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Final Report

PULSED GAS CHROMATOGRAPHIC SEPARATION

Prepared for
Technical Information Division
Ames Research Center
Moffett Field, California 94035
Attention: Frank C. DeRosa, Contract Monitor
Joel Leonard, Technical Monitor

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Prepared by

K. Lui
L. Ferder
E. Findl, Program Manager

Approved by


A. Gruber, Manager
Micro-Data Operations

ELECTRO-OPTICAL SYSTEMS, INC. - PASADENA, CALIFORNIA
A Subsidiary of Xerox Corporation

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1. INTRODUCTION

In the development of closed-cycle life-support systems, chemical processes play a primary role in maintaining an environment suitable for human habitation. These processes are unfortunately plagued by a number of problem areas, one of which is the separation of gaseous reactants and waste products. There are a number of mechanisms being investigated to solve the problem of gas separation. The mechanisms under study fall into two general categories: (1) physiochemical techniques and (2) biochemical techniques. The report presented herein is concerned with a physiochemical separation technique related to gas chromatography which has been termed pulsed-gas chromatography (PGC). It is expected that the successful application of this technique for "continuous" gas separation/enrichment will play an important role in the development of environmental control systems for long-duration manned-space missions.

Contract NAS2-3209 was awarded to Electro-Optical Systems, Inc. (EOS) on 30 August 1965 to evaluate the feasibility of the Pulsed Gas Chromatographic (PGC) separation technique. The PGC separation study had as its objective the evaluation of the effectiveness of a pulsed mode of operation in separating gases encountered in spacecraft systems. A number of parameters were to be investigated, including chromatographic column size, packing material and temperature, in conjunction with three gas mixtures: 80 percent CO_2 to 20 percent air, 1 percent CO_2 to 99 percent air, and 80 percent CH_4 to 20 percent H_2 .

The PGC technique is inherently light in weight and offers a possible improvement in separation efficiency over presently available

gas separation techniques. Application of the PGC technique to life-support systems is principally aimed at the removal and concentration of CO₂ and the reclamation of O₂. Other potential applications include the separation of gaseous products from Bosch or Sabatier reactors, separation of electro dialysis-reaction products, contaminant removal, etc. In principle, any simple gaseous mixture can be separated by the PGC technique.

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2. SUMMARY

Work conducted under Contract NAS2-3209 on the PGC concept has demonstrated the feasibility of separating binary-gas mixtures based upon a pulsed-mode gas adsorption/desorption. Certain critical parameters affecting separation have also been demonstrated, the primary one being the necessity for adequate pumpdown (evacuation) of the separation column between cycles. (Poor pumpdown results in poor separation.)

Author

3. PRINCIPLES OF PULSED GAS CHROMATOGRAPHY

There are a number of principles upon which chemical separations are based, such as distillation, diffusion, mass discrimination, absorption, adsorption, extraction, leaching, etc. Each of these techniques is useful under a certain set of boundary conditions. For gaseous separations, under the boundary conditions set up for a space vehicle, these methods are generally not feasible due to gravity, thermal energy, large mass of working fluid requirements, etc. One separation technique, gas chromatography (based on adsorption), appears to have certain highly desirable features such as gravity insensitivity, high separation efficiency and low energy requirements. The conventional techniques of frontal analysis, displacement analysis, or elution, are, however, unacceptable: frontal analysis, because of poor component separation, and the latter two because of the requirement for a large flow of carrier gas.

These objectives proved to be a stumbling block in our thinking until a system for bypassing them was conceived. The concept is quite simple in principle, and is a modification of the frontal-analysis technique combined with recent advances in preparative-column technology.

Frontal analysis is the term used to describe the technique whereby a gas-mixture sample is passed continuously through an adsorbent. Separation is poor because the use of continuous-sample injection causes a large overlapping of the various constituents, even though the gaseous components are selectively adsorbed and desorbed. Preparative-column chromatography is the term used to describe that phase of gas chromatography (GC) dealing with the preparation of relatively large volumes of pure chemicals using relatively large diameter columns. (The recent GC literature contains a number of papers relating to this subject.)

The modification to the frontal-analysis technique which we propose is the use of a time-sequenced, pulse-injection system, whereby the sample is rapidly injected into an evacuated-separating column. The time-sequenced technique differs from the conventional adsorption/heat-removal technique in that heating of the column is not required. Gas separation is accomplished by an adsorption/flow process. A simplified drawing of such a sequenced system for the separation of two gases (A and B) is shown in Fig. 1.

Operation of the device is as follows: A gas mixture, in this case nonadsorbed A and highly adsorbed B, is rapidly injected into the column at time (t_0) from the feed gas manifold. Gas A, having less tendency to be adsorbed than gas B, will diffuse much more rapidly through the column than will gas B. Gas A will, therefore, reach the outlet valve prior to gas B. When gas A reaches the outlet valve (t_1), the valve opens, permitting gas A to flow to its outlet line. When gas B starts to arrive at the outlet valve (t_2) the valve switches to feed into the gas B outlet line. Pressure traces taken at the inlet and outlet of the separation column would look somewhat like that shown on Fig. 2. Note that gas separation is not the same as in conventional analytical-gas chromatography. Instead of sharp peaks, somewhat overlapping type of separation will occur. The mixed-gas band is due to nonuniform gas distribution both through and across the column. One can, however, minimize this zone by lengthening the column, having a uniform packing density, using smaller injection volumes (by increasing the inlet pressure) and by using high efficiency columns. The mixed-gas zone will also be minimal if the percentage of gas B in gas A is small.

A typical case for such a separation would be a space-vehicle atmosphere containing oxygen and carbon dioxide. In this case, if one were to use a column containing silica-gel or Poropak, oxygen would come through the column first, then CO_2 . Since the CO_2 will be present in less than 2.5 volume percent, the mixing zone will be minimal. An

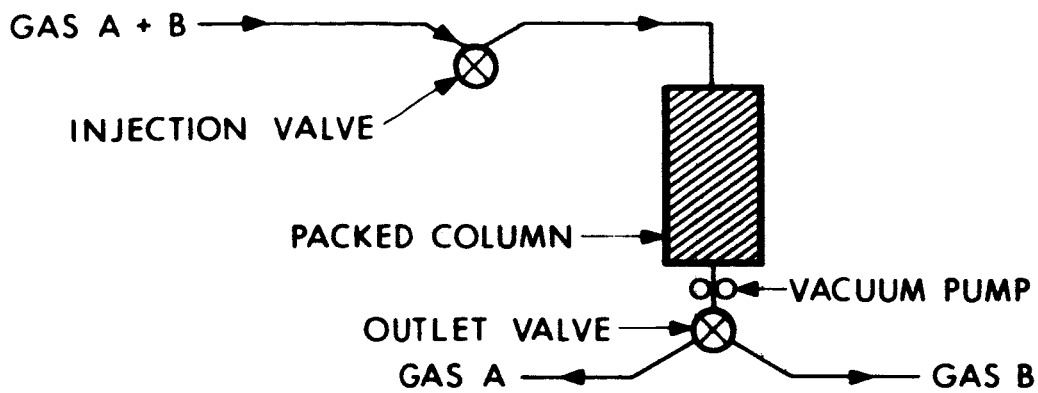


FIG 1 VENTED PGC COLUMN

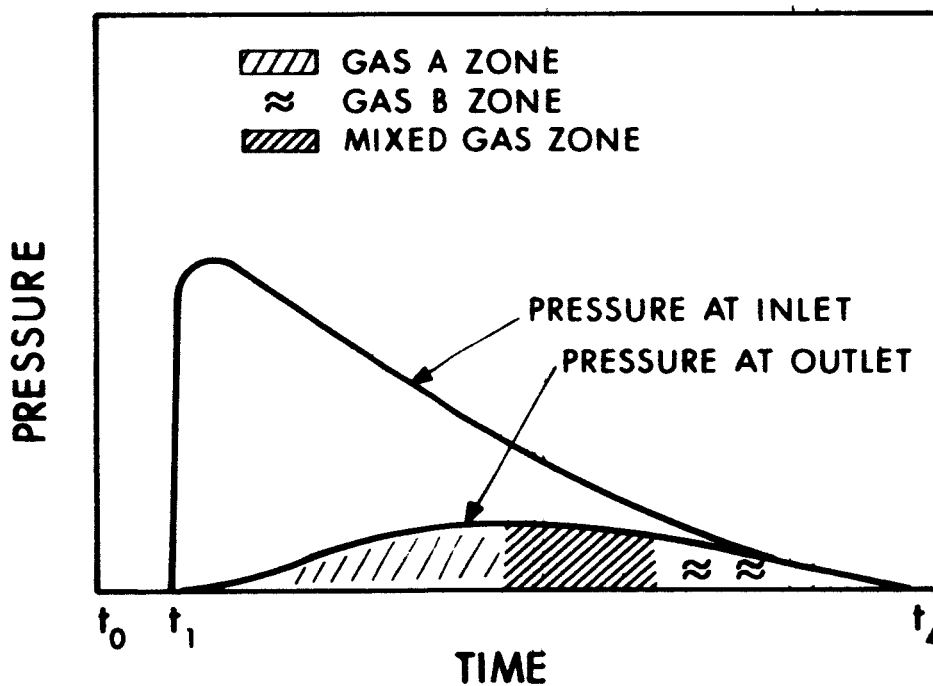


FIG. 2 GENERALIZED TWO COMPONENT PGC PRESSURE PLOT

outlet pressure-time plot for this system actually would look like Fig. 3. (The CO₂ and mixed-gas zones are greatly exaggerated.)

In the ideal case, with perfect time-phase separation between the two gas phase constituents (A and B), no overlapping of gases will occur in the effluent of the separation column. Thus a time-concentration graph would look as shown in Fig. 4. The interpretation of this graph (Case I) is simply that from injection time 0 until time X, the column effluent is 100 percent constituent A. At time X, all of the constituent A has evolved and constituent B starts to evolve (at the 100 percent concentration level). At time Y, all of constituent B has evolved and the cycle is ready to begin again.

In a column in which A and B are overlapped for a portion of the cycle but are completely separated at the initial and final portions of the cycle, the time-percent chart would appear as shown in Fig. 5. Thus, for Case II (Fig. 5) between time 0 and X, the effluent is 100 percent A. Between times X and Y the effluent is mixed A and B. Between times Y and Z the effluent is 100 percent B.

In the case where the initial separation is good but the overlap is extensive for the final gaseous effluent, one would obtain a curve such as shown in Case III (Fig. 6). Between times 0 and X, the effluent is 100 percent A. However, between times X and Y, the effluent is mixed A and B.

When one does not completely purge the injected sample between cycles and has poor separation efficiency, a fourth case occurs, as shown in Fig. 7.

Thus at time 0, the effluent contains residual gas from the previous run which is principally B plus new cycle gas which is principally A. At time Y, the effluent is mainly B. Between times Y and Z the concentration of Y gradually increases.

The case of complete failure to separate is given in Fig. 8.

In all of the preceding discussion, we have only considered separation as a function of concentration and time. A third factor

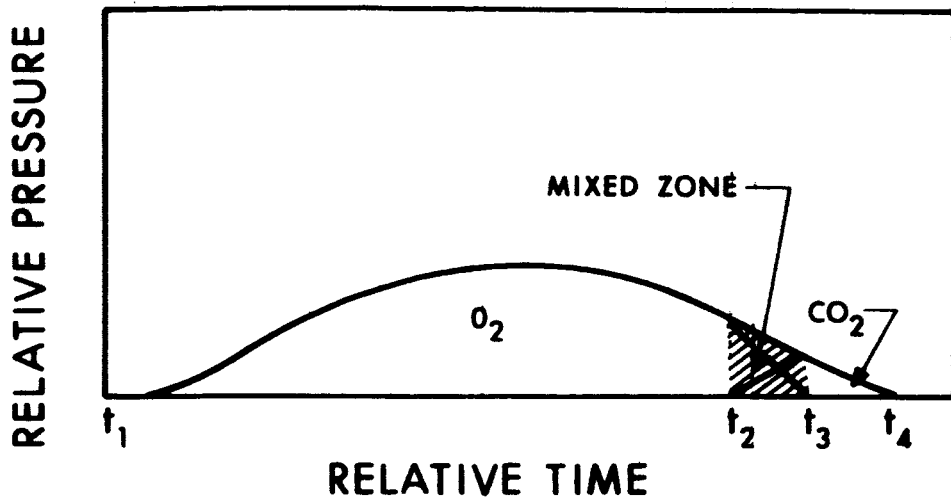


FIG. 3 O_2 - CO_2 PRESSURE PLOT

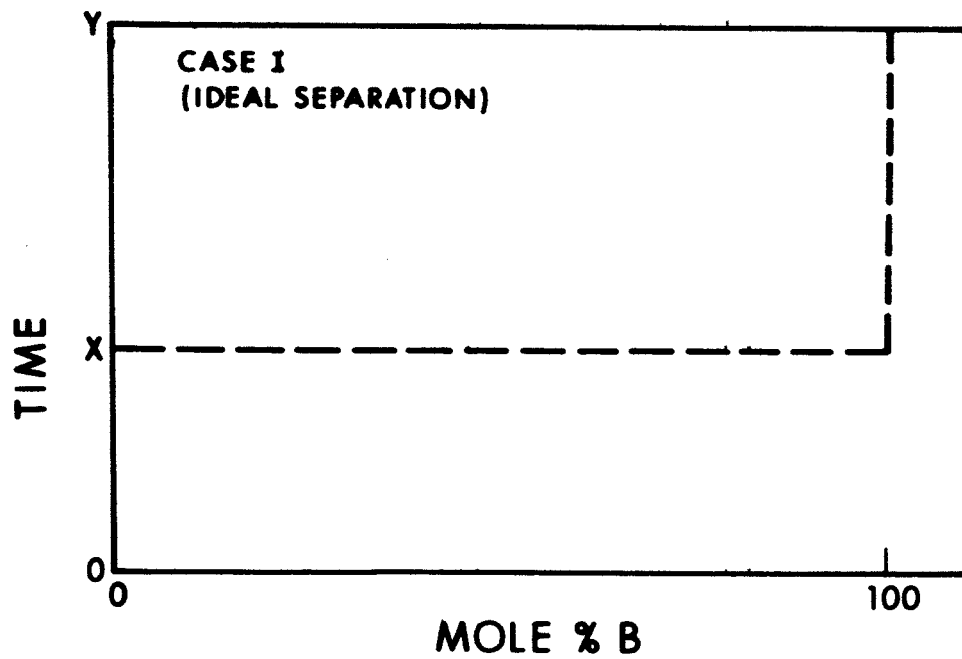


FIG. 4 TIME CONCENTRATION PLOT

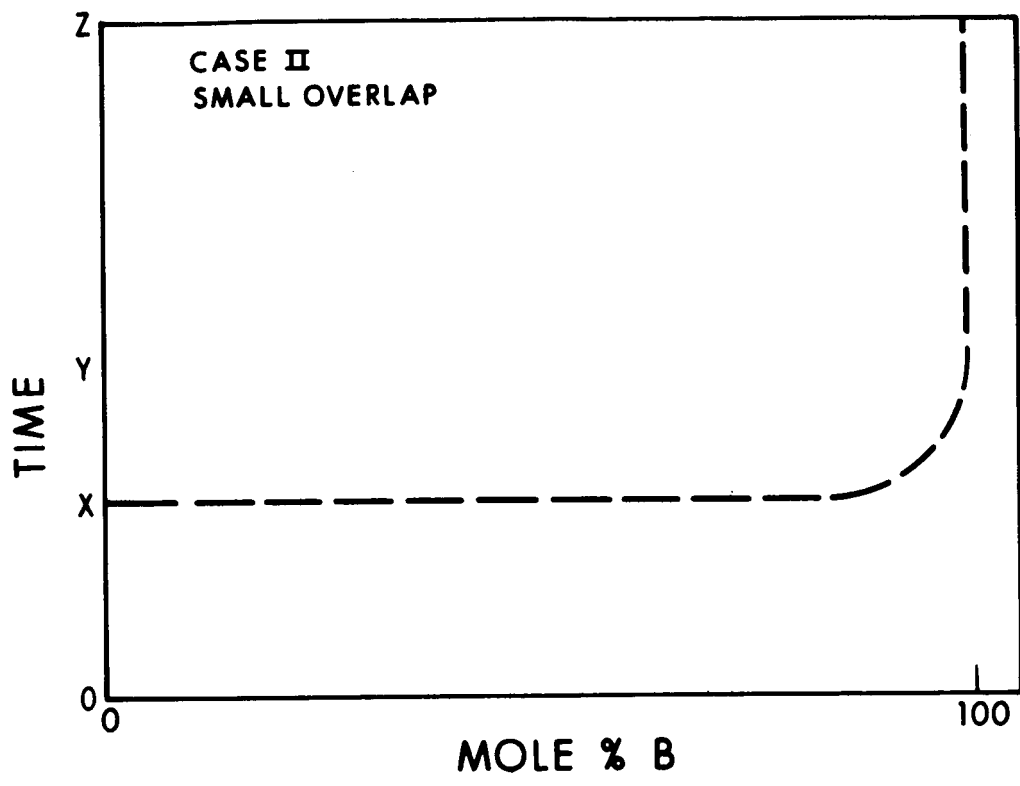


FIG. 5 TIME CONCENTRATION PLOT - CASE II, SMALL OVERLAP

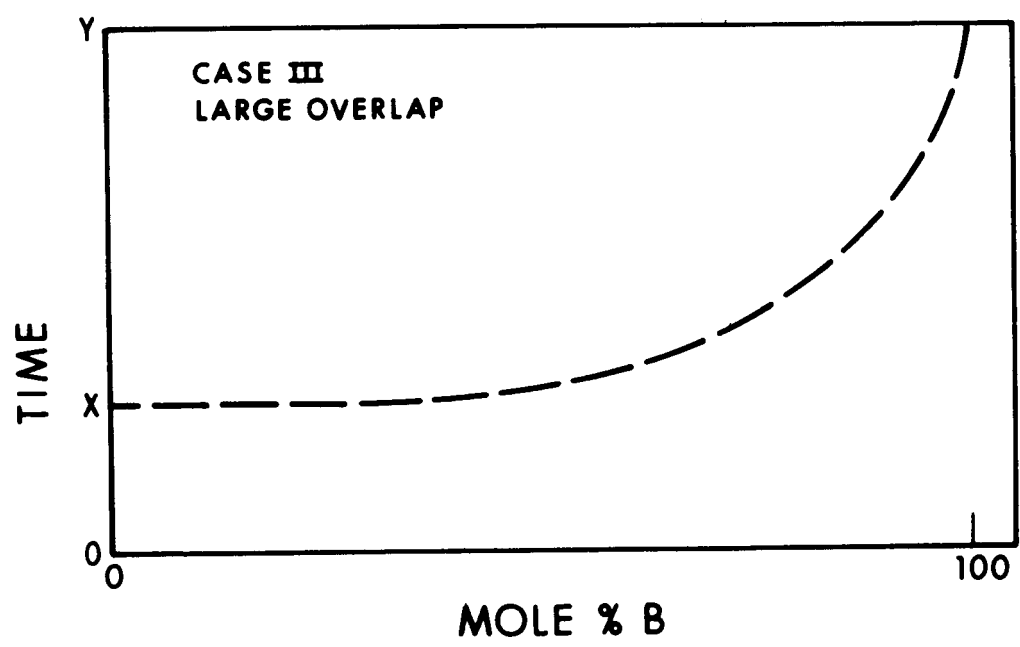


FIG. 6 TIME CONCENTRATION PLOT - CASE III, LARGE OVERLAP

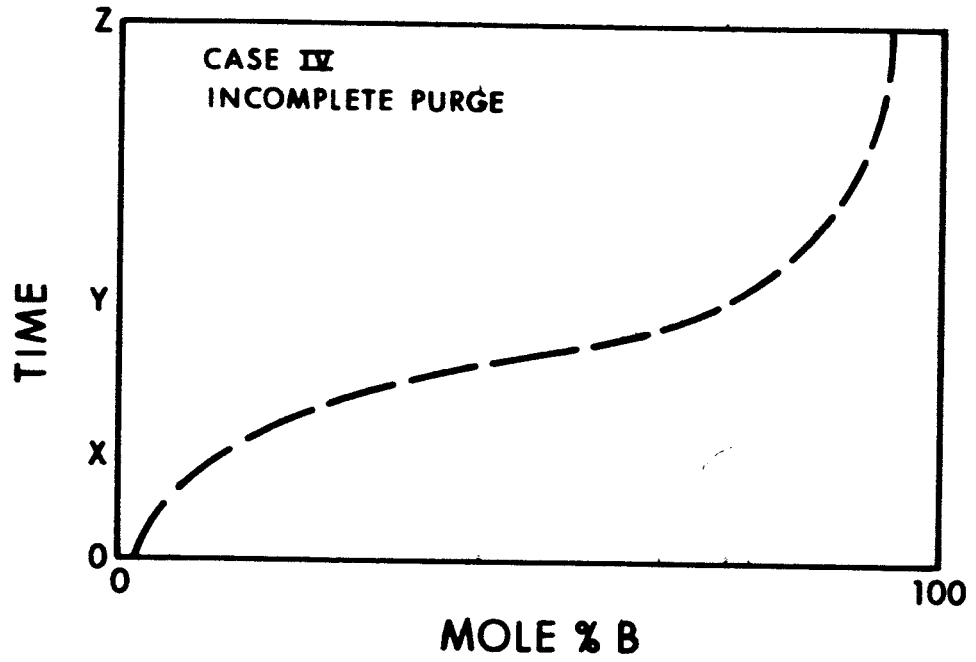


FIG. 7 TIME CONCENTRATION - CASE IV, INCOMPLETE PURGE

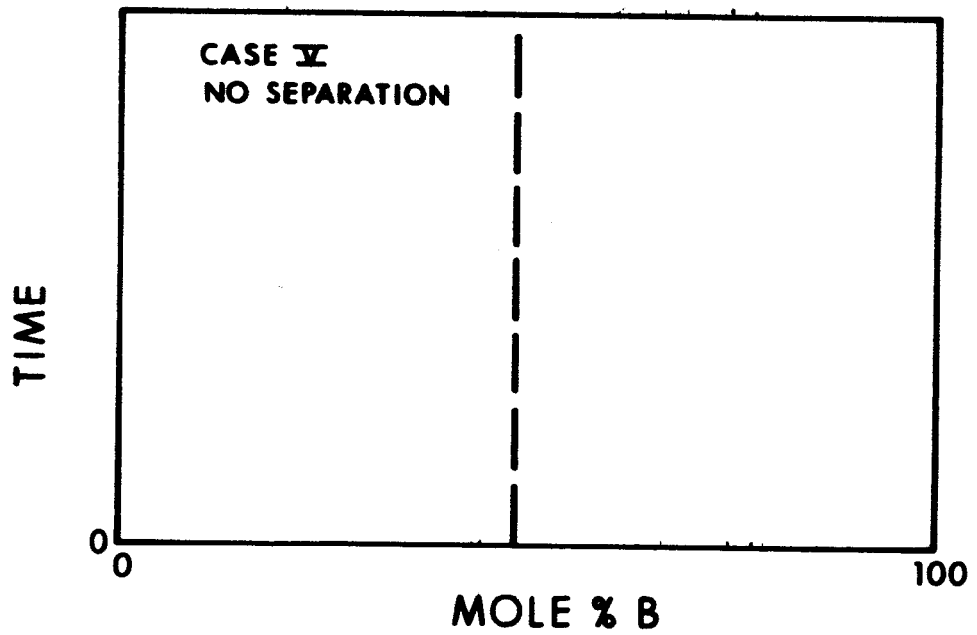


FIG. 8 TIME CONCENTRATION - CASE V, NO SEPARATION

must also be included in order to provide engineering design information. This factor is the mass-flow rate as a function of time. In the case of the PGC technique, a useful presentation is shown in Fig. 9 (for the ideal case). Here again, from time 0-X all of component A is eluted, thus a mass fraction of 1.0 is reached at time X. Between X and Y, all of component B is eluted.

The nonideal cases would look as follow in Fig. 10.

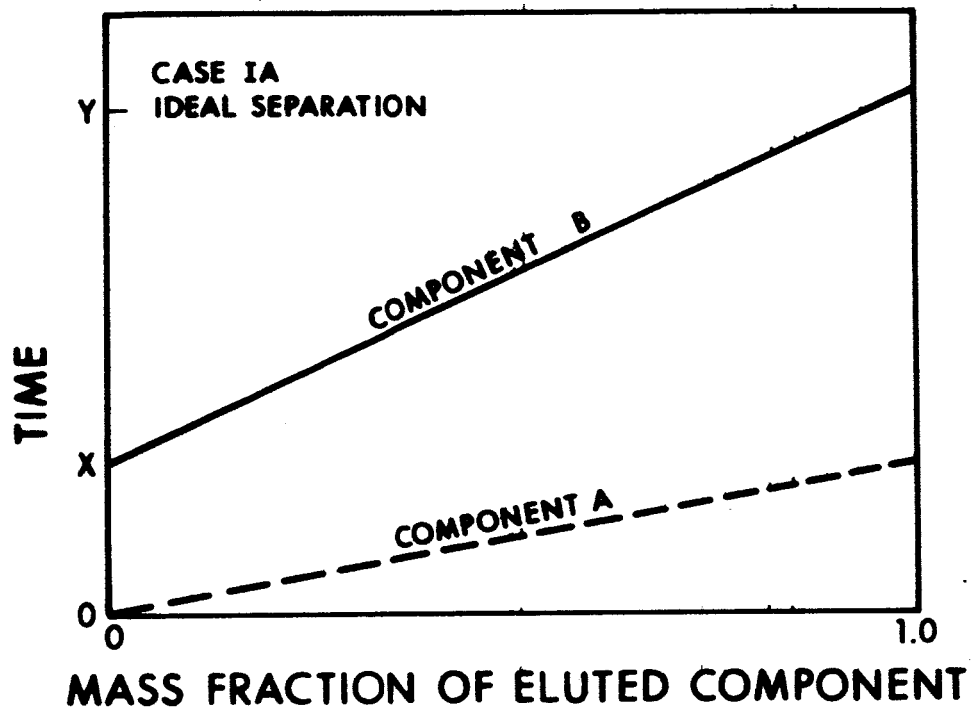


FIG. 9 MASS FRACTION OF ELUTED COMPONENT, IDEAL

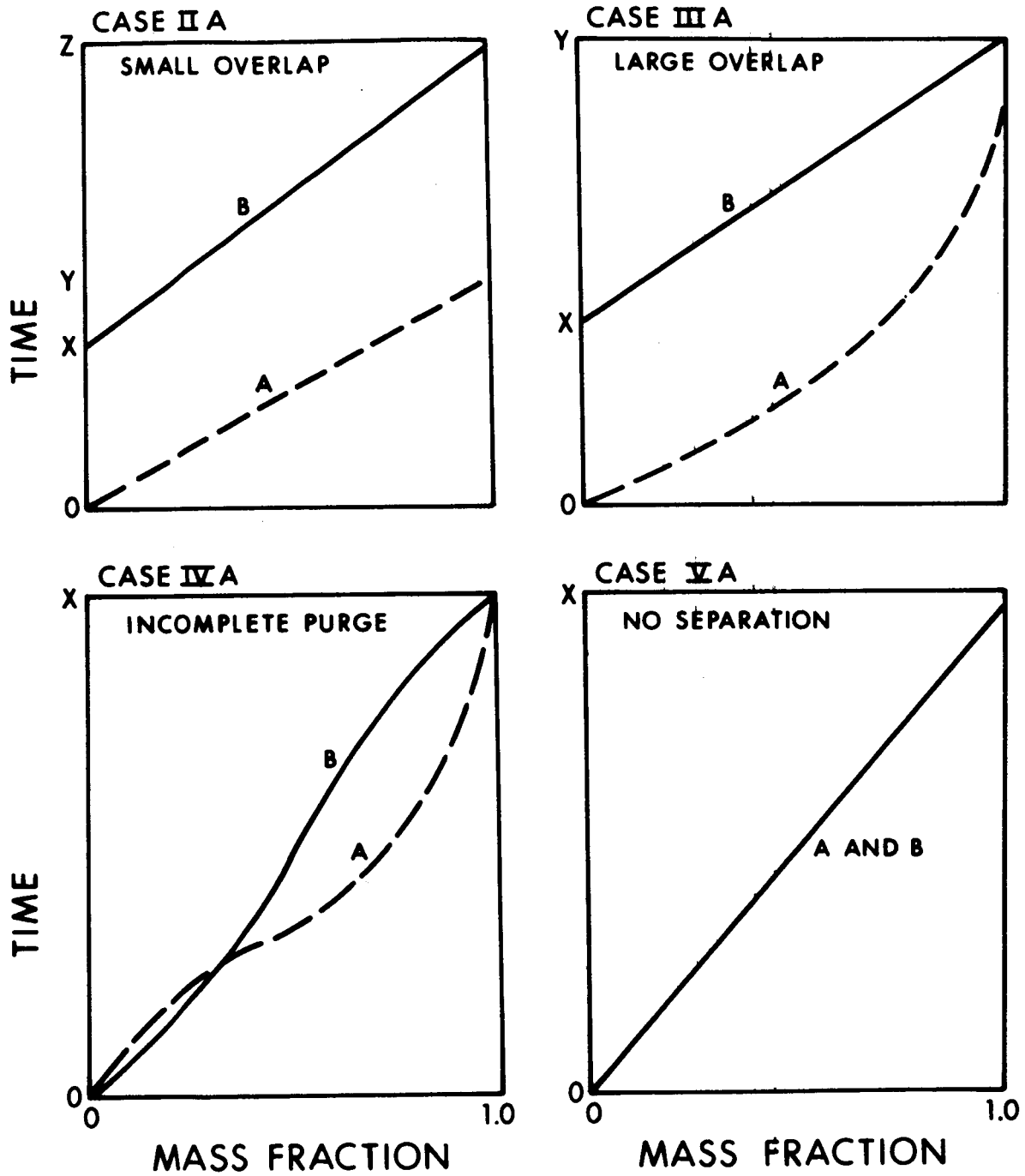


FIG. 10 MASS FRACTION OF ELUTED COMPONENT, NONIDEAL

4. EXPERIMENTAL APPARATUS

During the course of the program, a number of significant variations in experimental apparatus were employed. These variations, in general, came about as a result of limitations placed upon the test results due to system constraints. Each of the major variations is described in the following sections along with equipment calibration procedures.

4.1 Initial System Design and Operation

The design of the initial test apparatus is shown schematically in Fig. 11. Components of the apparatus were as follows:

1. Separation column (with provision for heating)
2. Solenoid valves
3. Cycle timers
4. Column vacuum system
5. Five-station thermocouple vacuum gauge
6. McLeod gauge
7. Gas sample bottle
8. Mercury reservoir
9. Calibration mixture manifold
10. U-tube manometer
11. Analysis chromatograph
12. Analysis vacuum system

The separation column consisted of a stainless-steel tube packed with an adsorbent material suitable for the gas separation to be made. Five-column materials, i.e., molecular sieves, silica gel, silicone rubber, and an organic amine were evaluated in conjunction with three gas mixtures: 80 percent CO_2 to 20 percent air, 1 percent CO_2 to 99 percent air, and 80 percent CH_4 to 20 percent H_2 . The column was heated (when required) by using a heating tape regulated by a Variac.

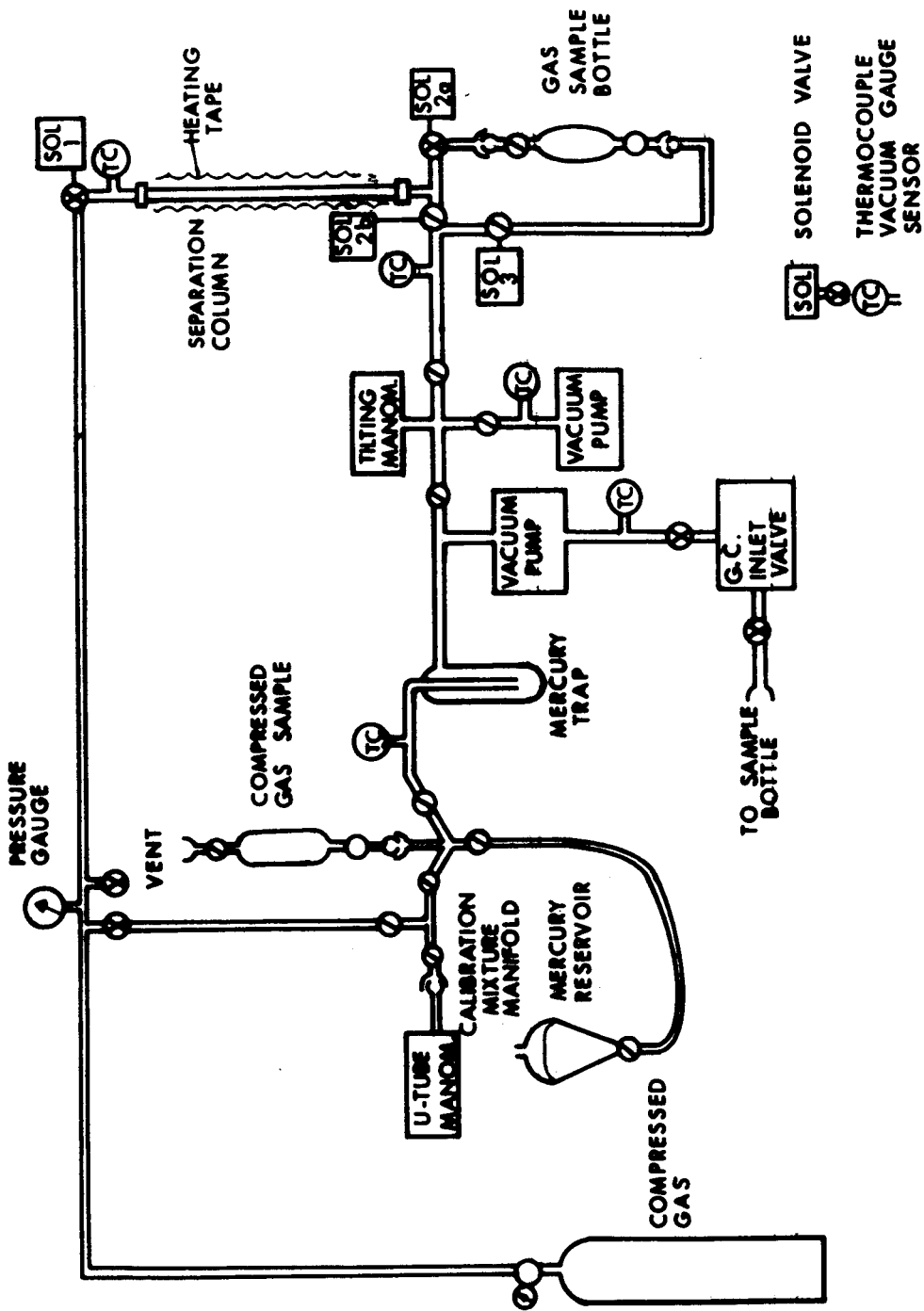


FIG. 11 TEST APPARATUS

Solenoid valves, in conjunction with a recycling timer apparatus, Fig. 12 were used to sequence the injection and removal of the various gas mixtures.

Timer No. 1 controls the length of the injection pulse into the separation column, and can provide injection times of up to 60 seconds. Timer No. 2 controls the length of the total cycle consisting of sampling time and pumping time. These can be as long as 180 seconds. Timer No. 2 also resets Timer No. 1, ensuring that the next cycle (beginning with gas injection) will not begin until the previous one is completed. The operating sequence of the system may be summarized as follows.

Injection, sampling, and pumpdown duration are set on the appropriate timers. The cycle is begun by Timer No. 1 energizing the injection solenoid valve, allowing a pulse of gas mixture to enter the separation column. Simultaneously Timer No. 2 opens the gas-sampling solenoid valves, which remain open for the duration of the sampling time, allowing the separated gas stream to flow through the sampling bottle. At the end of the sampling interval, the sampling valves are closed and the pumpdown valve is opened, enabling the sampling bottle to be removed for analysis while the separation column is purged. The next cycle begins when the pumpdown time has elapsed.

Following collection of the gas sample, which is at a sub-atmospheric pressure, it is compressed in the sampling bottle by the use of mercury compression from the reservoir. It is then analyzed by injection into the analytical gas chromatograph.

A manual switching arrangement allows for automatic cycling to be bypassed, if desired.

One of the vacuum pumps is utilized as the prime mover of the separation system. The use of a vacuum or pressure gradient, as the separation driving force in conjunction with a pulsed mode of operation, represents the major difference between PGC and conventional chromatographic separation techniques. The other vacuum system is

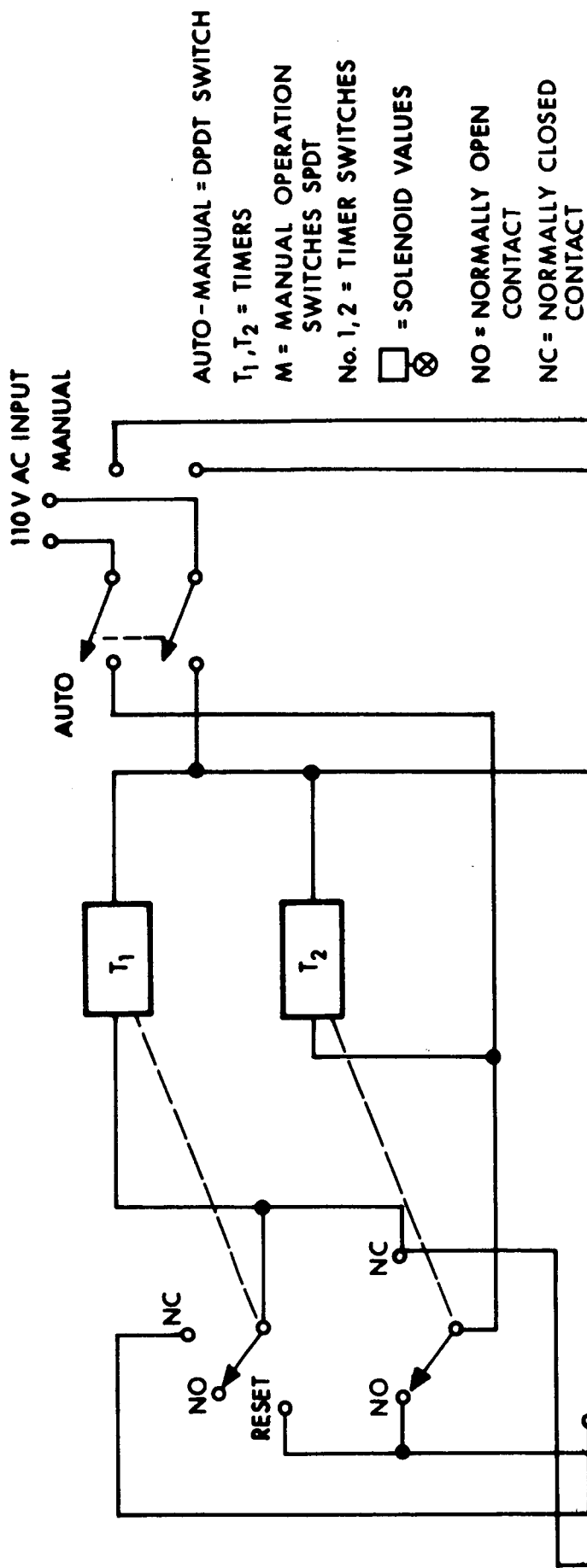


FIG. 12 TIMING CIRCUIT SCHEMATIC

used, by manipulating the appropriate valves in the system, to evacuate the various lines and manifolds prior to compressing the gas sample, and also to purge the sample inlet-valve assembly on the chromatograph before injecting a sample for analysis. Vacuum levels in the system are monitored by means of a Veeco 5-station thermocouple vacuum gauge. The thermocouple sensors are located at critical areas in the two-vacuum-system lines, as shown in Fig. 11. A McLeod tilting manometer gauge is also in the system as a calibration gauge.

Following compression of the gas, it is analyzed with an FM Model 720 gas chromatograph. The instrument was optimized for Air-CO₂ separation analysis by using the following parameters:

Column: 1/4 in. D x 12 in. L silica gel 130 mesh at 25^oC

Carrier gas: Helium, at 55-60 cc/min

Detector: Thermal conductivity type, with bridge current set at 178 mA

Sample size: 2 cc

The column was pretreated by baking at 150^oC for 24 hours. A short, 130-mesh silica-gel column was chosen as the best compromise between good separation of the air-CO₂ signals, sharp peaks for both gases, and minimum tailing of the CO₂ peak. Reproducibility of the ratios of the air and CO₂ peak heights has been found to be very good with this set of parameters.

4.2 Mass Flowmeter Modification

The following additional equipment was incorporated into the test apparatus to provide the flow-rate-measurement capability;

1. Mass flowmeter
2. Flow totalizer
3. Two cold-traps
4. Gas-drying tube

The mass flowmeter is composed of a flow transducer and matched-signal conditioner. The output is a dc voltage which varies linearly with mass-flow rate through the flow transducer. The

transducer mass-flow range is 0-0.4 lb/min and the full scale output is 5 volts for maximum-flow rate. The effluent from the column vacuum pump is demisted of oil vapors through a cascade of two cold-traps before transmitted through the transducer. The chart recorder traces the instantaneous output of the transducer. The output is also integrated even at zero flow. This is caused by a constant leakage voltage from the transducer and this leakage value must be subtracted from the final value to obtain the actual value.

A gas-drying tube was added to eliminate water vapor as a possible variable during initial-feasibility testing. It is readily acknowledged that water vapor is an important variable in typical air-CO₂ separations, but it was felt at this time it might mask other results.

Deleted from the test apparatus at this time was the tilting manometer, which had served its usefulness and was no longer needed. A schematic of the modified apparatus is shown on Fig. 13.

4.3 Final System Modification

Based on test results and observations of pressure instrumentation on the PGC column during testing, it was apparent that many of the columns previously studied were not satisfactorily purged within a cycle before starting a second cycle. Continuous efforts had been made in adjusting the several column parameters to realize a reasonable pumpdown time. The ranges of change of these parameters are as follows:

<u>Parameter</u>	<u>Range of Change</u>
Column Diameter	From 1/4 to 3/4 in.
Column Length	From 72 to 6 in.
Injection Time	From 15 to 5 sec

It was observed that the 3/4 x 6-in. and 3/4 x 12-in. silica gel columns both required 4 minutes to reach 1-mm Hg of pressure. This indicated that the pumpdown time cannot be further reduced by reducing the length of the 3/4-in-diameter column. A test was then performed

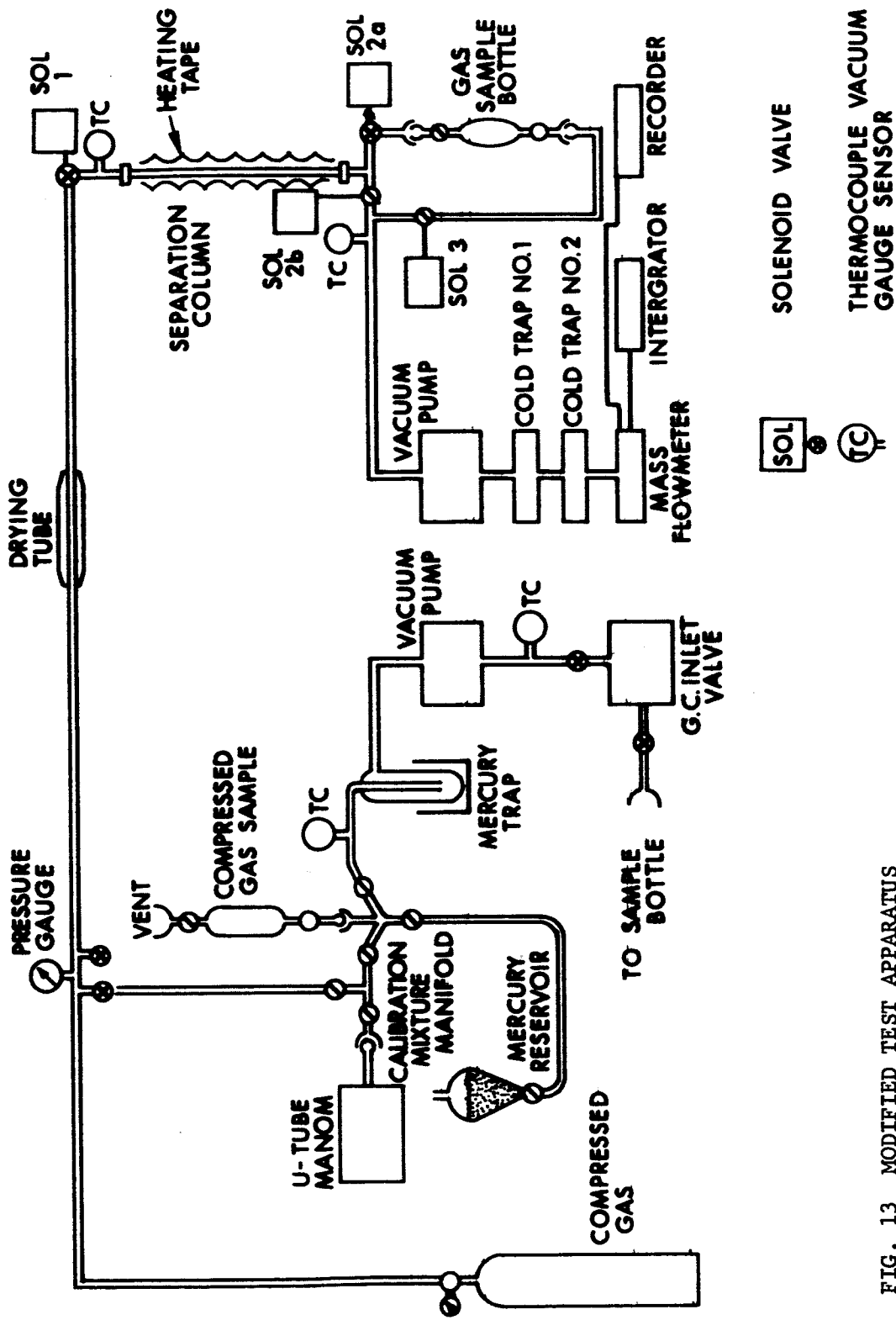


FIG. 13 MODIFIED TEST APPARATUS

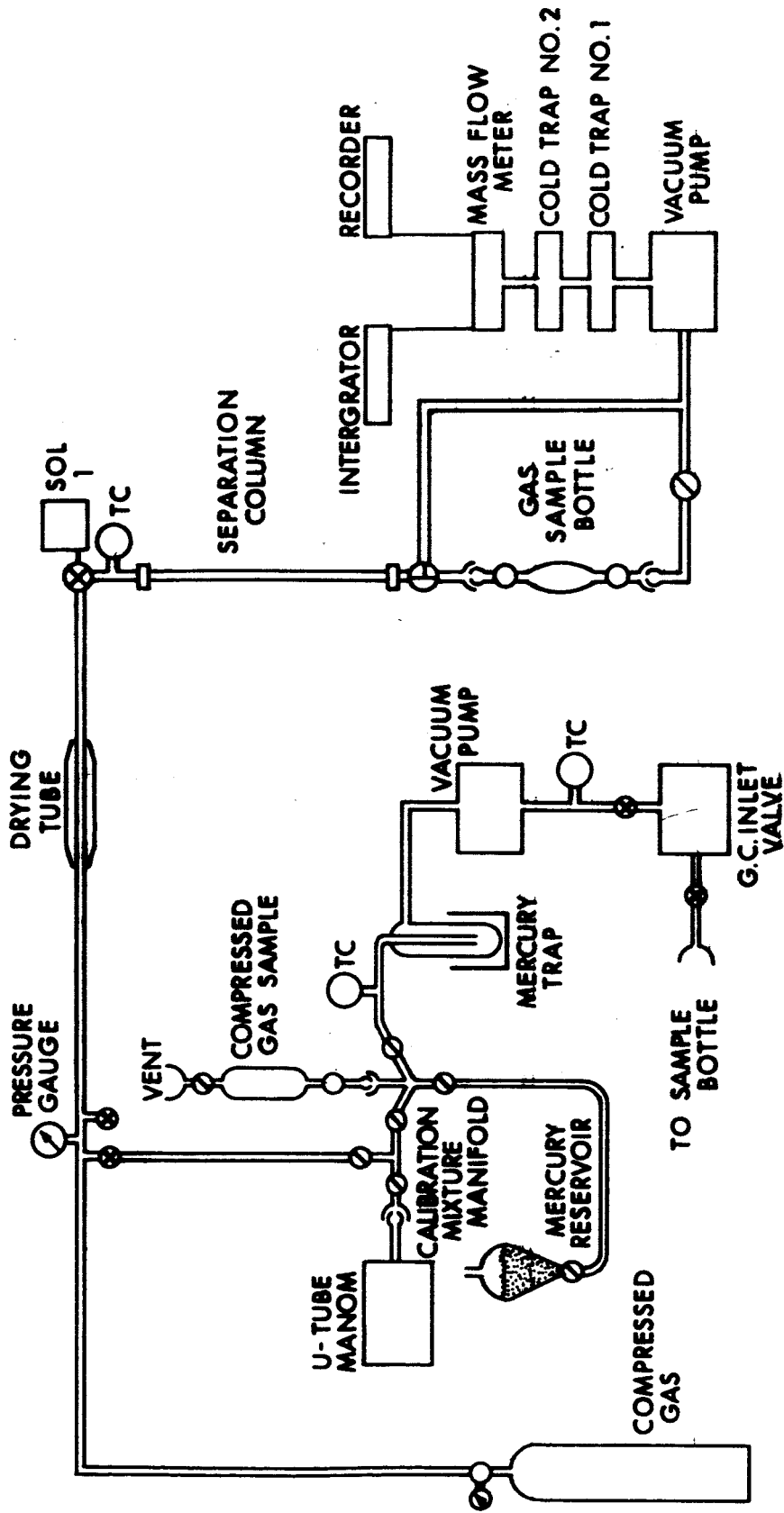
by connecting a 3/4 x 6-in. silica gel column directly to the vacuum pump. It was observed that by bypassing the sampling portion of the apparatus, the column was pumped down to below 1-mm Hg of pressure within 30 seconds. Thus the sample line impedance has accounted for the largest delay in pumpdown time. The sampling portion of the test apparatus was therefore modified by replacing the solenoid valves with glass stopcocks and the 1/8-in. lines with 3/16-in. OD vacuum tubings. The schematic of the modified test apparatus is shown in Fig. 14.

4.4 Gas Chromatograph Calibration

As the various gas-mixture samples are analyzed on the gas chromatograph, ratios of peak heights of air and CO₂ are obtained. In order to determine the extent of separation by the system, it is necessary to convert these ratios to relative concentrations of the two gases. This has been accomplished by the use of standard gas mixtures for which peak height ratios were obtained. A calibration plot thus was drawn, which allows volume percent CO₂ to be read directly once the peak height ratio of an unknown mixture is obtained.

The standard gas mixtures were produced by evacuating a sample bottle to the lowest possible system pressure (< 50 micron) and back-filling with pure CO₂ to a certain subatmospheric pressure as read on the U-tube manometer. The bottle was then brought up to atmospheric pressure, or just below it, by admitting air into the system. Since the ratio of CO₂ pressure to the total system pressure is equivalent to the volume percent of CO₂ in the bottle, any calibration mixture may then be made. As a double check on our procedure, selected samples were analyzed mass spectrometrically. Results of the mass spectrometric analysis showed deviations of < ±1 percent from that calculated by pressure measurement. Figure 15 shows the results obtained of air/CO₂ mixtures.

As with the CO₂-air system, volumetric calibration plots are required for the methane and hydrogen gas chromatograms to determine the extent of separation by the PGC technique. The



SOL

TC

SOLENOID VALVE

THERMOCOUPLE VACUUM GAUGE SENSOR

FIG. 14 FINAL SYSTEM TEST APPARATUS

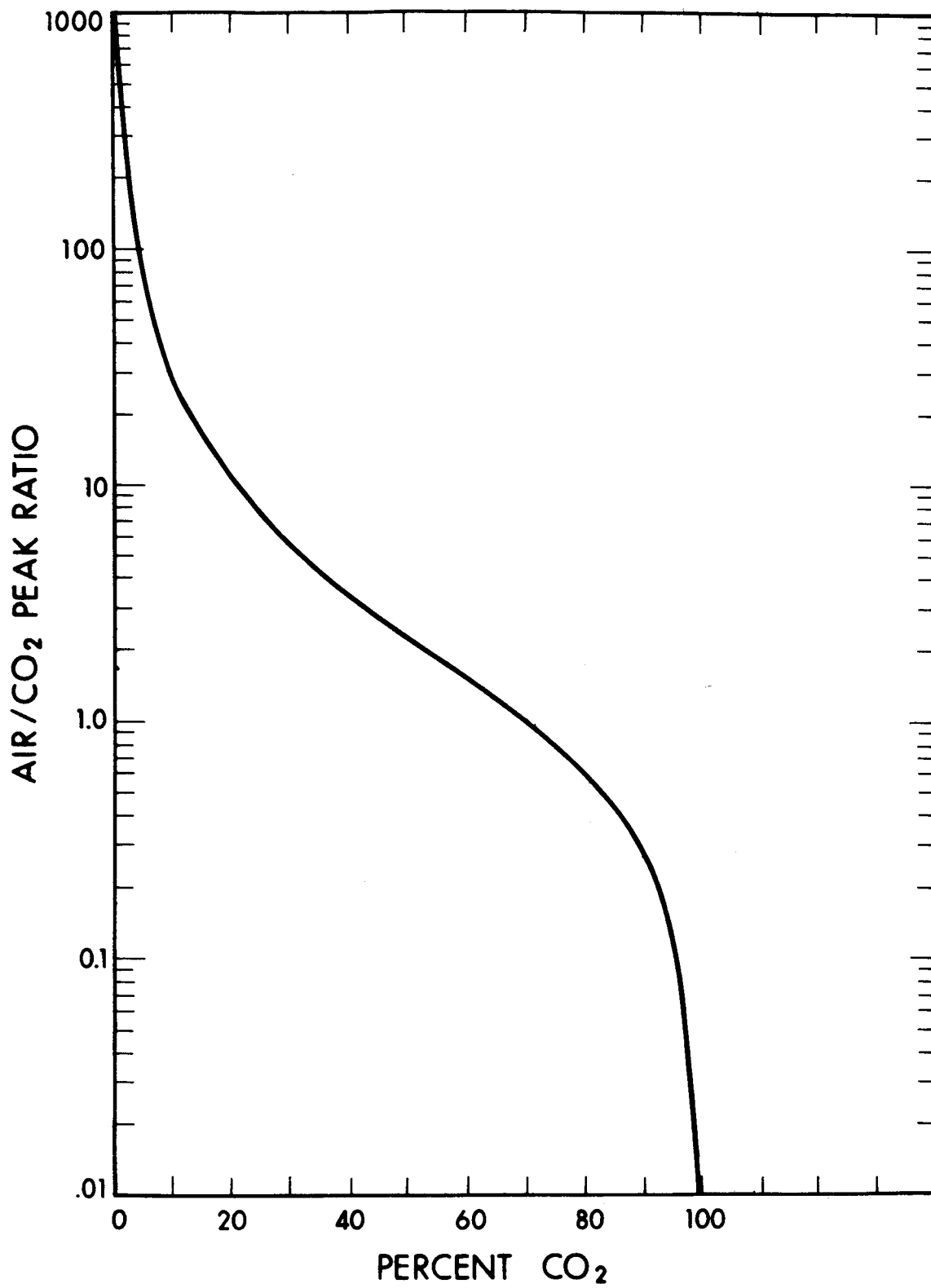


FIG. 15 CALIBRATION PLOT FOR AIR-CO₂ MIXTURES

techniques used in preparing standard CO₂-air mixtures for calibrating the chromatograph, however, could not be used. Therefore a calibration plot which allowed the volume percent of each gas to be read directly from peak height ratios was not feasible. Other techniques, consequently, were adopted for obtaining calibration plots of methane and hydrogen gases.

If the separation of a gas mixture by the analysis column is good, the composition of the gas mixture may be analyzed by reading directly from a calibration plot of peak height versus pressure (concentration) for each gas component. In the case of H₂ and CH₄ mixtures using a thermal conductivity detector, an additional problem arises; namely, when using standard carrier gases such as He, N₂ and A, the detection sensitivity is not uniform. Thus, when using He as a carrier, sensitivity for H₂ is very poor while CH₄ sensitivity is excellent. Conversely, when using N₂ or A as the carrier, sensitivity for H₂ is excellent while CH₄ sensitivity is poor. A compromise was reached by using a carrier composed of 50 percent He and 50 percent N₂. In this case, the detector electrical output was reversed between the H₂ and CH₄ peaks to maintain a positive trace on the recorder.

The calibration curves for methane and hydrogen using a 1/4 x 24-in. silicon-rubber-analyzing column are shown in Figs. 16 and 17 respectively. Another set of calibration curves for methane and hydrogen using a 1/4 x 36-in. molecular-sieve-analyzing column are shown in Figs. 18 and 19 respectively. Silicon-rubber column yields a more linear hydrogen plot, while the sieve yields a more linear methane plot. The hydrogen curve for both columns, however, begins to change polarity at low pressures, i.e., below 100-mm Hg for the silicone-rubber column and below 250-mm Hg for the molecular-sieve column. Due to this reversal effect, accurate low-percentage H₂ concentrations could not be obtained. Test results were therefore analyzed mass-spectrometrically.

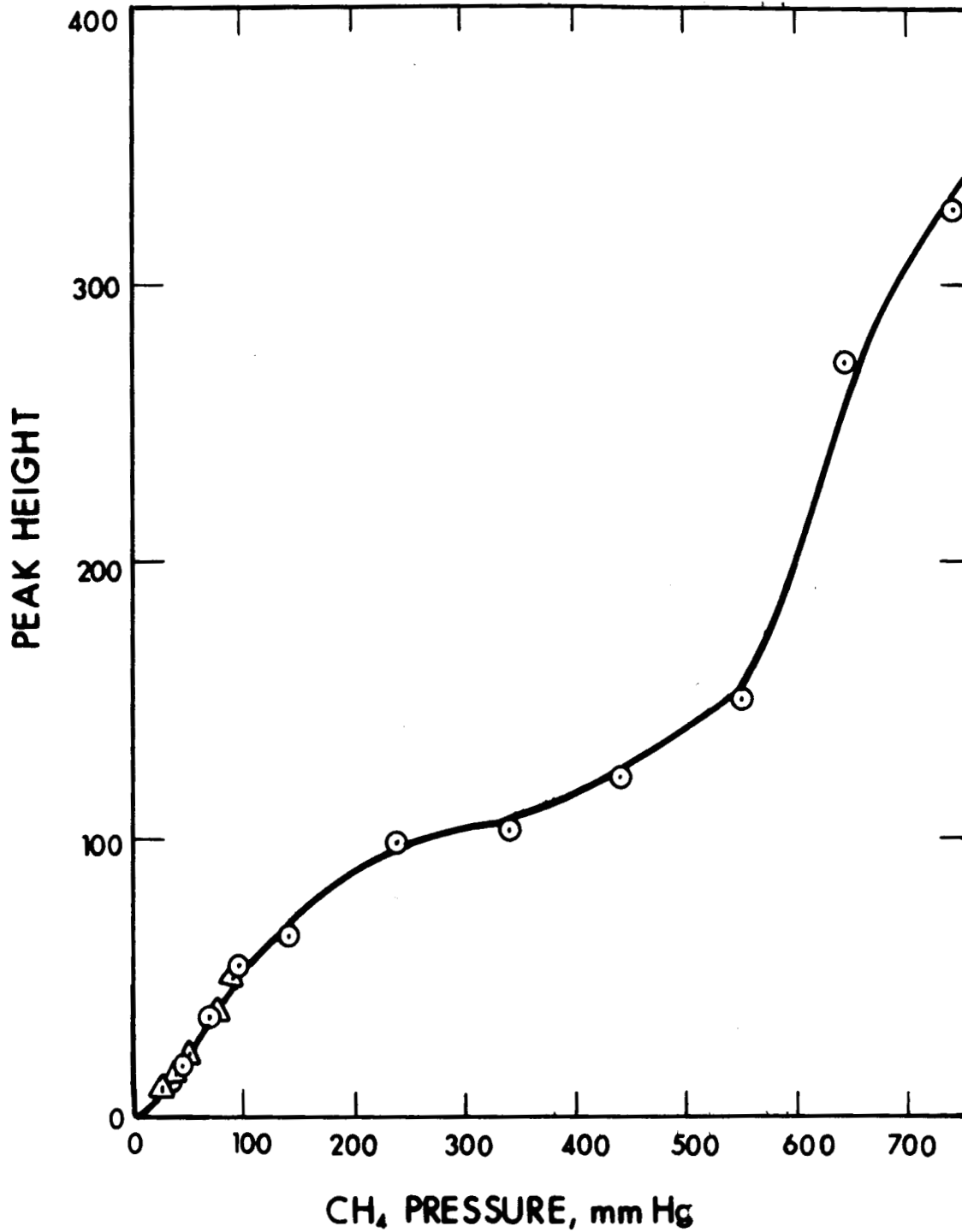


FIG. 16 CALIBRATION CURVE FOR METHANE 1/4 x 24 INCH SILICONE RUBBER ANALYZING COLUMN AT ROOM TEMPERATURE

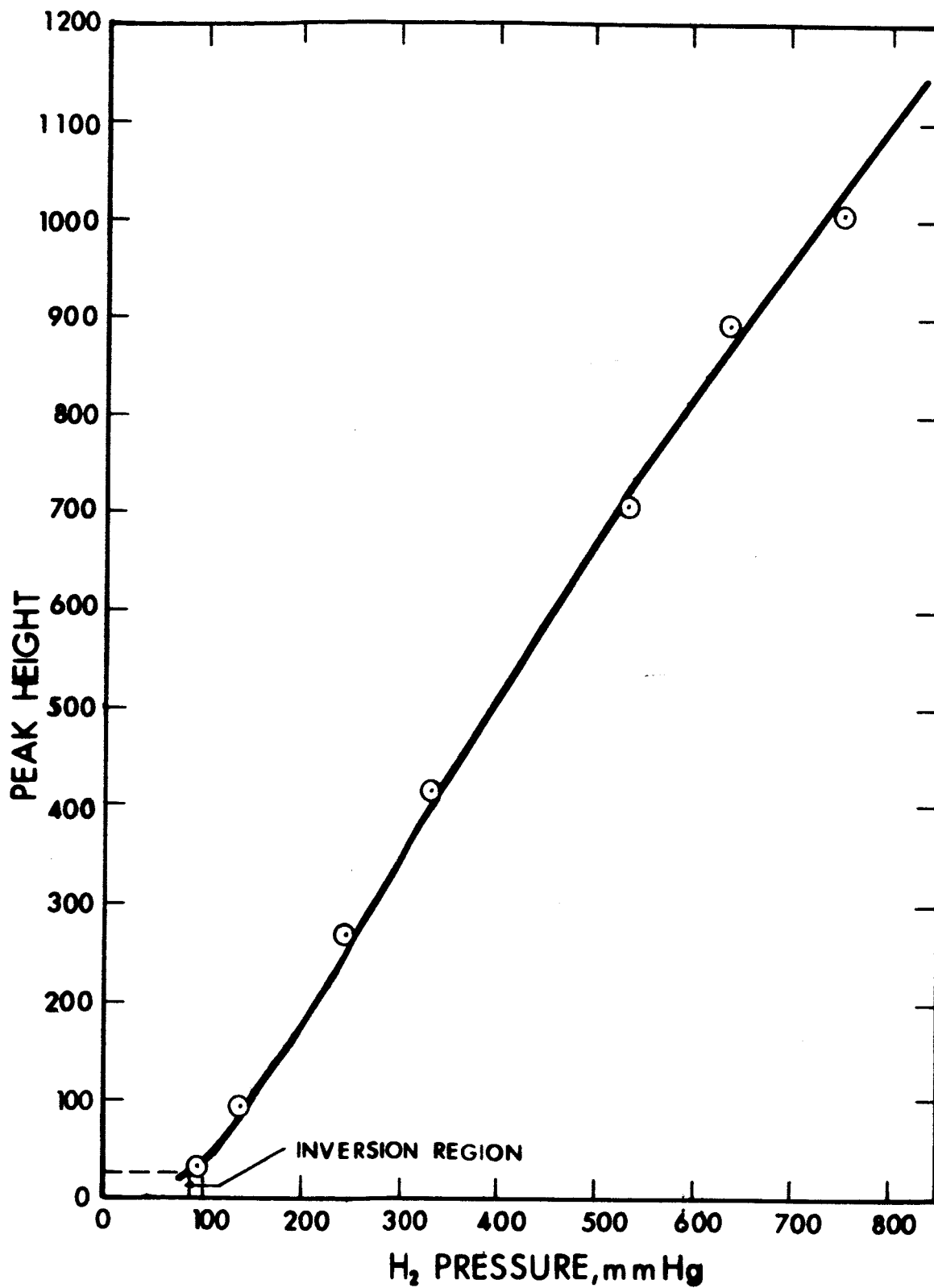


FIG. 17 CALIBRATION CURVE FOR HYDROGEN 1/4 x 24 INCH SILICONE RUBBER ANALYZING COLUMN AT ROOM TEMPERATURE

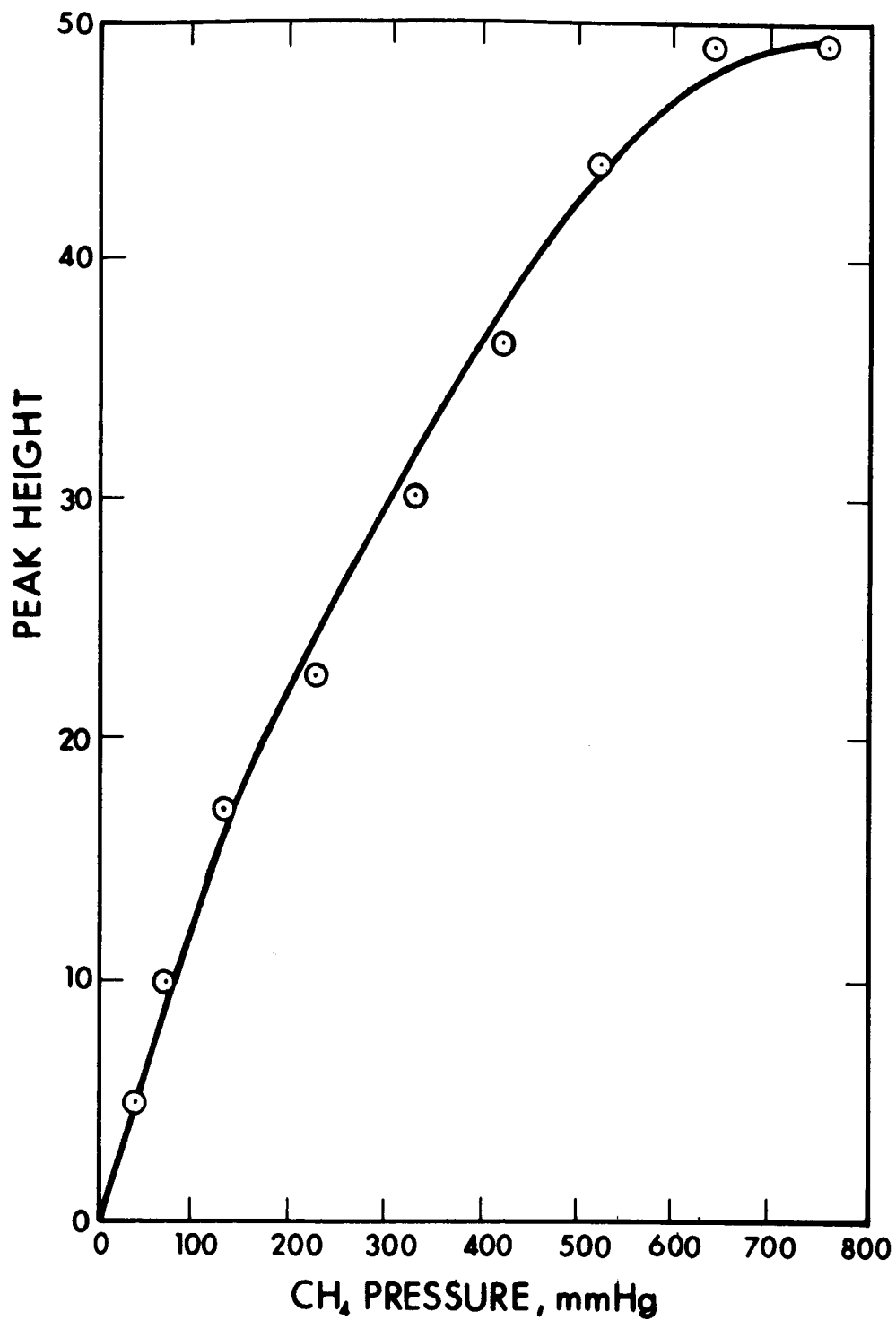


FIG. 18 CALIBRATION CURVE FOR METHANE, 1/4 x 36 INCH MOLECULAR SIEVE ANALYZING COLUMN AT ROOM TEMPERATURE

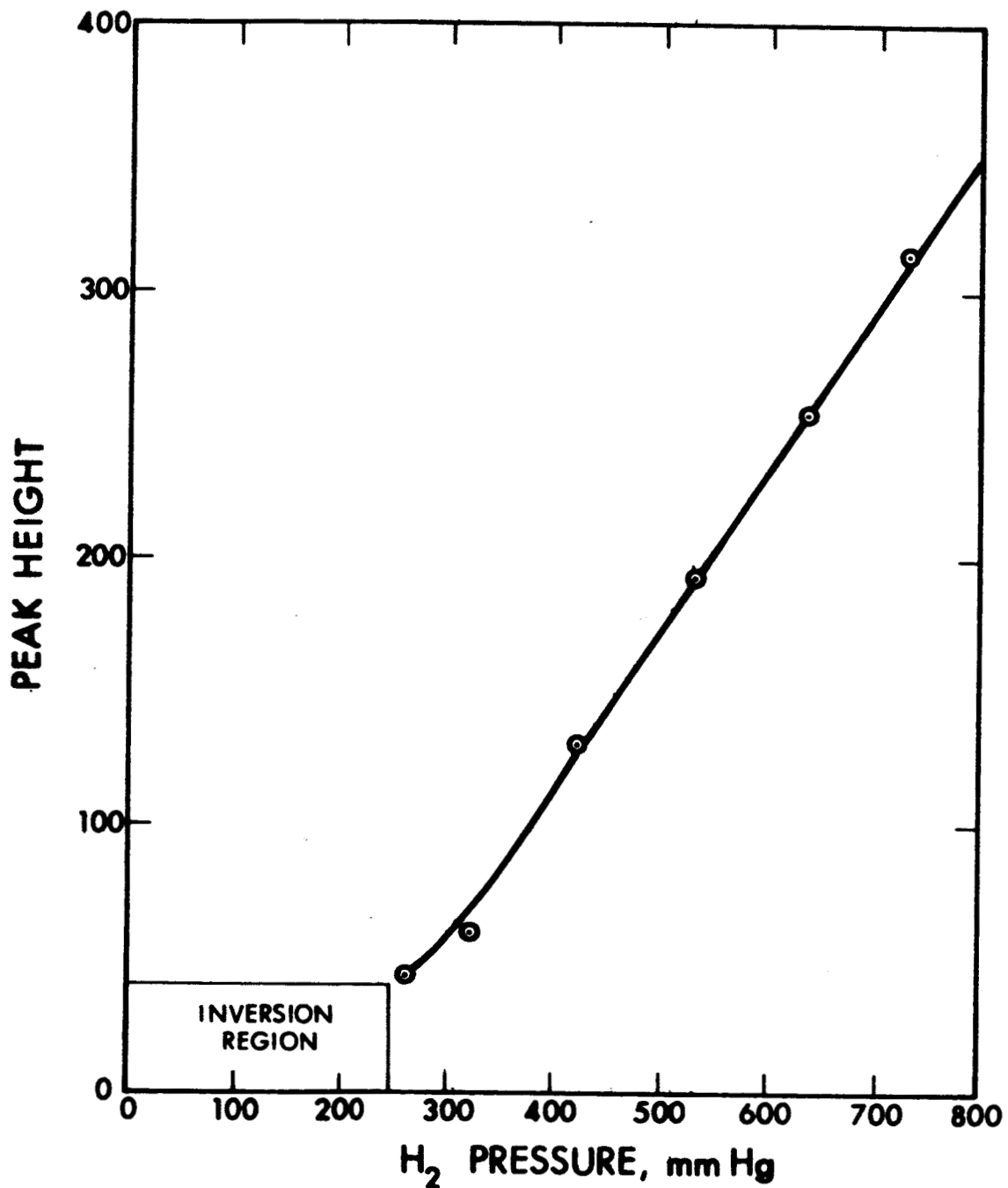


FIG. 19 CALIBRATION CURVE FOR HYDROGEN, 1/4 x 36 INCH MOLECULAR SIEVE ANALYZING COLUMN AT ROOM TEMPERATURE

4.5 Calibration Curves for Mass Flowmeter

Individual calibration curves of transducer output voltage and mass flow for CO₂ and air were furnished by the manufacturer. Since the transducer output voltage is linear with the mass-flow rate of the individual gas, it was assumed that flow rates for mixtures of CO₂ and air could be made by linear interpolation of the CO₂-air calibration curves. Calibration curves for CO₂-air mixtures were constructed and are shown in Figs. 20 and 21. A one-point check with the 80 percent CO₂ to 20 percent air mixture to verify this assumption was done as follows:

Conditions: 80 percent CO₂, 20 percent air mixture, inlet pressure setting at 5 psig.

1. Flow-rate measurement at 5 psig by displacement method.

Volume flow = 145 cc/sec

$$\text{Mass flow} = (0.145) \left(1.85 \frac{\text{g}}{\text{l}}\right) \left(\frac{273}{296}\right) \left(\frac{1}{454}\right) (60)$$

$$= 0.0327 \text{ lb/min}$$

2. From linear interpolation of CO₂-air transducer voltage - mass flow curves 80 percent CO₂, 20 percent air at 0.0327 lb/min = 0.147 volt
3. Transducer voltage for 80 percent CO₂, 20 percent air at 5 psig setting = 0.150 volt
4. Error calculations:
 - a. Comparative error = 0.003 volts or 2 percent which would represent 0.5 percent change in CO₂ concentration

Tests were conducted on a 3/4 x 24-in. column packed with 6-16 mesh silica gel. The column effluent is pumped through two cold-traps to remove the oil vapor prior to being transmitted into the flow transducer. Cold traps were found to be more efficient in removing oil vapor than filters and also traps have much less pressure drop. The response time, which is the delay time between the effluent's exit

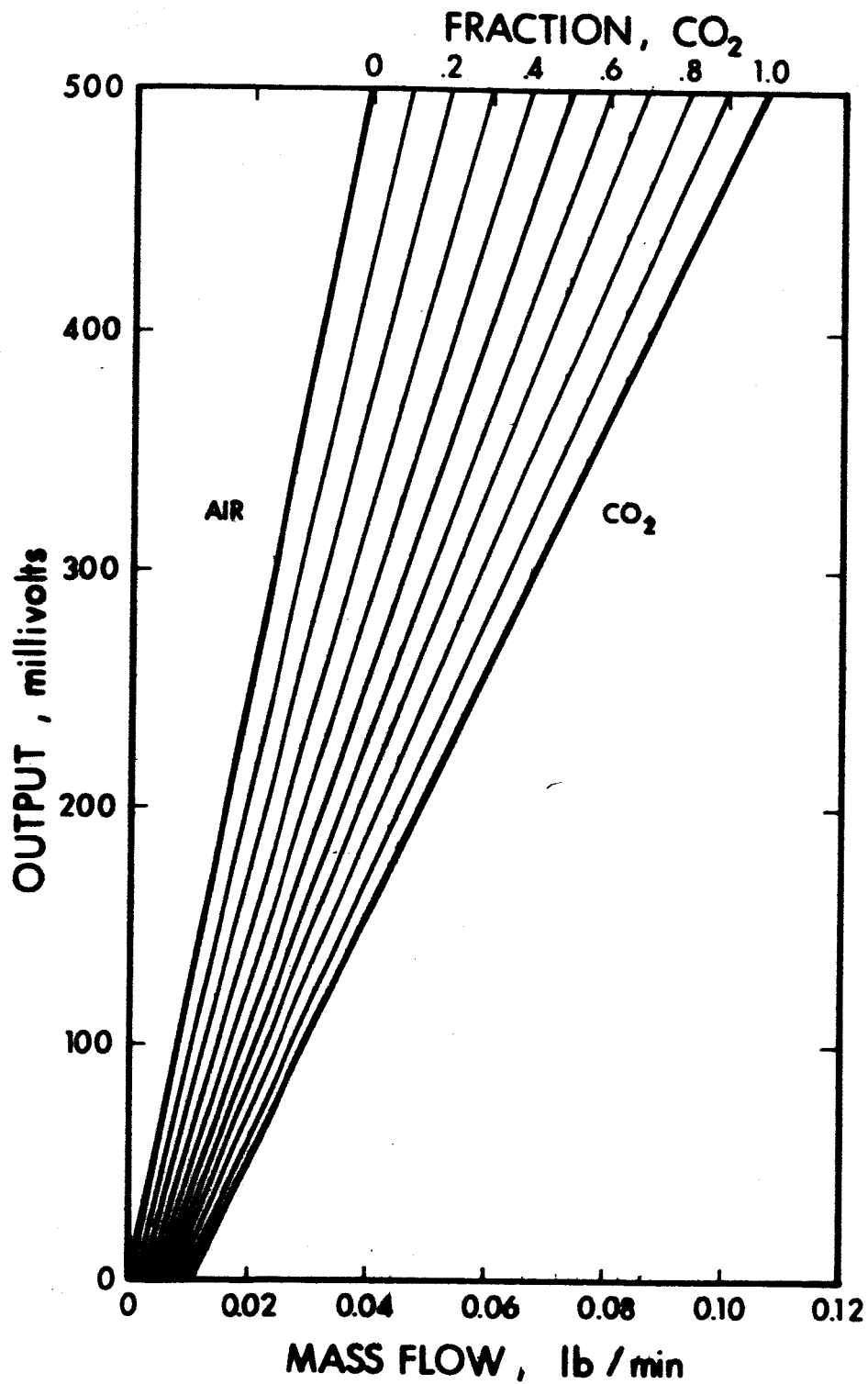


FIG. 20 CALIBRATION DATA FOR MASS FLOWMETER
CO₂-AIR BINARY MIXTURE

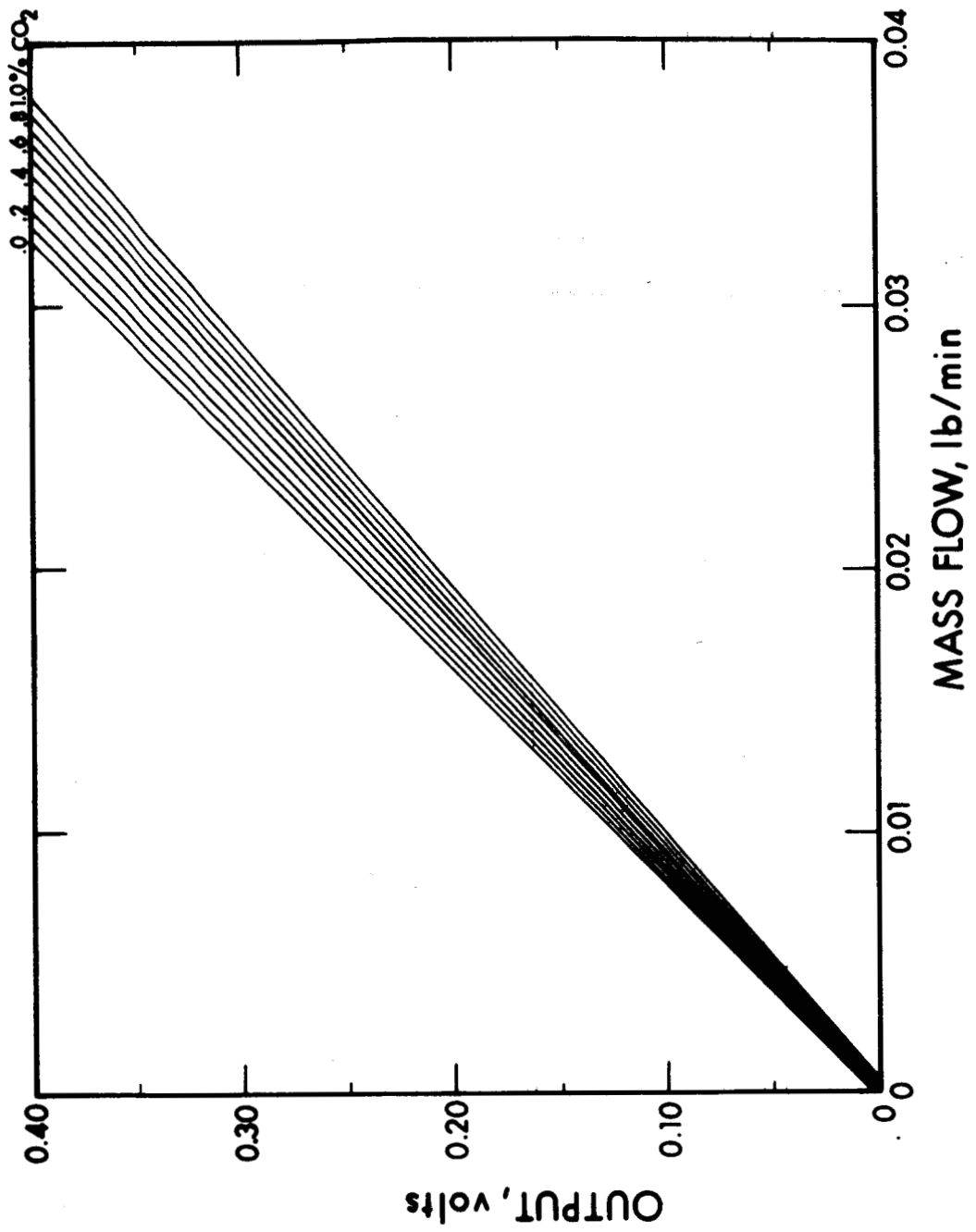


FIG. 21 CALIBRATION DATA FOR MASS FLOWMETER CO₂-AIR BINARY MIXTURE

from the column and its measurement by the transducer, is approximately 0.1 second. An output trace for a 5 second injection of 80 percent CO_2 , 20 percent air and a total cycle time of 180 seconds is shown in Fig. 22. This curve gives the instantaneous transducer-voltage output for the CO_2 -air effluent. To reduce this curve into instantaneous mass flow of the individual gas, the separation curve for 80 percent CO_2 to 20 percent air and the calibration curve for CO_2 -air were used. The results of this data reduction process are a plot of the mass-flow characteristic of CO_2 and air in the column effluent and are shown in Fig. 23. This curve, however, only qualitatively illustrates the separation of CO_2 and air.

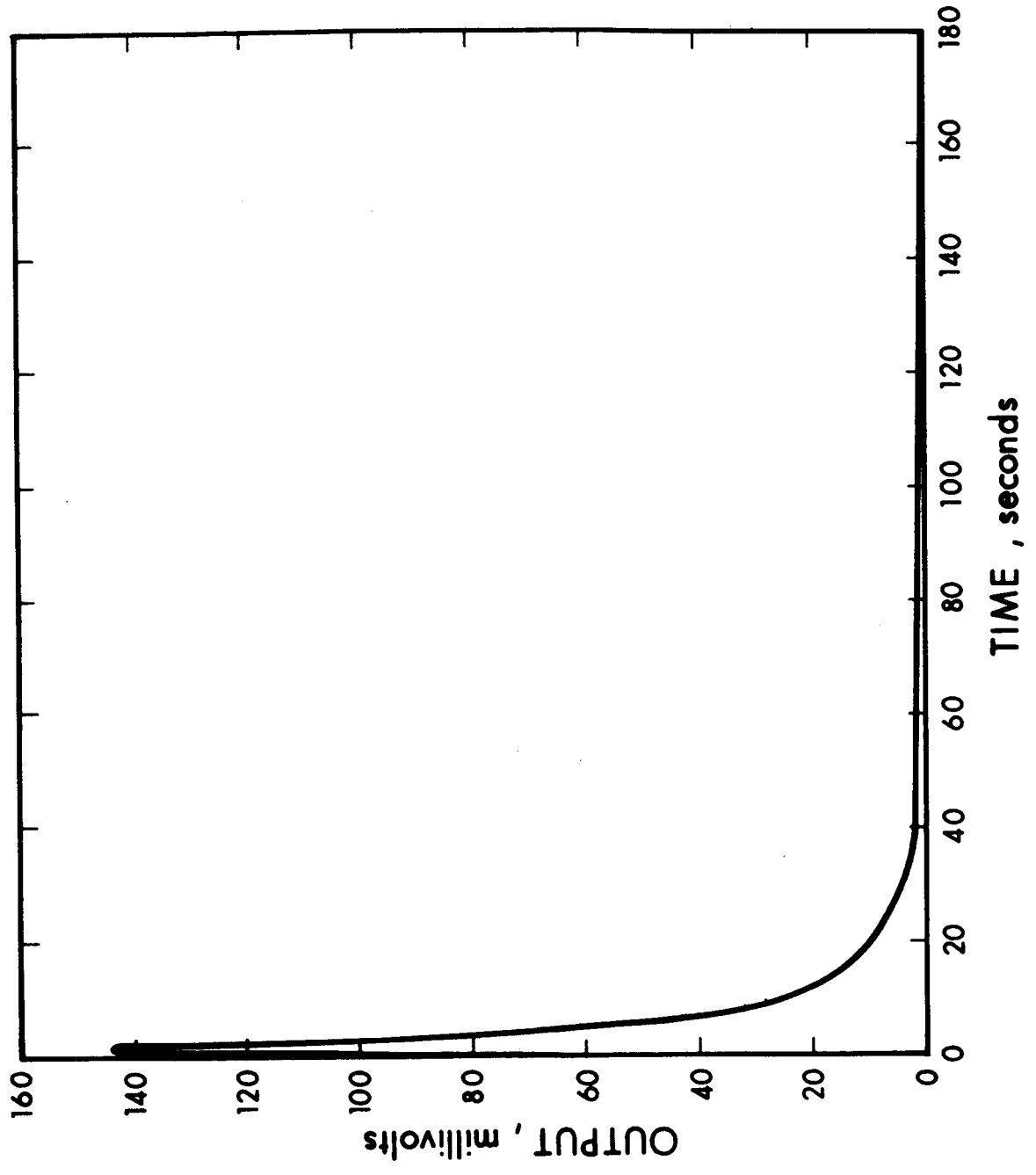


FIG. 22 TRANSDUCER OUTPUT TRACE FOR 5-SECOND INJECTION OF 80 PERCENT CO₂,
20 PERCENT AIR

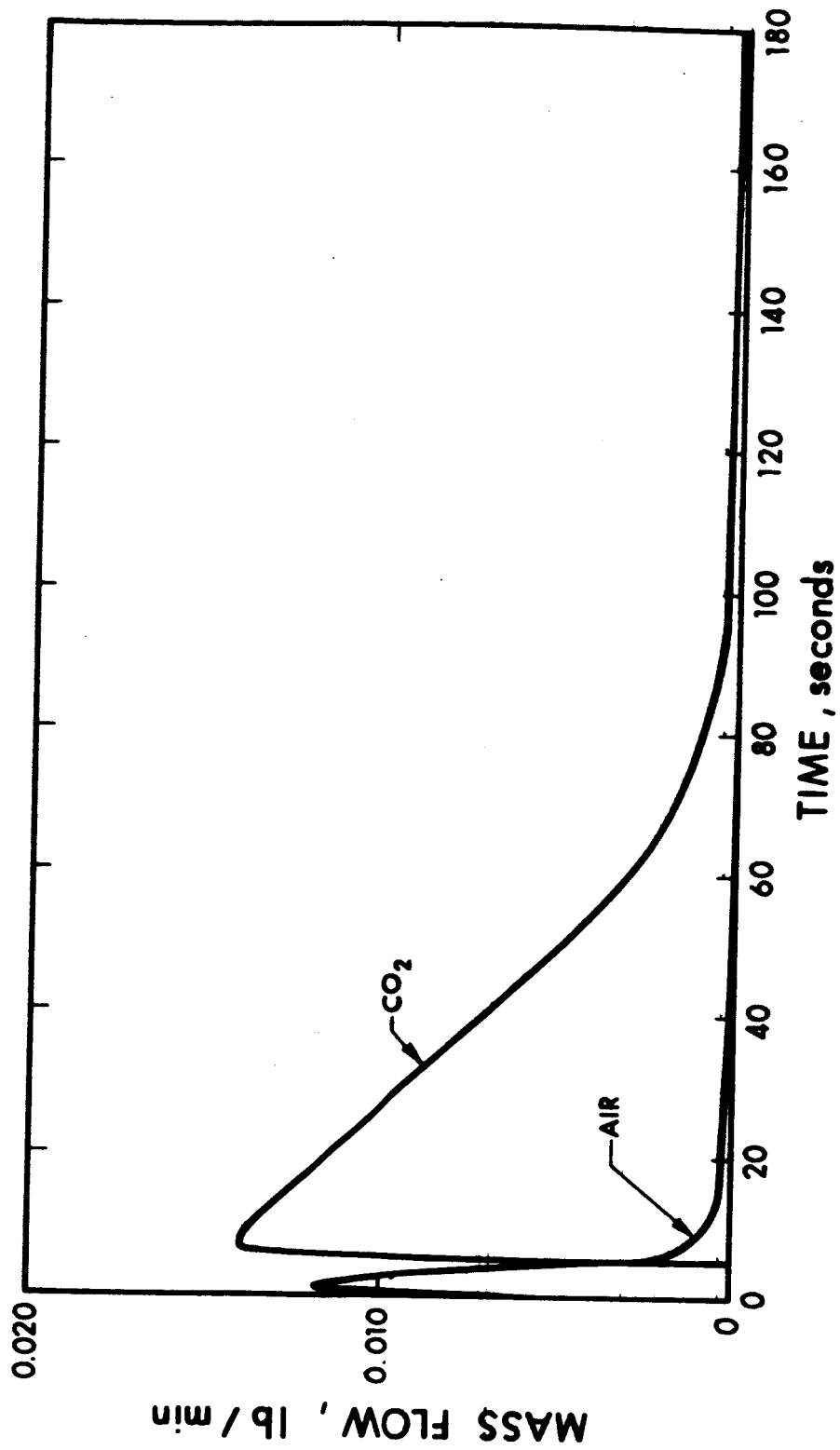


FIG. 23 OUTPUT TRACE OF AIR AND CO₂ WITH TIME

5. EXPERIMENTAL PROGRAM

5.1 Initial Test Results

The test program was designed to evaluate the following variables on PGC column performance.

1. Column length
2. Operating temperature
3. Column diameter
4. Injection volume
5. Injection pressure
6. Column-packing material
7. Moisture-removal equipment

Three gases were investigated during the course of the program; 80 percent CO₂ to 20 percent air, 1 percent CO₂ to 99 percent air, 80 percent CH₄ to 20 percent H₂.

Initial testing was conducted using the 80 percent CO₂ to 20 percent air mixture, a 2-foot column length and a 200-mesh silica gel packing material. Various gas-injection times and cycle times were investigated. The effect of temperature was investigated at 25°C and 50°C. Two column diameters, 3/8-in. and 3/4-in., were tested.

The separation system parameters were varied according to the following schedule:

- Injection times: 5 and 15 seconds
Sampling times: 5, 10, 15, 25, 35, 45 and 55 seconds
Total cycle times: 1, 1-1/2, 2, and 3 minutes

Results of the experiments conducted are presented in two forms:

(1) the data are shown in tabular form, and (2) these data are then plotted as concentration of CO₂ versus sampling time for each injection period and total cycle duration. Tables 1 through 12 present the tabular data. Figures 24 through 35 present the graphical data.

TABLE 1
SEPARATION DATA (Fig. 24)

GAS MIXTURE 80% CO₂, 20% Air
 SEPARATION COLUMN 3/8" x 24" Silica Gel at 25°C
 ANALYSIS COLUMN 1/4" x 12" Silica Gel at 25°C

INJECTION TIME (SEC.)	SAMPLE TIME (SEC.)	TOTAL CYCLE (SEC.)	AIR PEAK	CO ₂ PEAK	AIR: CO ₂ RATIO	VOL. % CO ₂
15	5	180	96.0	4.9	19.6	13.5
			64.0	3.5	18.3	14.0
	10	180	110.4	4.2	26.3	10.5
			72.8	2.8	26.0	10.5
	14.5	180	62.0	35.0	1.77	57.0
			43.2	22.8	1.89	54.0
	26	180	30.0	30.4	0.99	71.0
			20.0	18.4	1.08	69.5
	34	180	15.6	20.8	0.78	75.0
			9.8	12.8	0.76	76.0
	45.5	180	8.8	13.4	0.65	79.0
			5.3	7.6	0.69	78.0
	54	180	4.2	8.9	0.47	84.0
			6.4	13.4	0.48	83.5

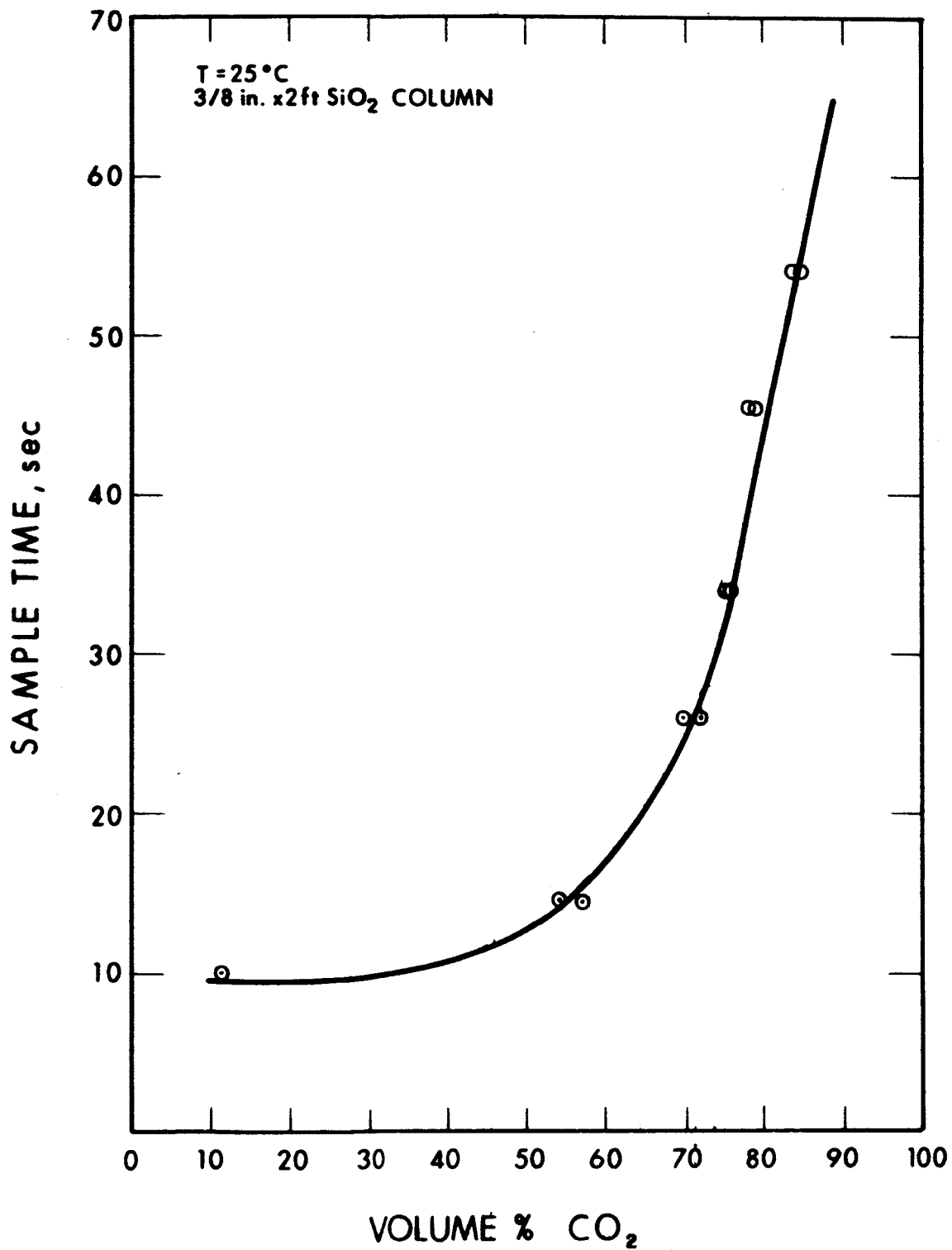


FIG. 24 SEPARATION PLOT (80% CO₂ - 20% Air, 15-second injection, 180-second cycle)

TABLE 2
SEPARATION DATA (Fig. 25)

GAS MIXTURE 80% CO₂, 20% Air
 SEPARATION COLUMN 3/8" x 24" Silica Gel at 25°C
 ANALYSIS COLUMN 1/4" x 12" Silica Gel at 25°C

INJECTION TIME (SEC.)	SAMPLE TIME (SEC.)	TOTAL CYCLE (SEC.)	AIR PEAK	CO ₂ PEAK	AIR: CO ₂ RATIO	VOL. % CO ₂
15	5	120	64.8	3.4	19.06	13.5
			44.8	2.4	18.67	14.0
	10	120	120.0	9.6	12.50	18.5
			83.2	7.5	11.09	20.0
	16	120	166.4	21.2	7.85	25.0
			118.4	13.4	8.84	23.0
	25	120	30.8	24.4	1.26	65.0
			21.2	15.6	1.36	63.0
	36	120	12.8	14.8	0.86	73.0
			45.5	120	10.2	17.0
	54	120	6.2	9.8	0.64	79.0
			3.9	7.8	0.50	83.0
			6.6	14.5	0.45	84.0

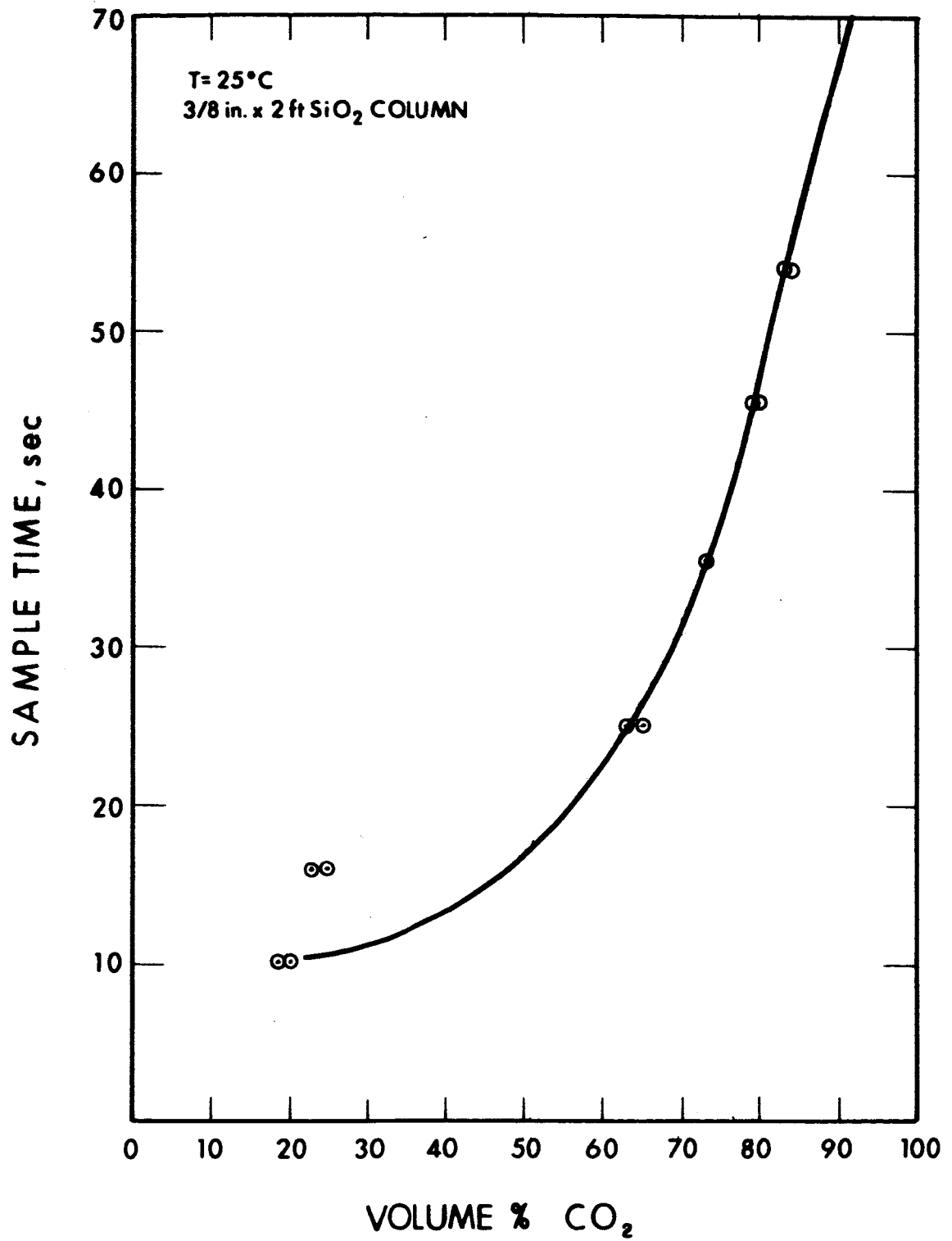


FIG. 25 SEPARATION PLOT (80% CO₂ - 20% Air, 15-second injection, 120-second cycle)

TABLE 3
SEPARATION DATA (Fig. 26)

GAS MIXTURE 80% CO₂, 20% Air
 SEPARATION COLUMN 3/8" x 24" Silica Gel at 25°C
 ANALYSIS COLUMN 1/4" x 12" Silica Gel at 25°C

INJECTION TIME (SEC.)	SAMPLE TIME (SEC.)	TOTAL CYCLE (SEC.)	AIR PEAK	CO ₂ PEAK	AIR: CO ₂ RATIO	VOL. % CO ₂
15	16	90	56.8	26.4	2.15	51.0
			40.0	18.2	2.20	50.5
	25.5	90	26.4	24.0	1.10	68.0
			18.2	15.6	1.17	67.0
	36	90	12.6	16.6	0.76	76.0
			11.2	12.8	0.87	73.0
	45.5	90	6.3	10.6	0.59	80.0
			7.8	12.6	0.62	79.5
	54	90	4.5	8.6	0.52	82.0
			7.1	16.4	0.43	85.0

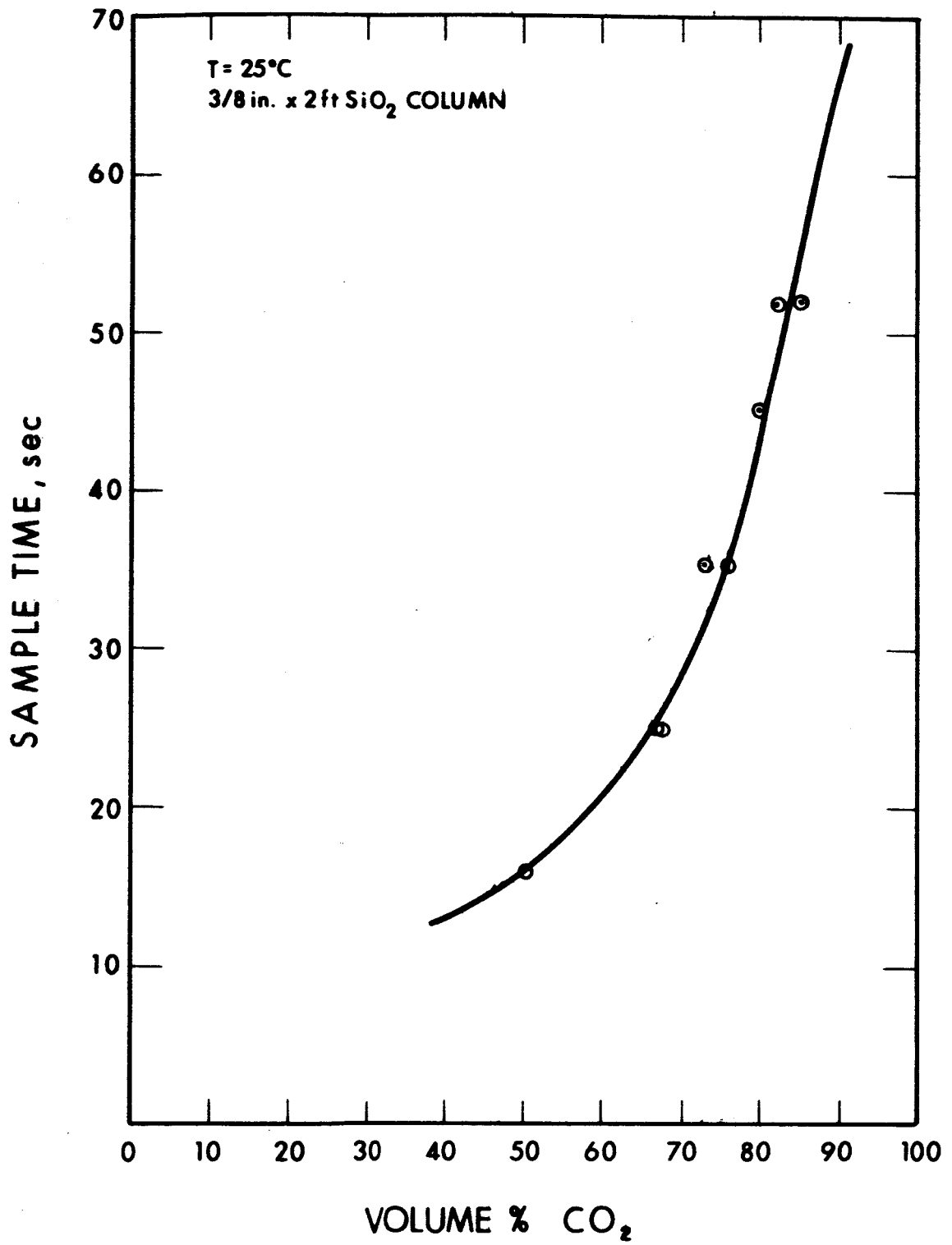


FIG. 26 SEPARATION PLOT (80% CO₂ - 20% Air, 15-second injection, 90-second cycle)

TABLE 4
SEPARATION DATA (Fig. 27)

GAS MIXTURE 80% CO₂, 20% Air
 SEPARATION COLUMN 3/8" x 24" Silica Gel at 25°C
 ANALYSIS COLUMN 1/4" x 12" Silica Gel at 25°C

INJECTION TIME (SEC.)	SAMPLE TIME (SEC.)	TOTAL CYCLE (SEC.)	AIR PEAK	CO ₂ PEAK	AIR: CO ₂ RATIO	VOL. % CO ₂
15	5	60	192.0	16.0	12.0	19.0
			144.0	12.2	11.8	19.0
	10	60	105.6	23.2	4.6	34.0
			85.7	16.4	5.2	31.5
			52.2	11.6	4.8	32.5
	16	60	70.4	31.6	2.21	50.0
			41.6	19.2	2.16	50.0
	25	60	45.6	22.8	2.0	53.0
			33.2	13.4	2.45	47.0
	35	60	14.8	15.8	0.94	71.5
			10.6	10.0	1.06	69.0
	45	60	8.7	12.4	0.70	77.0
			6.1	9.6	0.64	79.0
	54	60	5.8	12.8	0.45	84.0
			3.7	7.1	0.52	82.0
	3	60	5.95	22.6	0.26	91.0
			8.1	13.1	0.62	79.0
			6.2	8.1	0.77	75.5

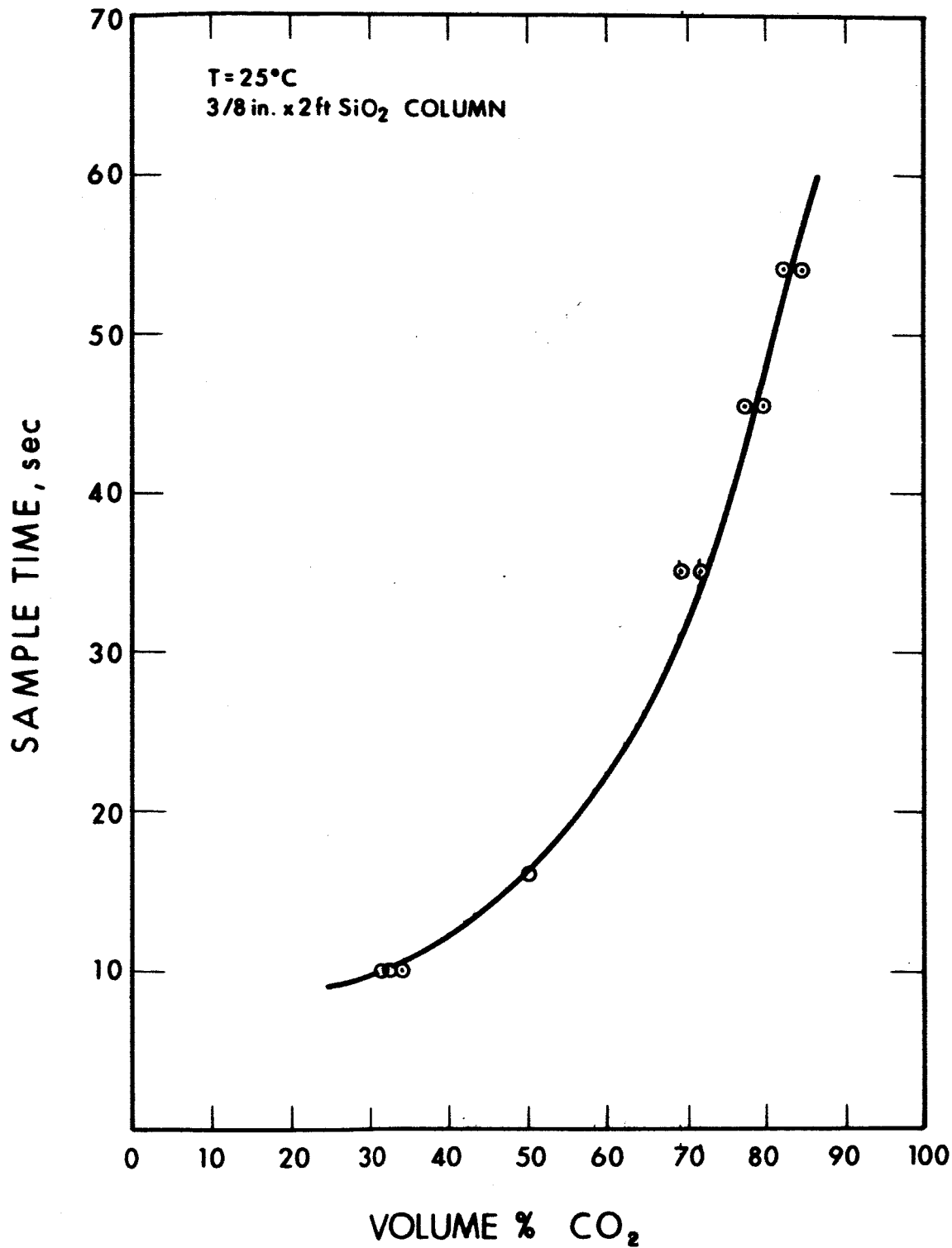


FIG. 27 SEPARATION PLOT (80% CO₂ - 20% Air, 15-second injection, 60-second cycle)

TABLE 5
SEPARATION DATA (Fig. 28)

GAS MIXTURE 80% CO₂, 20% Air
 SEPARATION COLUMN 3/8" x 24" Silica Gel at 25°C
 ANALYSIS COLUMN 1/4" x 12" Silica Gel at 25°C

INJECTION TIME (SEC.)	SAMPLE TIME (SEC.)	TOTAL CYCLE (SEC.)	AIR PEAK	CO ₂ PEAK	AIR: CO ₂ RATIO	VOL. % CO ₂	
5	4	180	518.0	---	----	---	
			493.0	---	----	---	
	10	180	118.4	5.6	21.14	12.5	
			13.5	180	66.8	3.1	21.55
	26	180	45.6	2.2	20.73	13.0	
			20.6	22.9	0.90	72.5	
	34	180	12.6	13.6	0.93	72.0	
			12.6	12.9	0.98	71.0	
	44	180	8.5	9.05	0.94	72.0	
			11.2	3.1	3.61	39.5	
	56	180	8.5	2.5	3.40	40.0	
			8.7	12.2	0.71	77.0	
				5.2	6.0	0.87	73.0

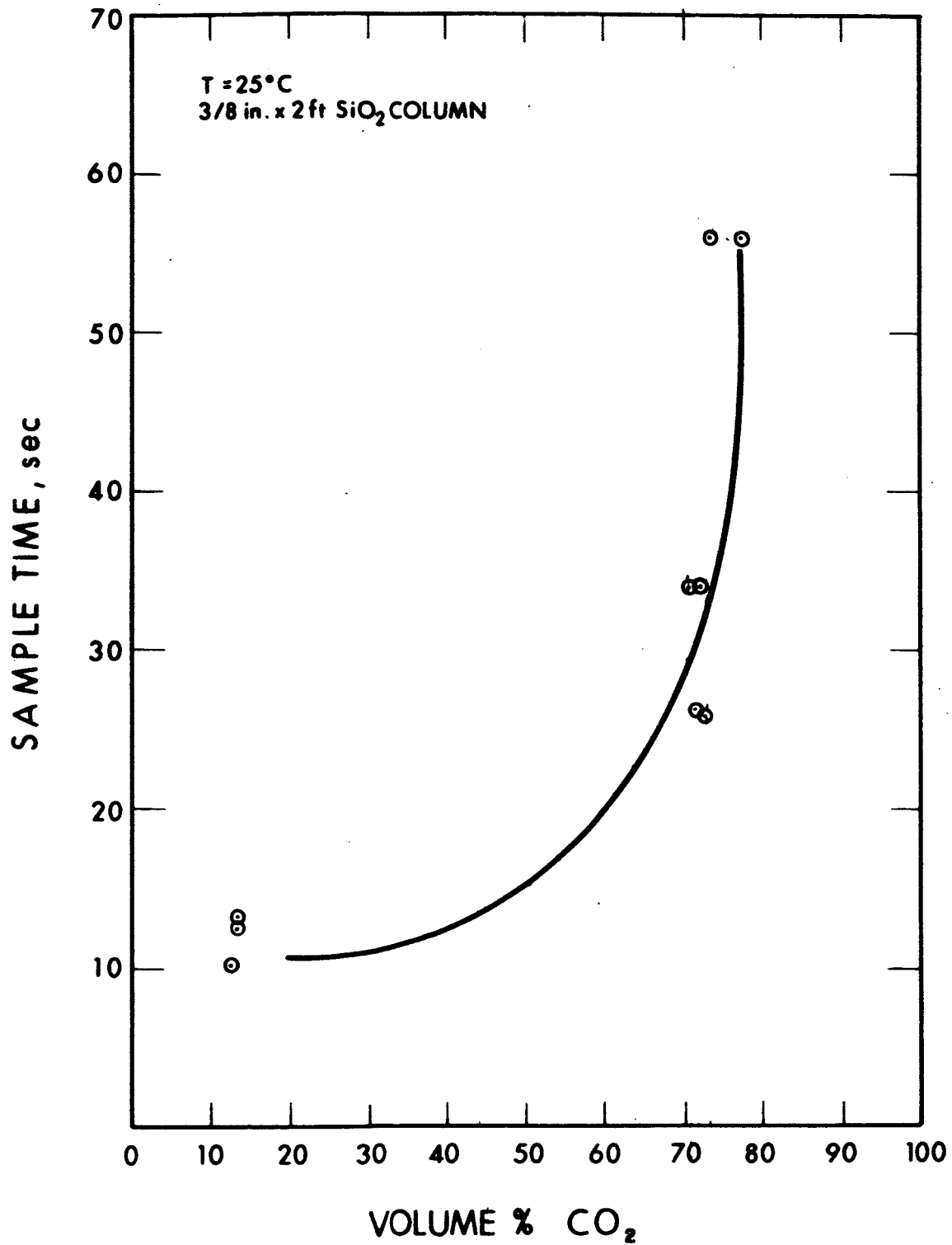


FIG. 28 SEPARATION PLOT (80% CO_2 - 20% Air, 5-second injection, 180-second cycle)

TABLE 6
SEPARATION DATA (Fig. 29)

GAS MIXTURE 80% CO₂, 20% Air

SEPARATION COLUMN 3/8" x 24" Silica Gel at 25°C

ANALYSIS COLUMN 1/4" x 12" Silica Gel at 25°C

INJECTION TIME (SEC.)	SAMPLE TIME (SEC.)	TOTAL CYCLE (SEC.)	AIR PEAK	CO ₂ PEAK	AIR: CO ₂ RATIO	VOL. % CO ₂
5	5	120	70.4	8.7	8.09	24.0
			45.6	5.3	8.60	23.0
	10	120	86.4	6.75	12.80	18.5
			56.0	4.05	13.83	17.5
	14.5	120	52.4	30.0	1.75	57.0
			32.8	17.7	1.85	55.0
	25	120	18.2	21.2	0.86	74.0
			11.0	13.0	0.85	74.0
	35	120	13.8	22.8	0.61	80.0
			8.8	12.6	0.60	80.0
	45.5	120	9.0	11.4	0.79	75.0
			5.3	7.0	0.76	76.0
	55	120	9.7	17.4	0.56	81.0
			5.85	10.2	0.57	81.0

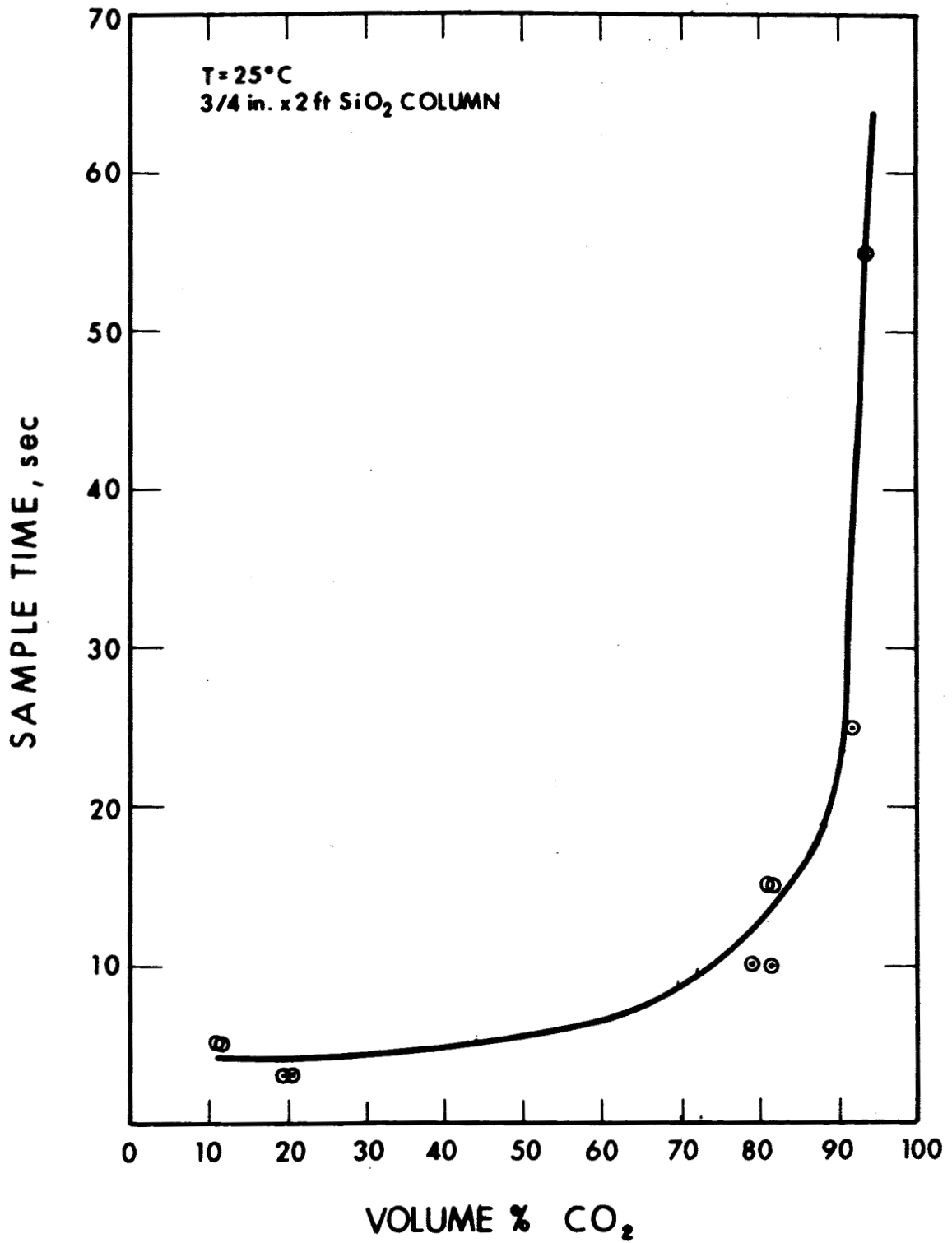


FIG. 32 SEPARATION PLOT (80% CO₂ - 20% Air, 15-second injection, 180-second cycle)

TABLE 10
SEPARATION DATA (Fig. 33)

GAS MIXTURE 80 o/o CO₂, 20 o/o Air
 SEPARATION COLUMN 3/8" x 24" S_iO₂ at 50°C
 ANALYSIS COLUMN 1/4" x 12" S_iO₂ at 25°C

INJECTION TIME (SEC.)	SAMPLE TIME (SEC.)	TOTAL CYCLE (SEC.)	AIR PEAK	CO ₂ PEAK	AIR: CO ₂ RATIO	VOL. o/o CO ₂
5	15	60	20.0	40.4	0.495	83.0
			14.2	29.2	0.486	83.0
	5	60	38.0	24.8	1.72	57.0
			24.6	15.5	1.59	60.0
	9.5	60	33.8	38.0	0.89	73.0
			25.4	29.2	0.87	73.0
	25	60	9.25	25.8	0.36	87.0
			5.80	14.9	0.39	86.0
	35.5	60	8.90	26.0	0.34	88.0
			5.40	14.4	0.375	86.0
	55	60	4.50	11.8	0.38	86.0
			2.52	6.18	0.41	85.0

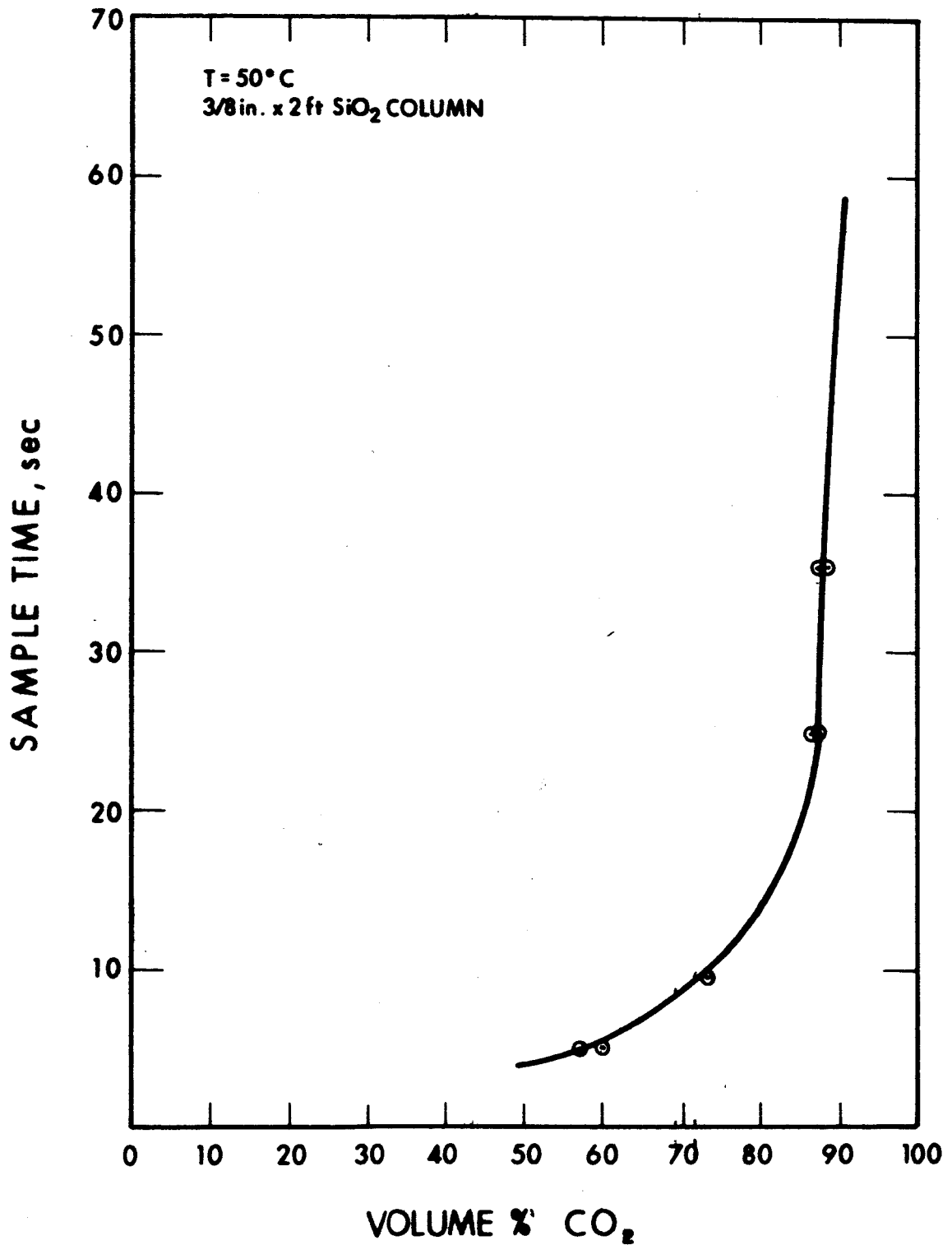


FIG. 33 SEPARATION PLOT (80% CO₂ - 20% Air, 5-second injection, 60-second cycle)

TABLE 11

SEPARATION DATA (Fig. 34)

GAS MIXTURE 80 o/o CO₂, 20 o/o Air
 SEPARATION COLUMN 3/8" x 24" S_iO₂ at 50°C
 ANALYSIS COLUMN 1/4" x 12" S_iO₂ at 25°C

INJECTION TIME (SEC.)	SAMPLE TIME (SEC.)	TOTAL CYCLE (SEC.)	AIR PEAK	CO ₂ PEAK	AIR: CO ₂ RATIO	VOL. o/o CO ₂
15	55	60	6.80	20.4	0.33	88.0
			3.95	10.7	0.37	86.5
	35	60	10.0	28.6	0.35	87.0
			6.30	17.2	0.36	87.5
	25.5	60	21.2	46.8	0.45	84.0
			13.4	28.8	0.465	83.5
	15	60	31.6	51.6	0.61	79.5
			20.8	34.0	0.61	79.5
	10	60	40.0	54.4	0.735	76.0
			29.6	37.6	0.79	75.5
	5	60	50.4	19.8	2.55	46.0
			32.6	11.8	2.76	42.5

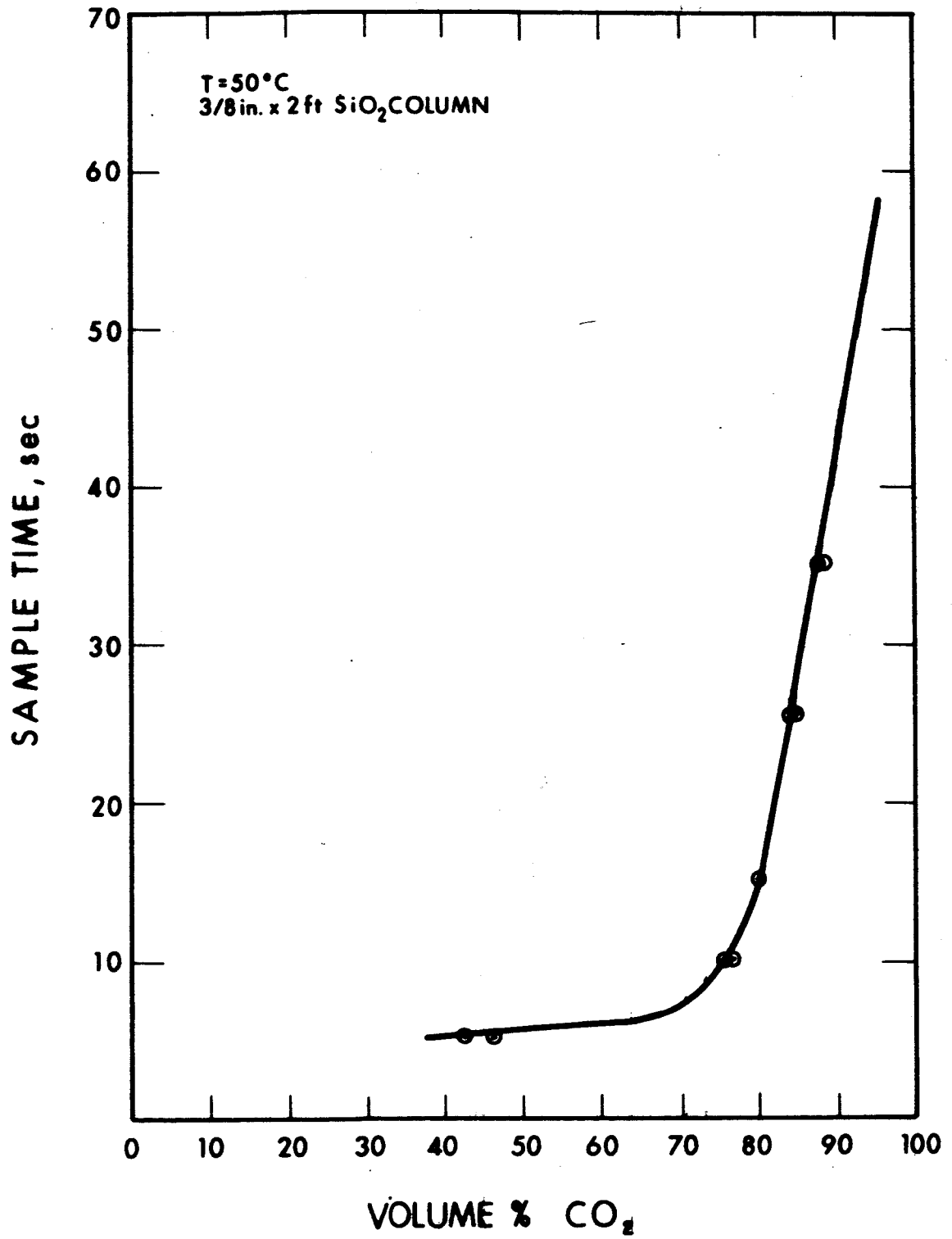


FIG. 34 SEPARATION PLOT (80% CO₂ - 20% Air, 15-second injection, 60-second cycle)

TABLE 12
SEPARATION DATA (Fig. 35)

GAS MIXTURE 80 o/o CO₂, 20 o/o Air
 SEPARATION COLUMN 3/4" x 24" S_iO₂ at 50°C
 ANALYSIS COLUMN 1/4" x 12" S_iO₂ at 25°C

INJECTION TIME (SEC.)	SAMPLE TIME (SEC.)	TOTAL CYCLE (SEC.)	AIR PEAK	CO ₂ PEAK	AIR: CO ₂ RATIO	VOL.o/o CO ₂
15	15	60	58.4	108.8	0.54	81.5
			49.6	96.0	0.52	82.0
25.5	25.5	60	22.4	71.2	0.31	88.5
			15.0	46.4	0.32	88.5
			14.2	52.8	0.27	90.0
			9.4	34.6	0.27	90.0
55.5	55.5	60	6.8	22.8	0.30	89.0
			3.3	10.0	0.33	88.0
			10	60	63.6	126.4
10	10	60	40.2	101.6	0.40	86.0
			5	60	84.8	102.4
3	3	60	72.4	84.8	0.85	73.5
			92.8	52.0	1.78	56.5
			71.2	38.0	1.87	55.0

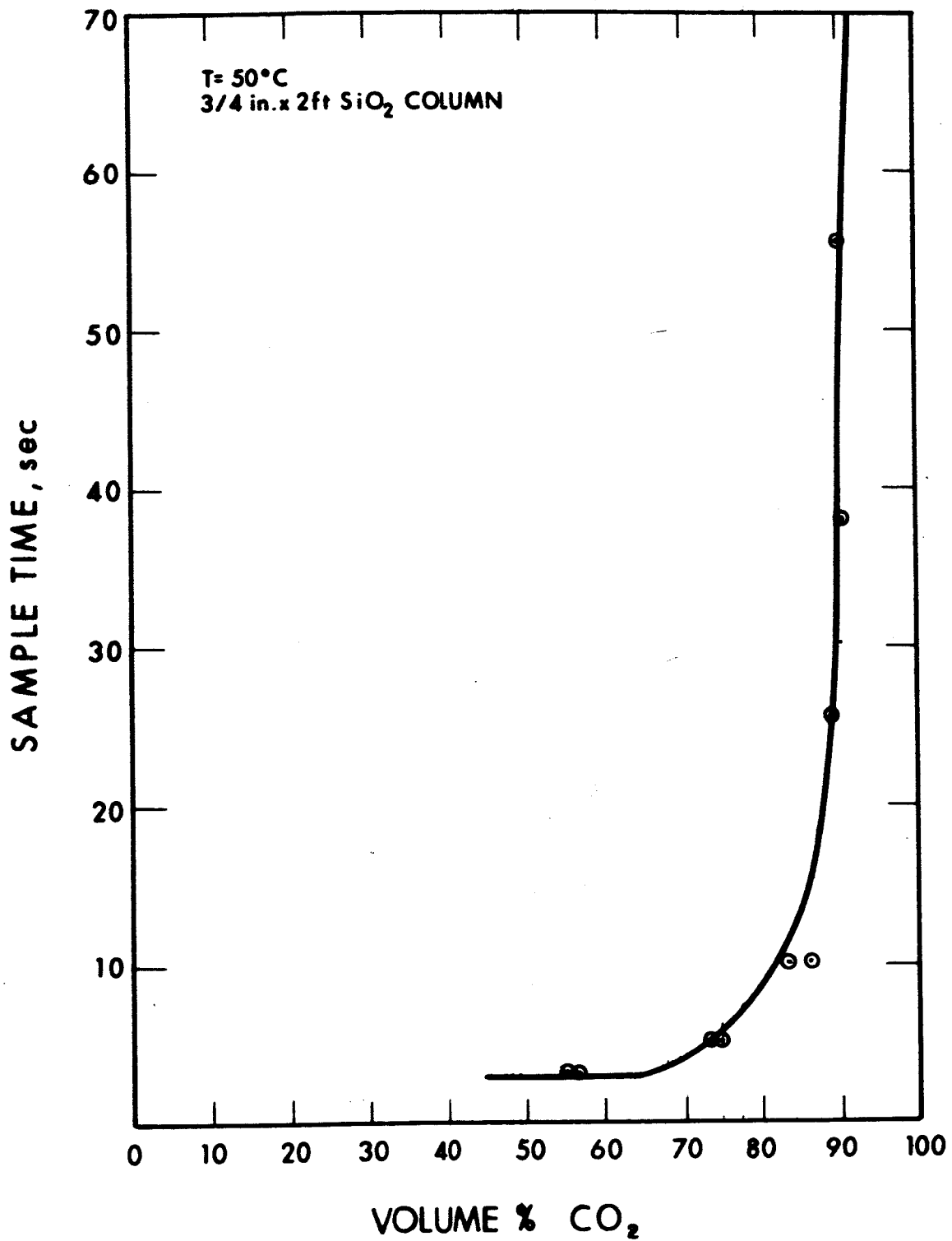


FIG. 35 SEPARATION PLOT (80% CO₂ - 20% Air, 15-second injection, 60-second cycle)

Analysis of the test results indicated one major factor, i.e., pumpdown between cycles was the controlling parameter. Any variable that tended to improve pumpdown time improved the separation characteristics. Thus 5-second injections were better than 15-second injections; 3-minute cycles were better than 1-minute cycles, etc.

As a result of this first series of tests, the column-packing material was changed from a fine silica-gel powder to a coarse-grain material. This noticeably improved pumpdown time.

5.2 Long Term Cycling Test

In order to evaluate long-term cycling effects, the gas separation apparatus was allowed to cycle continuously for 101 hours to determine the effects on the column-separation efficiency of extended operation. The conditions for this run were:

Gas mixture:	80 percent CO ₂ , 20 percent air
Separation column:	24 x 3/4-in. packed with 6-16 mesh silica gel
Column operating temperature:	60°C
Injection time:	5 sec
Total cycle time:	180 sec

At the beginning of the run, the system was run through a complete schedule of sampling times. Following the 100 cycles, the same schedule was followed and the results compared. The data are tabulated in Table 13 and plotted on Fig. 36.

It may be seen from comparison of the pre- and post-extended run data that column efficiency is negligibly affected by extended-time operation. The results also show that separation has been dramatically improved by more rapid pumpdown due to the coarse silica gel.

The separation curve in Fig. 36 is in volume percent of CO₂. To expedite weight calculations and analyses, the volume percent was converted to weight percent. The conversion curves are shown in

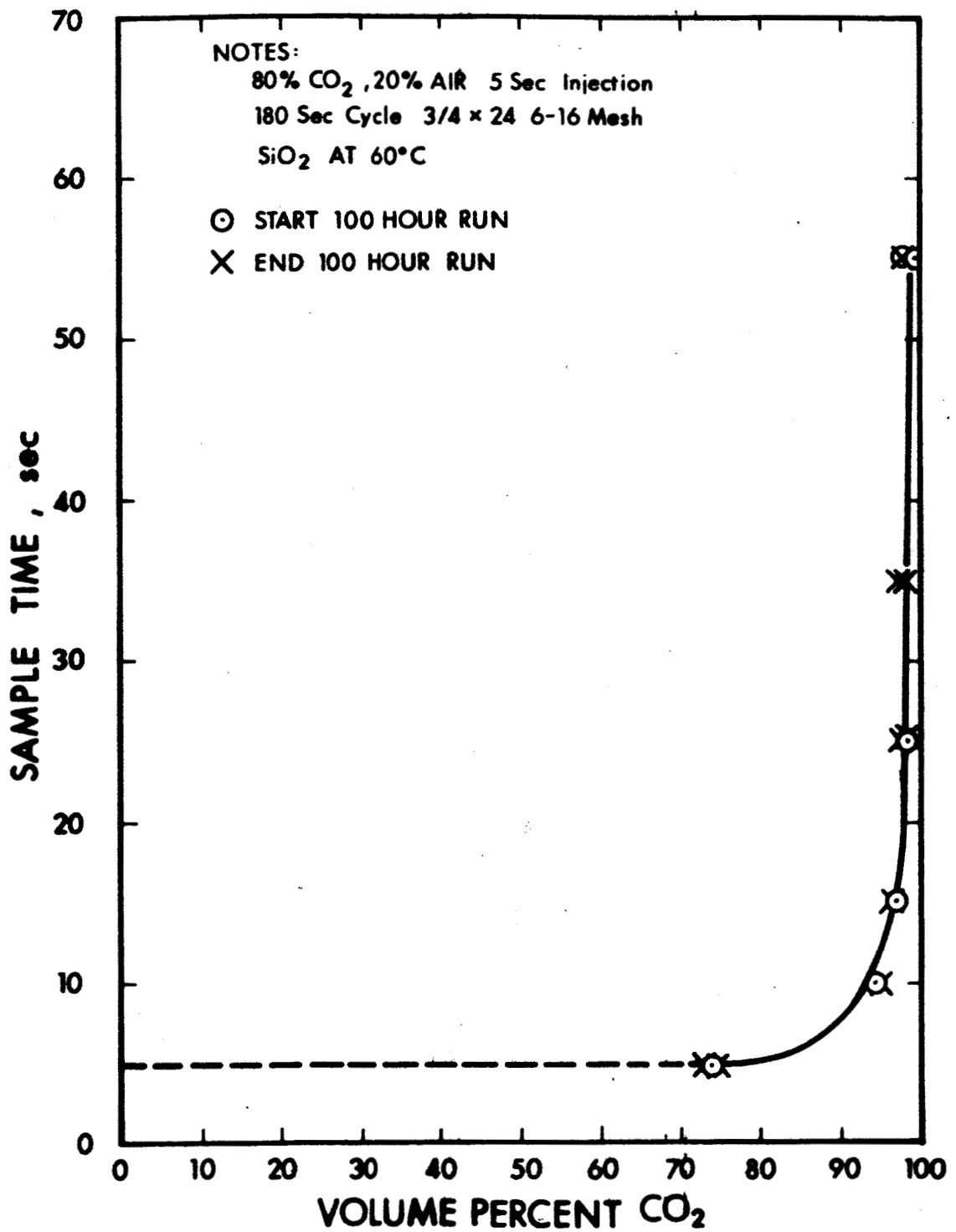


FIG. 36 SEPARATION PLOT (80% CO₂ - 20% Air, 5-second injection, 101-hour cycling)

TABLE 13
SEPARATION DATA

GAS MIXTURE 80% CO₂, 20% Air
 SEPARATION COLUMN 3/4" x 24" Coarse SiO₂ at 60°C
 ANALYSIS COLUMN 1/4" x 12" SiO₂ at 25°C
 START 101 Hr. Run

START OF RUN						
INJECTION TIME (SEC)	SAMPLE TIME (SEC)	TOTAL CYCLE (SEC)	AIR PEAK	CO ₂ PEAK	AIR: CO ₂ RATIO	VOL.% CO ₂
5	5	180	147.1	183.9	0.805	74
			147.0	180.4	0.816	73.8
	10	180	17.9	134.4	.133	94
	15	180	8.95	141.6	.0625	96.5
			7.46	105.7	.0706	96.1
	25	180	2.65	92.9	.0285	98
			2.35	72.8	.0323	98
	55	180	0.8	46.4	.0172	99
			0.7	29.2	.0239	98
AFTER 101 HOURS						
5	5	180	168	195	0.86	72.8
			153.6	192	0.80	74.0
	10	180	20.6	160	0.13	94.5
			18.2	139.2	0.13	94.5
	15	180	9.8	121.6	0.081	96.0
			8.1	99.9	0.082	96.0
	25	180	3.7	94.4	0.039	97.3
			3.35	73.6	0.046	97.0
	35	180	2.0	73.6	0.027	98.0
			1.9	56.8	0.034	97.5
	55	180	1.25	60.0	0.021	98.2
			0.80	30.6	0.026	98.0

Fig. 37 and 38. Data from Table 13 are converted by an appropriate factor to yield a separation plot for CO₂ in weight percent. The weight percent CO₂ versus sampling time curve is shown in Fig. 39.

5.3 Test Results After Mass Flowmeter Installation

Preliminary test results indicated the desirability of measuring the actual mass separation achieved by the PGC technique in order to provide quantitative data for engineering calculations and estimations of separation efficiency. A mass flowmeter was approved for purchase and after a 2.5 month delivery period, installed in the test apparatus. (The test program was halted during this period.) Methods for defining separation efficiency were also initiated at this time.

The definition of efficiency of separation for chemical systems is quite arbitrary. In general, the term is taken to mean the degree to which a desirable quantity can be obtained from a system as compared to that for an ideal system. When trying to compare two different systems, the definition falls apart. This is especially true when trying to compare batch-separation systems with continuous-separation systems. The only practical comparison method is to totalize the outputs of the two systems being compared and determining the degree to which each approaches the desired quantity of acceptable separation.

Three approaches to determining efficiency have been undertaken with varying degrees of success. These are described in the following discussion using an air/CO₂ binary gas for discussion purposes.

Method 1

An efficiency of separation can be defined based upon the quantity of CO₂ in the effluent from the column. Under this definition the efficiency is equal to 100 percent when the effluent contains 0 percent CO₂.

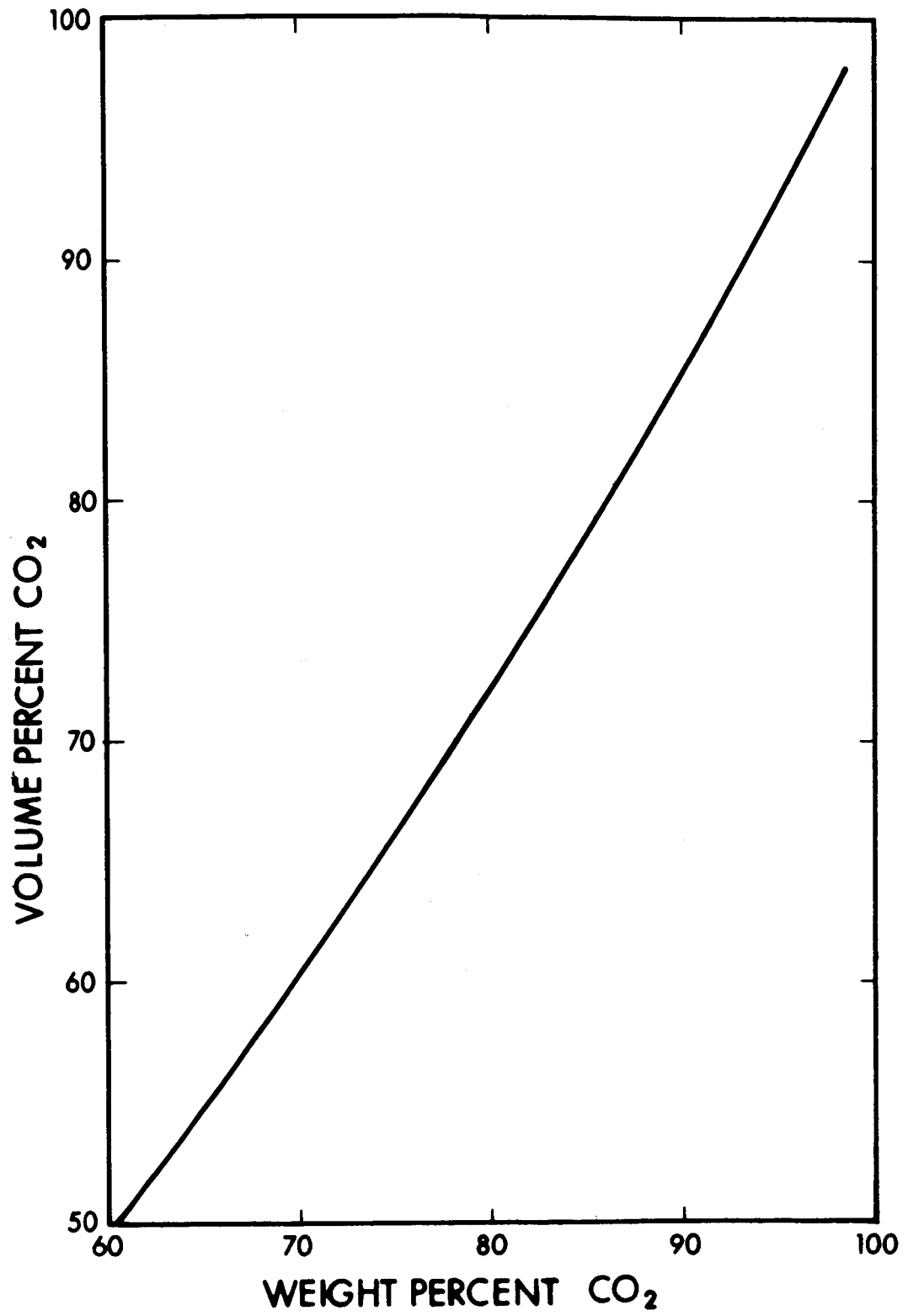


FIG. 37 CONVERSION CURVE, VOLUME PERCENT CO₂ TO WEIGHT PERCENT CO₂

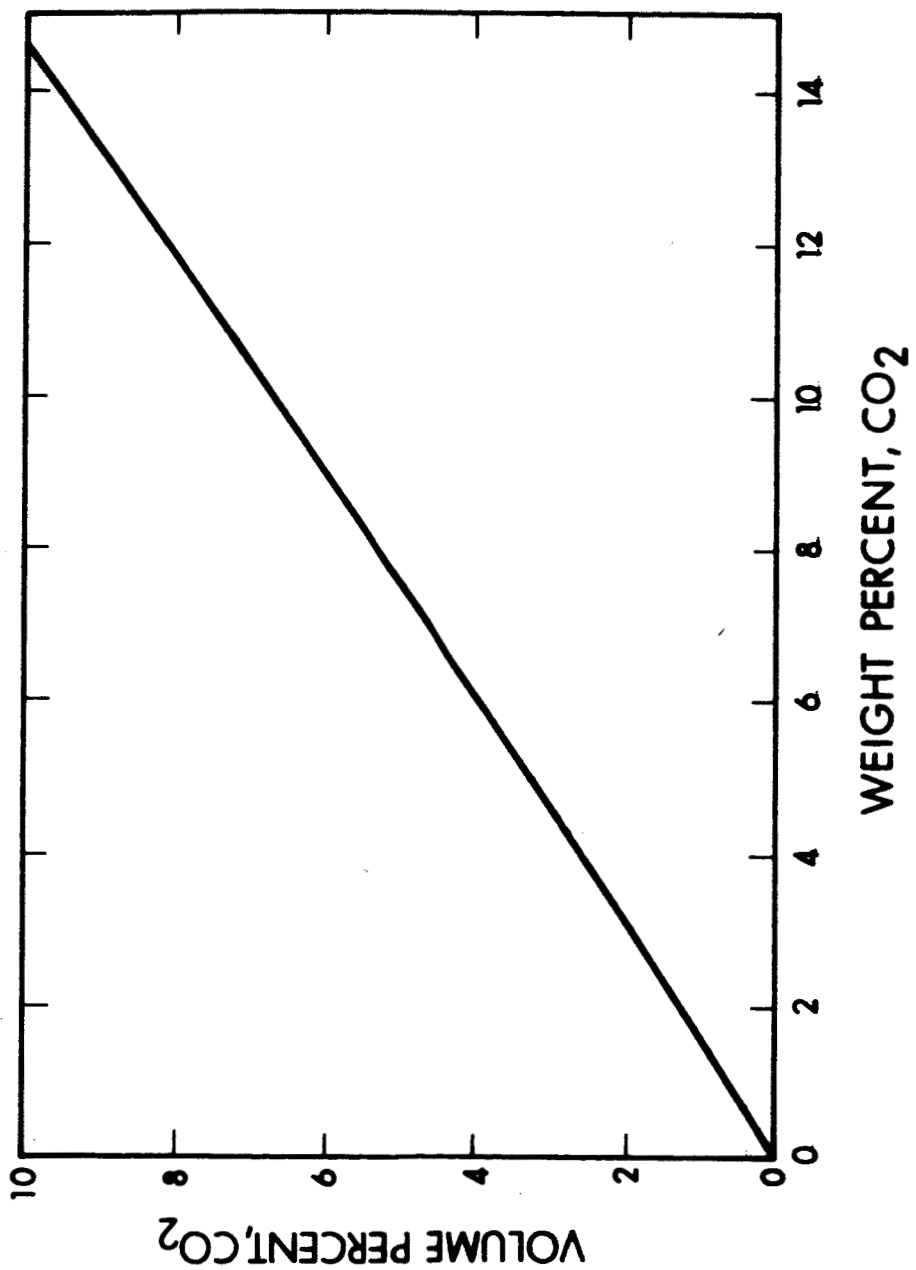


FIG. 38 VOLUME-WEIGHT CONVERSION FOR CO₂

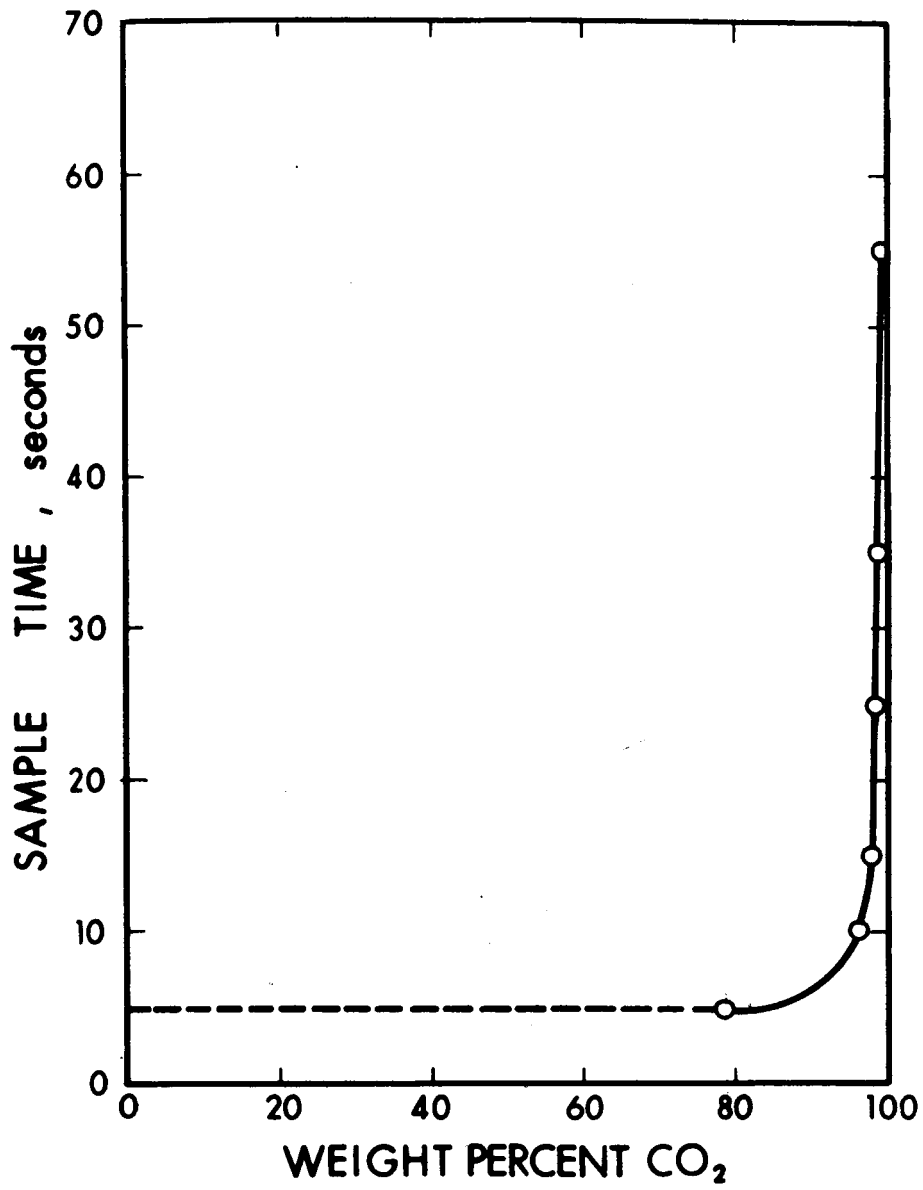


FIG. 39 SEPARATION PLOT (80% CO₂ - 20% Air, 5-second injection, 101²-hour pumpdown)

$$\text{Efficiency} = \left(1 - M_1/M_2\right)$$

where

M_1 = weight of CO_2 in effluent stream

M_2 = weight of CO_2 in input stream

Figure 40 shows such a curve for a 99 percent air, 1 percent CO_2 gas run on a 1 foot long, 3/4-inch-diameter silica gel column. This method neglects the factor that the efficiency value does not have any relationship to the total quantity of gas being processed. Thus, if one were to choose arbitrarily a process time of 6 seconds for this column, the air returned to the cabin would contain 0 percent CO_2 but would only be 30 percent of the initial weight of air admitted to the column. We would, in other words, be dumping or recycling 70 percent of the air, an unsatisfactory situation. It can be seen, therefore, that the efficiency term must somehow be constrained by the mass of the air as well as the CO_2 .

Method 2

This method has been employed for the analysis of the PGC data. The column efficiency is defined as follows:

$$\text{Column Efficiency (\%)} = \frac{M_1}{M_2} \cdot \left(1 - \frac{M_3}{M_4}\right) \cdot 100$$

where

M_1 = mass of CO_2 in bypass effluent

M_2 = mass of CO_2 in input pulse

M_3 = mass of air in bypass effluent

M_4 = mass of air in input pulse

(The term "bypass" is used to indicate the gas has not returned immediately to the cabin.)

Thus both gases can be related to the efficiency value.

Figure 41 shows such a determination for the same 1-foot SiO_2 column. If all the CO_2 is in the bypass effluent, the M_1/M_2 term = 1.

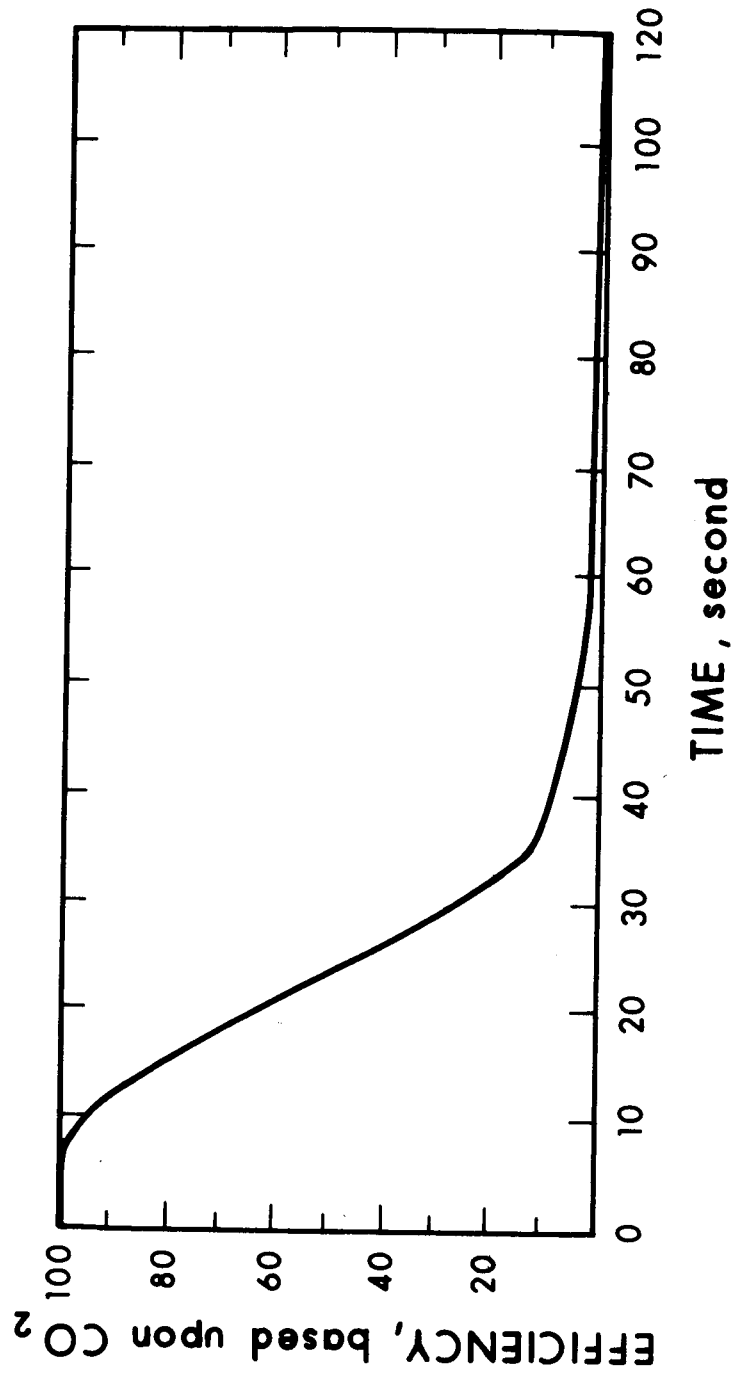


FIG. 40 EFFICIENCY BASED UPON CO₂ ALONE

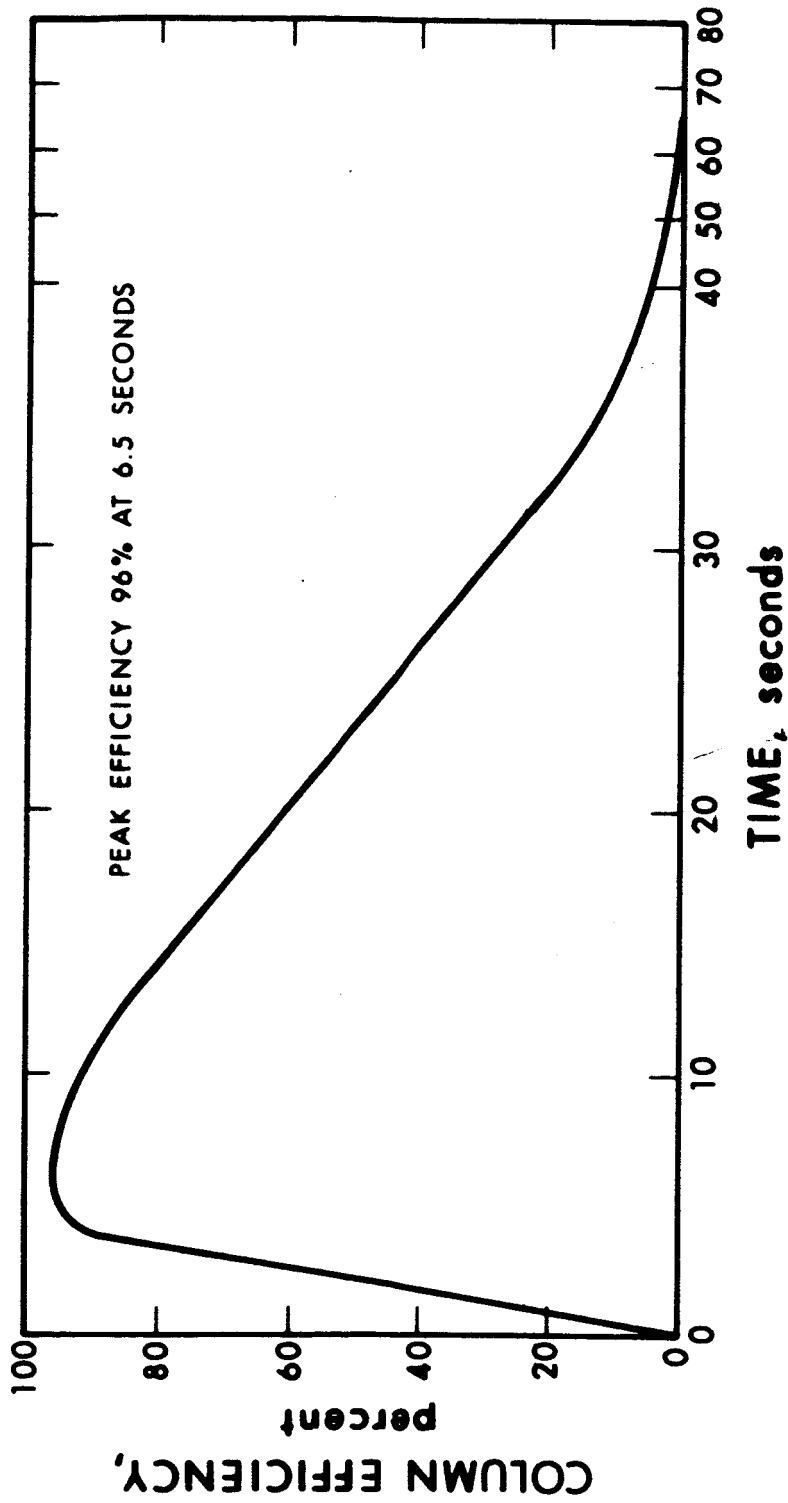


FIG. 41 COLUMN EFFICIENCY BASED UPON BOTH AIR AND CO₂

Likewise if all the air is removed before the effluent is bypassed, the $(1 - \frac{M_3}{M_4})$ term is 1, and a 100 percent efficiency would result. If the value of M_1 were low, i.e., very little CO_2 in the bypass effluent, efficiency would be low. Similarly, if the M_3 terms were high, i.e., a lot of air in the bypass effluent, the efficiency would be low. Thus, 100 percent efficiency represents complete gas separation and 0 percent efficiency represents no separation. This expression is ideally suitable for any binary-gas mixture. Note, however, the peak efficiency requires the highest multiple of both gas quantities and this requirement itself can impose a penalty, i.e., the efficiency is lowered by the quantity of CO_2 , even though the quantity of CO_2 in the bulk is acceptable for recirculation. A more practical method would be to consider the acceptable level of CO_2 in computing the efficiency.

Method 3

This method is based on the weight percent of air in the effluent multiplied by an importance factor. For the 99 percent air, 1 percent separation, it is assumed that a 0.5 percent CO_2 effluent air stream is wholly acceptable and the acceptability of higher concentration is linearly derated as shown on Fig. 42. The importance factor is multiplied against the weight percent of the air. The resultant efficiency curve is shown in Fig. 43. Note that from this curve, the switch can be extended from 6 seconds to 20 seconds and still be above a "defined" 95 percent efficiency.

However, inasmuch as this is a general binary gas feasibility study, Method 2, the ideal case has been used for calculation purposes since importance factors for other than 99 percent air to 1 percent CO_2 mixtures have not been determined.

5.3.1 Initial Efficiency Calculation

The first test involving the use of efficiency calculation was run with the 80 percent CO_2 to 20 percent air mixture discussed in Subsection 4.5.

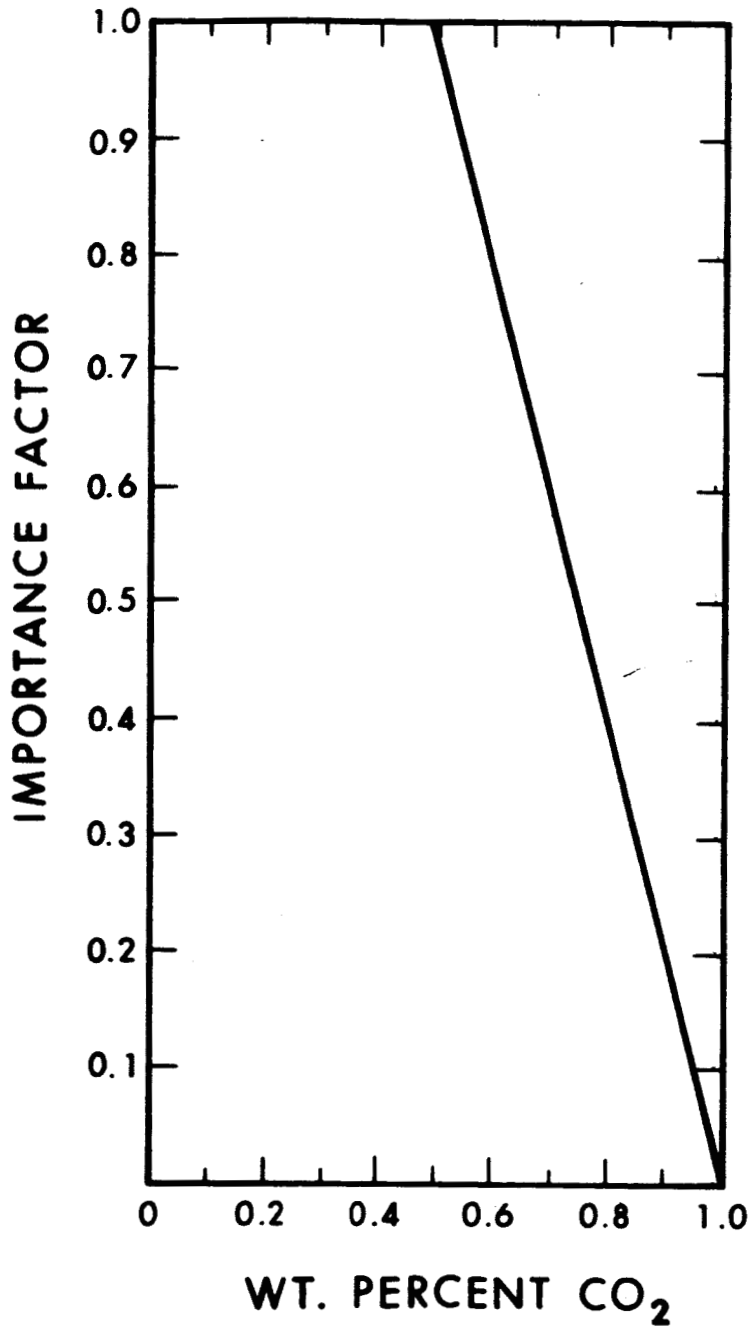


FIG. 42 IMPORTANCE FACTOR CURVE

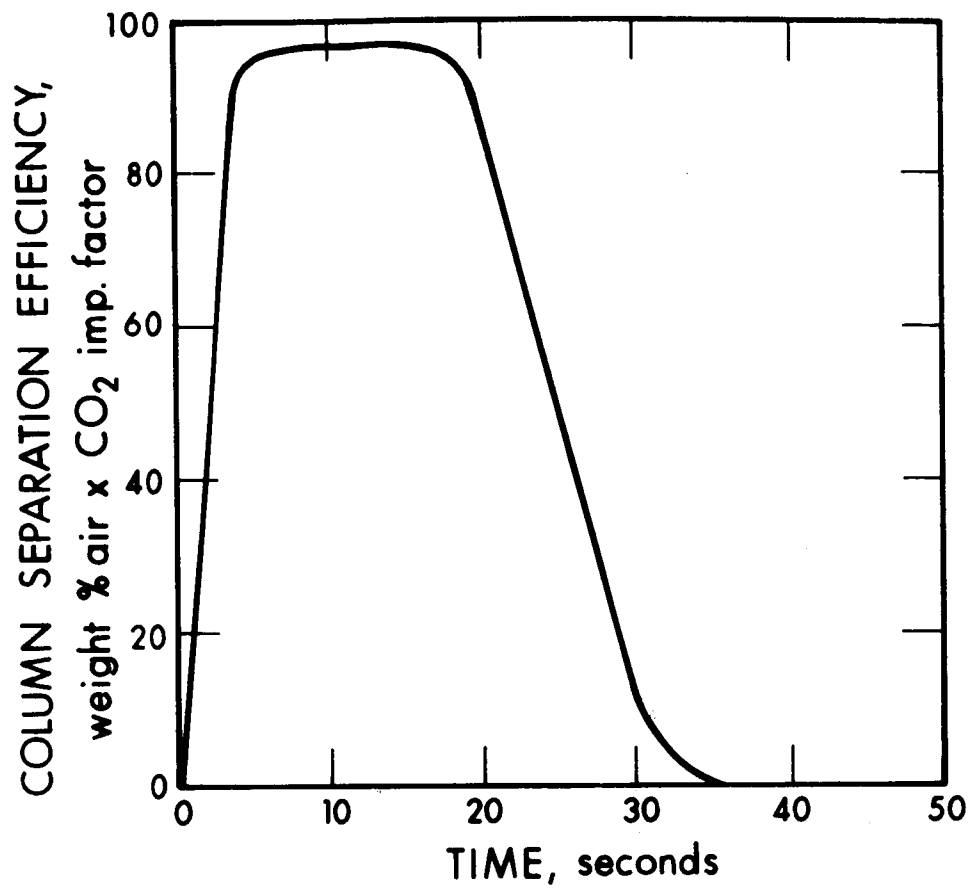


FIG. 43 EFFICIENCY WITH IMPORTANCE FACTOR

The terms for the efficiency equation for given elapsed times are tabulated in Table 14. The plot of column efficiency with elapsed time is shown in Fig. 44. The curve takes on a lopsided bell shape with a peak column efficiency of 88 percent at elapsed time of 8 seconds.

5.3.2 Additional Experimental Results

Tests were next conducted on eight different columns. These column/gas mixture combinations were as follows:

<u>Column</u>	<u>Gas Mixture</u>
3/4 x 12-in. silica gel	80 percent CO ₂ , 20 percent air
3/4 x 6-in. silica gel	80 percent CO ₂ , 20 percent air
3/4 x 12-in. silica gel	99 percent air, 1 percent CO ₂
3/4 x 6-in. silica gel	99 percent air, 1 percent CO ₂
3/4 x 6-in. monoethanolamine	99 percent air, 1 percent CO ₂
3/4 x 24-in. molecular sieve	80 percent CH ₄ to 20 percent H ₂
3/4 x 12-in. molecular sieve	80 percent CO ₂ to 20 percent air

(In all above cases a 5-second injection time, a 5 psig injection pressure, and total cycle time of 180 seconds was employed.)

3/4 x 12-in. molecular sieve 99 percent air, 1 percent CO₂

(A 15 second injection time, a 7.5 psig injection pressure and a total cycle time of 180 seconds was employed in this latter case.)

The experimental results of these columns are discussed in detail in the following sections.

5.3.2.1 3/4 x 12-in. Silica Gel - 80 Percent CO₂, 20 Percent Air

This experiment was intended to reduce the pumpdown time by utilizing a shorter column. It was noticed that the pumpdown time was (to < 1 mm Hg) reduced from 16 minutes for a

TABLE 14

TERMS IN COLUMN EFFICIENCY EQUATION AS AREAS UNDER THE CURVE IN FIGURE 44.

Time (Sec.)	M ₁ (Area Units)	M ₂ (Area Units)	M ₃ (Area Units)	M ₄ (Area Units)	$\frac{M_1}{M_2}$	$\frac{M_3}{M_4}$	$1 - \frac{M_3}{M_4}$	% Eff. $= \frac{M_1}{M_2} \left(1 - \frac{M_3}{M_4}\right) 100$
0	0	55.2	0	5.6	0	0	0	0
1	55.2	"	4.5	"	1	.804	.196	19.6
2	55.2	"	3.5	"	1	.625	.375	37.5
3	55.2	"	2.7	"	1	.482	.518	51.8
4	55.2	"	2.1	"	1	.375	.625	62.5
5	55.2	"	1.6	"	1	.286	.714	71.4
6	54.1	"	1.3	"	.952	.233	.767	73.1
7	52.6	"	0.5	"	.953	.090	.910	86.4
8	51.2	"	0.25	"	.927	.045	.955	88.5
9	49.9	"	0.17	"	.887	.031	.969	86.0
10	48.6	"	0.10	"	.864	.017	.983	84.7
11	47.3	"	0.06	"	.842	.011	.989	83.3
12	46.0	"	0.03	"	.834	.0054	.995	83.0
13	44.7	"	0.02	"	.810	.0037	.996	80.5
14	43.4	"	0.015	"	.785	.0027	.997	78.4
15	42.1	"	0.010	"	.763	.0018	.998	76.2
16	40.9	"	0.005	"	.742	.001	.999	74.2
20	35.2	"	0	"	.636	0	1	63.6
40	16.4	"	0	"	.297	0	1	29.7
80	7.2	"	0	"	.131	0	1	13.1
180	0	"	0	"	0	0	1	0

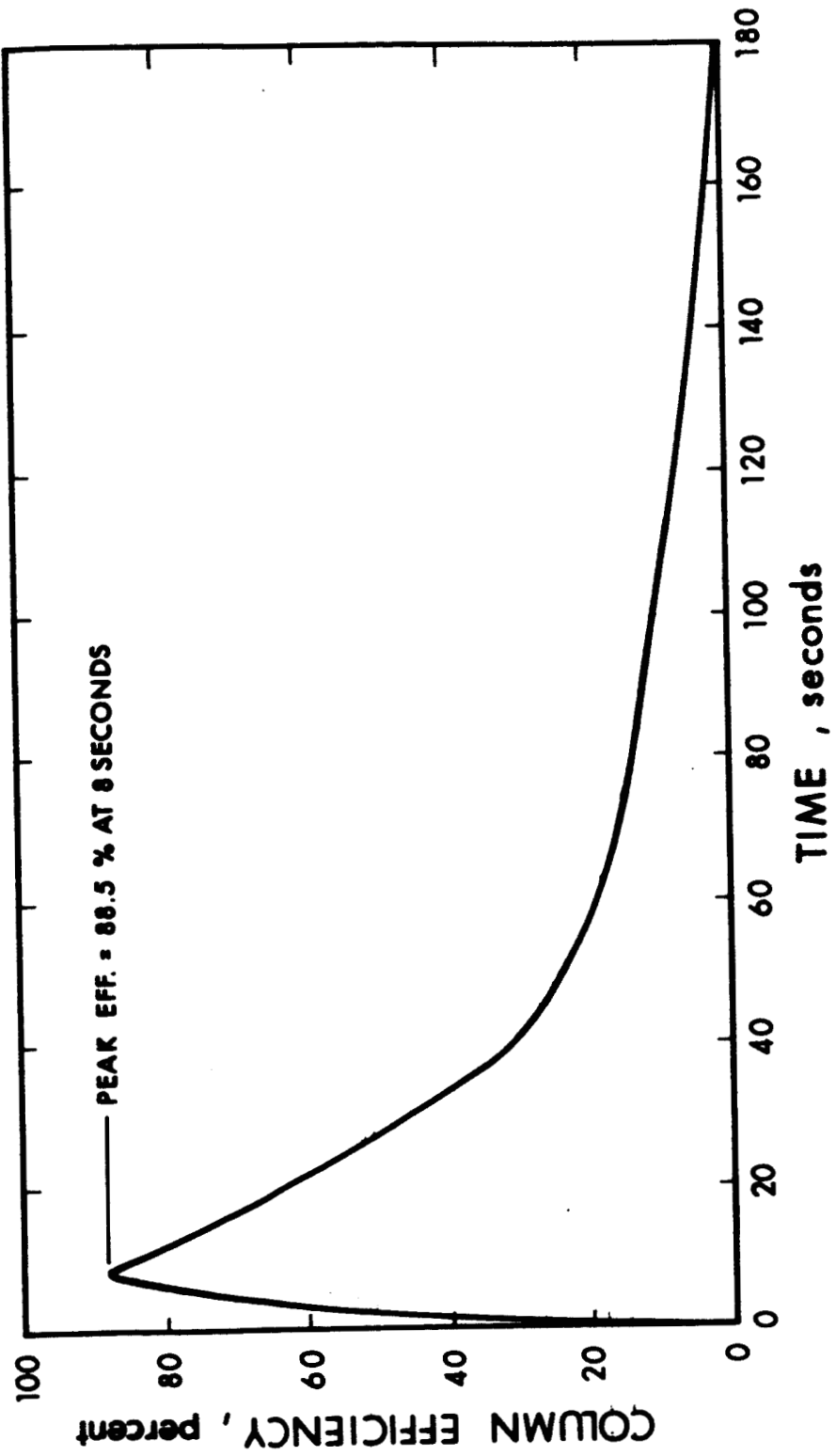


FIG. 44 PLOT OF COLUMN EFFICIENCY WITH TIME

24-in. column to 4.5 minutes for a 12-in. column. A cursory analysis of the separation curve and mass flow transducer output curve for a 5 second injection of 80 percent CO₂ to 20 percent air at 5 psig very much resembles that for the 24-in. column of Subsection 5.3.1. Thus, no detailed analysis was made on the data gathered from this column, since the results would be identical to those obtained on the 24-in. column presented in Subsection 5.3.1.

5.3.2.2 3/4 x 6-in. Silica Gel - 80 Percent CO₂,
20 Percent Air

This experiment was a further attempt to reduce the pumpdown time by using an even shorter column. It was noticed that the pumpdown time still required about 4 minutes. With this observation, it was suspected that some of the pumping energy was expended by the impedance in the small orifices and lines in the gas-sampling portion of the test apparatus. This apparatus was then modified as described in Subsection 4.3. After modification, the 3/4 x 6-in. column could be pumped down to 1 mm Hg of pressure within a minute.

The separation data obtained with this column are presented in Table 15, and the curve is shown in Fig. 45. It was noted that the CO₂ concentration at a 5-second sample time for the 6-in. column was much higher than for the 24 or 12-in. column. It was suspected that the column was flooded, and very little separation occurred during the injection time period. However, this could not initially be confirmed since no sampling was done at a time of less than 5 seconds, and also since the separation curve after 5 seconds was very similar to the separation obtained from the 24 and 12-in. columns.

Results of the efficiency analysis are shown in Figs. 46, 47, 48, and Table 16. The peak column efficiency was found to be 76.8 percent at 5 seconds. A mass balance for CO₂ and air was made to check the accuracy of the analysis. The calculations

TABLE 15

SEPARATION DATA FOR 80 PERCENT CO₂, 20 PERCENT AIR
WITH 6 x 3/4-IN. DIAMETER SILICA GEL COLUMN

GAS MIXTURE	80% CO ₂ , 20% Air
SEPARATION COLUMN	6" x 3/4" Dia. 8-16 Silica Gel at R.T.
ANALYSIS COLUMN	1/4" x 12" Silica Gel at R.T.

Injection Time (Sec)	Sample Time (Sec)	Total Cycle (Sec)	Air Peak	CO ₂ Peak	Air: CO ₂ Ratio	Vol. % CO ₂	Wt % CO ₂
5.0	5.0	120	121	174	0.694	77.0	82.5
			63	94.4	0.667		
	10	120	2.27	24	0.095	95.8	97.0
			5.16	56.4	0.091		
	15	120	1.52	18.5	0.082	96.2	97.5
			0.8	9.90	0.089		
	20	120	.040	2.08	0.052	97.0	98.0
			.063	3.02	0.048		

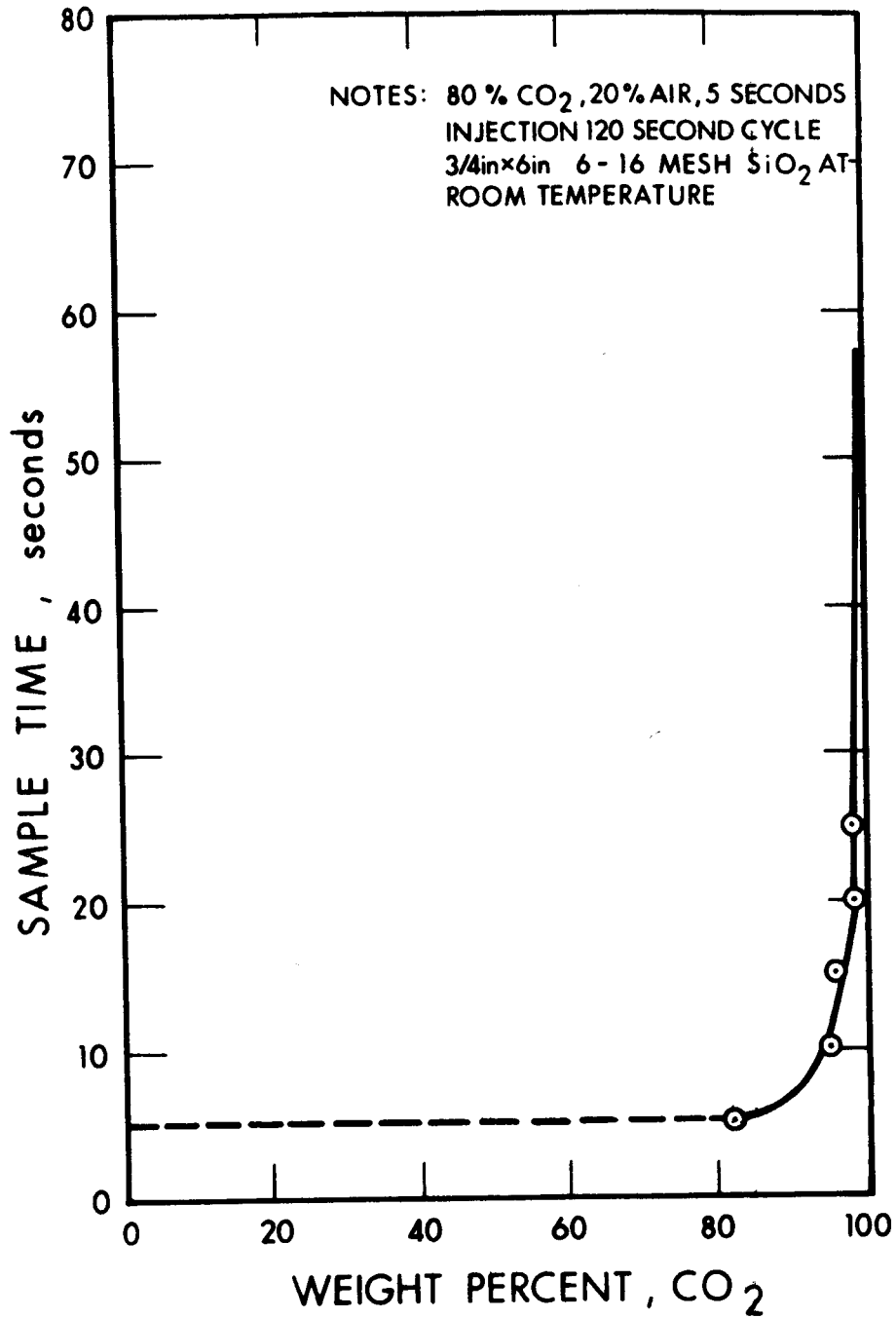


FIG. 45 SEPARATION PLOT (80% CO₂ - 20% Air,
5-second injection)

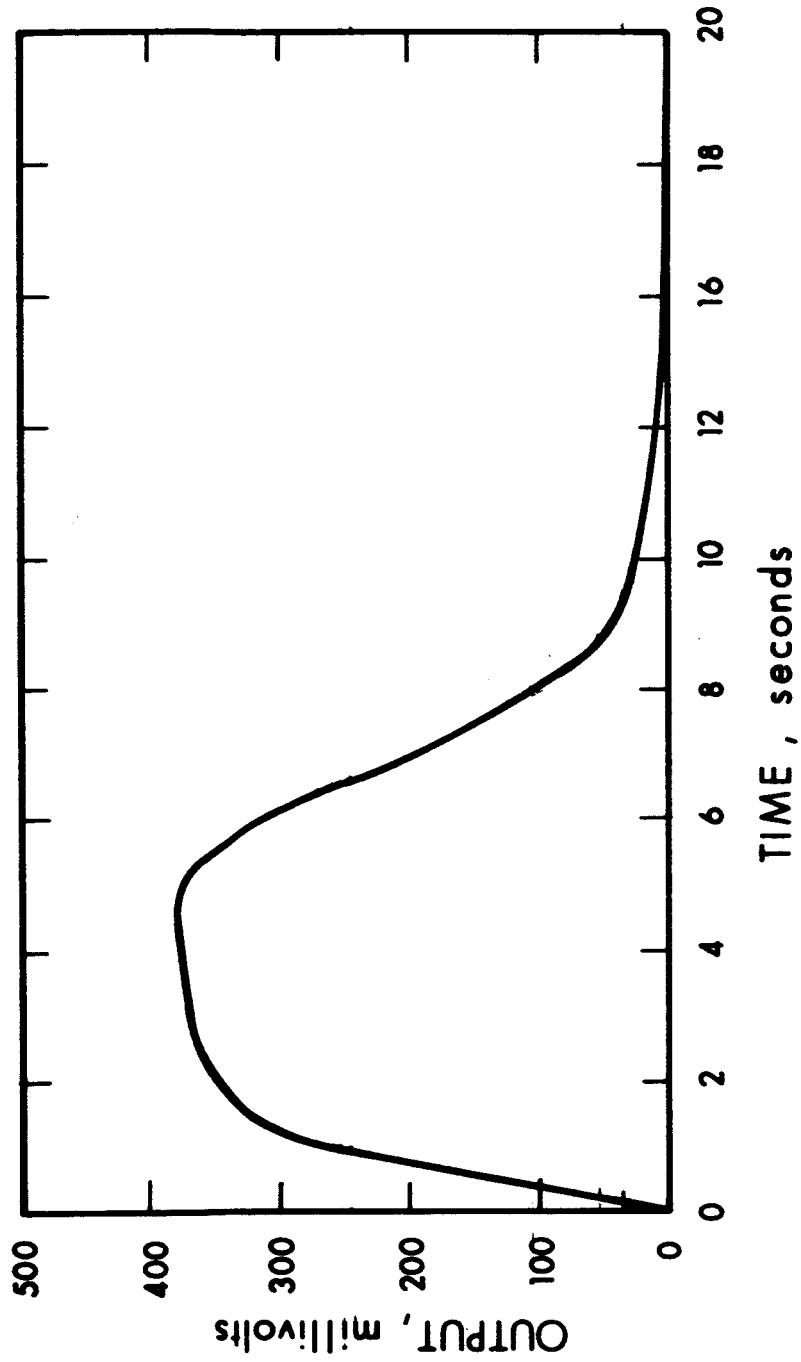


FIG. 46 TRANSDUCER OUTPUT TRACE FOR 5-SECOND INJECTION OF 80% CO₂,
20% AIR, 3/4 INCH X 6 INCH SILICA GEL COLUMN

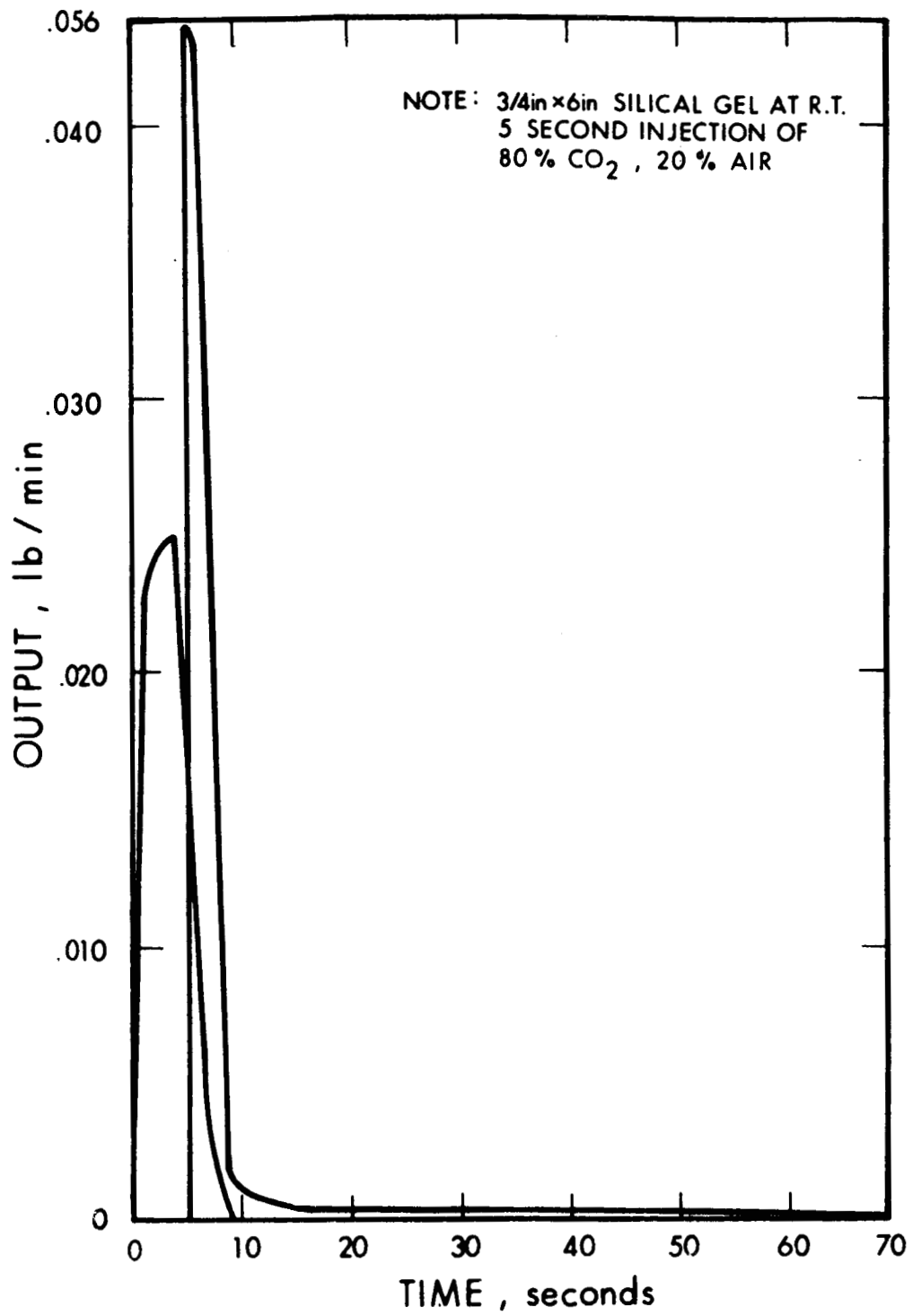


FIG. 47 OUTPUT TRACES OF AIR AND CO₂ WITH TIME

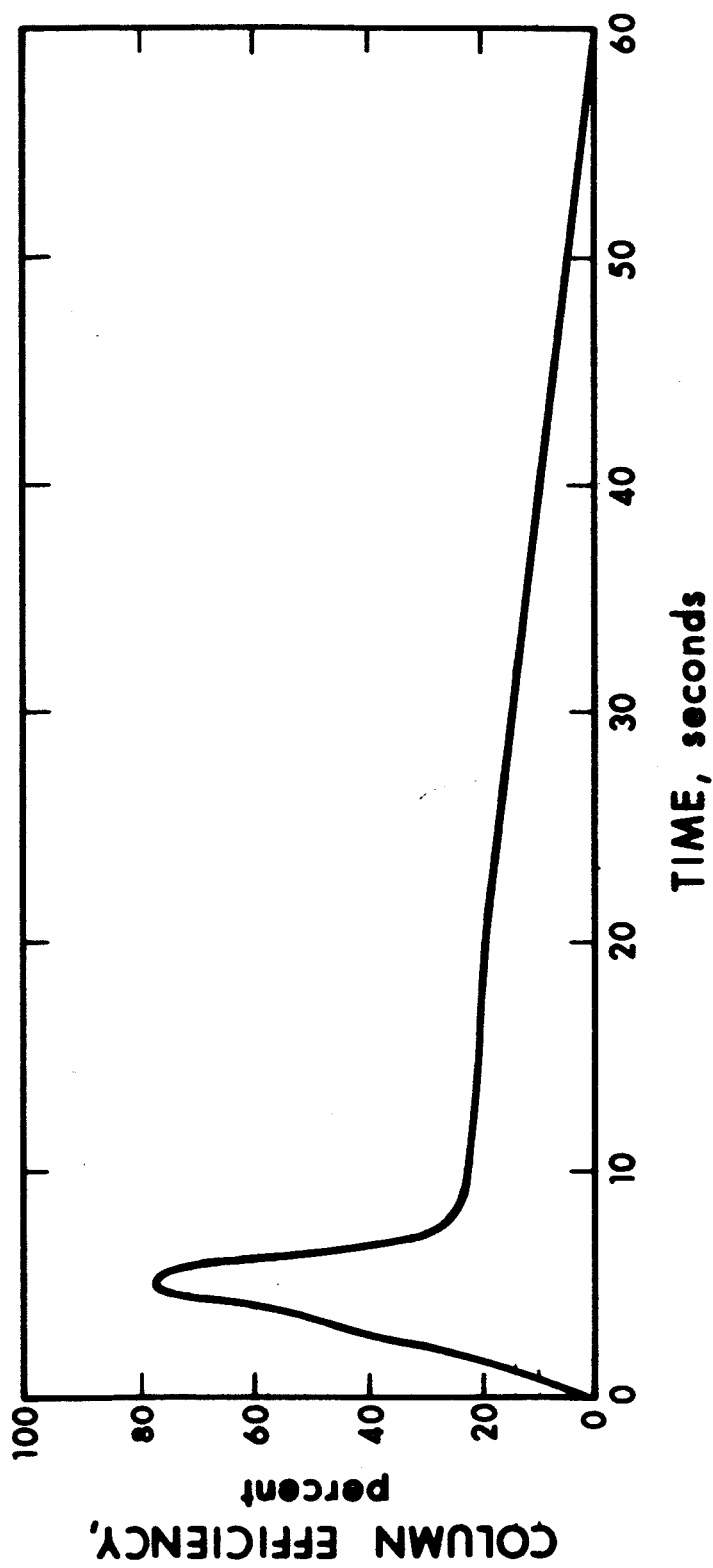


FIG. 48 COLUMN EFFICIENCY - 3/4 INCH X 6 INCH SILICA GEL AT ROOM TEMPERATURE,
5-SECOND INJECTION, 5 PSIG, 80% CO₂, 20% AIR

TABLE 16

TERMS IN COLUMN EFFICIENCY EQUATION AS AREAS UNDER THE CURVE IN FIGURE 48

Time (Sec)	M_1 (Area Units)	M_1 (Area Units)	M_3 (Area Units)	M_4 (Area Units)	$\frac{M_1}{M_2}$	$\frac{M_3}{M_4}$	$1 - \frac{M_3}{M_4}$	$\left[\frac{M_1}{M_2} \left(1 - \frac{M_3}{M_4} \right) \right]$
0	0	17.4	0	13.7	0	0	0	
1	174	"	12.1	"	1	.884	.116	11.6
2	174	"	9.9	"	1	.724	.276	27.6
3	174	"	7.5	"	1	.548	.452	45.2
4	174	"	5.02	"	1	.367	.633	63.3
5	174	"	3.18	"	1	.232	.768	76.8
6	129	"	2.61	"	.742	.191	.809	60.0
7	6.8	"	2.30	"	.391	.167	.833	32.6
8	5.17	"	2.18	"	.297	.159	.841	25.0
9	4.96	"	2.10	"	.285	.153	.847	24.1
10	4.84	"	2.04	"	.278	.149	.851	23.7
11	4.74	"	1.99	"	.272	.145	.855	23.1
12	4.64	"	1.94	"	.264	.141	.859	22.6
13	4.54	"	1.85	"	.261	.135	.865	22.3
14	4.44	"	1.80	"	.255	.131	.869	22.0
15	4.34	"	1.75	"	.249	.128	.872	21.6
16	4.24	"	1.70	"	.243	.124	.876	21.3
17	4.14	"	1.65	"	.238	.120	.880	21.0
18	4.04	"	1.60	"	.232	.117	.883	20.5
19	3.94	"	1.55	"	.226	.113	.887	20.0
20	3.84	"	1.50	"	.221	.109	.891	19.7
40	1.84	"	0.50	"	.106	.027	.973	10.3
60	0	17.4	0	13.7	0	0	1	0

showed that the gas mixture in the analysis was 66 percent CO₂ and 34 percent air. The actual values were 80 percent CO₂ and 20 percent air. This confirmed the suspicion that the 6-in. column was initially flooded.

5.3.2.3 3/4 x 12-in. Silica Gel, 99 Percent Air -
1 Percent CO₂

This experiment was performed in accordance with a technical directive expressing the desirability of testing the PGC technique using a 99 percent air, 1 percent CO₂ mixture in place of the 95 percent air, 5 percent CO₂ mixture originally called for. The separation plot for the 99 percent air, 1 percent CO₂ is distinctively different from those obtained with a mixture of higher CO₂ content. That is, the CO₂ concentrations are at a very low range (0.4 - 8 percent).

Results of the detailed analyses on the PGC data gathered on this column-gas mixture are shown in Figs. 49, 50, 51, 52 and Tables 17 and 18. The plot of column efficiency with lapsed time curve has a relatively broad peak, and the maximum column efficiency is 97 percent at 6.5 seconds. A mass balance check was performed to check the accuracy of the results. The calculations showed that the gas mixture in the analysis was 99.2 percent air and 0.8 percent CO₂. The actual mass spectro-analysis of the gas mixture was 99.03 percent air and 0.97 percent CO₂.

5.3.2.4 3/4 x 6-in. Silica Gel - 99 Percent Air,
1 Percent CO₂

A cursory examination of the separation data and transducer output for mass flow indicated flooding had occurred. A detailed analysis was therefore not performed on the PGC data gathered with this column.

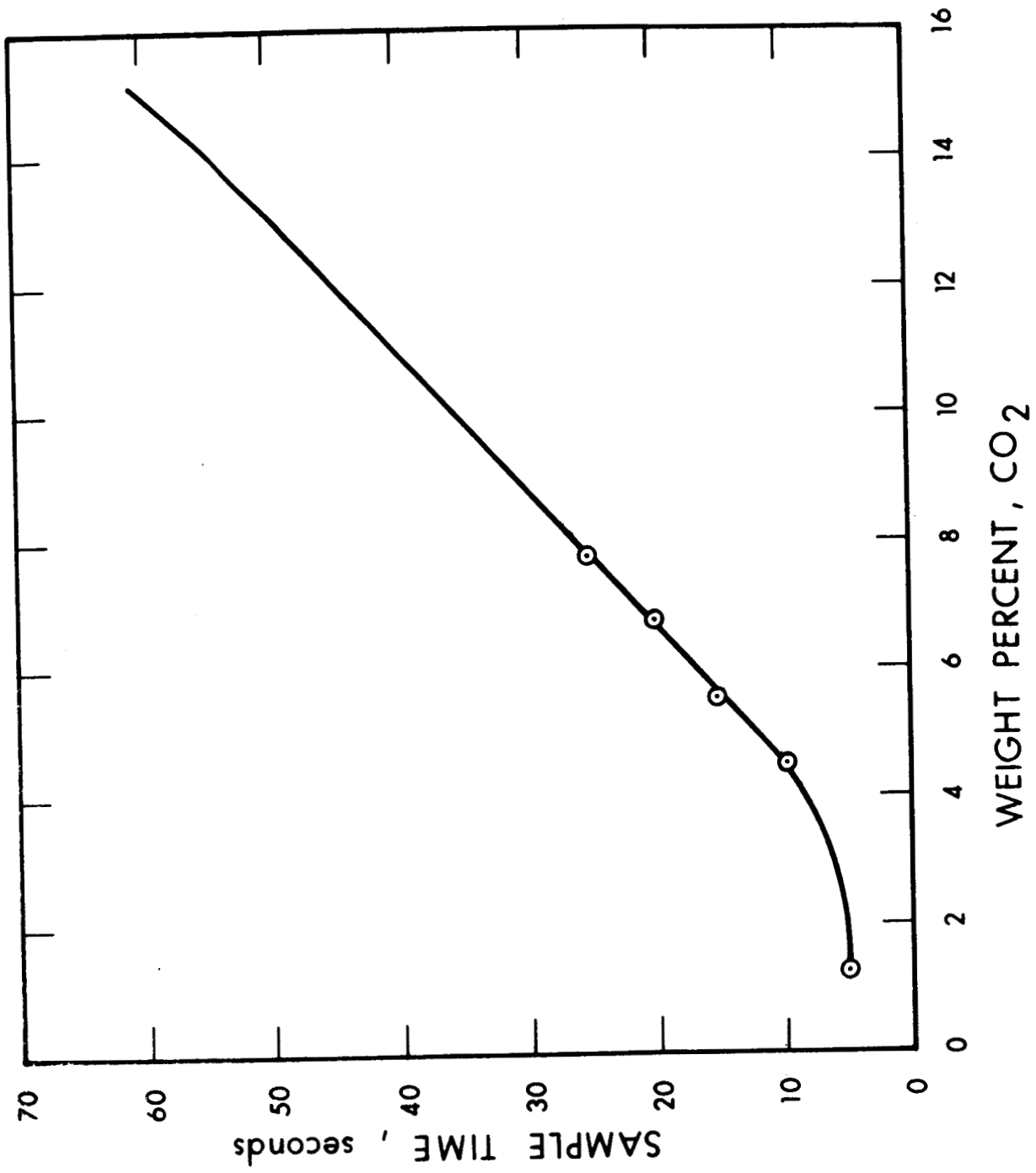


FIG. 49 SEPARATION PLOT (99% Air, 1% CO₂, 5-second injection, 120-second total cycle)

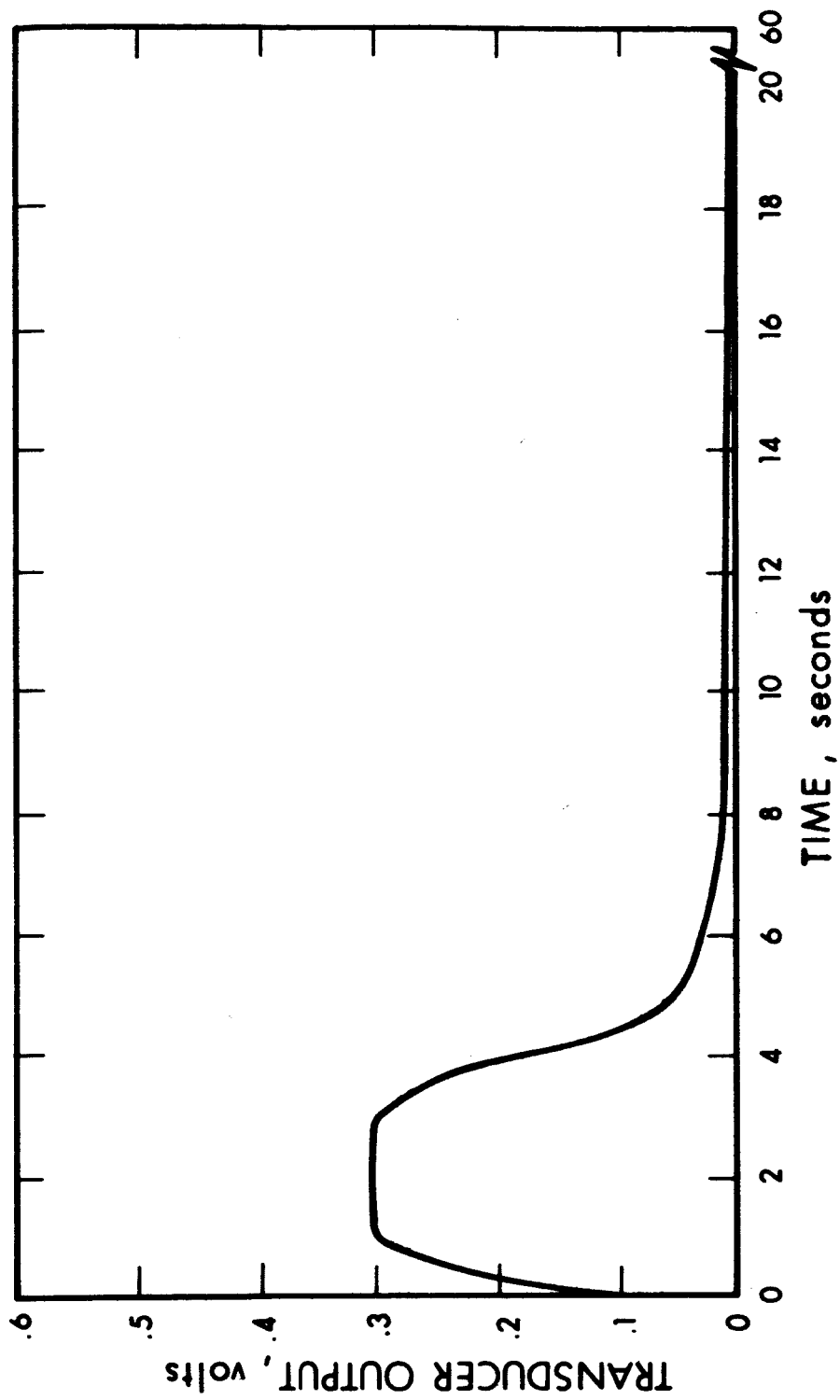


FIG. 50 TRANSDUCER OUTPUT TRACE FOR 5-SECOND INJECTION OF 99% AIR, 1% CO₂

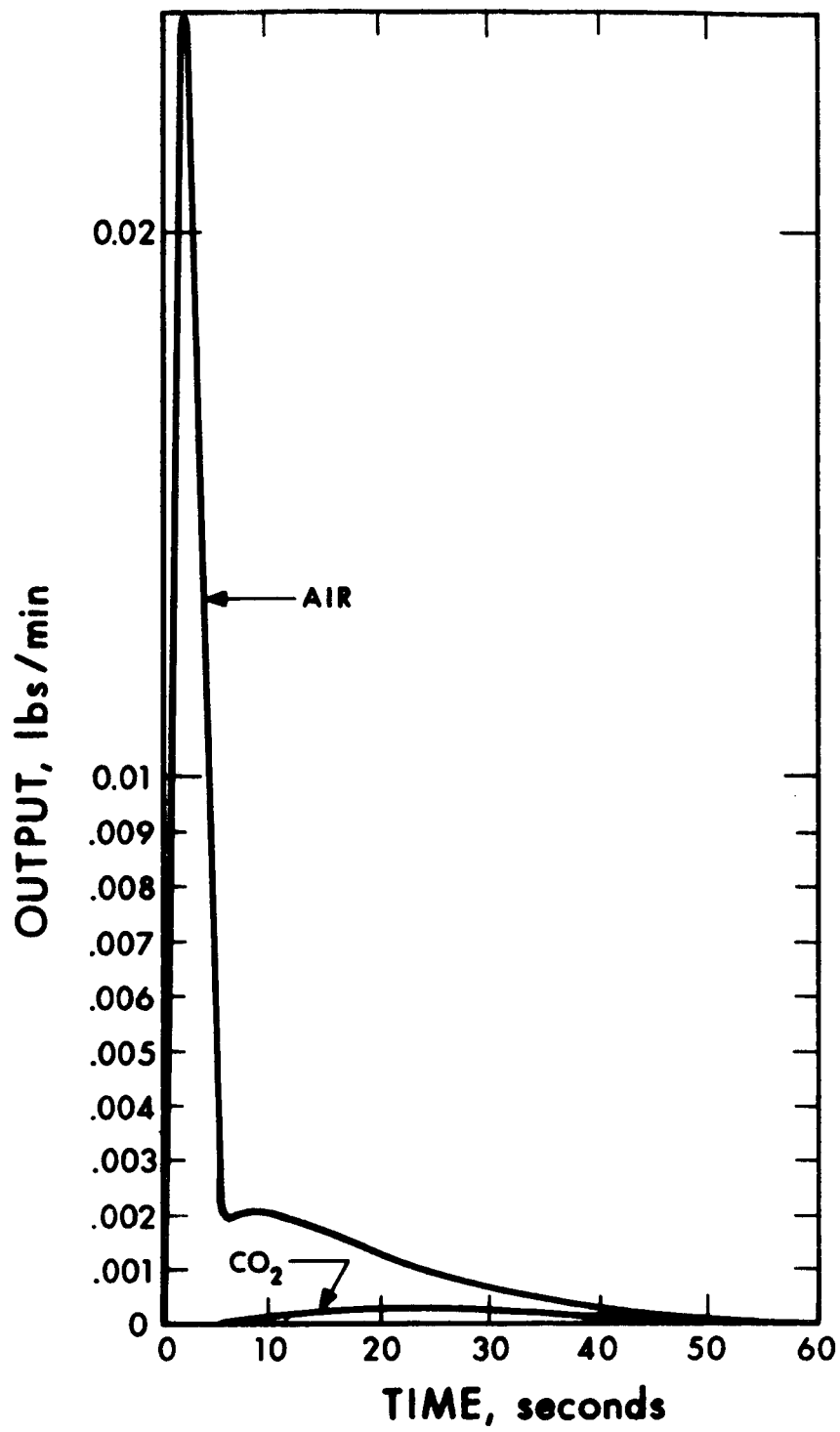


FIG. 51 OUTPUT TRACE OF AIR AND CO₂ WITH TIME

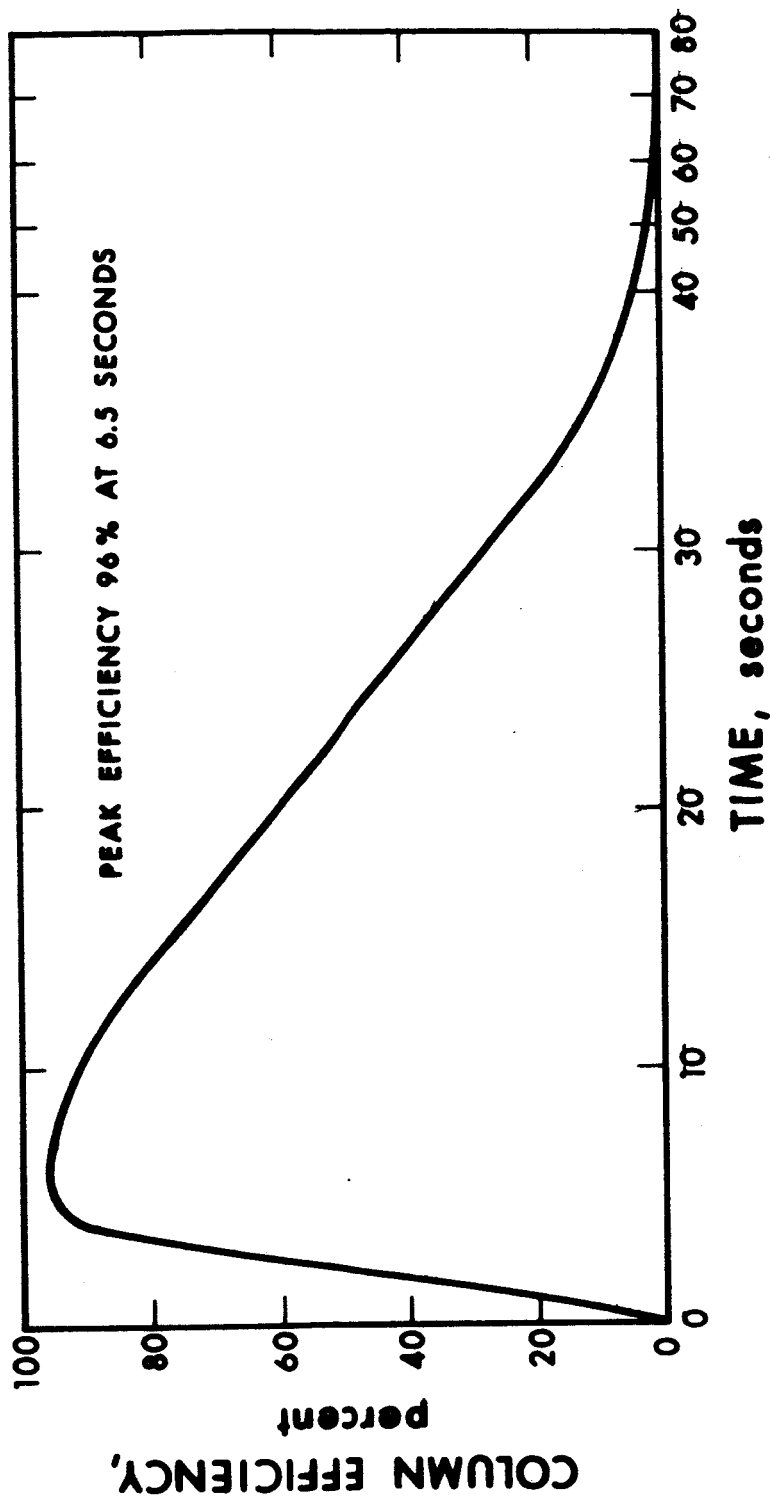


FIG. 52 COLUMN EFFICIENCY, 3/4 INCH X 12 INCH SILICA GEL AT ROOM TEMPERATURE,
5-SECOND INJECTION, 5 PSIG, 99% AIR, 1% CO₂

TABLE 17
 SEPARATION DATA FOR 99 PERCENT AIR, 1 PERCENT CO₂
 WITH 3/4 x 12-IN. SILICA GEL COLUMN

GAS MIXTURE	99% Air - 1% CO ₂
SEPARATION COLUMN	3/4" x 15" (8 - 16) Silica Gel at R.T.
ANALYSIS COLUMN	12" x 1/4" Silica Gel at R.T.

Injection Time (Sec)	Sample Time (Sec)	Total Cycle (Sec)	Air Peak	CO ₂ Peak	Air: CO ₂ Ratio	Vol. % CO ₂	WH % CO ₂
5	5	180	336	0.36	934	0.75	1.2
			320	0.30	1062	0.8	1.3
	10	180	44.8	.41	189	2.9	4.4
			137	.80	172	3.1	4.7
	15	180	31.4	.25	126	3.8	5.8
			20.0	.14	142	3.6	5.5
	20	180	39.2	.40	98	4.6	6.9
			31.6	.30	105	4.4	6.6
	25	120	18.8	.20	96	4.6	6.9
			26.8	.35	76.5	5.3	7.9

TABLE 18

TERMS IN COLUMN EFFICIENCY EQUATION AS AREAS UNDER THE CURVE IN FIGURE 52

Time Sec	M ₁ (Area Units)	M ₂ (Area Units)	M ₃ (Area Units)	M ₄ (Area Units)	$\frac{M_1}{M_2}$	$\frac{M_3}{M_4}$	$1 - \frac{M_3}{M_4}$	$\left[\frac{M_1}{M_2} \left(1 - \frac{M_3}{M_4} \right) \cdot 100 \right]$
0	0.65	0.65	48.30	48.30	1	1	0	0
1	0.65	"	40.08	"	1	0.829	0.171	17.1
2	0.65	"	27.83	"	1	0.526	0.474	47.4
3	0.65	"	13.58	"	1	0.281	0.719	71.9
4	0.65	"	3.08	"	1	0.064	0.936	93.6
5	0.65	"	2.48	"	1	0.051	0.949	94.9
6	0.6485	"	2.02	"	0.998	0.042	0.958	95.7
7	0.6455	"	1.914	"	0.993	0.040	0.960	95.3
8	0.642	"	1.826	"	0.986	0.0378	0.9622	94.8
9	0.630	"	1.801	"	0.970	0.0374	0.9626	93.4
10	0.618	"	1.781	"	0.953	0.0369	0.9631	91.8
11	0.605	"	1.762	"	0.931	0.0365	0.9635	89.6
12	0.588	"	1.743	"	0.906	0.0361	0.9639	87.3
13	0.569	"	1.726	"	0.876	0.0357	0.9643	84.0
14	0.538	"	1.705	"	0.828	0.0353	0.9647	80.0
15	0.516	"	1.680	"	0.794	0.0348	0.9652	76.6
20	0.406	"	1.525	"	0.625	0.0316	0.9684	60.5
25	0.294	"	1.401	"	0.452	0.0290	0.9710	43.8
30	0.184	"	1.114	"	0.283	0.0231	0.9769	27.6
35	0.073	"	0.965	"	0.112	0.020	0.980	11.0
45	0.019	"	0.611	"	0.029	0.013	0.987	2.9
60	0.006	"	0.273	"	0.009	0.006	0.994	0.9
80	0.002	"	0.007	"	0.003	0.001	0.999	0.3
120	0	0.65	0	48.3	0	0	1.000	0

5.3.2.5 3/4 x 6-in. Monoethanolamine Impregnated Firebrick

Solutions of monoethanolamine (MEA) have been shown to be a good adsorption media for carbon dioxide. MEA, being a liquid, has to be supported. Firebrick (30/60 Mesh) was chosen because of its chemical inertness and relatively high porosity. MEA has a boiling point of 175°C at atmospheric pressure. At 1 mm Hg pressure, it will boil at 30°C. Thus, during pumpdown (to < 1 mm Hg), the MEA would probably vaporize. Nevertheless a 3/4 x 12-in. column was constructed to attest to the stability of the MEA at low pressure. However, it was found that the MEA chemically reacted with the copper tubing and fittings to form a bright blue substance. At this point the experiment was discarded.

5.3.2.6 3/4 x 24-in. Molecular Sieve - 80 Percent CH₄, 20 Percent H₂

This experiment was performed as a preliminary test to evaluate the PGC technique for gas separations in the Sabatier reaction system. A 3/4-in. diameter, 24-in.-long column was packed with 13 x molecular sieves and used for this evaluation. Due to analysis problems described in the chromatographic calibration section, i.e., Subsection 4.4 sample analyses were made mass spectrometrically. The data showed that all the hydrogen came out in the effluent during the 5-second injection time. Since samples cannot be taken between 0 and 5 second, with the present arrangement and the mass flowmeter had not been calibrated for H₂ and CH₄, the test results were quantitatively meaningless. Qualitatively, however, it appears that H₂ can readily be separated from CH₄.

5.3.2.7 3/4 x 12-in. Molecular Sieve - 99 Percent Air, 1 Percent CO₂

This experiment was performed to ascertain the ability of a molecular-sieve column to separate air contaminated with CO₂; a 15-second injection time and a 7.5 psig injection pressure

was used to increase throughput. Results of the detailed analyses on the PGC data gathered on this column/gas mixture are shown in Figs. 53, 54, and 55 and in Table 19. It was noted that no carbon dioxide was found in the effluent up to 15 second sample time. The plot of column efficiency with lapsed time curve shows a relatively linear rise and drop with small flat peak and a maximum column efficiency of 99.7 percent at 15 seconds. A mass balance check was performed to check the accuracy of the results. The calculation showed that the gas mixture in the analysis was 98.2 percent air and 2.02 percent CO₂. The actual mass spectro-analysis of the gas mixture was 99.03 percent air and 0.97 percent CO₂.

5.3.2.8 3/4 x 12-in. Molecular Sieve - 80 Percent
CO₂, 20 Percent Air

This experiment was performed to evaluate the ability of the molecular-sieve column in separating high percentages of CO₂ from air. It was observed that the 5-second samples repeatedly showed large quantities of CO₂ when they were analyzed chromatographically. Samples were also sent out for mass spectrographic analysis. The mass spectral analysis indicated that there was poor separation at both 5 seconds and at 10 seconds. Further experiments should be performed to describe the factors which give rise to the distinctive differences for the molecular sieve for separating 99 percent air, 1 percent CO₂, and 80 percent CO₂, 20 percent air.

5.4 Discussion of Test Results

Certain conclusions can be drawn from the test results achieved to date. First, the PGC is capable of separating gaseous mixtures in the manner described in Section 3, Principles of Pulsed Gas Chromatography. Second, the variables investigated, i.e., column length, column diameter, temperature, injection pressure, injection time, etc., affect separation principally by varying the pumpdown time in the range investigated. Details of these effects are described in the following section.

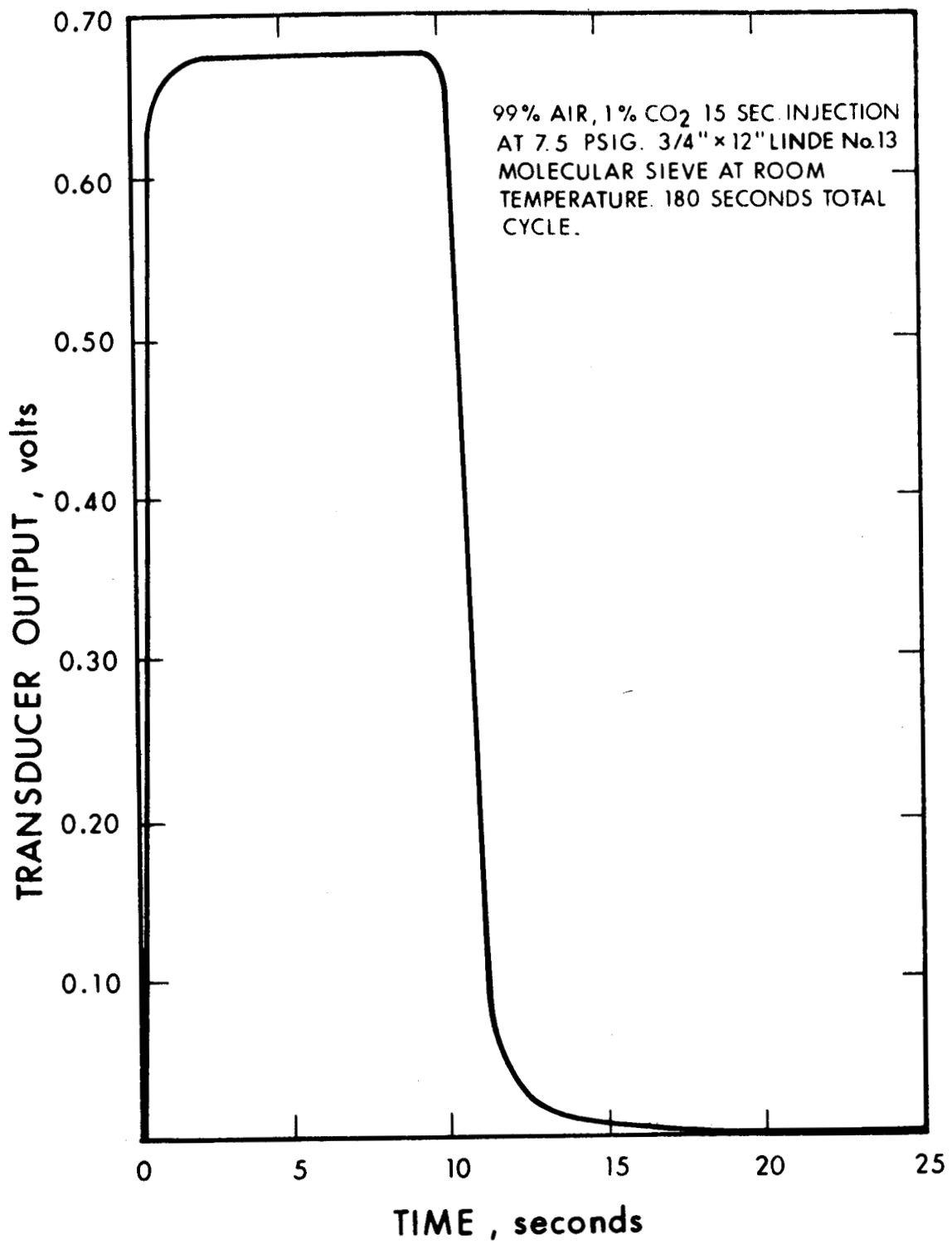


FIG. 53 TRANSDUCER OUTPUT TRACE FOR 15-SECOND INJECTION OF 99% AIR, 1% CO₂

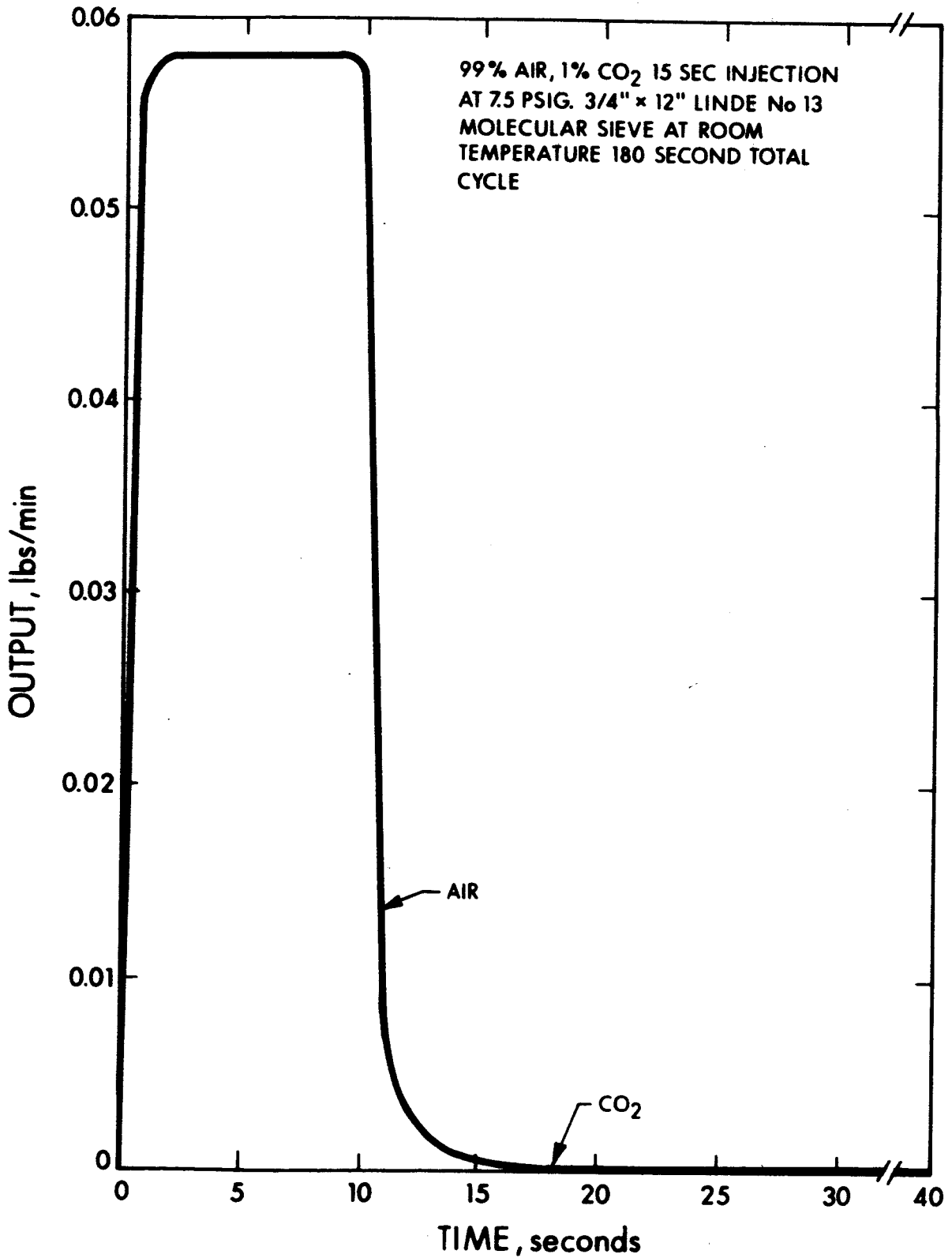


FIG. 54 OUTPUT TRACE OF AIR AND CO₂ WITH TIME

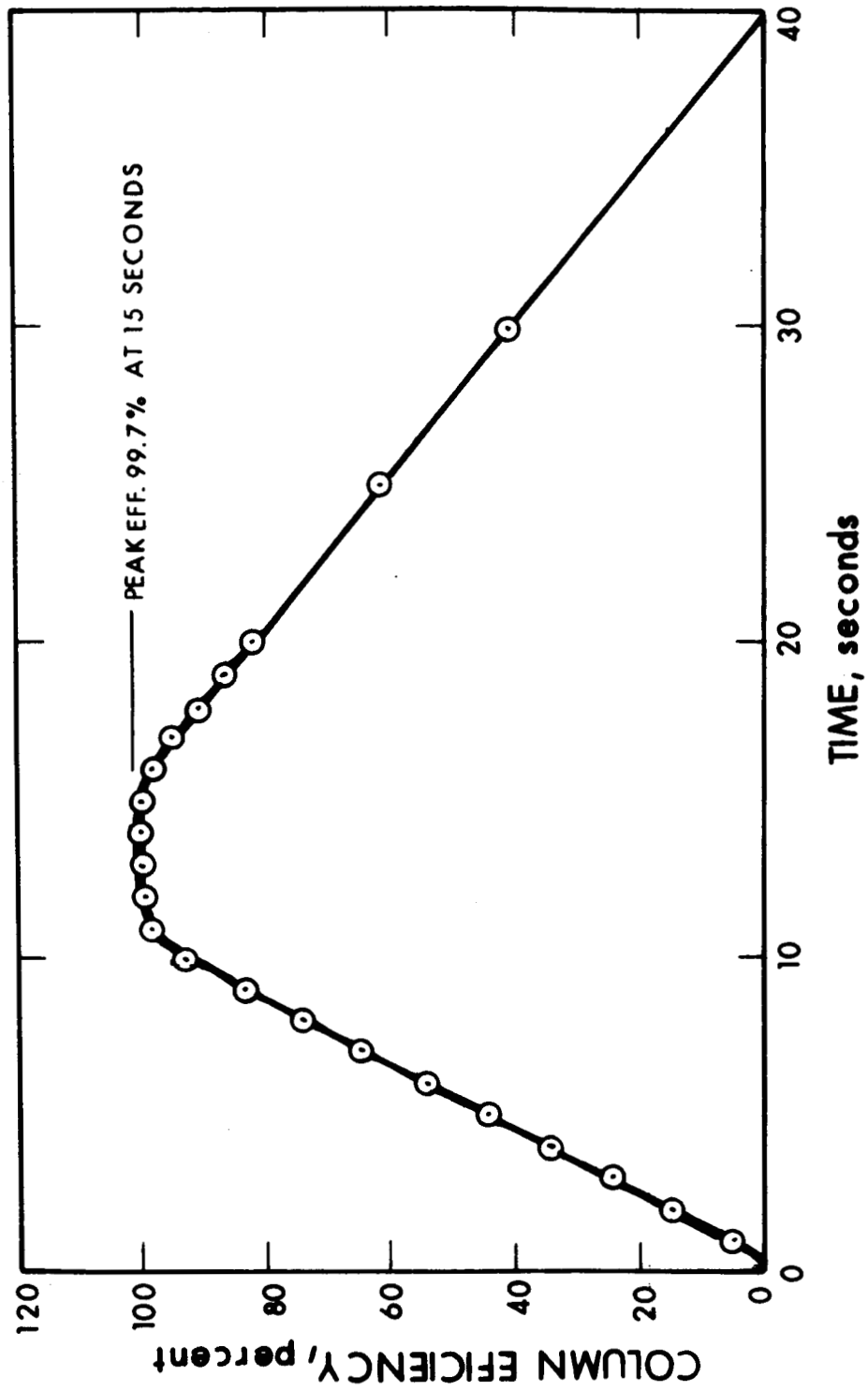


FIG. 55 COLUMN EFFICIENCY 3/4 INCH X 12 INCH MOLECULAR SIEVE AT ROOM TEMPERATURE,
 15-SECOND INJECTION, 7.5 PSIG, 99% AIR, 1% CO₂

TABLE 19
TERMS IN COLUMN EFFICIENCY EQUATION AS AREAS UNDER THE
CURVE IN FIGURE 54

TIME (SEC)	M_1 (AREA UNITS)	M_2 (AREA UNITS)	M_3 (AREA UNITS)	M_4 (AREA UNITS)	$\frac{M_1}{M_2}$	$\frac{M_3}{M_4}$	$1 - \frac{M_3}{M_4}$	$\frac{M_1}{M_2} (1 - \frac{M_3}{M_4})$ (PERCENT)	100
0	2.45	2.45	0	118.5	1	1	0	0	
1	"	"	112.5	"	"	0.947	0.053	5.3	
2	"	"	101.0	"	"	0.852	0.148	14.8	
3	"	"	89.4	"	"	0.754	0.246	24.6	
4	"	"	77.8	"	"	0.656	0.344	34.4	
5	"	"	66.2	"	"	0.558	0.442	44.2	
6	"	"	54.6	"	"	0.461	0.539	53.9	
7	"	"	43.0	"	"	0.363	0.637	63.7	
8	"	"	31.4	"	"	0.265	0.735	73.5	
9	"	"	19.8	"	"	0.167	0.833	83.3	
10	"	"	8.3	"	"	0.070	0.930	93.0	
11	"	"	2.0	"	"	0.017	0.983	98.3	
12	"	"	1.05	"	"	0.009	0.991	99.1	
13	"	"	0.63	"	"	0.006	0.994	99.4	
14	"	"	0.47	"	"	0.004	0.996	99.6	
15	2.45	"	0.37	"	1	0.003	0.997	99.7	
16	2.40	"	0.27	"	0.978	0.002	0.998	97.7	
17	2.32	"	0.18	"	0.946	0.0015	0.9985	94.6	
18	2.21	"	0.10	"	0.903	0.001	0.999	90.3	
19	2.11	"	0.03	"	0.861	0.0003	1.000	86.1	
20	2.00	"	0.0	"	0.816	0	1	81.6	
25	1.50	"	0.0	"	0.613	0	1	61.3	
30	1.0	"	0.0	"	0.407	0	1	40.7	
40	0.0	2.45	0.0	"	0	0	1	0	

5.4.1 Effect of Column Length

Column lengths in the range 6 inches to 6 feet were investigated. Test results indicate that the 6-inch length columns tend to flood while the 6 foot columns tend to restrict flow, decrease throughput and increase pumpdown time. For the gases and packing materials tested, column lengths of between 1 and 3 feet appear optimal.

5.4.2 Effect of Operating Temperature

No major effects on separation were noted at temperatures of 25° and 50°C.

5.4.3 Effect of Column Diameter

Columns ranging from 0.25-inch to 0.75-inch diameter were studied. Separation generally improved with an increase in diameter, contrary to conventional gas chromatography experience, due to an improvement in pumpdown time. However, one can expect a lowering in separation efficiency with larger-diameter columns if gas-flow correction devices are not employed.

5.4.4 Effect of Injection Volume

Injection volume was varied by changing the injection time. Two cycles for achieving this were employed, namely 5 and 15 seconds. In general, with a fixed-pumping speed, as used in our test apparatus, increasing injection time decreases separation efficiency. Conversely, however, throughput is increased with increased injection time. Optimizing this factor will depend greatly on the gas mixture to be separated and the separation efficiency deemed satisfactory.

5.4.5 Effect of Injection Pressure

Injection pressure was varied from 14.7 psia to 22.2 psia. The effect of increasing injection pressure is similar to that of increasing injection time.

5.4.6 Effect of Column-Packing Material

This factor is the major variable in the PGC concept. Experience with separations using conventional gas chromatographic data is directly applicable to the PGC concept. Thus, CO₂ can be separated satisfactorily on silica gel, but tends to remain on molecular sieves. Sieves and silicone-rubber columns on the other hand are quite useful for separating H₂ from CH₄, while silica gel is not as good for this separation.

The particle size of the packing material is also an important variable. One would expect better separation using small particles having high surface areas. However, small particles tend to increase flow impedance and thus increase pumpdown time which degrades separation efficiency.

5.4.7 Effect of Moisture-Removal Equipment

The only equipment employed for moisture removal on the test apparatus was a column of Drierite in the injection gas line. Quantitatively, during the course of the program, it was noted that when room air was cycled through the column during checkout runs, room air moisture (30-50 percent relative humidity) had no effect on column performance. However, long term effects of high humidity atmospheres may tend to degrade silica gel columns. A recent packing material having the commercial name Poropak^{1,2} should, however, eliminate moisture as a degrading factor while providing excellent CO₂ - air separation.

6. PRELIMINARY SYSTEM ANALYSES

As a first step in comparing the PGC concept with other gas separation schemes, estimates of system weights have been made. For comparison purposes, we have selected a 4-man spacecraft application and a CO₂-air separation.

Data taken during the program indicates that a 2-foot, 0.75-inch-diameter-packed column will pass $\approx 1 \times 10^{-2}$ pounds of atmospheric pressure air during a 1-minute period with a 15-second injection pulse. Based upon these data and the requirement of removing 2.25 pounds of CO₂ per man per day, one can estimate the size and weight of a PGC system for life support in a spacecraft.

- Assumptions: (1) Input to the PGC column contains 99 percent air, 1 percent CO₂
- (2) Outputs for PGC column contained essentially pure air and pure CO₂ as demonstrated in the experimental program

The quantity of air + CO₂ to be processed is determined as follows:

$$\begin{aligned} M_1 &= 4 \times 2.25/0.01 = 900 \text{ lb/day} \\ &= 0.25 \text{ lb/min} \end{aligned}$$

where

M_1 = mass flow of air required for 4-man system

Since flow rate is proportional to column frontal area or the square of the diameter, we can estimate the column diameter required for a 4-man system, since we have data for a 0.75-inch-diameter column.

$$M_1/M_2 = (d_1)^2/(d_2)^2$$

where

- M_2 = mass flow of 0.75-inch column
- d_1 = diameter of column for a 4-man system
- d_2 = 0.75 inches

$$d_1^2 = M_1(d_2)^2/M_2$$

$$d_1^2 = 0.25 \cdot (0.75)^2/0.01 = 14.1$$

$$d_1 = (14.1)^{0.5} = 3.74 \text{ inches}$$

This diameter is well within the state of the art for gas chromatography, since 4-inch-diameter columns have been commercially available for over two years and columns to 12-inch diameter have been demonstrated in the literature.

Based upon the use of silica-gel having the same packing fraction as that presently used with the 0.75 inch column, the weight of a 3.74-inch diameter can be estimated.

$$\frac{W_1}{W_2} = \frac{(d_1)^2 L_1}{(d_2)^2 L_2}$$

where

- W_1 = weight of silica gel in 3.74 inch-diameter column
- W_2 = weight in 0.75-inch column i.e., 84 grams
- L = length of column = 2 ft in both cases
- d_1 = 3.74 inches
- d_2 = 0.75 inches

$$\begin{aligned} W_1 &= 84 \times (3.74)^2 / (0.75)^2 = 1,840 \text{ grams} \\ &= 4.06 \text{ pounds} \end{aligned}$$

Other system-component weights are estimated to be as given in Table 20.

TABLE 20

	<u>Quantity Required</u>	<u>Weight (lbs)</u>
1. Column tubing (thin wall Al)	2 ft	0.8
2. Fittings and miscellaneous accessories		1.0
3. Solenoid valve	2 ea	2.0
4. Vacuum pump	1 ea	20.0
5. Controls and electrical accessories		2.5

Total system weight thus comes to \approx 30.4 pounds.

A search of the available commercial literature indicates that a two-stage pump composed of a rotary carbon vane roughing section and a Rootes blower first stage would be a logical type of system to be employed. Based upon extrapolation of power requirements for commercial pumps, power requirements are estimated at 0.5 horsepower or 373W. Additional power to operate the solenoids and controls should not exceed 25 watts, so total power requirements should approximate 400W.

7. RECOMMENDATIONS

The pulsed gas chromatographic separation technique has been shown to be capable of separating and/or enriching various gas mixtures. Work performed under this contract (NAS2-3209) has indicated certain technical facets of the approach that will require additional investigation before the full potential of the PGC technique can be determined. Among the facets requiring additional effort are:

1. Separation efficiency as a function of mass flow
2. Extended time operational behavior
3. Scale-up effects
4. Effect of contaminants on separation efficiency
5. Optimization of column packing

It is recommended that EOS expand the effort started under NAS2-3209 to evaluate these parameters and to conduct a system-analysis study for comparison of the PGC technique with other systems being investigated for gas separation in spacecraft.

REFERENCES

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2. Anon, "Poropak," *Perco Notes, Perco Supplies*, Vol. 3, No. 3, Jul 1966