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ANALYSIS SYSTEM FOR MEASUREMENT OF THE CO_2 CONCENTRATION IN FLASK AIR SAMPLES

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A system for measuring the concentration of CO_2 in flask air samples from the NOAA/CMDL worldwide flask sampling network is described. Up to 180 samples per day can be analyzed using a non-dispersive infrared CO_2 analyzer. All data acquisition and instrument control operations are handled by a Hewlett-Packard Series 300 desktop computer. A non-contaminating diaphragm pump transfers the sample from the flask to the NDIR CO_2 analyzer. Tests conducted using flasks filled from dry tanks of air showed either no systematic offsets or a small offset of about 0.1 ppm. The precision of the analysis system is estimated to be better than 0.1ppm.

1. INTRODUCTION

The measurement of carbon dioxide (CO_2) concentrations in air samples collected in flasks is one of the main methodologies for obtaining the global distribution of carbon dioxide in the atmosphere (see e.g., *Keeling et al.*, 1976, *Beardsmore et al.,* 1978, *Komhyr et al.*, 1985a, *Wong et al.*, 1984, *Conway et al.*, 1988). The Climate Monitoring and Diagnostics Laboratory (CMDL) of the National Oceanic and Atmospheric Administration (NOAA) currently collects air samples from a global network of sampling sites. These samples are returned to the main laboratory in Boulder, Colorado, where they are analyzed by gas chromatography for methane (*Steele et al.*, 1987, *Lang et al.*, 1990) and carbon monoxide, for carbon dioxide with a non-dispersive infrared (NDIR) analyzer, and for stable isotopic ratios with a mass spectrometer.

The NOAA/CMDL CO_2 sampling program began in 1968 with samples collected at Niwot Ridge, west of Boulder, and in the North Atlantic on Ocean Weather Station 'Charlie'. These samples were analyzed with a manually operated apparatus, which incorporated a mercury displacement pump for transferring the sample to an NDIR analyzer. The analyzer output was recorded on a strip chart recorder, from which flask concentrations were calculated by hand. By 1981, the NOAA/CMDL flask sampling program had expanded to 20 globally distributed stations, with a pair of samples collected once or twice per week. The large increase in the number of samples necessitated the development of a semiautomatic apparatus for the analysis (*Komhyr et al.*, 1983). This apparatus employed a free floating piston mechanism to transfer the sample to the NDIR analyzer. The gas flows were controlled by a microprocessor (*Harris et al.*, 1980) which also digitized the voltage output of the analyzer. The digitized output was then sent to a desktop computer, which computed the CO_2 concentration of the sample and stored the results as well as the sampling information for each flask.

Since 1981, the sampling network has expanded to over 30 sites. In addition, flask samples are collected aboard two cargo ships traversing the Pacific Ocean between the United States and New Zealand, an oil tanker operating in the South China Sea, and on special missions of aircraft and ocean going research ships. The increase in the number of flask samples again required that a new analysis system be built. The system described here has been in use since December, 1988.

2. ANALYSIS SYSTEM

The analysis system is shown schematically in Figure 1. Twelve sample flasks are connected via two-way solenoid valves to a central manifold. Four reference gases (W, X, Y, and Z) are also connected to the manifold so that the reference gases go through the same analysis path as the flask samples. A diaphragm vacuum/pressure transfer pump pulls the air from the flasks or the reference gases and momentarily compresses the air between the pump and the outlet solenoid valve (Vout). The solenoid valve opens, and the sample is pushed through a particle filter, a mass flow controller, a cold trap for removing interfering water vapor, and into the CO_2 NDIR analyzer. The pump is then turned off, and the sample is allowed to stabilize inside the analyzer. The response of the analyzer is measured with a digital voltmeter, and the results transferred to the computer.

The computer is the heart of the system, controlling the timing and sequence of events, prompting the operator for attention when needed, storing sample information, and calculating, storing and plotting flask sample concentrations. The computer is a Hewlett-Packard series 300 instrument controller, and the analysis program is written in HP BASIC. Raw data from the analysis is stored on 3 1/2" flexible disks. Processed results are merged into an existing database of flask data on a central file server, where the data is then available for analysis on a small network of computers. The flexible disk drive, digital voltmeter, switching unit and thermocouple pressure gauge controller are all connected to the computer via an IEEE-488 standard interface bus. A strip chart recorder is also used to provide a visual indication of the analysis, as well as a backup data logger.

The voltmeter is configured so that when triggered by the computer, begins taking readings at a rate of 2 readings per second for 30 seconds. The readings are then averaged by the voltmeter and the result sent to the computer. The solenoid valves operate on 24 volt DC, and are activated by a RACAL-

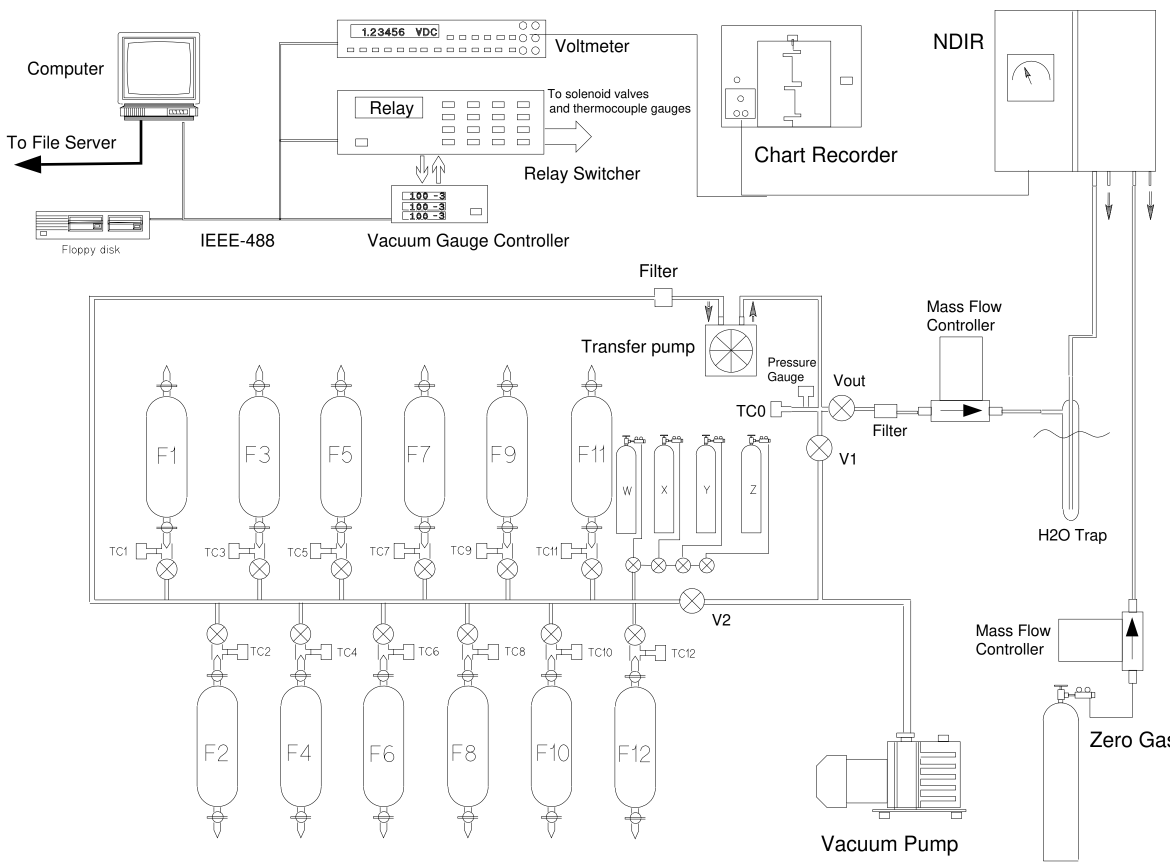

Figure 1. Schematic diagram of flask analysis system.

DANA Universal switching unit based on commands sent to the switching unit by the computer. The vacuum gauge controller is a Granville-Phillips model 316, with three channels operating thermocouple gauges. Channel A is dedicated to thermocouple TC0. The odd numbered thermocouples from TC1 to TC11 are connected through a multiplexer in the switching unit to channel B. The even numbered thermocouple gauges from TC2 to TC12 are connected through a multiplexer in the switching unit to channel C. A two stage direct drive vacuum pump (capacity ~1 cfm) evacuates the system between samples when the two solenoid valves V1 and V2 are open.

The flasks are connected to the system by inserting them into stainless steel ground joints (ground glass joints with glass to metal seals were used initially, but replaced with stainless steel joints due to concern about breakage). Wire mesh screens are placed in the joints to prevent large particles from entering the system. A particle filter is also placed in the tubing before the pump inlet to prevent damage to the pump valves. All tubing in the system, except for the water vapor trap, is 1/8" or 1/4" O.D. stainless steel. In addition, the interior surfaces of the tubing have been electropolished in order to reduce absorption of CO_2 on the walls of the tubing. The water vapor trap is Pyrex glass of conventional design, approximately 15cm long and 1.5 cm in diameter, and is immersed in an alcohol bath maintained at about -70° C. A glass wool plug is inserted in the trap to prevent frost particles from entering the analyzer.

A pressure transducer is connected to the system between the pump and solenoid valve Vout to monitor the performance of the pump. Flow rates of the gases to the analyzer are controlled using two mass flow controllers. Flow rates are set to 1000 cc/min for gases (flask samples and reference gases) flowing through the analyzer sample cell, and 10 cc/min for "zero" gas flowing through the reference cell. The analyzer is a Siemens Ultramat 3 model (S/N U08-450), fitted with sample cells 8 cm in length and 2.5 cm in diameter.

3.0 OPERATING MODES

There are three modes of operation for the analysis system. Mode 1, performed weekly, is for checking the nonlinearity

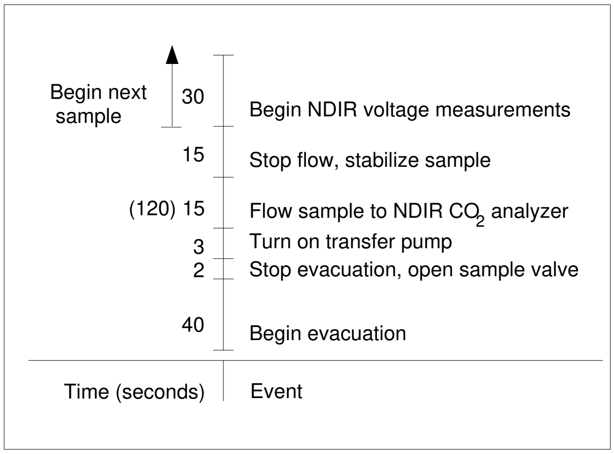

Figure 2. Sequence of events for analysis of one sample. Time indicated in parentheses is for analysis of reference gases.

characteristics of the analyzer. Mode 2, performed prior to analyzing flask samples, is used to allow the system to stabilize from zero and span drifts of the analyzer. Mode 3 is for analysis of CO_2 flask samples. Common to all modes is the sequence of events for each sample analyzed. This sequence is shown in Figure 2. The system is evacuated for 40 seconds by opening V1 and V2. Except for the first sample of the day, this time overlaps with the acquisition of voltages from the NDIR analyzer. V1 and V2 are then closed and the flask solenoid valve (or reference gas solenoid valve) is opened. After two seconds, the pump is turned on and the sample is compressed between the pump and Vout for 3 seconds, typically reaching a pressure of 30 psia. Vout opens and the sample flows to the analyzer. After 15 seconds (or 2 minutes for reference gases), Vout closes, the transfer pump is turned off, V1 and V2 open, and the sample is allowed to stabilize in the analyzer for 15 seconds. The voltage from the analyzer is then read by the voltmeter for 30 seconds at 2 readings per second.

The flow rate of the gas through the analyzer is set by the mass flow controller at 1000 cc/min. The time that the reference gas sample flows through the analyzer is two minutes, and the time for the flask sample is 15 seconds. The difference is due to the fact that there is a tendency for the pressure regulators on the reference gas tanks to absorb CO_2 between samples. A time of two minutes is necessary to safely insure that the depleted gas is flushed through the system. The total time to analyze a reference gas is 3 minutes, and to analyze a flask sample is 1.25 minutes.

3.1 WEEKLY ANALYZER CHECK.

Normal flask analysis in Mode 3 uses two reference gases and assumes linear response of the analyzer. However, because the CO_2 NDIR analyzer is actually nonlinear, it is necessary to determine the error when deriving concentrations linearly. Mode 1 is used to check on the magnitude of the nonlinearity of the analyzer. The sequence of gases used in this mode is shown in Figure 3a. All four reference gases are used, increasing in concentration from W to Z, and decreasing from Z to W. This represents one cycle, with a total of 5 cycles performed. For each cycle, the voltages for each reference gas are averaged. These mean voltages are plotted versus the corresponding assigned concentrations, and a quadratic function

$$C = a + bV + cV^2 \qquad (1)$$

is fitted to the data using least squares regression analysis. C represents the CO_2 concentration and V represents analyzer voltages. For each pair of working gases, W and X, X and Y, Y and Z, a linear function is computed

$$C' = d + eV \qquad (2)$$

which represents the apparent CO_2 concentration based on an assumed linear response of the analyzer.

Table 1. Typical corrections due to nonlinearity of CO2 analyzer.

C',ppm	ΔC, ppm For reference gases W and X	ΔC,ppm For reference gases X and Y	ΔC,ppm For reference gases Y and Z
334	0.04	0.16	0.35
336	0.02	0.13	0.30
338	0.01	0.10	0.26
340	0.00	0.07	0.22
342	-0.01	0.05	0.18
344	-0.01	0.04	0.15
346	-0.01	0.02	0.12
348	-0.01	0.01	0.09
350	0.00	0.00	0.07
352	0.01	-0.01	0.05
354	0.02	-0.01	0.03
356	0.04	-0.01	0.02
358	0.06	0.00	0.00
360	0.08	0.00	0.00
362	0.11	0.01	-0.01
364	0.13	0.03	-0.01
366	0.17	0.04	-0.01
368	0.20	0.06	-0.01
370	0.24	0.09	0.00
372	0.28	0.11	0.01
374	0.32	0.14	0.02

C' are linearly derived CO_2 concentrations; ΔC are corrections to apply due to nonlinearity of CO_2 analyzer. Concentrations of reference gases are: W ~340 ppm, X ~ 350 ppm, Y ~359ppm, Z ~370ppm.

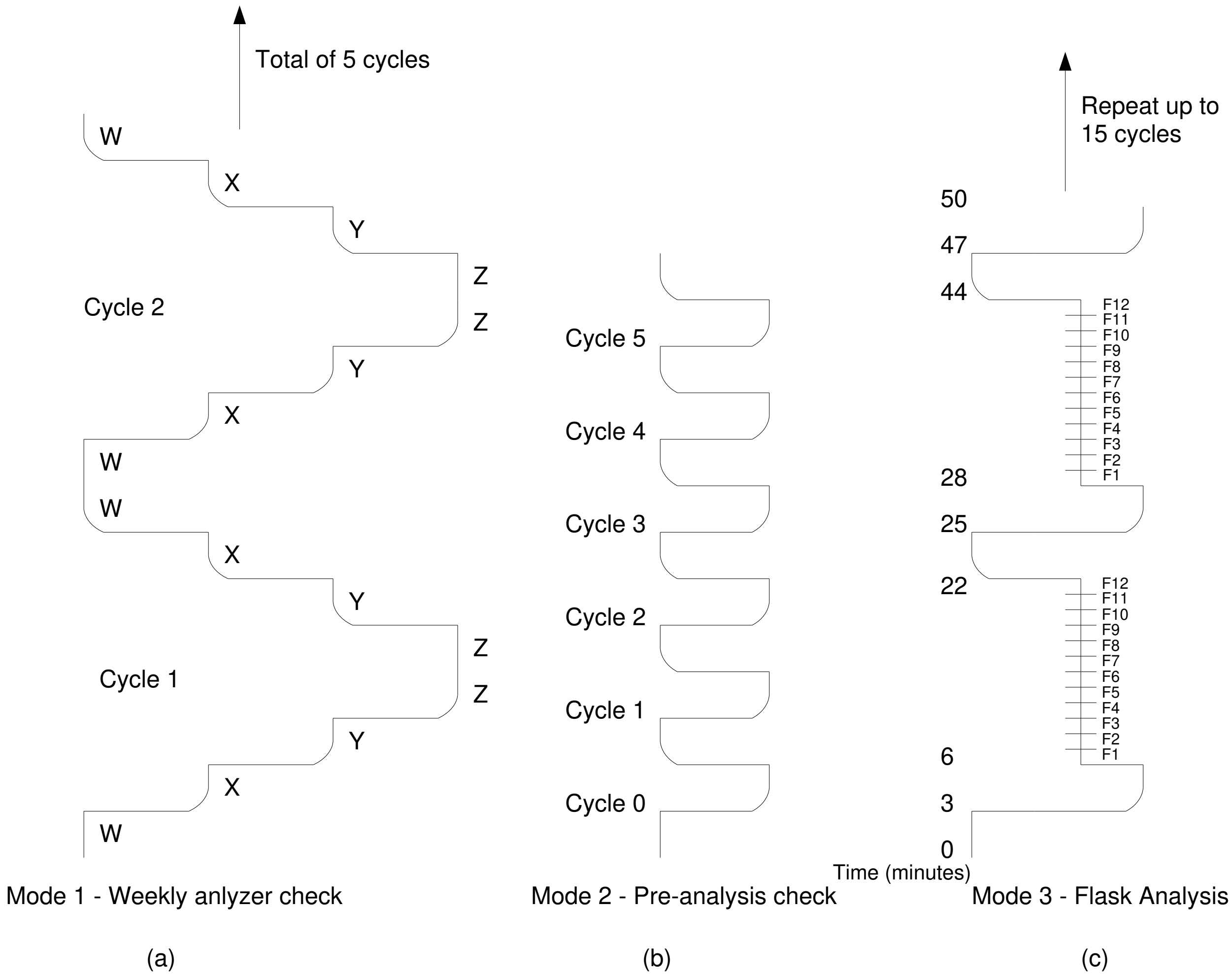

Figure 3. Operating modes of the CO2 flask analysis system.

Combining equations (1) and (2) gives

$$C'' = a + b(C'-d)/e + c((C'-d)/e)^2 \qquad (3)$$

which expresses the true nonlinear concentration in terms of the linearly derived concentration. The error correction $\Delta = C'' - C'$ is then computed. Typical values for Δ as a function of C' are given in Table 1. By keeping the span between two reference gases at about 10 ppm, the errors when using linear interpolation between the reference gases are negligible.

3.2 MODE 2: PRE-ANALYSIS CHECK.

This mode is used in preparation for CO2 flask analysis and is shown in Figure 3b. It allows for adjustment of reference gas flow rates as well as conditioning the system and allowing the analyzer to stabilize from drift. Two reference gases are alternated, and the voltage drift and sensitivity drift are calculated after each cycle. The sensitivity is calculated as

$$S = (C2 - C1)/(V2 - V1) \qquad (4)$$

where C2 and C1 are the concentrations of the high and low reference gases respectively, and V2 and V1 are the voltages of the high and low reference gases, respectively. Voltage drift is simply the difference in voltages for each gas from one cycle to the next. Table 2 shows the results from a typical pre-analysis check. Seven cycles are run, where each cycle is a pair of gases. The first cycle is ignored, and the last 6 cycles are used to compute the average voltage drift and sensitivity. If the absolute values of the average voltage drifts for both V1 and V2 are acceptable , then sample analysis in mode 3 can begin.

3.3 MODE 3: FLASK SAMPLE ANALYSIS.

The gas sequence for the analysis of flask samples is shown in Figure 3c. Two reference gases, approximately 10 ppm apart, are chosen from the 4 available (W, X, Y, Z) to bracket the expected concentrations of the flask samples. These gases are analyzed followed by 12 flask samples. The two reference

TABLE 2. Typical results of pre-analysis check

Cycle	Sensitivity (ppm/volt)	Reference gas X drift (volts)	Reference gas Y drift (volts)
0	4.896	-------	------
1	4.890	-0.00103	0.00114
2	4.890	0.00119	0.00117
3	4.892	0.00058	-0.00002
4	4.891	0.00198	0.00218
5	4.888	0.00029	0.00141
6	4.889	-0.00095	-0.00108
Average	4.890	0.00062	0.00073
Sigma	0.002	0.00109	0.00128

gases are again analyzed to allow correction for drift and sensitivity changes in the analyzer. This cycle can be repeated up to 15 times, so that up to 180 flasks can be analyzed in a typical day. The concentrations of the flasks are calculated as follows:

First the drift corrected voltages for the reference gases are computed;

$$V_h'' = V_h + (V_h' - V_h)k/14 \quad (5)$$

$$V_l'' = V_l + (V_l' - V_l)*(k+1)/14 \quad (6)$$

where V_h and V_l are the high and low reference gas voltages which preceded the 12 flasks, V_h' and V_l' are the high and low reference gas voltages which follow the 12 flasks, k is the number of aliquots since V_h. The flask concentration C_f is calculated with

$$C_f = C_l + (C_h - C_l)/(V_h'' - V_l'')*(V_f - V_l'') \quad (7)$$

where V_f is the analyzer voltage for the flask, and C_h and C_l are the assigned concentrations for the high and low reference gases respectively.

The manifold is evacuated between each sample by opening valves V1 and V2. At the beginning of each cycle the system is also evacuated up to the stopcocks of the flasks by opening the solenoid valves F1 through F12. A value of 200 x 10^{-3} Torr is used as the pressure below which the manifold must be evacuated for normal operation to continue. Usually the manifold is evacuated to a pressure below 100 x 10^{-3} Torr in the allotted evacuation time. However, experience shows that the ground joint where the flask connects to the manifold often leaks, so that the manifold can not always be evacuated to the required pressure. In order to detect these leaks quickly, a thermocouple vacuum gauge is connected at every flask-manifold connection point. If one of the flasks is leaking, then the pressure in the manifold, as measured by thermocouple gauge TC0, will be too high. When this occurs, the computer enters a routine to find the location of the leak. First, all twelve flask solenoid valves are closed and the manifold only is evacuated. Then the first flask solenoid valve is opened, and an attempt is made to evacuate the system. After 30 seconds of evacuation, the pressure of the thermocouple gauge TC1 is read by the computer. If the pressure is too high (above 200 x 10^{-3} Torr), a message is displayed on the computer screen. The solenoid valve is closed and the pressure check is made for the second flask. This process is repeated for all twelve flasks. After all the flasks have been checked, the operator has a list of which flask connections are leaking. The computer then enters a mode in which the operator can manually switch the solenoid valves in order to fix the leaks and to properly evacuate the system. Automatic sequencing of events then resumes.

CMDL currently uses two sizes of sample flasks, 0.5 liters and ~3 liters. Because the flow rate of the mass flow controller is set at 1000 cc/min for each sample, there usually is not enough gas in the 0.5 liter sample flasks to maintain this flow rate for the required 15 seconds. The flow rate gradually declines to about 700 cc/min after 15 seconds. Therefore a total of about 200 cc of sample is used. But because the volume of the water vapor trap, tubing, and analyzer sample cell that needs to be flushed for each sample is only about 60 cc, there is adequate sample available to insure proper flushing. The voltage output of the analyzer is read before turning the pump off to check for highly contaminated samples. If a sample is contaminated, forcing the analyzer off scale, the low reference gas valve is turned on and the system is flushed until the analyzer response returns on scale.

4. TEST RESULTS

The main objective in testing the flask analysis system was to see if any systematic offsets occurred when analyzing flasks. In order to remove any errors due to CO_2 calibration scales, the flasks used for testing were filled from both the high and low reference gas tanks. Therefore the results only needed to be compared to the assigned concentrations of the reference gas tanks. The system was first tested to determine the safety margin of using 15 seconds of flushing time at 1000 cc/min for flasks. This was done by analyzing groups of 6 flasks with flushing times of 5, 10, 15 and 20 seconds which were filled from the low reference gas tank with an assigned CO_2 concentration of 350.02 ppm. The flushing time for a group of 24 test flasks filled from the high reference gas tank was held at 15 seconds. In addition, the test flasks were alternated between high and low concentrations, so that any memory effects from sample to sample would be apparent. The results from this test are shown in Figure 4. It is obvious that 5 seconds of flushing time was not enough. However,

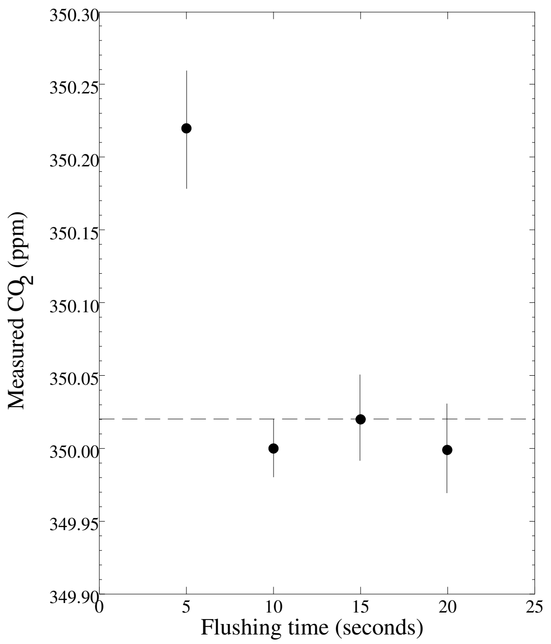

Figure 4. Results of test flasks with varying flushing time. The dashed line is the assigned value for the reference tank from which the flasks were filled.

there was no significant difference between the flasks analyzed at the longer flushing times. From this it was concluded that 15 seconds was adequate for flushing the system for each sample. The mean of the high concentration test flasks was 358.93 ±0.04 ppm for 24 flasks, a difference of only 0.01 ppm from the assigned value.

In order to confirm the results from the previous test, a large number of test flasks were analyzed in random order which were filled from both the high and low reference gas tanks as well as a third test gas tank. This test was conducted on December 12, 1988. The results are shown in Table 3. No significant offsets were found. The mean of the high concentration test flasks was -0.02 ppm from the assigned value, and the mean for the low concentration test flasks was -0.01 ppm from the assigned value. In addition, the mean for the flasks from the third test gas tank was 355.08 ± 0.02 ppm, which differs from the assigned value of 355.05 by only 0.03 ppm. This test was repeated on September 20, 1990, using a smaller number of flasks. Twelve flasks from the low reference gas and twelve flasks from the high reference gas were filled and analyzed. The mean of the high concentration test flasks was -0.02 ±0.05 ppm from the assigned value, and the mean for the low concentration test flasks was -0.03 ± 0.04 ppm from the assigned value. Thus it appears that no significant systematic offsets are present in the system.

During normal flask analysis, up to 16 test flasks are analyzed during the day. From the time that the new flask analysis system began operation in December 1988 until the end of 1991, 12 test flask reference gas tanks were used. The results of the analysis of these flasks are shown in Table 4 . Two of these tanks, 74240 and 287174, exhibited significant drift in concentration during their period of use. In order to account for this drift, the results of the test flasks for each analysis day were compared with the value for that day of a linear least-squares regression line through the available calibration points of the tanks. The mean and standard deviation of the residuals about the regression line was calculated. The results show that generally there was a small offset of about 0.1 ppm between the flask value and the assigned tank value. Except for one tank, 64031, nearly all test flasks were below the assigned value for the corresponding tank. This offset did not appear for flasks filled directly from reference gas tanks as previously mentioned. The method for filling both normal test flasks and flasks for special tests is the same. A group of 10 to 12 flasks are connected in series, with a flow meter attached to the outlet of the last flask in line. Gas from the tank then flows through the flask at a flow rate between 5 and 10 liters/minute for about 10 minutes. The outlet stopcock on the last flask is closed, and the flask are pressurized to a few psi above ambient pressure. The stopcocks on all the flasks are then closed. The system of calibrating tanks (*Komhyr et al.*, 1985b, *Thoning et al.*, 1987) was checked carefully for the

TABLE 3. Results of analysis of test flasks filled from reference gas tanks.

Date	Gas	Assigned CO_2 concentration (ppm)	Number of samples	Mean value (ppm)	Difference from assigned value (ppm)
December 12, 1988	Low test	350.02	30	350.01 ± 0.05	-0.01
	High test	358.94	30	358.92 ± 0.04	-0.02
	Mid test	355.05	24	355.08 ± 0.02	+0.03
September 20, 1990	Low test	350.55	12	350.52 ± 0.04	-0.03
	High test	359.14	12	359.12 ± 0.05	-0.02

Uncertainties are 1 standard deviaition about the mean.

Table 4. Results of analysis of test flasks

Serial Number	Date of Usage	Assigned CO2 (ppm)	Number of flasks analyzed	Mean difference (ppm)
74240*	December 8, 1988 - May 17, 1989	355.12	522	-0.06 ± 0.06
287174*	May 18, 1989 - January 17, 1990	356.82	523	-0.03 ± 0.07
53928	September 14, 1989 - December 7, 1989	346.77	234	-0.09 ± 0.05
64031	January 23, 1990 - February 5, 1990	356.54	66	0.05 ± 0.06
71657	February 9, 1990 - June 12, 1990	356.71	192	-0.05 ± 0.08
71652	March 6, 1990 - June 5, 1990	355.46	211	-0.07 ± 0.07
71594	July 6, 1990 - July 20, 1990	355.38	52	-0.14 ± 0.04
71561	July 25, 1990 - August 24, 1990	354.93	110	-0.13 ± 0.06
71647	June 14, 1990 - November 16, 1990	354.86	394	-0.06 ± 0.16
71594	November 21, 1990 - April 5, 1991	350.35	586	-0.09 ± 0.15
71652	April 9, 1991 - August 19, 1991	356.52	629	-0.06 ± 0.07
71561	August 20, 1991 - December 31, 1991	354.82	684	-0.16 ± 0.06

* - These tanks exhibited significant drift. Differences are from a linear regression line to the calibration values on these tanks. Uncertainties are 1 standard deviaition about the mean.

reference tanks involved, and a possible correction of about 0.03 ppm could be applied to all the tanks. However, this correction would not account for the offset, since both the reference tanks and the analyzed flask values would change equally. The cause of this offset is unknown.

5. DISCUSSION

Results of the tests show that under best conditions, the short term (one day) precision of the analysis system is less than 0.05 ppm. Longer term precision over several months, based on test flasks filled from a calibrated compressed air tank, is about 0.07 ppm. This value includes uncertainties due to filling and analyzing flasks, as well as uncertainties in the calibration system used for assigning CO_2 concentrations to reference gas tanks.

The CO_2 flask analysis system has been configured to analyze up to 180 flasks per analysis day. In practice, about 100 to 120 are analyzed, which takes approximately 6 hours to complete. It is felt that the new system will be able to handle the ever increasing requirements for determining from flask samples the global distribution of CO_2 concentration in the atmosphere for several years.

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