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SEPTEMBER 1979
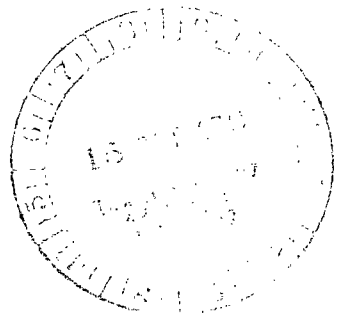
NASA

NASA Technical Paper 1526

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SUMMARY

Carbon monoxide in the upper troposphere and lower stratosphere (6 to 13 km altitude) was measured as part of the NASA Global Atmospheric Sampling Program (GASP). GASP measurement systems were installed on four airline-operated aircraft in commercial service to measure atmospheric constituents in order to determine, if possible, whether aircraft are contributing to pollution of the upper atmosphere. Carbon monoxide (CO) levels encountered on the GASP flight routes ranged from 0.03 to 0.4 parts per million by volume (ppmv).

The CO analyzer is a modified version of a commercial instrument manufactured by Beckman Instruments, Inc., Anaheim, California. The major modification made by Beckman was a twentyfold increase in sensitivity, resulting in a 1-ppmv full-scale analyzer. Other modifications included changes in the readout; the addition of control circuits to permit automatic, unattended operation; and repackaging to meet Federal Aviation Administration (FAA) and Boeing Company environmental requirements for operation on Boeing 747 aircraft.

The analyzer operates on the infrared (IR) absorption principle with dual-isotope fluorescence and has a single IR source, a single sample cell, and a single solid-state detector. These features provide long-term stability and minimize the problems associated with high vibration levels. Calibrations were performed with Standard Reference Materials obtained from the National Bureau of Standards and with a closed-loop volume-ratio technique. Calibrations were also performed with span gases obtained at NASA.

Uncertainty in the CO measurement resulted from calibration errors, change in analyzer sensitivity between calibrations, GASP measurement system error, and random fluctuation of the output signal. Measurement errors over a 2-year period ranged from ±3 to ±13 percent of reading plus an error due to random fluctuation of the output signal of ±3 to ±15 parts per billion by volume (ppbv).

INTRODUCTION

This report describes the measurement of carbon monoxide (CO) as part of the Global Atmospheric Sampling Program (GASP). The CO analyzers are a modified

version of a commercial 20-parts-per-million-by-volume (ppmv) full-scale infrared (IR) absorption instrument manufactured by Beckman Instruments, Inc., Anaheim, California. The major modification made by Beckman for GASP use was a twentyfold increase in sensitivity to achieve a 1-ppmv full-scale output with a limit of detectability of 0.02 ppmv. This represents an extension of the state of the art for a field instrument. Other modifications included changes in the readout; the addition of control circuits to permit automatic, unattended operation; and repackaging into standard avionics enclosures. The modified analyzers met Federal Aviation Administration (FAA) and Boeing Company environmental requirements for operation on Boeing 747 aircraft. Seven analyzers were purchased for GASP.

In this program, managed by the NASA Lewis Research Center, daily global measurements were made of such atmospheric constituents as carbon monoxide, ozone, condensation nuclei, and water vapor. These measurements were made in the upper troposphere and lower stratosphere (6 to 13 km altitudes) with fully automatic instrumentation systems installed on four airline-operated B-747 aircraft in commercial service. A NASA Convair 990 capable of carrying a GASP measurement system was used to survey off-airline routes on an assignment basis. The purpose of the program was to obtain baseline data and to monitor the constituents associated with aircraft-engine emissions to determine, if possible, whether aircraft are contributing to pollution of the upper atmosphere.

Details of the aircraft system are given in references 1 and 2. A series of reports (refs. 3 to 9) describe the flight routes, dates, data-processing procedures, and data tape specifications. In this report, the GASP measurement system and the carbon monoxide analyzer are described in sufficient detail so that a potential user can judge the quality of the CO measurements. Analyzer performance details, calibration procedures, and measurement errors are discussed.

GASP MEASUREMENT SYSTEM

The GASP aircraft installation, its operation and control, and the data-acquisition system are described. Air-sampling details for the CO measurement and a description of in-flight analyzer operation are included.

Operation and Control

The GASP measurement system was installed near the nose of the B-747 below the passenger level (fig. 1). The system had three functional subsystems: the air-sampling system, the constituent-measuring instruments, and the management and control system.

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A schematic of the air-sampling system is shown in figure 2. Air was sampled by two probe assemblies mounted on the aircraft skin. The geometry of the probes ensured sampling outside the boundary layer. One assembly, dedicated solely to the water-vapor measurement, had the sensor attached. No ducting was required. All other constituent measurements were made with the second assembly, which contained two inlets. One inlet was for isokinetic sampling to measure particle number density. The other inlet provided an air sample to a filter mechanism for collecting airborne particles and also to the constituent-measuring instruments. Sample air for the ozone and carbon monoxide measurements was pressurized to 100 kilopascals. Sample flow rate for each measurement was determined by a choked venturi downstream of each instrument. Spent air was dumped overboard through a static vent in the aircraft skin.

The GASP installation contained instruments for measuring carbon monoxide, ozone, condensation nuclei, water vapor, and particle number density. A particulate filter collection unit with several individual filter holders, which could be sequentially exposed, was also installed on two GASP aircraft.

Automatic control of all system operations was provided by the data management and control unit (DMCU). This unit contained a small, special-purpose computer programmed to provide the automation. Essentially, there were three operating modes: standby, calibration, and data. The GASP system was powered before takeoff. At this time, the system was on standby. That is, there was no sample flow and no data were recorded. After takeoff, the DMCU, upon receiving a pressure signal at 6 kilometers altitude, opened the air-sampling probe inlets and exhaust vents, started the pump, and initiated the operating cycle. The operating cycle had a period of 1 hour and consisted of twelve 5-minute segments. Six of these segments were data segments during which constituent measurements were made. Interspersed between these data segments were six 5-minute calibration segments during which control signals were activated to place the instruments in a calibration mode. The number and nature of calibration segments that each instrument underwent depended on that instrument's operating characteristics. Data were recorded during the last 16 seconds of each 5-minute segment. The operating cycle repeated until aircraft descent. At the conclusion of each flight, when the aircraft descended to 6 kilometers, the DMCU returned the system to standby status. The air-sampling pump was shut down, the probe inlets were capped, and the exhaust vents were closed to prevent possible contamination of the air-sampling ducts.

The DMCU could also recognize certain failures and fault conditions and modify the system accordingly. In case of major data-acquisition or system control problems, a cockpit light was activated requesting the flight engineer to deactivate the system until it was checked out. If the probe inlets did not open at 6 kilometers, the flow system was not activated. A manual override was provided to allow operation of the system for a ground checkout.

Data-Acquisition System

The DMCU also managed the data flow between the various subsystems and for-matted the data for output to a digital cassette tape recorder. A block diagram showing the relationship between system control, data acquisition, and the aircraft is presented as figure 3. In addition to data from the air-sampling instruments, such supportive data from the flow system as pressures and temperatures were recorded. Status information, including valve positions, instrument identification signals, etc., were also recorded. Aircraft flight data were collected at the time of air constituent measurements. Latitude, longitude, heading, and the computed wind direction and velocity were obtained from the aircraft inertial navigation system. Altitude, air speed, and static air temperature were collected from the central air-data system in the aircraft. Date and time were provided by a separate clock-calendar unit.

At intervals of about 2 weeks, data tape cassettes were replaced and data were transcribed onto computer-compatible tape for further processing. Electronic instrument identification codes were recorded with the data and used, when applicable, to select the proper calibration curves. Data tape reports were prepared at the Lewis Research Center. Data tapes are available through the National Climatic Center, Ashville, North Carolina.

Carbon Monoxide Measurement

The analyzer, shown in figure 4, is packaged in two cases to meet weight-per-unit specifications of the GASP equipment rack. Total weight is 30 kilograms. The electronics case is 23 centimeters wide, 50 centimeters long, and 18 centimeters high. The optics case is 35 centimeters wide, 62 centimeters long, and 18 centimeters high. Plumbing connections are made at the front panel, and all electrical connections are made through connectors mounted on the rear panel of each case. Cooling is provided by a fan installed in the top cover of each case with air ingestion through screened cutouts in the side panels.

The air sample for the CO measurement was obtained through the pressurized portion of the GASP flow systems. Absolute sample pressure was maintained at 100 kilopascals ±5 kilopascals at altitudes from 6 to 12 kilometers by the pressure-regulating system. All sample lines from the probe inlet to the pump and all components in the pressurized portion of the system upstream of the analyzer were fabricated from Teflon or were Teflon coated on the inside. A schematic of sample flow through the analyzer is shown in figure 5. A flow rate of 5 liters per minute, established by a choked venturi downstream of the analyzer, was monitored by measuring the pressure

between a fixed orifice and the venturi. Inlet pressure and temperature were measured to permit corrections for density effects.

Flow inside the analyzer depended on the operating mode; namely, DATA, ZERO, or GAIN. The operating mode was selected by control signals from the DMCU. In the DATA mode (CO concentration measurement), the air sample passed through a dessicant cartridge to remove water vapor and then through a particulate filter before it entered the sample cell for analysis. In the ZERO mode, flow was similar except that a solenoid valve, activated by a control signal, diverted the air sample through a CO scrubber and a second particulate filter before it entered the sample cell. The scrubber, which contained heated Hopcalite particles, was sized to remove all traces of CO from a gas with an original content of 1 ppmv at a flow rate of 5 liters per minute. The ZERO output level was monitored three times during the DMCU operating cycle at 20-minute intervals. In the GAIN mode, sample flow was identical to ZERO-mode flow, but simultaneously an electronic signal replaced the IR detector output signal. The level of the electronic signal, adjusted in the laboratory, was such as to result in an output equivalent to 0.5 ppmv and served as a check on the electronic gain of the analyzer. The GAIN output level was monitored once per hour.

The analyzer environment was approximately the same as the passenger-cabin environment. Air from the passenger cabin was circulated around the GASP equipment rack for heat dissipation. In flight, the analyzer ambient-temperature range was 285 to 300 K. Cabin pressure was maintained about 60 kilopascals above altitude pressure at altitudes above 7 kilometers. This was less than the CO air-sampling pressure so that small leaks in the sampling system would not affect the accuracy of the CO measurement.

The analyzer output was a linear 0- to 5-volt dc signal corresponding to the CO concentration of the air sample. Sensitivity, adjusted in the laboratory during calibration, was 0.25 ppmv per volt. Because a decrease in analyzer ambient temperature caused a zero shift, and because the data system could not accept a negative voltage, the ZERO output level was set at 2 volts dc. A 5-volt dc output, then, corresponded to 0.75 ppmv. Carbon monoxide levels encountered on the GASP flight routes ranged from 0.03 to 0.4 ppmv.

Each analyzer was calibrated before it was installed aboard an aircraft. Upon the analyzer's removal, the calibration was checked to determine any change in sensitivity. Carbon monoxide concentration was computed from

$$\text{ppmv CO} = \frac{P_0}{P_{meas}} \times \frac{T_{meas}}{T_0} (\text{DATA} - \text{ZERO}) S$$

where

P_0	pressure, 101 kPa
P_{meas}	analyzer inlet pressure, kPa
T_{meas}	analyzer inlet temperature, K
T_0	temperature, 298 K
DATA	analyzer output, DATA mode, V dc
ZERO	analyzer output, ZERO mode, V dc
S	analyzer sensitivity, ppmv/V dc

The values of P_0 and T_0 were the conditions under which the analyzer calibration took place. The value S was an average of the sensitivities obtained before analyzer installation and after its removal from the aircraft. Uncertainty of the CO measurement is discussed later in this report.

ANALYZER FUNCTIONAL DESCRIPTION

The Beckman CO analyzer with dual-isotope fluorescence (ref. 10) has a single IR source, a single sample cell, and a solid-state detector. These features improved the reliability of the CO measurement under conditions imposed by the GASP environment. Because the detector has high mechanical stability, its performance was not affected by the vibration levels encountered in flight. And the use of a single source and a single sample cell minimized the drift problems associated with traditional analyzers.

Dual-Isotope Fluorescence Technique

In the Beckman dual-isotope fluorescence technique, pulses of IR radiation are alternately produced at wavelengths that correspond to the vibrational-rotational absorption bands of $C^{12}O^{16}$ and $C^{13}O^{16}$. These two IR radiation spectra are passed through a single sample cell. The CO present in the air sample (98.9 percent of all naturally occurring carbon monoxide is $C^{12}O^{16}$) will absorb the $C^{12}O^{16}$ radiation but not the $C^{13}O^{16}$ radiation. Thus, the $C^{13}O^{16}$ radiation pulses are a reference against which the absorption of $C^{12}O^{16}$ is measured. After passing through the sample cell, the alternating radiation pulses are converted to electrical signals by an IR detector. Ratio comparison of the two signals yields a voltage level that corresponds to the CO concentration in the sample chamber.

The dual-isotope technique is depicted in figure 6. As shown, a broadband, black-body IR source stimulates fluorescence of the $C^{12}O^{16}$ and $C^{13}O^{16}$ species contained in a single sealed cell. The fluoresced radiation is allowed to pass through two gas-filled filter cells mounted on a rotating wheel. One filter cell contains the $C^{12}O^{16}$ species, the other contains the $C^{13}O^{16}$ species. Each cell, when appearing in the optical path, will filter, by absorption, either the $C^{12}O^{16}$ or $C^{13}O^{16}$ IR radiation. The net result is IR energy that consists of alternating pulses of $C^{12}O^{16}$ and $C^{13}O^{16}$ radiation, as shown in figure 6. To eliminate the large background caused by the black-body source, a chopper wheel is mounted on the rotating shaft with windows oriented out of phase with respect to the absorption cells. As a result, only the vibrational fluorescent energy is transmitted through the chopper assembly.

These IR radiation pulses are passed through the sample cell. The $C^{12}O^{16}$ (A pulse) is reduced in intensity as a result of absorption by the CO contained in the sample cell but the $C^{13}O^{16}$ (B pulse) remains unchanged. The photoconductive detector converts the A-B-A-B pulse train to an electrical signal. Particulate matter or moisture, either present in the gas sample or accumulated on the optical windows, will attenuate both pulses equally. Thus no ratio difference is detected, and the drift problems associated with analyzers using a separate reference chamber are eliminated. Similarly, any change in the IR energy emanating from the chopper assembly or any change in the sensitivity of the detector will again affect both pulses equally.

Signal Processing

A block diagram of the analyzer is shown in figure 7. A low-noise preamplifier amplifies the detector output signal to a higher level. Further amplification is attained by a postamplifier, and the signal is then sent to the automatic gain control (AGC) board located in the electronics unit. A variable-gain amplifier receives the signal and, by feedback action, maintains the output signal at a constant peak-to-peak level even though the postamplifier signal level may vary.

The output of the variable-gain amplifier is synchronously demodulated. The demodulator output is equal to the difference between the A and B pulses. An electronically generated zeroing signal is then added to form a direct-current voltage that represents the CO concentration. This zero signal is adjustable so that analyzer output voltage for a CO-free gas can be set at an appropriate level. The demodulator also functions as a low-pass filter amplifier. Another direct-current amplifier follows that has similar gain and filter characteristics.

Linearity correction and compensation for GAIN and ZERO temperature coefficients are then performed. The temperature coefficients are compensated for by a thermistor located in the chopper assembly and by an amplifier. This temperature signal is

scaled and applied to the demodulator to correct for the normal sensitivity of instrument zero to temperature changes. An analog multiplier is used to correct for both nonlinearity and the sensitivity of instrument span to temperature changes.

Timing signals are generated by circuitry on the automatic frequency control (AFC) board. The AFC receives a trigger pulse from a magnetic pickup in the chopper assembly. This once-per-revolution pulse is amplified and applied to a phase-locked loop containing an oscillator. The oscillator signal is divided for comparison with the trigger frequency. The phase-locked loop will adjust its oscillator until the frequencies and phases are exactly matched. The circuit, because of its nature, follows any change in power-line frequency.

Analyzer Performance

A strip-chart recording of an analyzer output signal after a calibration is shown in figure 8. Chart speed was 1 division per minute. Several performance characteristics are apparent, such as repeatability, random fluctuation of the output signal, and response time. These characteristics, as shown in the figure, are typical of all the GASP CO analyzers. For this recording, the analyzer was alternately operated in the ZERO, GAIN, and DATA modes, which was equivalent to introducing a step change in CO concentration of the air sample. The air sample contained 0.65 ppmv of CO in nitrogen at a flow rate of 5 liters per minute.

With a sensitivity of 0.25 ppmv per volt, the DATA output was 2.60 volts dc above the ZERO level. Similarly, the half-scale GAIN output was 2.00 volts dc above ZERO. At a flow rate of 5 liters per minute, the time constant (the time required to reach 63 percent of final reading) was 1.5 minutes. Random fluctuation was ±0.05 volt dc, which is equivalent to ±0.012 ppmv.

During the time period shown on the recording, about 100 minutes, the ZERO output level increased from 1.55 volts dc to 1.65 volts dc. This zero drift was typical when the analyzer had been powered for less than a few hours. However, the sensitivity remained constant.

Modifications for GASP

The modifications by Beckman Instruments, Inc., were made to meet the GASP requirements of a highly sensitive instrument capable of automatic, unattended operation. Also, installation in a commercial aircraft imposed stringent safety precautions and a high use-factor with limited accessibility for servicing.

Increasing the sensitivity of the commercially available analyzer by a factor of 20 was the primary performance modification. Extensive changes in the optics were made to achieve a full-scale range of 1 ppmv. A single-pass sample cell was replaced with a multipass sample cell with an optical path length of about 10 meters. The cell, containing gold-plated mirrors for high reflectivity, has a volume of 2.5 liters. The IR source and the fluorescent cell were selected for maximum efficiency and high output. The detector geometry and housing were modified to improve the optical coupling to the sample cell. The detector is maintained at 253 K by a thermoelectric cooler to enhance the signal-to-noise ratio. The hermetically sealed detector housing contains carbon dioxide and oxides of nitrogen to minimize interference from traces of these gases in the air sample.

Packaging into ARINC (Aeronautical Radio, Inc.) cases was necessary to meet airline requirements. Front-panel mounting of a flowmeter and a dessicant cartridge provide a visual check of sample flow and dessicant condition. Special mounting hardware and fabrication procedures were employed by Beckman to meet the shock and vibration test requirements. The main optics case subassembly, containing all the optical components, is shock mounted inside the case. Electrical connections are made through an ARINC connector mounted on the rear panel of each case. All input-output lines are EMI-filtered to meet Boeing Company standards for both electromagnetic interference generation and susceptibility.

As shown in figure 7, alternating-current power (115 V, 400 Hz) is brought into the electronics case and routed through an interconnect cable to the optics case. A circuit breaker and a thermal switch, mounted in each case, are wired in series so that the opening of any of these devices interrupts power to both cases.

Two voltages are wired to the output connector to provide discrete signals that were recorded to indicate case overtemperature or analyzer fault conditions. A TEMP indication occurs when analyzer power is interrupted by the opening of a thermal switch. A FAULT indication occurs when detector cooler servoloop control is lost, the signal from the detector is insufficient, or AFC sync control is lost. Case temperatures were continuously monitored by recording the resistance of a thermistor inside each case.

Each analyzer was identified in the GASP data recording by means of a voltage drop across a potentiometer mounted in each case. The potentiometer was set so that the resultant voltage corresponded to the analyzer serial number. This identification in the data recording made it possible to document the history of each analyzer. Periodic removal of the analyzer for maintenance or calibration was easily made, and data could be corrected for any change in sensitivity.

ANALYZER HISTORY AND RESULTS

All GASP instrumentation was subjected to reliability-and-quality-assurance tests and to extensive acceptance tests. Test programs for the CO analyzer were conducted by both Beckman and Lewis personnel. The time required to perform these tests resulted in about 400 hours of analyzer operation before it was installed aboard an aircraft. These procedures are described, along with calibration procedures and measurement errors. The measurement history is briefly discussed. Typical data from a GASP flight are included.

Tests

Burn-in and thermal cycling tests were performed by Beckman. The burn-in required 168 hours of operation, with a performance test and a two-point calibration conducted at 24-hour intervals. In the event of a failure, the analyzer was repaired and the test was continued until 168 hours of operation were completed. Thermal cycling tests were conducted with the analyzer in an environmental chamber. Chamber temperature was cycled from 333 K, down to 253 K, and back to 273 K, at which time a performance test and a two-point calibration were performed as in the burn-in tests. This cycle was repeated 20 times. The final four cycles had to be failure free.

Electromagnetic interference tests, based on procedures given in Boeing Company standards, were conducted and certified by a test laboratory under contract to Beckman. These tests were conducted on one analyzer for both interference generation and susceptibility effect. Any design changes made for compliance with Boeing requirements were made to all analyzers.

At Lewis, one analyzer was subjected to shock and vibration tests, as described in reference 11. Several minor hardware problems were corrected by more securely fastening some large components, circuit boards, and cable runs. Again, any changes made to the test analyzer were duplicated on all analyzers. Experience has shown that shocks encountered in handling and shipping were more severe than those specified in the test procedure even though the analyzers were shipped in padded containers.

A five-part acceptance test program was conducted at Lewis on each analyzer. This program consisted of an initial inspection, functional tests, electrical power and transient tests, temperature and altitude tests, and performance tests. These tests were performed to ensure compliance with specifications under laboratory and in-flight environmental conditions. Electrical power tests were made to determine the effect of various steady-state alternating-current voltage and frequency combinations that might be encountered on B-747 aircraft. Temperature tests were made to ensure that

analyzer sensitivity remained constant over an ambient-temperature range of 283 to 313 K. Ambient-temperature effects were eliminated by electronic adjustments in the temperature compensation circuitry.

Ambient-temperature transients, however, were accompanied by a zero shift, as shown in figure 9. The zero shift shown in the figure was the result of a decrease in ambient temperature from 298 to 286 K. This decrease approximated the GASP installation environment shortly after takeoff. For this test, the analyzer was operated in the ZERO mode while the temperature of the environmental chamber was changed. The test was then repeated with the analyzer operating in the DATA mode with an air sample containing 0.71 ppmv of CO. As shown, during the transient repeat, the analyzer was also periodically operated in the ZERO mode. Within the accuracy of the experiment, the response and the shape of both curves are the same, and the DATA-minus-ZERO output corresponds to the CO content of the air sample. Similar results were obtained with an increase in ambient temperature. The treatment of data obtained during cabin-temperature transients is discussed in the section Operating Experience.

Calibration

Since accurately known span gases with CO concentrations of less than 1 ppmv were not available, a precise means of producing CO-in-nitrogen-gas mixtures was required for analyzer calibration. Also, to establish the desired sensitivity, it was equally important that the "zero" gas be CO free. A block diagram of the two primary techniques employed at Lewis for calibration is shown in figure 10; namely, the flow-blending technique and the closed-loop technique.

For the flow-blending technique shown in figure 10(a), CO-in-nitrogen-gas bottles were obtained from the National Bureau of Standards. These were aluminum cylinders with a treated lining whose CO content was accurately known so as to serve as NBS Standard Reference Materials (SRM). Since the lowest concentration of CO obtainable as an NBS SRM is about 10 ppmv, this mixture had to be blended with proportionate amounts of CO-free nitrogen to obtain sample concentrations in the range 0.1 to 1.0 ppmv. A precision flow-blender, manufactured to NASA specifications, was used to obtain the proper flow rates. Accuracy of the flow-blender was checked at Lewis' flow-meter calibration facility, where calibrations are accurate to within ±1/4 percent.

The "zero" gas was obtained from liquid-nitrogen boiloff passed through an external, heated Hopcalite scrubber. To verify that this gas was CO free, the analyzer was alternately operated in the DATA and ZERO modes. In the ZERO mode, the air sample was routed through a second Hopcalite scrubber inside the analyzer. If there was no CO in the "zero" gas, DATA and ZERO output levels were identical. As a

further check, with "zero" gas flow and the ZERO operating mode, the air-sampling lines were valved off and the sample cell was evacuated with a pump at the analyzer outlet. Again, with acceptable "zero" gas, there was no change in output before and after the sample cell was evacuated.

The NBS SRM mixtures are reputed to be stable for 1 year. At the time of the initial calibrations, cylinder composition was certified as 9.82±0.14 ppmv of CO. After approximately 1 year, this cylinder was returned to NBS for analysis, which identified the composition as 9.78±0.14 ppmv. Taking into account the uncertainties of the NBS SRM and the flow controllers, calibrations were estimated to be accurate to within ±2 percent.

Initial calibrations were also done with the closed-loop technique shown in figure 10(b). The loop included the sample cell, a mixing plenum, a circulating pump, tubing, and a rubber septum for injection of pure CO by syringe. To determine loop volume, the loop was evacuated and closed off and the pressure was noted. The known volume was then filled with filtered, dry air at ambient pressure and closed off. It was then expanded into the closed loop and final pressure in the loop was noted. Loop volume was then calculated from the pressure-volume relation.

For calibration, the loop was purged with CO-free nitrogen gas and closed off and the pressure was adjusted to 101 kilopascals. An appropriate amount of CO was injected into the loop. A circulating pump was started to thoroughly mix the gas and then stopped to allow the pressure to equalize in the loop. Carbon monoxide concentration in the loop was the ratio of the volume of injected CO (corrected for purity, temperature, and pressure) to the total volume of the loop. Random error of the closed-loop calibration was within ±2 percent. Details of the closed-loop calibration technique are given in reference 12.

A single, straight line fits the calibration data obtained from the flow-blending and closed-loop techniques with a standard deviation of 0.014 ppmv.

The apparatus required to calibrate an analyzer, as previously described, was also used for other GASP instrumentation calibrations. To minimize turnaround time of an analyzer checkout, span gases were obtained for calibration. These were gas cylinders of liquid-nitrogen boiloff whose CO content was determined from a comparison with a flow-blending calibration. The CO content of these span gases was checked at about 6-month intervals. The change in CO concentration over this period was variable and in some cases excessive. Similar instabilities in CO concentration are reported in reference 13. Span-gas analyses were subsequently performed on a monthly basis.

Measurement Error

Each analyzer was calibrated before it was installed on an aircraft. A calibration check was performed when the analyzer was removed from the aircraft to determine any change in its sensitivity. The uncertainty of the CO measurement was estimated for each installation interval, which encompassed the initial calibration, the installation period, and the calibration check. This uncertainty was the result of calibration errors, change in analyzer sensitivity between calibrations, GASP system error, and random fluctuation of the output signal.

As stated in the previous section, the uncertainty of an NBS SRM flow-blending calibration was within ±2 percent. When CO-in-nitrogen-span-gas bottles were used, the calibration errors varied from ±2 percent to ±11 percent. The error due to a change in analyzer sensitivity ranged from 0 to ±3.1 percent, based on an average sensitivity determined from the calibrations during an installation interval. The GASP system error, estimated to be ±1 percent, was due to inaccuracies in the measurement of air-sample inlet pressure and temperature. These errors are expressed as a percentage of reading. The error due to random fluctuation of the output signal varied from analyzer to analyzer and for each analyzer with time. The magnitude of this error, expressed as ± ppbv, was independent of the CO concentration level.

For installation intervals from early 1977 to late 1978, the total measurement uncertainty ranged from ±3 percent to ±13 percent of reading plus an error of ±3 ppbv to ±15 ppbv due to random fluctuation. The measurement uncertainty is published in each data tape report for the installation intervals contained therein.

Operating Experience

The CO analyzers became part of the GASP measurement system in January 1977. Considering the environmental requirements, the high use-factor with limited servicing, and the sensitivity required to measure the low CO levels encountered in flight, the analyzers proved to be reliable instruments. Some had 8000 hours of operation. Failures were minimal. About 70 percent of the removals from an aircraft were for routine maintenance and calibration.

Before January 1977, during the initial installation intervals, the analyzers were subject to excessive changes in sensitivity. These changes were caused by shocks received during shipping and/or by vibration levels on the aircraft that changed the sample-cell mirror alinement. This problem was corrected by using more positive locking procedures on the mirror mountings. Also, with time, fine particles of Hopcalite from the CO scrubber migrated into the sample lines and into the sample cell. This migration contributed to the measurement error by "absorbing" CO in the

air sample and by diminishing the reflectivity of the mirror surfaces. A highly efficient, air-sampling filter was installed downstream of the scrubber to eliminate this problem.

Because a change in analyzer ambient temperature caused a zero shift, some CO data were precluded from use. This zero shift usually occurred shortly after takeoff, when the ambient temperature decreased approximately as shown in figure 9. Although the most current ZERO value was used in the CO calculation, large variations in successive ZERO levels can introduce errors in the reported CO level. To assist in identifying data that may have a significant error due to ZERO-level variation, any data recorded between ZEROS that differed by more than 100 millivolts (25 ppbv) were tagged. All data recorded between ZEROS that differed by more than 200 millivolts were edited out. All data, however, are included in the tapes sent to the National Climatic Center. Changing ZERO levels would require interpolation to eliminate these errors.

Carbon monoxide concentrations recorded on a meridian flight around the world are shown in figure 11. Flight altitude and levels of ozone concentration and condensation nuclei are included in the figure. Each data point in the figure is a 30-minute average of the constituent measurement. The flight was operated by Pan American World Airways. It began on October 28, 1977, from San Francisco, went over the North Pole to London, England, and then to Capetown, South Africa. From Capetown, the flight went directly over the South Pole to Aukland, New Zealand, and then back to San Francisco. The flight lasted 54 hours with 2-hour refueling stops in London, Capetown, and Aukland.

Air constituent measurements made between San Francisco and London and between Capetown and Aukland are stratospheric data. The high levels of ozone, the low levels of carbon monoxide and condensation nuclei, and the absence of clouds are typical of stratospheric measurements. Conversely, tropospheric data, obtained between London and Capetown and between Aukland and San Francisco are typified by high levels of carbon monoxide and condensation nuclei, low levels of ozone, and frequent cloudiness. In general, ozone levels correlated inversely with carbon monoxide and condensation nuclei levels.

The air constituent levels shown in figure 11 exhibit hemispheric and longitudinal differences. Carbon monoxide and condensation nuclei concentrations were higher for Northern Hemispheric air flowing south, illustrating that regions of heavy industrial releases have a measurable influence on atmospheric concentrations. The data obtained on this flight are analyzed in reference 14.

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CONCLUDING REMARKS

Carbon monoxide (CO) in the upper troposphere and lower stratosphere (6 to 13 km altitude) was measured as part of the NASA Global Atmospheric Sampling Program (GASP). The CO analyzer is a modified version of a commercial dual-isotope-fluorescence, infrared absorption instrument manufactured by Beckman Instruments, Inc., Anaheim, California. The major modification, made by Beckman, was a twentyfold increase in sensitivity, resulting in a 1-part-per-million-by-volume (ppmv) full-scale analyzer. Other modifications included changes in the readout; repackaging in standard avionics enclosures; and the addition of control circuits to permit automatic, unattended operation in an aircraft.

Uncertainty of the CO measurement was estimated for each installation interval, which encompassed the calibration before installation, the installation period, and the calibration after removal from the aircraft. This uncertainty was the result of calibration errors, change in analyzer sensitivity between calibrations, GASP system error, and random fluctuation of the output signal. For installation intervals from early 1977 to late 1978, uncertainty of the measurement ranged from ±3 to ±13 percent of the reading plus an error of ±3 to ±15 parts per billion by volume due to random fluctuation of the output signal. Carbon monoxide levels encountered on the GASP flight routes ranged from 0.03 to 0.4 ppmv.

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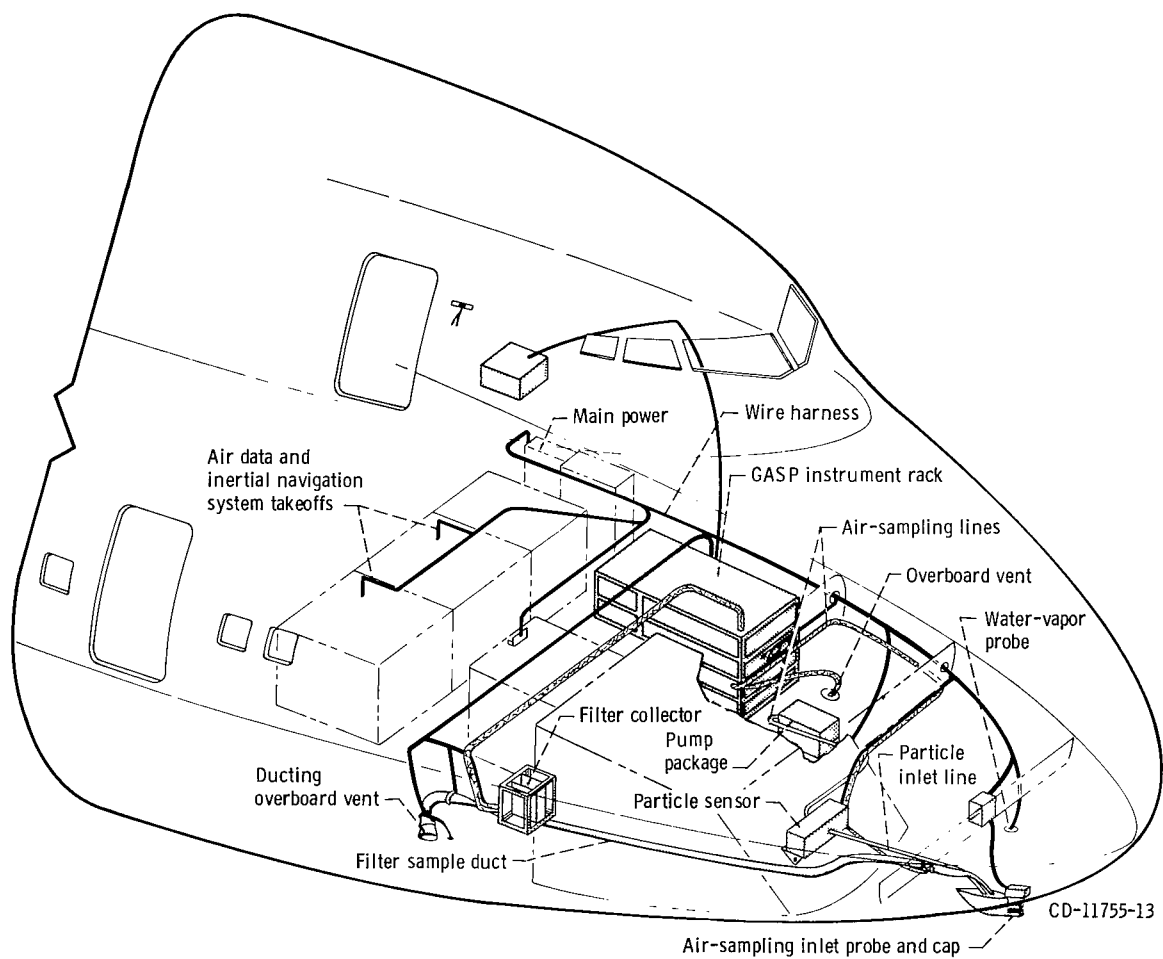
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Figure 1. - GASP system installation on Boeing 747.
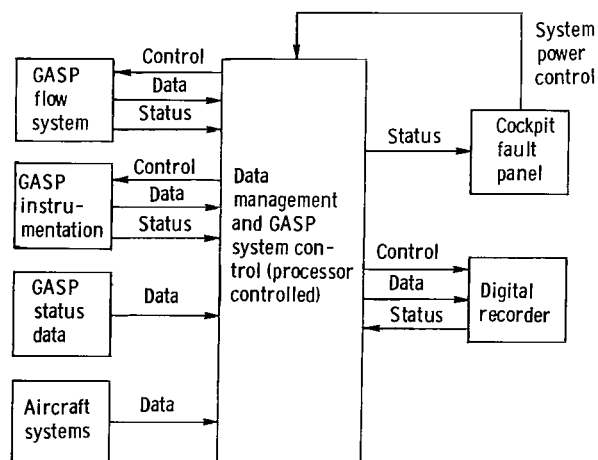
Air data and
inertial navigation
system takeoffs

Main power

Wire harness

GASP instrument rack

Air-sampling lines

Overboard vent

Water-vapor
probe

Filter collector

Pump
package

Particle
inlet line

Ducting
overboard vent

Particle sensor

Filter sample duct

Air-sampling inlet probe and cap

CD-11755-13
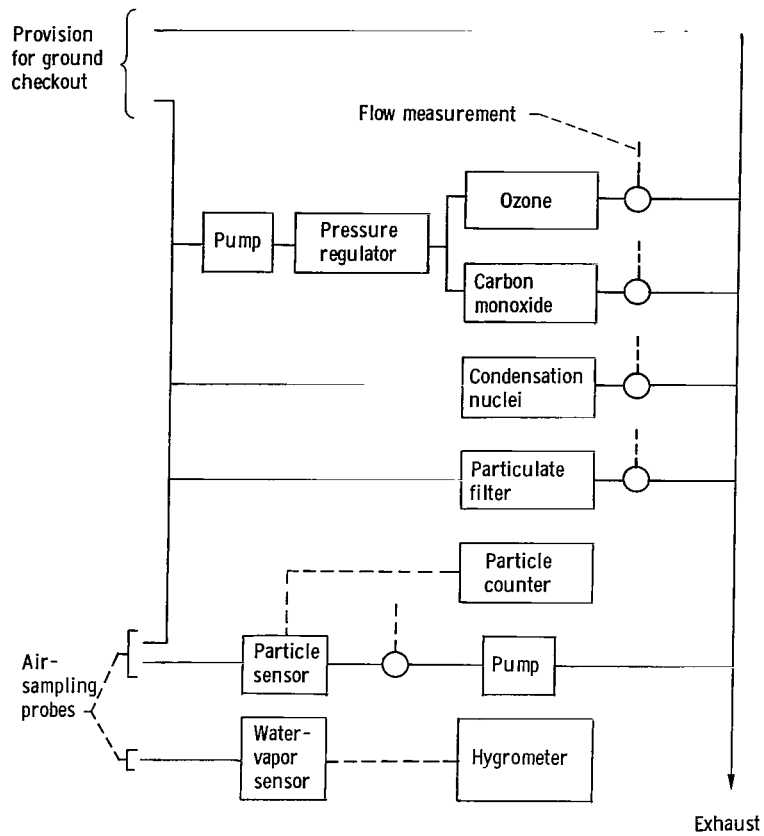
Figure 2. – GASP air-sampling flow system.

Figure 3. – GASP data management and system control.

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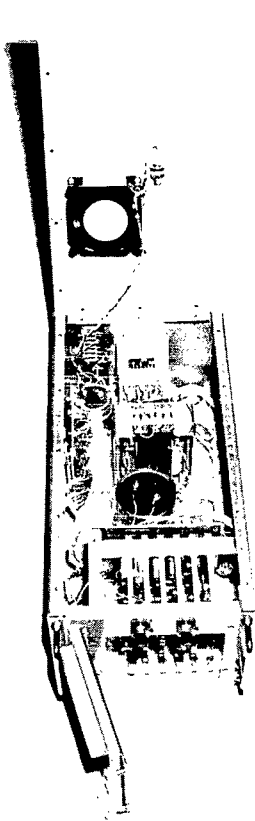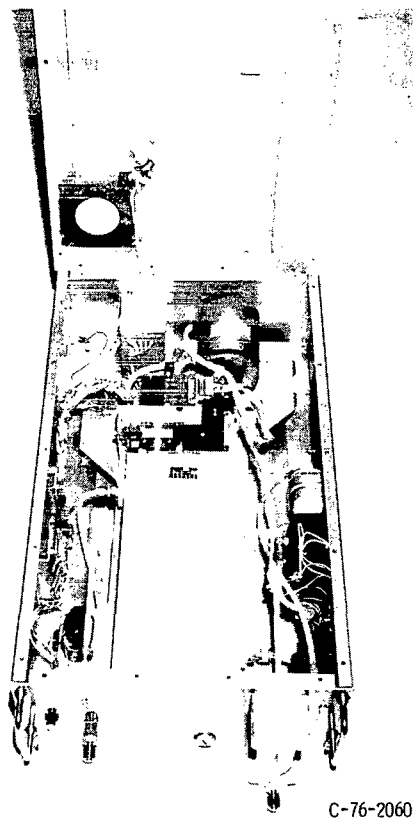
C-76-2059   C-76-2060

(a) Electronics case, top cover open.   (b) Optics case, top cover open.

Figure 4. – Beckman carbon monoxide analyzer.
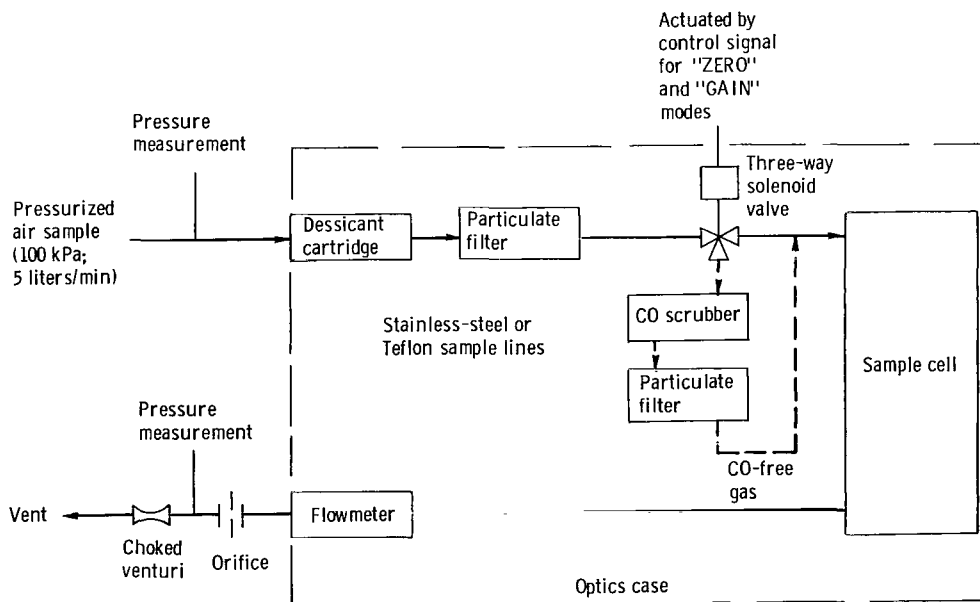
Figure 5. – Air-sample flow for CO measurement.
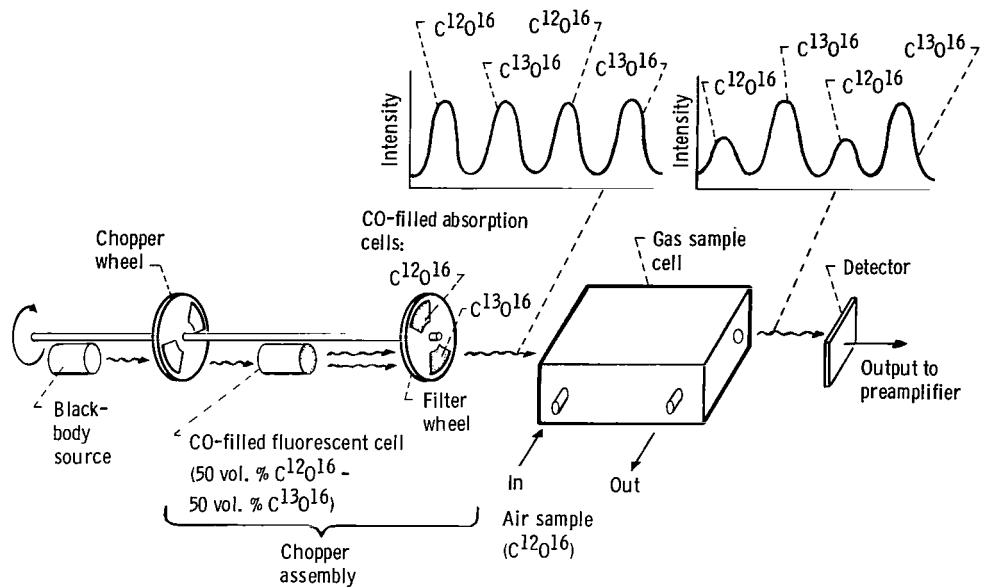
Figure 6. – Infrared absorption analyzer with dual-isotope fluorescence.
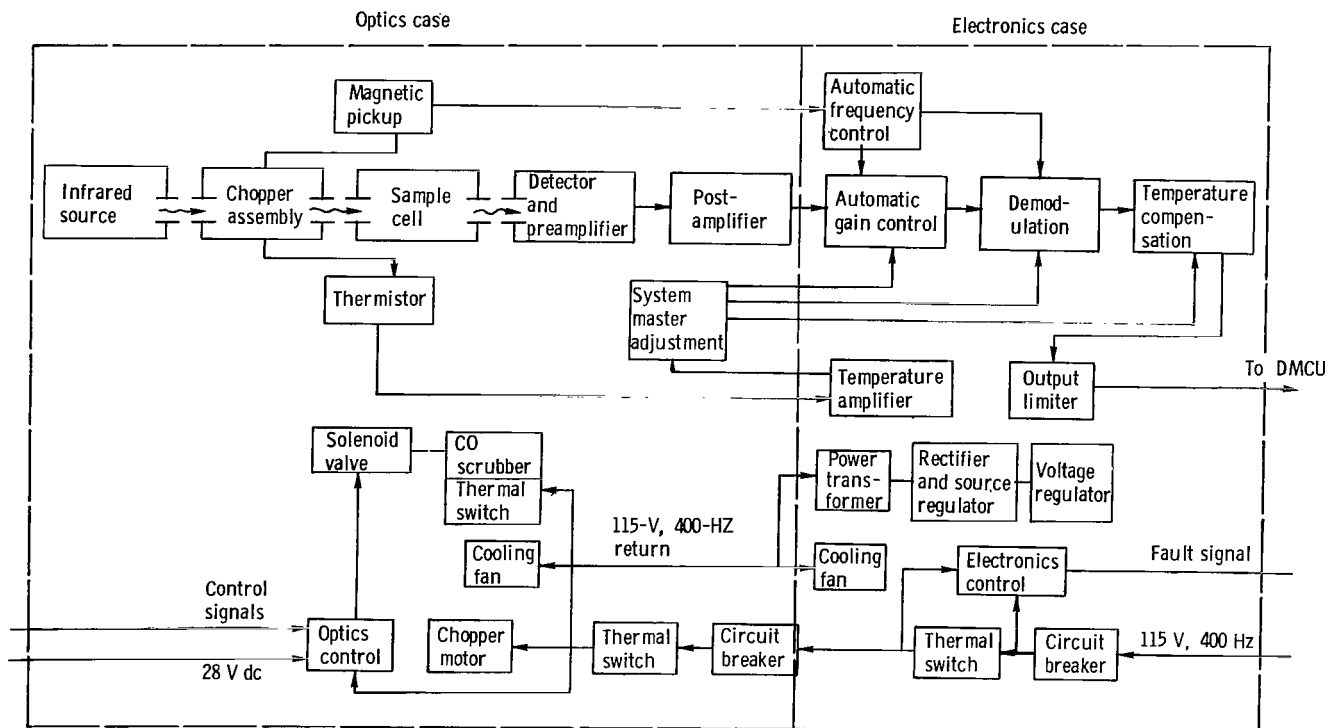
Figure 7. – Block diagram of 1-ppm CO analyzer.

20
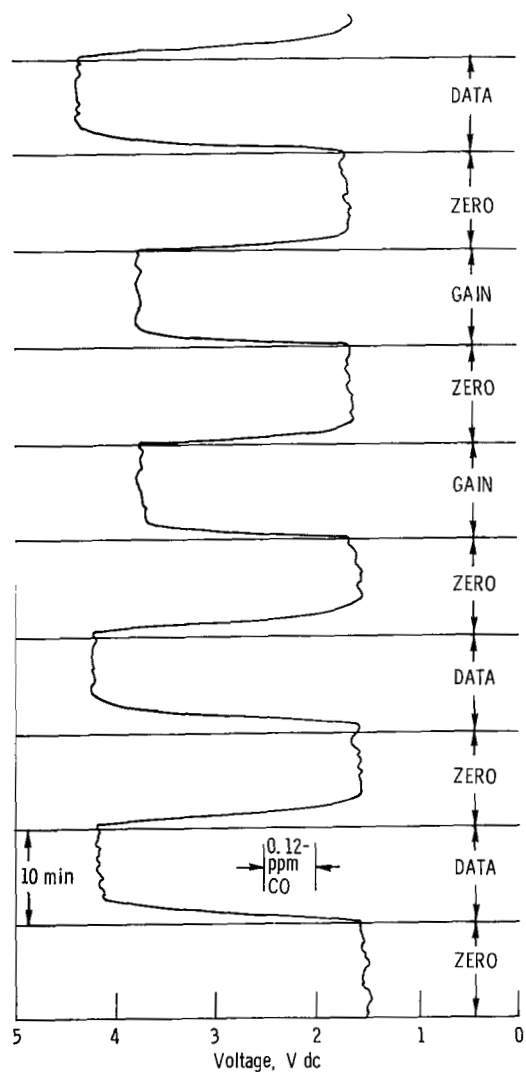
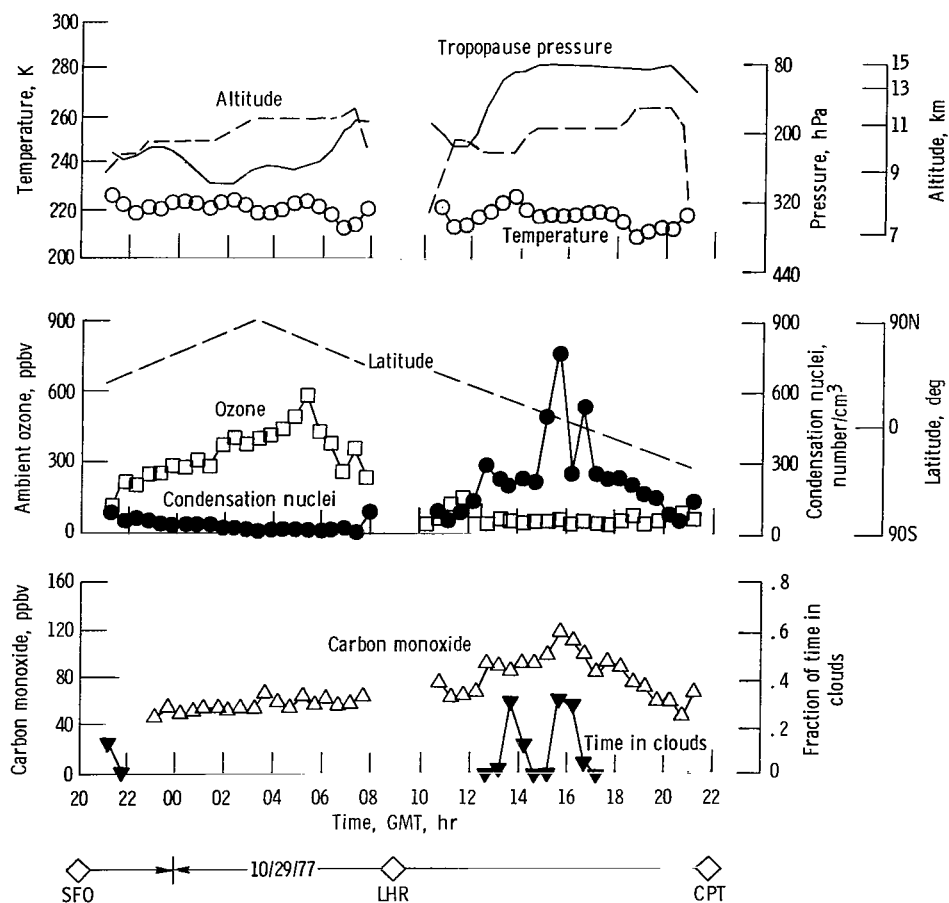Figure 8. - Recording of analyzer output. Span gas, 0.65 ppmv CO; flow rate, 5.0 liters/min.
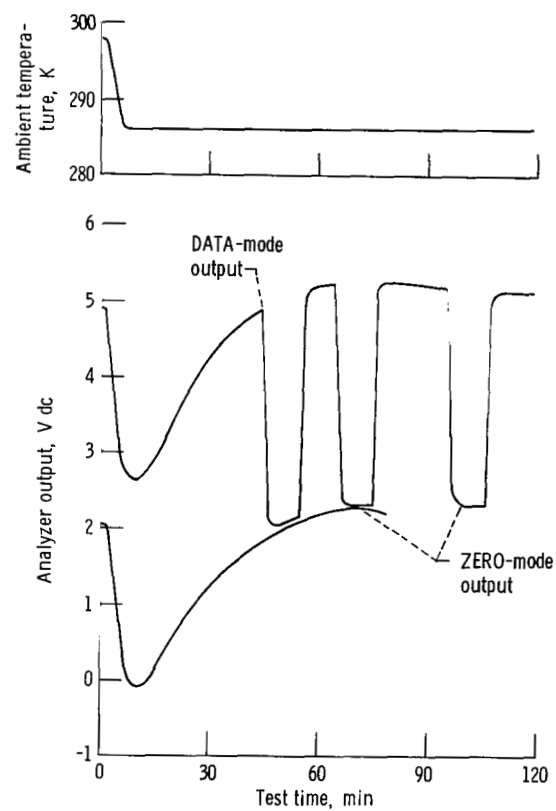
Figure 9. - Effect of ambient-temperature decrease on analyzer output. Span gas, 0.71 ppmv CO.
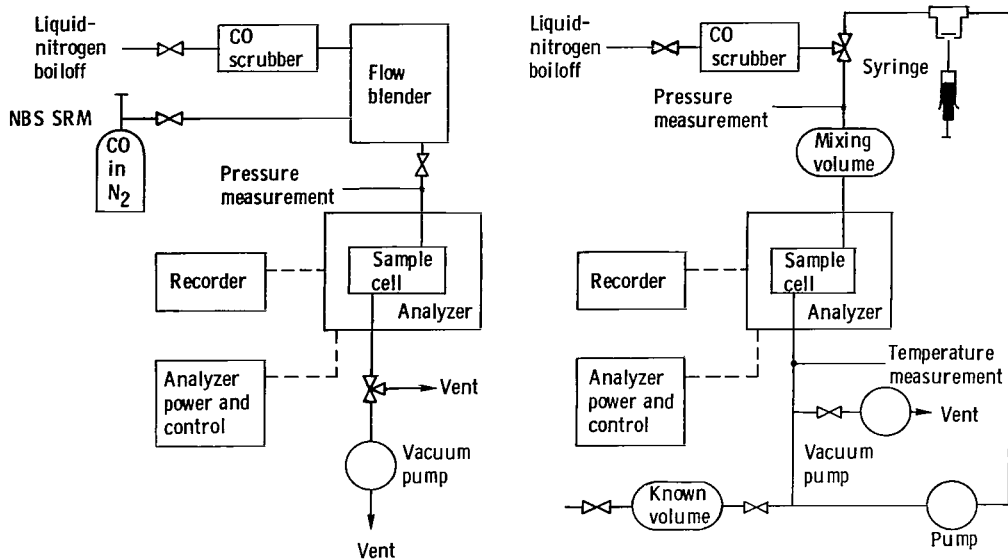
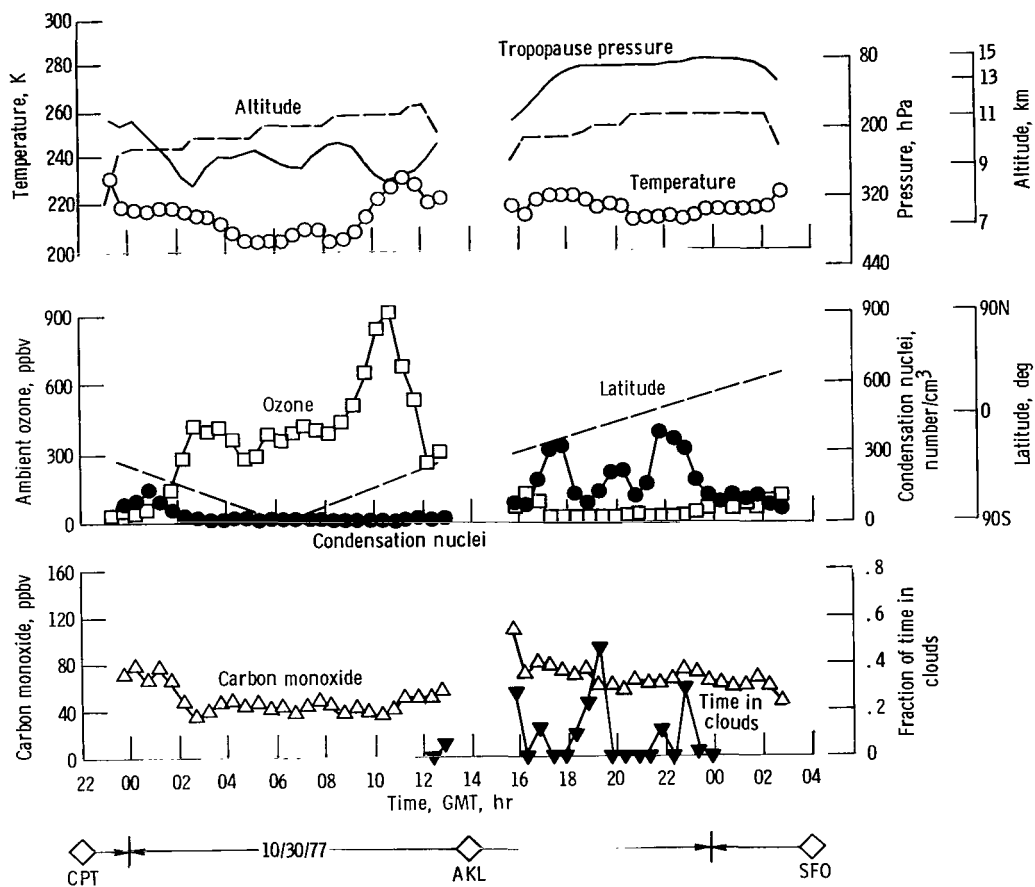(a) Flow-blending calibration system.   (b) Closed-loop calibration system.

Figure 10. - CO analyzer calibration techniques.

(a) San Francisco to London to Capetown (SFO-LHR-CPT).

Figure 11. - Flight record from Pan American World Airways 50th-
anniversary flight, October 28-31, 1977.

(b) Capetown to Aukland to San Francisco (CPT-AKL-SFO)

Figure 11. - Concluded.

1. Report No. NASA TP-1526	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle CARBON MONOXIDE MEASUREMENT IN THE GLOBAL ATMOSPHERIC SAMPLING PROGRAM		5. Report Date September 1979
		6. Performing Organization Code
7. Author(s) Thomas J. Dudzinski		8. Performing Organization Report No. E-9972
		10. Work Unit No. 198-10
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135		11. Contract or Grant No.
		13. Type of Report and Period Covered Technical Paper
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The carbon monoxide measurement system used in the NASA Global Atmospheric Sampling Program (GASP) is described. The system used a modified version of a commercially available infrared absorption analyzer. The modifications increased the sensitivity of the analyzer to 1 ppmv full scale, with a limit of detectability of 0.02 ppmv. Packaging was modified for automatic, unattended operation in an aircraft environment. The GASP system is described along with analyzer operation, calibration procedures, and measurement errors. Uncertainty of the CO measurement over a 2-year period ranged from ±3 to ±13 percent of reading, plus an error due to random fluctuation of the output signal of ±3 to ±15 ppbv.

17. Key Words (Suggested by Author(s)) Carbon monoxide Calibration Pollution monitoring Infrared absorption Earth atmosphere Instrumentation	18. Distribution Statement Unclassified - unlimited STAR Category 45		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 25	22. Price* A03

National Aeronautics and
Space Administration

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