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A high-precision fast-response airborne CO₂ analyzer for in situ sampling from the surface to the middle stratosphere

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Abstract

Two in situ CO₂ analyzers have been developed for deployment on the NASA ER-2 aircraft and on stratospheric balloons. The ER-2 instrument has had more than 150 flights during 21 deployments from 1992 to 2000, resulting in a dataset with nearly pole-to-pole coverage that includes data from all seasons in both hemispheres except austral summer. In-flight calibrations show that the typical long-term (i.e. flight-to-flight) precision of the instruments is better than ±0.1 ppmv. The flight standards are traceable to standards held by the Scripps Institute of Oceanography and the National Oceanic and Atmospheric Administration's Climate Monitoring and Diagnostics Laboratory. The balloon instrument has had 8 balloon flights since September 1996, providing the first in situ observations of CO₂ above ~21 km. In addition, the balloon instrument has been flown onboard a Cessna Citation II aircraft for sampling between the surface and 10 km. In this paper, the instrumentation and calibration procedures for both instruments are described in detail. An intercomparison of the two instruments during the Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) project showed that, on average, the instruments agreed to within 0.05 ppmv.
1. Introduction

Mixing ratios of carbon dioxide measured at the Earth's surface exhibit a latitudinally varying seasonal cycle due to uptake and release by vegetation and soils, superimposed a long-term increase due to fossil fuel combustion (e.g., Keeling and Whorf 1994; Conway et al. 1994). The seasonal cycle and the long-term increase propagate from the surface into the troposphere and eventually into the stratosphere, thus measurements of CO$_2$ can be used to diagnose transport rates throughout the atmosphere. For example, measurements of CO$_2$ in whole air samples collected using commercial aircraft have been used to study the movement of air through the troposphere and into the lower stratosphere (Nakazawa et al. 1991; Maseuda and Inoue 1996), and CO$_2$ mixing ratios in air samples obtained using high-altitude balloons have been used to calculate the average length of time for air to travel from surface to altitudes as high as 30 km (e.g., Bischof et al. 1980, 1985; Schmidt and Khedim 1991; Nakazawa et al. 1995).

We have developed two fast-response instruments for in situ measurement of stratospheric CO$_2$ mixing ratios. The first instrument was designed to fly on the NASA ER-2 aircraft and has reported data for more than 150 flights during major NASA sampling campaigns from 1992 to 2000. The second instrument was built for sampling from high-altitude balloons and has flown 8 times since September 1996 during the Observations of the Middle Stratosphere (OMS) experiment. A water trap has been designed for use with the balloon instrument during tropospheric sampling from aircraft. Both instruments measure CO$_2$ by nondispersive infrared absorption using a modified commercial detector and are calibrated in flight with a long-term precision of ± 0.1 ppmv. Our standards are traceable to standards maintained by the Scripps Institute of
Oceanography and by the National Oceanic and Atmospheric Administration (NOAA)/Climate Monitoring and Diagnostics Laboratory (CMDL). Thus, our data can be compared to any other data reported on either of these scales. The major difference between the instruments is that the balloon instrument has a more powerful pumping system, allowing it to operate to altitudes up to 32 km (~10 mbars, 107 kft). The maximum altitude of the ER-2 aircraft is 21 km (~40 mb, 70 kft).

In situ observations obtained using the instruments described in this paper have greatly increased the spatial and temporal coverage of available stratospheric CO₂ data. These data have been used in several studies of stratospheric transport rates (e.g., Boering et al. 1994, 1995, 1996; Strahan et al. 1998; Andrews et al. 1999, 2001a, 2001b; Neu and Plumb 1999; Park et al. 1999; Hall et al. 1999; Jones et al., 2001) and to calculate emission indices for pollutants in aircraft exhaust sampled during wake crossings (Fahey et al., 1995). We have recently configured the balloon instrument for tropospheric sampling and participated in the CO₂ Budget and Rectification Airborne (COBRA) experiment, a study designed to measure CO₂ uptake by ecosystems on a regional scale (J. C. Lin et al., manuscript in preparation). The high precision and rapid response time incorporated for stratospheric work have proven to be valuable for resolving features in the planetary boundary layer associated with turbulent transport that are usually regarded as "noise" in flask sampling.

The ER-2 and OMS payloads include instruments for measuring many other important trace species and meteorological parameters. Mixing ratios of N₂O, CH₄, CFC-11, CFC-12, SF₆, H₂O, and O₃ are measured on both platforms, providing information about stratospheric transport rates over a wide range of timescales and
providing a powerful framework for studying the combined effects of chemistry and transport on stratospheric O₃ concentrations.

In this paper, we describe the operation and calibration of the ER-2 and balloon CO₂ instruments and the modifications required for tropospheric sampling. We also present results from three intercomparison flights, when the ER-2 and balloon instruments were flown nearly simultaneously, and the results of an intercomparison flight between the ER-2 instrument and the NASA Langley (LaRC) CO₂ analyzer flown on the NASA DC-8 (Anderson et al. 1996; Vay et al. 1999).

2. Instrumentation

a. ER-2

A schematic of the ER-2 instrument is shown in Figure 1. We use the light source, gas cells and solid-state detector from a nondispersive infrared CO₂ analyzer (Li-Cor, Inc., Lincoln, Nebraska, model LI-6251). The infrared source is maintained at a constant color temperature of 1000° K, and a chopping shutter (500 Hz) alternately sends the light through the sample and reference cells. A 150 nm bandpass filter is mounted between the gas cells and the detector. Absorption at 4.26 μm, corresponding to the asymmetric stretch of CO₂, is measured using a lead selenide solid state detector that is thermoelectrically cooled to -12° C. Interference from water vapor by absorption and pressure broadening is negligible. The CO₂ mixing ratio is reported with respect to dry air. Dilution corresponding to H₂O mixing ratios ≤ 85 ppmv causes errors in the CO₂ mixing ratio < 0.03 ppmv, and we commenced sampling in the upper troposphere to avoid humidities higher than this value. The response time of the detector is 0.1 s and the cutoff
frequency is 5 Hz. In flight, data are recorded at 4Hz and typically median-filtered in data blocks of 2 seconds. The instrument is operated in differential mode, with a CO$_2$-in-air standard of known, near-ambient concentration flowing through the reference cell at all times.

The wide range of ambient temperatures and pressures encountered during stratospheric flight necessitated careful control of temperatures and pressures within the instrument and frequent in-flight calibrations, in order to meet the specifications for accuracy and precision. The detector is vibrationally isolated and housed in a temperature controlled pressure vessel (dot-dashed line in Figure 1). The temperature of the sample and reference cells is maintained at 36.5 ± 0.2°C by controlling the temperature of the detector pressure vessel to 30°C. Heating and sensing devices control the temperature of the pressure vessel, rather than of the Li-Cor itself, to avoid coupling thermal oscillations from the heaters into the detector. Calibration gases are housed in a separate heated enclosure, and both calibration gases and sample air are heated to ~35°C before entering the detector pressure vessel. Custom-built high-frequency (1 kHz) temperature control circuits are used for the detector pressure vessel, the calibration gas deck and other critical components, including the pressure controllers and several pressure transducers. Less temperature sensitive components are thermally controlled using commercially available heaterstats (Minco Products, Inc., Minneapolis, MN, model CT198) or thermostats (Elmwood Sensors, Inc., Pawtucket, RI, model 3100).

Constant pressure in the sample cell is maintained using a bypass circuit with active pressure control. Air is drawn into the inlet and compressed using a single-stage diaphragm pump (KNF Neuberger, Inc., Trenton, NJ, model N726.1.2.ST.9R) with a
Teflon valve plate and diaphragm. The pump is driven by a brushless DC motor (BEI Sensors and Motion Systems Co., Maurmelle, AR), and a custom aluminum pump head is used to minimize weight. Pressure upstream of the cell is controlled to 360.0 ± 0.2 torr using a pressure controller and valve (MKS, Andover, MA, type 1250A pressure/flow controller and type 0248A control valve) driven by a signal from an absolute pressure transducer (Micro Gage, Inc., El Monte, CA, model P-121). The pressure downstream of the sample and reference cells is controlled to a setpoint of 320.0 ± 0.2 torr using a signal from a second pressure transducer on the sample line, with a differential pressure transducer (MKS Baratron, Andover, MA, type 223BD) between the cells providing the signal for the control valve downstream of the reference cell.

Sample, reference and bypass flows are measured for diagnostic ("housekeeping") purposes (Microbridge Mass Airflow Sensors, Honeywell, Inc., Freeport, IL, Microswitch AWM3000 series). The flows through the sample and reference cells are 200 and 27 sccm, respectively, corresponding to a flushing time for the sample cell of 1.5 s (assuming plug flow). Flow through the bypass circuit depends strongly on the ambient pressure, and varies from 0 - 3500 sccm during a typical flight. A correction factor based on measured bypass flow and relevant volumes is applied to data submitted to the NASA archive to account for the delay between the time air enters the inlet until it reaches the sample cell. Typical delay times are 2-10 s.

The instrument is controlled by a datalogger (Campbell Scientific, Inc., Logan, Utah, model CR10) with a 16-channel AC/DC relay controller (model SDM-CD16), a 4-channel continuous analog output module (model SDM-AO4), and a custom built multiplexer to increase the number of signals that can be recorded. Measurements
typically begin at ~31 kft (9.45 km) on ascent and end on descent at ~29 kft (8.84 km) as indicated by a pressure sensor (Micro Gage, Inc., model P-121). For flights where it is desirable to sample in the upper troposphere, measurements begin at ~28.5 kft (8.69 km) and end at ~27 kft (8.23 km). We avoid sampling in conditions of "high" humidity (H$_2$O > ~300 ppmv), because residual moisture in the sample line can slow the response time of the instrument, potentially compromising the quality of data collected in the stratosphere, and because the dilution effect becomes non-negligible. As discussed below, we have recently developed a water trap for use with the balloon CO$_2$ analyzer to allow for sampling throughout the troposphere.

Four CO$_2$-in-air standards in 0.7 L fiber-wrapped aluminum gas cylinders (Structural Composites Industries, Pomona, CA) are used for in-flight calibrations. Each cylinder has two valves, one used only for filling and one leading to the detector (Swagelok, Solon, OH, model SS-OKM2-S2). The valves are closed between flights to protect against downstream leaks and to minimize the surface area to which the calibration gas is exposed. The delivery pressure for each standard is controlled by a two-stage brass regulator (Scott Specialty Gases, Plumsteadville, PA, 51-14D), and a 250 sccm frit is used to restrict the flow. Small, lightweight pressure transducers are used to measure the cylinder pressure (Entran Devices, Inc., Fairfield, NJ, model EXPM-A10-3000S) and delivery pressure (model EXPM-A10-150S).

Calibration gases are added as close to the sample inlet as possible, using 2-way and 3-way solenoid valves (General Valve Corp., Fairfield, NJ, series 9). The 2-way valves are located in the gas deck and are used to open and close each cylinder. The 3-way valve is located in the pump box and switches between ambient air and calibration
gas. This valve is operated using a reduced current driver (General Valve Corp., model 90-30-100) that supplies an initial voltage pulse of 28 V to open the valve and a lower “hold voltage” of ~8 V to keep the valve open. The reduced current driver was implemented after early flights indicated that, under certain conditions, heating of the valve by the operating current caused it to emit a significant amount of CO\textsubscript{2} when driven at full power. The only elements of the sample path that are not included in the calibration path are the aluminum inlet, an aluminum filter holder with a 3 µm filter (Gelman Sciences, Inc., Rossdorf, Germany), and a few short sections of Dekoron™ tubing (Dekoron/Unitherm Cable USA, Cape Coral, FL, type 1300, 3/8” OD, 1/16” wall). Laboratory analysis of these materials demonstrated that they neither absorb nor emit significant quantities of CO\textsubscript{2} under flight conditions.

The reference gas flows continuously during a flight. The zero of the detector is measured every ten minutes by sending reference gas through both cells, and the gain is measured every twenty minutes by sampling both high-span and low-span gases, which are chosen to bracket the range of CO\textsubscript{2} mixing ratios in the stratosphere. The zero and span gases flow for one minute each, and the average signals for the last thirty seconds are used to determine the quadratic calibration polynomial. A fourth-order interpolation scheme is used to derive continuous values for instrument response to each calibration standard between calibrations, and the calibration curve at each time during measurements of the ambient atmosphere is constructed from these values using second-order interpolation. The fourth standard gas is a long-term surveillance standard, which is sampled for two minutes every one or two hours depending on the duration of the flight. The calculated
The flight standards are filled as high as 1800 psi (depending on the pressure of the filling cylinder) and are used until the pressure drops to ~500 psi. Laboratory tests showed that concentrations of CO₂ can increase by several tenths of a part per million if the pressure drops to lower levels, presumably due to release of CO₂ bound to the cylinder walls. The reference standard must be refilled after one or two flights, and the span gases usually last 8-10 flights. The long-term surveillance standard typically lasts 14-18 flights. The flight-to-flight precision and accuracy of the instrument is better than 0.1 ppmv for all deployments, except for the September and December deployments of the Stratospheric TRacers of Atmospheric Transport (STRAT) experiment during which the degradation of an electronic component in the detector caused a slight reduction of instrument performance. The flight-to-flight precision for these deployments was ±0.15 ppmv. Short-term precision for all flights was ±0.03 ppmv.

The in-flight calibrations are augmented by calibrations of the flight standards on the ground relative to three "working standards", using a second CO₂ analyzer with a precision of 0.03 - 0.05 ppmv. The ground calibration unit is also a modified Li-Cor, Inc. LI-6251 infrared gas analyzer with temperature and pressure control. The working standards are used to determine the calibration polynomial for the ground calibration unit, and a fourth standard serves as the reference gas. Flight standards are calibrated relative to the cylinders from which they were filled both after filling and before being refilled. Differences of 0.1 ppmv between the flight standard and the filling cylinder are common,
with the flight standard always lower. In a few cases, differences as large as 0.3 ppmv have been observed.

The concentrations of the working standards are periodically measured relative to six "primary" lab standards, which have been measured several times by the Carbon Dioxide Research Group at the Scripps Institute of Oceanography (SIO). We are currently using our second set of working standards. Our stratospheric data have been reported on the Scripps-World Meteorological Organization SIO-WMO X95 Mole Fraction Scale. All of the primary and working standards are in aluminum cylinders, which are more stable for CO2-in-air than steel cylinders. There is no evidence that any of the primary or working standards have drifted significantly since they were purchased.

In 1997, we participated in a blind intercomparison (Francey 1997) overseen by the NOAA/CMDL Carbon Cycle Group, which is now responsible for maintaining the WMO CO2 standard, and we purchased a second set of six primary standards from the NOAA/CMDL group. Both the WMO intercomparison and our laboratory calibrations relative to the NOAA/CMDL primary standards indicate that the X95 values for our SIO primary standards are 0.1 - 0.2 ppmv higher than the NOAA/CMDL scale for CO2 mixing ratios from 340 to 380 ppmv. The mixing ratios of the six SIO primary standards are given on both scales in Table 1. The differences are systematic and reproducible, indicating that they are due to differences in the calibration scales rather than imprecision in our measurements. SIO and NOAA/CMDL both claim an uncertainty of ±0.1 ppmv for their CO2-in-air standards. Thus, the discrepancy between the scales lies within but near the outer edge of the expected uncertainty envelope. A second WMO blind intercomparison was conducted in 1999/2000, but the results were ambiguous because
recalibration of the gas cylinders when they were returned to NOAA/CMDL indicated that the concentrations had drifted by more than 0.1 ppmv over the course of the experiment (J. Butler, private communication).

An independently developed in situ CO₂ analyzer has been flown on the NASA DC-8 aircraft since 1991 (Anderson et al. 1996; Vay et al. 1999). An intercomparison between the DC-8 and ER-2 payloads during the ER-2 Stratospheric TRacers of Atmospheric Transport (STRAT) experiment and the DC-8 Vortex Ozone Transport Experiment (VOTE) indicated that the CO₂ instruments agreed to 0.14 ppmv on a flight leg at 10.7 km, but that there was a systematic difference of 0.44 ppmv on a second flight leg at 11.9 km with the ER-2 instrument reporting higher values (Weinheimer et al. 1998). This difference was larger than expected based on known instrumental uncertainties (~±0.11 ppmv for each instrument), but since the instruments were flying on different platforms, it is not possible to determine unambiguously whether they sampled the same air mass. These two instruments were compared again during the Sage III Ozone Loss and Validation Experiment (SOLVE) and were found to agree to within 0.1 ppmv on a flight leg at ~11 km when Harvard CO₂ values are reported on the NOAA\CMDL scale (Figure 2).

b. OMS

A second high-altitude sensor was designed and built for deployment on stratospheric balloons in response to a need for data above ER-2 altitudes. The primary difference between the balloon instrument and its predecessor is a more powerful pump system on the balloon instrument. Two teflon diaphragm pumps (KNF Neuberger), one
two-stage (model N726.3.ST.9R) and one single-stage (model N726.1.2.ST.9R) are used to maintain adequate sample flow up to ~32 km (~10 mb), the maximum altitudes reached by the balloons. The heads of the two-stage pump are run in parallel, with the single-stage pump in series downstream (Figure 3). As on the ER-2 instrument, the pumps are run with brushless DC motors and custom Al pump heads. The inlet of the two-stage pump is maintained at 40 mb using an additional active control valve (MKS, type 154A-200LSV, 0.25" orifice) to prevent excessive flow at lower altitudes. At altitudes above the 40 mb isobar, the inlet control valve is completely open, and the pumps operate at ambient pressure.

The pressure control downstream of the pumps is identical to that on the ER-2 instrument, but we use a lower sample flow of ~100 sccm, corresponding to the maximum flow the pumps can supply at the highest altitudes, in order to maintain constant conditions throughout the flight. The flushing time for the sample cell is ~3 s for this instrument. At altitudes with ambient pressure > 40 mb, the delay time between the inlet and the detector is constant at 6 s. At higher altitudes, the delay time increases to a maximum value of 15 s when the ambient pressure = 10 mb.

For an engineering flight in June 1996 and the first science flight in September 1996, calibration gas was added through a 3-way solenoid valve (General Valve Corporation, Series 9) upstream of the inlet pressure control valve in a configuration similar to that used on the ER-2 instrument. Unfortunately, the solenoid valve failed to operate reliably during both of these flights, resulting in significant loss of data, despite modifications to the control circuitry after the engineering flight. The sample solenoid was eliminated from the design by adding the calibration gas just downstream of the control
valve, which is forced to close during calibrations through software. Calibration gas is added through a custom fitting designed to direct the gas into the interior of the control valve before entering the pumps (see inset in Figure 3). Thus, the only portions of the sample pathway which are not also included in the calibration pathway are the inlet filter, a ~1.5 m length of Dekoron™ tubing (3/8" OD, type 1300), and the upstream side of the inlet control valve.

Data from the balloon instrument are received via telemetry for real-time monitoring and for storage in the event that the payload is not recovered. We also have the ability to turn the instrument power on or off and to force the instrument into a short or long calibration sequence at any time. The program is equipped with automatic control features that would provide nearly full data recovery even if communication with the gondola were lost. For example, the instrument automatically enters a standby mode to avoid overheating when the ambient pressure falls below 13 mb. In normal operation, a calibration sequence is initiated by a command sent from the ground, and the instrument resumes sampling prior to descent. However, if communications were lost, the instrument would automatically resume sampling when the ambient pressure reaches 16 mb.

In-flight calibrations are performed with the same frequency as on the ER-2 instrument. However, due to the longer intervals between flights, all of the gases are typically refilled after each flight, except when there is more than one flight per deployment, as in November 1997. Precision and accuracy for the balloon instrument are comparable to the ER-2 instrument.

c. Modifications for tropospheric sampling
Recent interest in tropospheric in situ sampling motivated design of a prototype system based on the balloon instrument. This system was designed to fly on the University of North Dakota Cessna Citation II aircraft, which has an altitude ceiling of \( \sim \)12 km. In order to obtain the same sample cell pressure used for stratospheric sampling, an additional two-stage diaphragm (KNF Neuberger, model N726.3ST.9I) was required for the outlet of the instrument. The instrument could be operated at a higher cell pressure, eliminating the need for the additional pump, but we opted to minimize the differences between the stratospheric and tropospheric configurations, and operating at reduced pressure prevents water vapor from condensing in the sample line. In tropospheric mode, the inlet control valve is set to a constant 33 mb, and the bypass flow and the delay time from the inlet to the detector are therefore constant (\( \sim \)8 s).

Auxiliary reference gas cylinders were used to allow more flight hours between refilling. This was necessary because the deployment plan involved traveling from airport to airport across the country, and transporting the filling cylinder and related equipment was impractical. Two additional 2.4 L fiber-wrapped Al gas cylinders (Structural Composites Industries) were plumbed in series with the built-in reference cylinder through the fill valve, giving a total volume for the reference gas of 5.5 L.

Obtaining accurate measurements of CO\(_2\) in the troposphere is complicated by conditions of high humidity. Water vapor can directly affect CO\(_2\) measurements by infrared absorption in three ways: 1) absorption at the wavelength of interest, 2) pressure broadening, and 3) dilution of the sample with varying amounts of water vapor. Water vapor can potentially also affect the measurement by displacement of CO\(_2\) molecules bound on instrument surfaces. These effects are negligible for absorption at 4.26 \( \mu \)m for
air with <300 ppmv H₂O, and thus it is not necessary to dry the airstream for stratospheric sampling. However, typical tropospheric humidities are sufficiently large to cause significant errors in reported CO₂ values.

To minimize issues associated with water vapor, a water trap was used to dry the air before it enters the CO₂ analyzer (Figure 4). The sample airstream passes through a Nafion™ membrane dryer (Perma Pure, Inc., Toms River, NJ, model PD-625), which removes the bulk of the water, before entering the pump unit. When the air exits the pump unit, it passes through a teflon dry-ice trap to further reduce the dew point. A stainless-steel 2 μm filter (Swagelok, model SS-4FW-2) is installed on the outlet side of the dry-ice trap to prevent ice particles that form in the trap from being drawn into the detector. The filter is housed within the dewar, so that trapped particles do not thaw and evaporate. Laboratory tests indicated that in this configuration the maximum mixing ratio for H₂O in the sample airstream was < 300 ppmv, corresponding to a maximum error in the CO₂ mixing ratio of 0.1 ppmv. The exhaust from the instrument serves as the purge gas for the Nafion™ dryer, eliminating the need for an additional source of dry air. Calibration gases are introduced upstream of the Nafion™ dryer in order to minimize differences between the calibration path and the sample path.

A major challenge in drying the sample air stream is to have enough dryer capacity to remove essentially all of the water, while minimizing the effect on the instrument response time. The Nafion™ dryer consists of a number of small tubes contained in a larger outer tube. The sample flows through the small tubes, while the dry purge gas flows around them through the outer tube. The sample airstream is thus subdivided, with the substreams taking different routes through the dryer. If the travel times for the
individual routes are significantly different, the instrument response time can be decreased. We initially hoped that a larger capacity Nafion™ dryer (model PD-1000) would eliminate the need for the dry ice trap, but laboratory tests showed that the larger Nafion™ dryer caused an unacceptable increase in the instrument response time. We also tested a large-capacity dry ice trap, hoping to avoid using two dryers, but although the trap was designed to minimize mixing of air within the volume of trap, enough mixing occurred to substantially increase the instrument response time.

In-flight calibrations of this prototype system for the troposphere indicated that precision during COBRA was ±0.25 ppmv, a factor of 2-5 worse than typical for stratospheric sampling. This was due in part to certain calibrations requiring more than the 60 s design period to equilibrate, resulting in a total uncertainty of up to ±0.5 ppmv for some data. The long equilibration time may have resulted from adsorption of CO₂ to the walls of a long (~2.5 m) 1/8” stainless steel tube used to introduce the calibration gas upstream of the dryer. Between calibrations, the pressure in the tube slowly increased. When calibration gas began flowing, the pressure in the tube dropped by ~10%, and some of the bound CO₂ may have been released. The pressure increase between calibrations may have resulted from a leak through one of the gas deck solenoids or from the surrounding air, since the pressure in the tube is sub-ambient during operation. On future flights, the length of the tube will be reduced by minimizing the distance between the sample inlet and the instrument. Comparison of our data with CO₂ values measured in flasks collected during the flights by the NOAA/CMDL whole air sampler indicated that on average, the instruments agreed to 0.25 ppmv during COBRA.
Optimization of the plumbing and the pressure and temperature control systems for future flights is expected to increase the in-flight precision of the tropospheric system to a level comparable to the stratospheric configuration (better than 0.1 ppmv). However, in order to obtain dry air mixing ratios accurate to 0.1 ppmv, it is necessary to dry the sample airstream leaving < 300 ppmv of water vapor. This corresponds to a dew point of -33°C near the surface (pressure = 1000mb) and a dew point of -48°C near 12 km (pressure = 200 mb). It is difficult to demonstrate that the drying system can perform at that level throughout a flight. To do so conclusively would require an extremely sensitive and accurate hygrometer measuring the instrument exhaust. Drying is also a potential problem for ground based CO₂ analyzers, although the competing need for rapid instrument response is diminished for a stationary measurement. Nevertheless, the ability to dry the sample airstream without also modifying the CO₂ concentration may set a practical limitation on accuracy for CO₂ measurements.

An alternative measurement strategy is simultaneous detection of CO₂ and H₂O without drying. However, the sensitivity of the H₂O measurement would probably limit the accuracy to which the CO₂ dry air mixing ratio could be measured. On an aircraft instrument in particular, the additional complication of H₂O being bound to and released from instrument surfaces as the ambient pressure changes could be a serious problem.

3. Deployments

A detailed description of the dates and latitude range corresponding to each of the ER-2 and OMS deployments is given by Andrews et al. (2001b). The ER-2 instrument has flown during five major sampling programs from 1992-2000, including SPADE.
(Stratospheric Photochemistry and Dynamics Expedition), ASHOE/MAESA (Antarctic Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft), STRAT (Stratospheric Tracers of Atmospheric Transport), POLARIS (Photochemistry of Ozone Loss in the Arctic Region in Summer) and the Sage III Ozone Loss and Validation Experiment (SOLVE). In addition, CO₂ data were acquired in November 1998 during two flights-of-opportunity from the NASA Dryden Flight Research Center in Edwards, CA. The ER-2 dataset includes observations during all seasons in both hemispheres except during Southern Hemisphere summer.

The balloon instrument has had 8 flights since September 1996 during the seven deployments of the OMS (Observations of the Middle Stratosphere) program. In addition, the balloon instrument was flown in June 1999 and in August 2000 on a Cessna Citation II aircraft to obtain tropospheric observations during the CO₂ Budget and Rectification Airborne (COBRA) experiment. COBRA test flights occurred during May and June 1998 out of Grand Forks, North Dakota. A more extensive COBRA flight series occurred during July and August 2000 with concentrated sampling over surface CO₂ monitoring stations at the WLEF TV tower in Wisconsin (Bakwin et al. 1998) and Howland Forest in Maine. Data were also obtained during a large-scale survey flight out of Denver, Colorado over Wyoming and Idaho and during transit flights between Grand Forks and Bedford, Massachusetts.

4. Intercomparison of the ER-2 and OMS CO₂ instruments

Nearly coincident ER-2 and balloon flights occurred on 21 September 1996 near Fort Sumner, New Mexico (35°N, 104°W), on 30 June 1997 near Fairbanks, Alaska
(65°N, 148°W) and on 5 March 2000 over Kiruna, Sweden (67°N, 21°E). Multi-platform intercomparisons are frequently complicated due to uncertainty about whether both platforms sampled the same air. This is the case for the flights in September 1996 and March 2000, as discussed below. However, on 30 June 1997, vertical profiles of tracer mixing ratios exhibited considerable structure, and the atmosphere was relatively stable. The flight paths of the two platforms are shown in Figure 5a and 5b. The balloon was launched at 5:52 am (local time) and landed at 11:23 am, and the ER-2 took off at 11:00 am and landed at 3:28 pm.

The results of the comparison are presented in Figure 5c-f. Pressure altitude (calculated from the pressure data assuming a constant scale height of 7 km) was chosen as the best vertical coordinate for the analysis. This may seem like a strange choice, since multi-platform intercomparisons are often more insightful when performed in tracer:tracer space. However, CO$_2$ and O$_3$ are the most precisely measured tracers on both payloads, and the relationship between these species is not monotonic, which complicates attempts to quantitatively compare the data from the two platforms (see Figure 5d). O$_3$ is measured on both platforms by UV absorption, according to the method described by Proffitt and McLaughlin (1983). The ER-2 instrument is operated by the NOAA Aeronomy Laboratory, and the balloon instrument is run by the NASA Jet Propulsion Laboratory. Comparison of correlations between CO$_2$ and other tracers (e.g., N$_2$O, CH$_4$ or the CFCs) are limited by the precision or temporal resolution of the other measurements.

The data were binned into 86 overlapping 250 m intervals from 10 km to the maximum altitude of the airplane (20.75 km), and the median CO$_2$ mixing ratio in each bin
was determined. The resulting profiles for both platforms are shown in Figure 5e. Differences between the OMS and ER-2 CO$_2$ measurements are shown as a function of pressure altitude in Figure 5f. The median value of the difference is 0.04 ppmv (OMS > ER-2), well within the combined precision of the instruments, and the few outliers can be explained by atmospheric variability. The mean difference was 0.05 ppmv, and most of the data fall within two standard deviations of the mean.

The same analysis was applied to the O$_3$ data, indicating a median difference of -7 ppbv (ER-2 > OMS) between the instruments, corresponding to 1.33%. The stated precision and accuracy are 1% and 3-5%, respectively, for the ER-2 and OMS instruments. Application of the method to the various N$_2$O and CH$_4$ measurements on board the two platforms also provides estimates of differences between instruments that are on the order of the stated accuracies. There were, however, a few species for which observed differences were significantly larger than expected given the combined uncertainties of the instruments. The results were not affected by considering only ascent or descent data for the balloon instruments or by excluding or using exclusively data for the level flight legs of the ER-2. Thus, although this method is crude, it seems to provide a robust estimate of cross-platform differences for these flights.

The balloon and ER-2 intercomparison flights on 21 September 1996 and 5 March 2000 are more difficult to interpret. Data from the four ER-2 flights from 13-21 September 1996 show that there was substantial variability in relationships among midlatitude N$_2$O, O$_3$, and CO$_2$ mixing ratios during that time period compared to other deployments (Figure 6; see also Andrews et al. 2001a). This may be because horizontal mixing by planetary scale waves is less efficient at homogenizing tracer mixing ratios.
during northern summer than other times of year. Due to a delayed take-off on September 21, the ER-2 began its profile ~3.5 hours after the balloon had landed. The flight plan had to be abbreviated, so the vertical profile at the most southerly point occurred from 34.7-35.6°N, while the latitude range for the OMS flight was from 34.1-34.49°N. Vertical profiles for CO₂, O₃ and N₂O all show significant differences between the ER-2 and OMS flights, indicating that, in this case, pressure altitude is not an appropriate coordinate for the intercomparison.

N₂O was measured on the ER-2 by the Airborne Tunable Laser Absorption Spectrometer (ATLAS) (Podolske and Loewenstein 1993) and on the balloon by the Airborne Laser Infrared Spectrometer II (ALIAS II) (Scott et al. 1999). While the CO₂:N₂O and CO₂:O₃ correlations from the OMS balloon flight fall within the range of values observed by the ER-2 during the deployment, they are slightly, but significantly, different than the relationships measured by the ER-2 on that day. For example, for a particular mixing ratio of N₂O, CO₂ measurements from the balloon varied from 0 to 0.5 ppmv higher than observed by the ER-2, with the largest discrepancies at the lowest N₂O (~200 ppbv). Similarly, for a particular O₃ mixing ratio, CO₂ measurements from the balloon varied from 0 to 0.8 ppmv higher than observed by the ER-2, with the largest differences at the highest O₃ (~2 ppmv). The corresponding N₂O:O₃ relationships for the ER-2 and OMS flights were nearly identical, pointing to a possible discrepancy between the CO₂ instruments. However, on September 13, the ER-2 encountered air with CO₂:O₃, CO₂:N₂O, and N₂O:O₃ correlations that were indistinguishable from those observed on the balloon flight one week later. In light of the excellent agreement of the CO₂ instruments in June 1997 and the scatter in the tracer relationships during September 1996, it seems
likely that the CO\textsubscript{2} differences observed on 21 September 1996 were due to atmospheric variability rather than to a discrepancy between the CO\textsubscript{2} instruments.

During SOLVE, the ER-2 was based at the Arena Arctica in Kiruna, Sweden, and the balloon was launched from the nearby Esrange launch facility operated by the Swedish Space Corporation. The nearly coincident ER-2 and balloon flights on March 5, 2000 occurred near the edge of the Arctic vortex. Thus, the air was characterized by large tracer gradients in the presence of strong winds. CO\textsubscript{2} and N\textsubscript{2}O data from the two platforms are compared as a function of pressure altitude in Figure 7. Agreement for both species is excellent above 17.6 km and from 15.4 - 16.4 km. However, agreement is not particularly good for either species below 15.4 km or from 16.4 - 17.6 km, suggesting that the two platforms encountered slightly different air masses in these altitude regions. For this analysis, N\textsubscript{2}O was measured by gas chromatography by the four channel Airborne Chromatograph for Atmospheric Trace Species (ACATS-IV) on the ER-2 (Elkins et al. 1996; Romashkin et al. 2001) and by the Lightweight Airborne Chromatography Experiment (LACE) on the balloon (F. L. Moore, manuscript in preparation). Since O\textsubscript{3} is not conserved in the polar vortex, it is not an especially good tracer in this case.

5. Conclusions

In situ measurements of atmospheric CO\textsubscript{2} can be extremely precise if temperatures and pressures are tightly controlled and the instrument is carefully calibrated in flight. Both the ER-2 and balloon CO\textsubscript{2} instruments have operated reliably over a wide range of conditions, resulting in a long-term precision for both instruments of better than ±0.1 ppmv, except during September and December 1996, when degradation of an
electronic component reduced the precision of the ER-2 instrument to ± 0.15 ppmv. The ER-2 dataset provides extensive latitudinal coverage and impressive temporal resolution from 1992 to 1998, while the OMS observations provide complementary information above ER-2 altitudes. Tropospheric data obtained during the COBRA mission will provide new information about sources and sinks of carbon on region scales.
Acknowledgements: We thank R. Keeling and D. Toohey for early development work on the measurement technique and for ideas about the calibration strategy; A. Bazzaz for engineering support; J. Lipson, C. Rosser, S. Alex, C. Gerbig, and J. Lin for field and laboratory support; M. Loewenstein and coworkers for data from ATLAS; C. R. Webster and coworkers for data from ALIAS-II; J. Elkins and coworkers for data from ACATS-IV and LACE; M. Proffitt, J. Margitan and coworkers for O$_3$ data; T. P. Bui and coworkers for ER-2 meteorological data; and S. Vay and B. Anderson for unpublished CO$_2$ data from the DC-8 flight of 20000123. We are grateful for the efforts of all the ER-2 investigators, pilots and crew and for the support of the National Scientific Ballooning Facility. Funding for the ER-2 instrument was provided by NASA's Upper Atmosphere Research Program and Atmospheric Effects of Aviation Project and for the balloon instrument by NASA's Environmental Research Aircraft Sensor Technology program and by the National Oceanic and Atmospheric Administration.
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Figure 1. Schematic of the ER-2 CO2 instrument. Dashed lines indicate heated enclosures; dot-dashed lines indicate the detector pressure vessel. See text for an explanation of the four flight standards, labeled REF, LTS (long-term surveillance), LOW, and HIGH.

Figure 2. (a) Intercomparison of CO2 measurements from the Harvard ER-2 CO2 analyzer (dark symbols) and the LaRC instrument on the DC-8 (light symbols) on 23 January 2001 at ~11 km over Sweden. The airplanes flew in formation for ~30 minutes, with the ER-2 starting ~60 seconds behind the DC-8 and falling to ~12 minutes behind by the end of the flight leg. (b) The difference between the CO2 values reported by the instruments when binned into 0.1 degree latitude intervals. The dotted line denotes the median difference, with the Harvard ER-2 instrument 0.09 ppmv higher than the DACOM DC-8 instrument on average. If binned with respect to longitude instead, a median difference of 0.10 ppmv is obtained. This analysis does not account for movement of the air (i.e., wind) over the course of the experiment or for possible errors in the reported latitude or longitude.

Figure 3. Schematic of the pump unit for the balloon CO2 instrument. Inset is a detail of the custom fitting for introducing calibration gas (see text for details). Symbols are the same as in Figure 1.
Figure 4. Schematic of the water trap designed for sampling in the troposphere. The dewar is filled with crushed dry ice before each flight. Symbols are the same as in Figure 1.

Figure 5. (a) Latitude-altitude and (b) longitude-altitude trajectories for the balloon (light) and ER-2 (dark) flights on 30 June 1997 from Fairbanks, AK. (c) CO₂ versus pressure altitude (calculated assuming a constant scale height of 7 km) for the balloon (light crosses) and the ER-2 (dark filled circles) flights. (d) CO₂ versus O₃ for the same flights, symbols are the same as in (c). (e) Median CO₂ mixing ratio from data shown in (c) binned in overlapping 250 m intervals from 10 km to the maximum altitude of the ER-2. (f) The difference between the binned CO₂ profiles for the balloon and the ER-2. Dashed line indicates the median difference of 0.04 ppmv.

Figure 6. (a-c) Tracer correlation plots for the ER-2 (light) and OMS (dark) intercomparison flights of 21 September 1996. ER-2 data are shown only for the vertical profile at the most southerly point in the flight track (34.7-35.6° N). The latitude range for the OMS flight was 34.1-34.5° N. The ER-2 was delayed on take-off, resulting in an abbreviated flight plan and a time delay of nearly 4 hours between the profiles. OMS CO₂ data is available at ER-2 altitudes only during the ascent portion of the flight. The dark open circles in panel (c) correspond to the balloon descent. (e-f) Same as (a-c), but the ER-2 data for the entire September deployment are shown for context (light grey filled circles). Data from the ER-2 flight on 13 September are shown separately (medium grey crosses) to highlight similarity to the OMS data.
Figure 7. (a) CO$_2$ and (b) N$_2$O from the ER-2 (light crosses) and OMS (dark filled circles) intercomparison flights of 23 January 2001. ER-2 data are shown only for the descent into Kiruna, Sweden, since that occurred at the same time the balloon was ascending from Esrange. The profiles were separated by 1.25 to 3.75 degrees latitude and 1 to 3 degrees longitude, with the largest separation at the highest altitudes.
Table 1: Primary CO₂-in-Air standards

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<th>SIO-WMO X95 Mole Fraction Scale (ppmv)</th>
<th>NOAA/CMDL Mole Fraction Scale (ppmv)</th>
<th>SIO-WMO X95 - NOAA/CMDL (ppmv)</th>
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<td>400.89</td>
<td>400.69</td>
<td>0.20</td>
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</tbody>
</table>
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A high-precision fast-response airborne CO$_2$ analyzer for in situ sampling from the surface to the middle stratosphere

B. C. Daube, Jr.; K. A. Boering; A. E. Andrews; S. C. Wofsy

Carbon dioxide concentrations at the Earth's surface exhibit a latitudinally varying seasonal cycle due to uptake and release by vegetation and soils, superimposed on a long-term increase due to fossil fuel combustion. The seasonal cycle and the long-term trend propagate from the surface into the troposphere and eventually into the stratosphere. Thus measurements of CO$_2$ can be used to diagnose transport rates throughout the atmosphere. In addition, carbon dioxide measurements can be used to infer surface fluxes, providing, for example, an indicator of how much carbon is being stored in forests and other ecosystems. Accurate carbon dioxide measurements will be needed in the future to monitor emissions and to evaluate the efficacy of carbon mitigation strategies. This paper provides a detailed description of two CO$_2$ analyzers designed to fly on the NASA ER-2 aircraft and on high-altitude balloons. These instruments provide extremely accurate measurements of CO$_2$ from the surface up to 32 km. The sensors can detect a change of 0.1 ppmv on an atmospheric background of approximately 370 ppmv. Data from these instruments have been used to determine the average age of stratospheric air, which provides information about how long pollutants will remain in the atmosphere, and to measure uptake of carbon by forests and croplands in North America.