning the range of observed mixing ratios. Mixing ratios were calculated by comparing the sample and standard responses, and correcting for the non-linearity using the ground calibration curve from our NOAHchrom programs created with Igor Pro software (WaveMetrics Inc., Lake Oswego, OR).

Results and Discussion

ACATS-IV test flights occurred in February 1994, followed by science flights for the ASHOE/MAESA campaign. Principal deployment locations were the NASA Ames Research Center Moffett Field, CA; Barbers Point, HI; and Christchurch, New Zealand during four separate periods (March-April, May-June, July-August, and October-November, 1994). Data for many of the species in Table 2 were collected on 22 flights. An example of a time series from the flight of November 4 is shown in Figure 3.

A wide variety of scientific issues can be addressed by the large group of species measured by ACATS-IV. The 5 Cl- and 1 Br-containing species compose about 80% of total organic Cl and about 12-18% of total organic Br entering the stratosphere, respectively. The remaining organic halogen-containing species can be estimated from other measured trace gases using correlations between long-lived species. These correlations, derived either from previous observations or from models, permit the calculation of total organic and inorganic Cl [*Woodbridge et al.*, 1995] and Br.

ACATS-IV also measures species with a range of atmospheric lifetimes from ~5 yr for CH_3CCl_3 to ~3200 yr for SF_6 (Table 2). The measurement of SF_6 permits the calculation of the mean age of an air mass because of its long lifetime and linear growth rate (~0.28 ppt yr^{-1}) [*IPCC*, 1995]. At the maximum altitude of the

ER-2 aircraft (~21 km), the average age of the midlatitude air samples in Figure 3 is about 3.5 yr, while for the tropics the age is less than 1.5 yr. The correlation slope between two long-lived species yields the ratio of their stratospheric lifetimes [*Plumb and Ko*, 1992]. When the correlation includes a species for which the lifetime is well-established (e.g., CFC-11 at about 50 yr, [*WMO* 1995]) the lifetime of the other species can be determined. When combined with separate ER-2 measurements of H_2O, the ACATS-IV measurements of CH_4 and H_2 can constrain the total hydrogen budget in the lower stratosphere. In Figure 3, H_2 shows very little variability during the flight, and is inversely correlated with CH_4. These, and other issues will be developed in forthcoming publications using the ASHOE/MAESA data set.

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Figure 1. (a) Schematic of the ACATS-IV instrument showing pressure transducers (P), electron capture detectors (ECD), gas sampling valves (GSV), and the stream selection valve (SSV). Shaded areas are temperature-controlled zones where the temperatures for the GSV, SSV, and flow module are indicated. ECD and sample loop pressure controllers use a valve (MKS Instruments, Inc., Andover, MA) servo-controlled to a pressure gauge (Micro Gage, Inc., El Monte, CA). (b) The first position of the 12-port GSV loads the sample loop, backflushes the pre-column, and moves the peaks of interest from the previous sample injection into the ECD. (c) Turning the rotor of the 12-port GSV injects the sample onto the columns and diverts the column exhaust away from the ECD.

Figure 2. Representative chromatograms of upper tropospheric air during ASHOE/MAESA for (a) channel 1 in 12-port mode, (b) channel 3 in 10-port mode, (c) channel 4 in 10-port mode, and (d) channel 2 in 12-port mode showing the peaks enlarged within the box insert.

Figure 3. ACATS-IV data for 10 trace gases, pressure (solid line), and latitude (dashed line) on the flight of November 4, 1994, shown vs. UTC time along the flight track. The flight began at Moffett Field, CA (37.4°N, 122.0°W) proceeded north along the 130.5°W meridian to ~60°N with two vertical profiles and then returned to Moffett Field.

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Table 1. Final Chromatographic Parameters for ACATS-IV During the Fourth Deployment of ASHOE/MAESA

Channel No. (Carrier Gas)	Gas Chromatographic Stainless Steel Columns: Packing Material, Outside DDiameter (Inside Diameter), Lengths	Main (Pre-column) Flow, sccm	Mode (GSV s Switch time, s)	Column Temp °C	Loop Size (cm^3)	ECD Temp. °C	ECD Current (nA)
1 (N_2)	3% OV-101 on Chromosorb, 3.2 (2.2) mm, Main: 3.6 m; Pre-column: 1.2 m	75 (48)	12-port (72)	45	2.5	350	1.3
2 (P-5)	Porapak Q, 4.8 (3.8) mm, Main: 3 m; Pre-column: 2 m	40 (52)	12-port (200)	95	7.5	360	0.18
3 (N_2)	Main: 20 % OV-101 on Chromosorb, 4 m, 4.8 (3.8) mm; Pre-column: Porasil B, 0.3 m	50 (90)	10-port (90)	45	5.0	260	0.07
4 (~15 ppm N_2O doped)	Main: Molecular Sieve 5A, 3.3 m, 4.8 (3.8) mm; Pre-column: Unibeads 1S, 2 m	120 (68)	10-port (85)	140	10.0	365	1.7

Table 2. Data for ACATS-IV During ASHOE/MAESA[a]

Species	Precision[b]	Calibration Gas Mixing Ratio[c]	Typical Stratospheric Mixing Ratio	Atmospheric Lifetime, yr [*WMO* 1995]
CFC-11	±0.4%	156.9 (272.1)	12-270 ppt	50
CFC-113	±0.7 ppt	48.8 (83.3)	18-85 ppt	85
CH_3CCl_3	±0.7 ppt	80.3 (129.5)	2-125 ppt	5.4
CCl_4	±0.8 ppt	63.7 (110.7)	5-115 ppt	42
N_2O	±0.9%	177.0 (311.7)	130-315 ppb	120
SF_6	±0.04 ppt	1.82 (3.10)	1.9-3.1 ppt	3200
CFC-12	±0.6%	299.0 (535.2)	150-550 ppt	102
Halon-1211	±0.05 ppt	1.9 (3.7)	0.3-3.8 ppt	20
H_2	±18 ppb	293.1 (545.7)	450-600 ppb	10
CH_4	±1.5%	1.058 (1.755)	1.0-1.8 ppm	10

[a]Accuracy is < ±2% absolute error (1 s.d.) plus precision. Detection limit is < 2% of tropopause value. ppb = parts per billion.
[b]The average precision during the last 7 flights is represented in percent for large SNR peaks and in mixing ratio for small peaks.
[c]Low and high (in parentheses) values of calibration standards are in the same units as in column of stratospheric mixing ratios (dry).