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THE PERKIN-ELMER CORPORATION  
AEROSPACE DIVISION  
2855 Metropolitan Place, Pomona, California 91767

FINAL REPORT  
CARBON MONOXIDE  
ACCUMULATOR CELL STUDY  
VOLUME 1 OF 6  
FOR  
COMBINED STUDY PROGRAM

By Mary Rotheram

March 1971

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Perkin-Elmer SPO 30006  
NASA Contract Number NAS1-9469

Prepared for  
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
LANGLEY RESEARCH CENTER  
Langley Station  
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## ABSTRACT

A program was conducted in which an instrument system concept was studied to optimize the application of a mass spectrometer as a sensor for monitoring the primary atmospheric constituents, as well as atmospheric contaminants, on board a manned spacecraft. The program was divided into six individual studies representing the primary system parts complementing the spectrometer: a Carbon Monoxide Accumulator Cell (Volume 1), an Ion Pump (Volume 2), an Ion Pump Power Supply (Volume 3), an Inlet Leak (Volume 4), an Ion Source (Volume 5), and an Undersea Atmospheric Analyzer (Volume 6). The principle goal of the combined study program was the achievement of an instrument concept of minimum power, weight and size without compromising the minimum detection limits of the instrument.

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## SUMMARY

Conceptual design of a flight test model Carbon Monoxide Accumulator Cell System has been completed. Several operational options were examined experimentally to establish a satisfactory set of operating parameters for the flight prototype system. Additional studies of the palladium-charcoal sorbent were carried out to confirm original observations and to obtain more information relevant to the sorbent characteristics. The accumulator cell technique can be used in a vacuum mode of operation to detect low concentrations of carbon monoxide in air.

The flight prototype Carbon Monoxide Accumulator Cell will be capable of detecting carbon monoxide at concentrations in the range from five to 100 parts per million. The analysis time is estimated at ten minutes with repetition intervals of twenty minutes. A peak power consumption of twelve and one-half watts is estimated for the system; a minimum of three watts power is required to heat the sample tube for monitoring the normal atmospheric components. Weight of the dual leak inlet system includes two pounds for the control units for the cell heaters and valves and one and one-half pounds for the inlet system hardware. A vacuum line, either to a rough pump or outer space, is required for operation of the system.

The dependence of the amount of carbon monoxide sorbed on the gas phase concentration was investigated. The total amount sorbed increased by a factor of four and one-half over the concentration range from eight to 5,150 parts per million. This result implies that operating the accumulator cell with a sample volume in excess of that required to saturate the cell, will not afford a sensitive measure of the carbon monoxide concentration. Two sorbent preparations were tested in the low concentration range and the reproducibility of sorption capability was demonstrated.

The results of the sorbent study program show that; first, with vacuum desorption and a fixed sample volume (less than that required to saturate the cell), carbon monoxide can be detected at concentrations of five parts per million; second, operation at atmospheric pressure using a carrier gas to transport desorbing carbon monoxide from the cell to a low conductance mass spectrometer leak does not afford sufficient sensitivity for detection of carbon monoxide, even at relatively high concentrations, on the order of 100 parts per million; and third, the palladium-charcoal sorbent can be prepared in a reproducible manner.

Results of the study program are used in the conceptual design of an inlet system to monitor both normal atmospheric constituents and carbon monoxide.



## INTRODUCTION

Measurement of the carbon monoxide concentration in spacecraft atmospheres is an important requirement to ensure the health and safety of the crew. While relatively high concentrations of carbon monoxide can be tolerated for short exposure periods, there is a general debilitation of personnel performance for continuous exposure to lower concentrations. In a manned space flight this is potentially hazardous. Therefore, being able to determine low concentrations of carbon monoxide, which signal the malfunction of some portion of the atmospheric control system is important in order to take preventive action before serious exposure problems are encountered.

A method for determining carbon monoxide at concentrations on the order of ten parts per million was developed as part of Laboratory Contaminant Sensor programs (Contract Number NAS1-7266 and NAS1-8258). This method is based on concentration of carbon monoxide by sorption on a suitable sorbent, removal of air from the system by vacuum pump out, followed by desorption of carbon monoxide by heat to a mass spectrometer for analysis. In this system the pressure due to desorption of carbon monoxide from the sorbent initially increases and then decreases as the gas is pumped out of the system. The carbon monoxide signal in the mass spectrometer at the peak of the desorption curve is used as the measure of the amount of carbon monoxide in the sample.

This program was undertaken to develop a test system that would approach hardware limitations imposed by flight conditions and to gain further insight into the factors involved in the detection of carbon monoxide by this technique. Modes of operations which are more suitable to flight requirements were tested. The program involved an effort to obtain more data on the performance of the sorbent, tests with a system which except for the valving requirements would be more compatible with flight hardware, and an evaluation of the power and weight requirements for a flight type unit. Conceptual design of a flight carbon monoxide detector was also undertaken.

The results of the test program with the small Accumulator Cell System are presented in the next section. Subsequent sections present the results of some additional tests with this sorbent, a conceptual design of a flight prototype system and a discussion of results.

## SMALL CARBON MONOXIDE ACCUMULATOR CELL

A small model Carbon Monoxide (CO) Accumulator cell was designed and tested to evaluate the performance of the carbon monoxide accumulation technique which except for the valves employed, approximates a flight type system. This unit was tested on the cycloidal mass spectrometer in three modes of operation; first, using vacuum desorption and linear temperature programming; second, vacuum desorption with a stepped temperature program; and third, carrier gas desorption with a single step temperature program. A description of the test model is presented in the following section, and the results of the test program are presented in subsequent sections.

## Test System

The test model consists of two Carle\* microvolume valves, Model 2013, and the tubulation necessary to connect the cell, sample lines, precut vacuum lines, and the mass spectrometer leak. The valves are eight-port, four-way switching valves of low internal volume. For this application the valves were obtained with a purge housing to minimize inward leakage of air during carbon monoxide determinations under vacuum. Argon was used as the valve purge gas in these experiments. Connections to the valves are made by Swagelok fittings to the one-sixteenth inch tubes (0.023 inch I.D.) which extend from the base of the valves. A schematic of the flow system for vacuum operation is shown in Figure 1 and a photograph of the test model is shown in Figure 2. By means of this flow system, performing sampling, precutting air from the accumulator cell and desorption of the cell to the mass spectrometer is possible by actuating the valves. The system was operated manually during the test program, although automatic actuators are available. The valves are considerably heavier than considered acceptable for a flight system, and power requirements for actuators are relatively high. Therefore, extending the evaluation of these valves to include automatic actuation was unnecessary.

The CEC model 21-614 mass spectrometer was used with a standard CEC gold leak with conductance of 0.15 cubic centimeter per second for the vacuum experiments. For the experiments with carrier gas, a sintered stainless steel leak with conductance of  $1 \times 10^{-5}$  cubic centimeters per second was obtained from Mott Metallurgical Company. This leak, as purchased, is housed in a one-fourth inch stainless steel tube, which was used to

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\*Carle Instruments, Inc., Fullerton, California

retain the leak in a special capsule holder designed to interface between the cell system flange and the mass spectrometer. This leak assembly is shown in Figure 3. A 150 mesh stainless steel screen was spot welded over the top of the capsule to prevent large particles of sorbent from passing through the valve and settling on the surface of the mass spectrometer leak.

The Carbon Monoxide Accumulator Cell consisted of a stainless steel tube, one-eighth inch in diameter, 0.010 inch wall, three inches in length, which is packed with 0.195 gram of palladium-charcoal sorbent (Batch 4)\*. The sorbent is retained with 150 mesh stainless steel screen inserted in the Swagelok reducing unions connected to the ends of the cell. The cell is equipped with an iron-constantan thermocouple attached to the midpoint of the tube; and is wrapped with resistance wire for heating and surrounded with glass wool insulation. The cell required six and four tenths watts to maintain a temperature of 270 degrees centigrade, this power was adequate to maintain the four degree centigrade per minute heating rate employed in the linear temperature program desorption experiments.

In operation, the sample gas lines are purged initially with the system in the PRECUT position (Figure 2) and the cap at valve A, port 4 open. The cap is closed and valve A switched to the SAMPLE position where the gas passes through the cell at a measured flow rate for a selected time interval. The system is returned to the PRECUT position to pump air from the system. A pressure surge is experienced back through the needle valve, but this is not large enough to overload the mass spectrometer system. At the end of the PRECUT period, valve B is switched to the DESORB position and the cell heated to desorb carbon monoxide. At the end of the analysis the system is returned to the PRECUT position, while the cell cools and the lines are purged for the next sample.

Initial tests with the system under vacuum showed that, whereas the valve leak rates were within the range quoted by the manufacturer for operation under pressure, there was appreciable inward leakage of air through the valves. The leak was traced to the bottom of the valve body where a tapered pin is inserted to prevent excessive purge gas outflow through the center pin of the valve. At the manufacturer's suggestion, this pin was removed and replaced with a one-eighth inch tube connected to the argon purge gas system to permit direct flooding of the center pin section of the valve body. This effectively reduced the level of nitrogen inward leakage in the system.

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\*Refer to section on Sorbent Experiments (Page 22).

Typical values for the inlet system pressures are shown in Table 1. These values were derived from the mass spectrometer signal, assuming a sensitivity equivalent to that measured in earlier experiments. Separate provision for monitoring the inlet system pressure in the test model was not made in order to minimize the system volume. The m/e 28 and 40 outputs were monitored daily as a check on the system performance and were found to be reasonably stable after the initial start up period.

TABLE 1.- INLET SYSTEM PRESSURES UNDER VACUUM OPERATION

| Position | Analyzer Pressure (torr) | Partial Pressure ( $\mu$ ) |       |
|----------|--------------------------|----------------------------|-------|
|          |                          | Nitrogen                   | Argon |
| Sample   | $1.2 \times 10^{-7}$     | 9.0                        | 6.8   |
| Precut   | $5.5 \times 10^{-8}$     | 0.1                        | 5.5   |
| Desorb   | $2.6 \times 10^{-7}$     | 0.6                        | 29.0  |

#### Carbon Monoxide Determination - Linear Temperature Program

A series of carbon monoxide determinations was carried out under conditions similar to those used in the Laboratory Contaminant Sensor Study Program. Samples of carbon monoxide in air were prepared by dilution of a stock mixture containing 115 parts per million carbon monoxide in nitrogen. The dual flowmeter gas proportioner unit was used for dilution. Sample volumes in the range from 200 to 300 cubic centimeters were used; flow rates varied from 50 to 120 cubic centimeters per minute. A precut time period of two minutes was found adequate to reduce the pressure to a value that would not overpressurize the ion source. The cell was heated at a rate of four degrees centigrade per minute and the mass spectra of the desorbing gases were scanned at twenty-five degree centigrade intervals. The mass spectrometer was operated in the low sensitivity mode, using twenty microamperes ionizing current. One division on the recorder is equivalent to 0.018 micron of carbon monoxide under these conditions.

Results of the analysis of samples containing carbon monoxide at concentrations in the range from six to 115 parts per million are shown in Figure 4. Typical desorption curves are shown in Figure 5. A summary of the test results in the linear temperature mode of operation is presented in Table 2. The nonlinearity of the curve at amounts of carbon monoxide in

TABLE 2.- SUMMARY OF TEST DATA IN LINEAR TEMPERATURE MODE OF OPERATION

| Test No. | Concn CO (ppm) | Sample Volume (cc) | Total CO ( $\mu\text{l}$ NTP) | Desorption Peak |                  | Value at 180°C (Div) |
|----------|----------------|--------------------|-------------------------------|-----------------|------------------|----------------------|
|          |                |                    |                               | Intensity (Div) | Temperature (°C) |                      |
| 2043     | 30.4           | 285                | 8.7                           | 310             | 228              | 280                  |
| 2044     | 15.9           | 240                | 3.8                           | 254             | 252              | 176                  |
| 2045     | 0              | 288                | 0                             |                 |                  | 78                   |
| 2046     | 0              | 280                | 0                             |                 |                  | 97                   |
| 2047     | 12.3           | 280                | 3.5                           | 248             | 246              | 177                  |
| 2048     | 26.6           | 286                | 8.8                           | 310             | 198-250          | 293                  |
| 2049     | 12.6           | 292                | 3.7                           | 205             | 247              | 152                  |
| 2050     | 6.3            | 290                | 1.5                           | 198             | 268              | 126                  |
| 2051     | 0              | 250                | 0                             |                 |                  | 84                   |
| 2052     | 0              | 300                | 0                             |                 |                  | 89                   |
| 2053     | 13.0           | 310                | 4.0                           | 210             | 252              | 157                  |
| 2054     | 6.3            | 291                | 1.8                           | 203             | 270              | 125                  |
| 2055     | 25.0           | 299                | 7.5                           | 280             | 204-225          | 260                  |
| 2056     | 39.8           | 230                | 9.2                           | 290             | 178-198          | 290                  |
| 2057     | 20.8           | 287                | 5.9                           | 267             | 200              | 240                  |
| 2058     | 0              | 255                | 0                             |                 |                  | 76                   |
| 2059     | 0              | 250                | 0                             |                 |                  | 66                   |
| 2060     | 0              | 220 Argon          | 0                             |                 |                  | 40                   |
| 2061     | 0              | 220 Argon          | 0                             |                 |                  | 38                   |
| 2068     | 0              | 300                | 0                             |                 |                  | 60                   |
| 2069     | 115.0          | 310                | 35.6                          | 675             | 140-174          | 675                  |
| 2070     | 73.5           | 282                | 20.8                          | 550             | 175              | 550                  |

excess of twenty microliters is due to saturation of the sorbent with the sample volume used. The peak height at 180 degrees Centigrade was chosen as the basis for relating the signal at m/e 28 to the carbon monoxide content.

At least squares line was calculated for the data shown in Figure 4 for total amounts of carbon monoxide from zero to twentieth microliters at standard temperature and pressures (STP); the resulting equation was

$$S_{180} = 87 + 23.2 V_{CO} \quad \text{or}$$

$$S_{180} = 87 + 6.96 C_{CO} \quad \text{for a 300 standard cubic centimeter sample.}$$

where S = Mass spectrometer signal in divisions (low sensitivity at twenty microamperes ionizing current) at a cell temperature of 180 degrees Centigrade.

$V_{CO}$  = Volume of carbon monoxide in the test gas sample in microliters.

$C_{CO}$  = Concentration of carbon monoxide in parts per million in a 300 cubic centimeter sample volume.

The standard deviation of the output predicted by this equation was twelve divisions. The blank value for the system corresponds to eighty-seven divisions. With the smallest concentrations tested, the total amount of carbon monoxide sorbed is about one and eight-tenths microliters, which is at the detectable limit for the technique. Although the blank value is high, it is relatively constant ( $\pm 20\%$ ), permitting detection of low concentrations of carbon monoxide with fair reliability.

As a matter of interest, the m/e 28 signal at 200 degrees centigrade and at the maximum in the desorbtion curve were examined for correlation with the carbon monoxide content. Neither value correlated as well as the 180 degree centigrade peak value. The area under the desorbtion curve was calculated and related to the total carbon monoxide using the estimated pump out rate and mass spectrometer sensitivity. The recovery of carbon monoxide under these conditions was twenty percent. The apparently low recovery is partly due to a minimum estimate of the pump out rate.

#### Stepped Temperature Operation

A stepped temperature heating program was tested to establish the sensitivity and the feasibility of operating the system in a basically simpler and less time-consuming mode. The operating time schedule shown

in Table 3 was chosen as a compromise between what might be considered a minimum control mode and the desire to obtain some data related to background levels in the system. In a flight system some of the operations would be omitted to achieve a minimum time period for carbon monoxide determination.

TABLE 3.- OPERATION TIME SCHEDULE - STEPPED TEMPERATURE PROGRAM

| Step | Time (min) | Operation                           |
|------|------------|-------------------------------------|
| 1    | 0 - 2.5    | Sample with cell at 50°C            |
| 2    | 2.5 - 4.5  | Precut                              |
| 3    | 4.5        | Switch to desorb                    |
| 4    | 5.5        | Scan mass spectra with cell at 50°C |
| 5    | 7.0        | Heat to 125°C                       |
| 6    | 8.0        | Scan at 125°C                       |
| 7    | 9.5        | Heat to 180°C                       |
| 8    | 10.75      | Scan at 180°C                       |
| 9    | 12.0       | Heat to 270°C                       |
| 10   | 16.0       | Scan at 270°C                       |
| 11   | 20.0       | Turn off heater                     |

This time cycle required approximately thirty-six minutes from the start of one sample to the start of the next.

A blank nitrogen level in this operation mode is no higher than those experienced in the slower linear temperature program mode and, in fact, actually appeared to be lower. This may be the result of changes in the sorbent cell, since a gradual decrease in blank values for air samples was noticed during the earlier tests. Therefore, the conclusion is that the two-minute precut time period reduces the nitrogen background from the cell to a minimal value.

Samples used in these tests were prepared in the same way as those used for linear temperature program operation. The results obtained are shown in Figure 6, and summarized in Table 4. Again, the m/e 28 signal at 180 degrees centigrade was used as a measure of the total carbon monoxide content of the sample. The sensitivity in the stepped temperature mode of

TABLE 4.- SUMMARY OF TEST RESULTS - STEPPED TEMPERATURE OPERATION MODE

| Run No. | CO Concn (ppm) | Volume (cc NTP) | Total CO ( $\mu$ & NTP) | 50°C | Output 125°C (Div) | 180°C |
|---------|----------------|-----------------|-------------------------|------|--------------------|-------|
| 2074    | 14.5           | 300             | 4.4                     | 180  | 108                | 228   |
| 2075    | 7.7            | 240             | 1.8                     | 147  | 60                 | 93    |
| 2076    | 35.6           | 295             | 12.0                    | 228  | 370                | 635   |
| 2077    | 95.0           | 235             | 22.4                    | 310  | 720                | 1020  |
| 2078    | 0              | 305             | 0                       | 177  | 93                 | 54    |
| 2079    | 87.0           | 218             | 1.9                     | 168  | 99                 | 96    |
| 2080    | 17.4           | 212             | 3.7                     | 162  | 102                | 189   |
| 2081    | 52.4           | 183             | 9.6                     | 198  | 480                | 700   |
| 2082    | 23.9           | 202             | 4.7                     | 189  | 138                | 264   |
| 2082A   | 27.2           | 288             | 7.8                     | 204  | 370                | 595   |
| 2083    | 46.5           | 302             | 13.7                    | 260  | 620                | 910   |
| *       |                |                 |                         |      |                    |       |
| 2097    | 0              | 238             | 0                       | 171  | 76                 | 51    |
| 2098    | 18.0           | 231             | 4.1                     | 192  | 105                | 162   |
| 2099    | 29.5           | 242             | 7.2                     | 225  | 243                | 417   |
| 2100    | 44.0           | 194             | 8.5                     | 179  | 272                | 452   |
| 2101    | 85.0           | 230             | 19.6                    | 306  | 620                | 850   |
| 2102    | 67.5           | 193             | 13.0                    | 279  | 570                | 820   |

\*Determinations after experiments with test gases containing hydrogen and oxygen.



operation is nearly double that of the slower, linear temperature program mode. On a qualitative basis, this is expected, since less of the desorbing carbon monoxide is pumped out of the system during the shorter heating period. (Also, note that the maximum water desorption pressure occurs at a later temperature because of this same effect.) On the basis of the desorption model the maximum in the carbon monoxide desorption curve should occur at higher temperatures for the faster heating rates. The apparent nonlinearity of response in the low concentration range (shown in Figure 6) may result from being farther away from the maximum point of the desorption curve in the stepped temperature operation. Therefore, improving the linearity and increasing the sensitivity might be possible, by using the m/e 28 peak at some higher temperature, possibly 200 to 220 degrees centigrade, as the measure of concentration.

The second line that appears in Figure 6 was obtained after some experiments with hydrogen/oxygen mixtures which are described in the following section.

#### Experiments with Oxygen, Nitrogen and Hydrogen Mixtures

Effects of bulk gas composition on carbon monoxide determination were investigated briefly. The diluent gases used had the following compositions:

|                | (1)     | (2)     |
|----------------|---------|---------|
| Hydrogen       | 1.004%  | 0.092%  |
| Nitrogen       | 37.687% | 1.776%  |
| Oxygen         | 53.818% | 97.605% |
| Carbon dioxide | 7.377%  | 0.366%  |
| Argon          |         | 0.161%  |

Blank values on both test gases showed relatively low m/e 28 background levels, comparable to those observed with argon. Water (m/e 18) intensities were high, particularly for mixture number one, which has the higher hydrogen content. The gas mixtures are dry; the water, therefore, arises from reaction of hydrogen and oxygen on the surface of the sorbent. This is proven by the fact that the water intensity is lower in the mixture containing the smaller amount of hydrogen. The initial water desorption pressure for mixture number one was high enough to depress the argon signal, indicating that the mass spectrometer leak was at pressures in the range for viscous flow. Pressures in the inlet system were well in excess of 300 microns initially. The effect was smaller with mixture number two. High values for carbon dioxide were also observed in the initial mass scan; all subsequent values were very low.

When these gas mixtures were used to dilute the standard carbon monoxide mixture in nitrogen, the water desorption pressures were reduced, although for mixture number one the pressures were still high enough to depress the argon peak.

Carbon monoxide (m/e 28) desorption curves for samples diluted with the test gases are shown in Figures 7 and 8 together with the desorption curves for comparable concentrations of carbon monoxide in air. A sample of carbon monoxide diluted with water saturated air was tested for comparison with the data shown in Figures 7 and 8. The desorption curves for this sample are shown in Figure 9. Comparing the three sets of desorption curves, it seems that the shift in the carbon monoxide desorption curve may reasonably be ascribed to the effects of sorbed water. Whether the effect is due to preferential sorption of water at high concentration to the exclusion of carbon monoxide or to some total pressure effect on the desorption of carbon monoxide, cannot be established from the available data. However, if it is due to a total pressure effect, eliminating the problem might be possible by using a longer precut time or a slightly higher temperature during precut. If the effect is due to preferential sorption of water, the problem can be eliminated by the use of a sorbent to scrub water, but this will not be effective for samples containing hydrogen. Since test gas samples will normally contain water, but probably not much hydrogen, the problem appears to be solvable but may require some additional development effort.

In order to establish whether the use of the test gases containing hydrogen and high concentrations of oxygen had changed the sorbent characteristics, a series of measurements of carbon monoxide were made in the stepped temperature mode. These data are shown in the second half of Table 4, and as the dashed line in Figure 6. There is an apparent drop in sensitivity of about twentieth percent maximum. Whether this is to be attributed to the effect of hydrogen or water on the sorbent remains to be established.

#### Summary of Scrubber Tests

The palladium-charcoal sorbent used to concentrate carbon monoxide will have sorption capabilities for other organic compounds as well; and providing for removal of these compounds from the sample gas stream is necessary before it encounters the palladium-charcoal sorbent. Any compound that has a fragment mass peak in the mass range from 26 to 30 represents a potential interference for the determination of carbon monoxide with the existing Two Gas Analyzer. This range will include almost the entire spectrum of organic compounds. The scrubber must be capable of removing these effectively to avoid interference with the carbon monoxide determination.

In the Laboratory Contaminant Sensor development program, charcoal was used as a sorbent for the lower molecular weight organic compounds, which are not retained on Porapak Q; and it was anticipated that this would prove to be a satisfactory scrubber material for most organics. Of particular concern, however, were the low molecular weight hydrocarbon gases, ethane and ethylene, since these two compounds both have base peaks at  $m/e$  28. Ethylene is expected to have sorption characteristics fairly similar to those of carbon monoxide, which is not retained to any significant extent on charcoal at ordinary temperatures. The test program was devoted to evaluating scrubber material for these two gases.

Three sorbent materials were tested in the program: Molecular Sieve 4A, Charcoal and Carbosieve B. The latter sorbent is a chromatographic material which is reported to have relatively long retention times for ethylene and ethane, but short retention for carbon monoxide. Scrubbers for water were not specifically investigated, but the effect of the scrubbers tested on the water content of the gas sample was noted.

A test gas mixture containing 100 parts per million each of ethylene and ethane in nitrogen was used to evaluate the scrubber. The sorption of this test gas mixture on palladium-charcoal was determined initially using the three inch cell in the linear temperature program mode of operation ( $4^{\circ}\text{C}/\text{min}$  program). Prior to tests with the ethylene-ethane mixture, nitrogen blank and carbon monoxide samples were checked. The response to carbon monoxide was somewhat erratic and the system exhibited higher sensitivity than previously. The argon leak rate of the valve had increased and  $m/e$  28 background values were higher than previously. These observations suggested that some change had occurred both in the mass spectrometer leak characteristics and the valve system. However, it was believed that valid results would be obtained on scrubber performance and no attempt was made to optimize system performance, since this could possibly involve purchase of new valves.

Desorption of ethylene and ethane from the palladium-charcoal sorbent is shown in Figure 10. Both ethylene and ethane desorb almost immediately from the cell at the start of the temperature program. At low concentrations, removing all of these compounds might be possible in the precut, or rapidly enough in the stepped temperature mode, so that they would not interfere with carbon monoxide determination.

Scrubber cells were prepared from six inch sections of one-eighth inch x 0.010 inch stainless steel tubing. They were packed with weighed amounts of sorbent and equipped with one-eighth to one-sixteenth inch Swagelok reducing unions which permitted them to be inserted in the one-sixteenth inch sample line. The sorbent was retained in the cell with small sections of 150 mesh screen inserted between the end of the tube and the fitting. Weights of sorbent in the scrubber cells are shown in Table 5.

TABLE 5.- SCRUBBER CELLS

| <u>Sorbent</u>     | <u>Weight (gms)</u> |
|--------------------|---------------------|
| Charcoal MI-1      | 0.395               |
| Molecular Sieve 4A | 0.600               |
| Carbosieve B       | 0.125               |

Scrubber cells were conditioned by heating at 300 degrees centigrade under helium flow for two to three hours. The cells were tested for retention of carbon monoxide at concentrations in the range of twenty to thirty parts per million using the Monoxor indicator tubes to detect carbon monoxide in the effluent gas. For Molecular Sieve 4A and Charcoal, the retention volume was very low, less than thirty cubic centimeters, or about the volume that would pass through the cell in the time required to sample the effluent gas through the indicator tubes. For Carbosieve B, the retention volume was slightly larger, on the order of forty to forty-five cubic centimeters. Retention of carbon monoxide is low enough on these sorbents that they may be considered for the scrubber cell applications.

Tests of the capacity of these sorbents were carried out by passing a measured volume of the test gas mixture through the scrubber cell and into the Carbon Monoxide Accumulator Cell System. The sample of gas in the carbon monoxide cell was desorbed under vacuum in the linear (4°C/min) temperature mode; precut time was two minutes.

Molecular Sieve 4A retained ethylene but not ethane from a 180 cubic centimeter sample of the test gas. Charcoal retained ethane from a sample volume of 300 cubic centimeters; ethylene breakthrough for charcoal occurs at less than 300 cubic centimeters. Carbosieve B retains both ethylene and ethane from a 180 cubic centimeter volume. Ethane does not break through until a volume of at least 280 cubic centimeters has passed through the six inch cell; ethylene breakthrough occurs between 180 and 280 cubic centimeters of the test gas mixture.

The results indicate that compounds which might interfere with the determination of carbon monoxide can be removed from the gas sample without significantly altering the carbon monoxide content of the sample. Break-through volumes for ethylene and ethane are comparable to the sample volume used to establish the sensitivity to carbon monoxide so that these sorbents should prove satisfactory for the scrubber cells. Other organic compounds are expected to be more strongly sorbed on these sorbents.

Also, in the particular case of ethylene or ethane, a longer precut could probably be used to remove them from the palladium-charcoal cell since they are not as strongly retained as carbon monoxide. However, assuming that the concentrations of organic contaminants in the samples to be analyzed are significant, using a combination of sorbents for the scrubber for the final system will be necessary; one scrubber material, particularly for ethane or ethylene, either Molecular Sieve 4A or Carbosieve B, and charcoal for the higher molecular weight organics. Both Molecular Sieve 4A and Charcoal are effective in retaining water at the relatively low concentration present in the test gas mixtures. The data obtained in these limited tests indicate that devising a scrubber system that will effectively remove contaminants that are potential interferences with carbon monoxide determination will be possible.

### Carrier Gas Mode of Operation

Part of the effort on this program was directed toward investigating the sensitivity for carbon monoxide detection which could be achieved using an inlet leak designed to operate at atmospheric pressure. If adequate sensitivity could be obtained, the Carbon Monoxide Accumulator Cell could be interfaced directly with the Mass Spectrometer Atmospheric Sensor in a relatively simple and, in terms of weight and power, efficient manner. However, since the inlet leaks differ in conductance by a factor of 15,000 (the vacuum leak has a conductance of 0.15 cc/sec and the atmosphere leak,  $1 \times 10^{-5}$  cc/sec), the peak pressure on desorption must be increased by the same amount in order to achieve the same sensitivity. According to the model derived to describe the desorption process, an increase in peak pressure can be achieved by decreasing the pump out or flow rate and increasing the heating rate. This experimental effort was undertaken to test the carrier gas mode of operation and to explore the sensitivity that can be achieved within practical limitations.

The low conductance leak described earlier was installed in the mass spectrometer, and the flow pattern in the test system was changed for carrier gas operation as shown in Figure 11. Carrier gas flow rate was regulated by the needle valve with upstream pressure controlled by a low pressure regulator. All gas lines were equipped with 0.22 micron Millipore gas line filters. During several weeks of operation, the leak conductance remained essentially constant, as indicated by the carrier gas mass spectrometer signal. Argon was used as carrier gas in most of the tests; helium was used in some later experiments. Typical background levels with argon carrier gas flowing through the system are shown in Table 6.

TABLE 6.- BACKGROUND VALUES FOR ARGON  
WITH LOW CONDUCTANCE LEAK

| <u>Component</u> | <u>Intensity*</u> |
|------------------|-------------------|
| Argon            | 55,000            |
| Nitrogen         | 120               |
| Oxygen           | 20                |

\*High Sensitivity Divisions at 20 Microamps

Based on an ambient pressure of 730 torr, the mass spectrometer sensitivity is calculated to be 75.5 divisions per torr for argon. The nitrogen levels are about equivalent to the analyzer background level with an evacuated inlet system and a high conductance leak.

Initial experiments were performed with gas samples containing carbon monoxide at concentrations of 115 parts per million or less. The three inch accumulator cell previously described was employed and samples of gas up to those required to saturate the cell were tested. Both linear and stepped temperature programming were tested. Flow rates of argon from one to three cubic centimeters per minute were used. It was established that a five cubic centimeter volume of argon was sufficient to remove bulk sample gas from the cell. In general, the results obtained on desorption were discouraging. However, a small signal, which appeared to be due to carbon monoxide desorption was obtained in one experiment in which the cell was nearly saturated with carbon monoxide at 115 parts per million. This result was obtained using the four degree Centigrade per minute linear temperature program and an argon flow rate of one and three-tenths cubic centimeters per minute. The signal was approximately 30 divisions at the peak above the m/e 28 background level of 120 divisions and spread over a wide range of temperature, but it was distinguishable by comparison with a blank sample which did not contain carbon monoxide.

Stopped flow desorption techniques were also investigated. In these experiments, after an initial purge with argon to remove the bulk sample gas, the argon flow was stopped and the gas exit was capped while the cell was heated to a preselected temperature, 180 or 250 degrees centigrade. When the selected temperature was reached, the exit line was opened and argon purge flow started to transport desorbed carbon monoxide from the cell to the leak. Results obtained with this technique were erratic and no positive evidence for a carbon monoxide desorption peak was obtained.

In order to establish whether the difficulties were associated with the mode of operation or with the carbon monoxide palladium-charcoal system and the relatively high instrument background level\*, two sets of experiments were undertaken. In the first, the system performance was evaluated for another contaminant-sorbent pair; in the second set of experiments, the carbon monoxide content of the system was increased by use of a larger cell and higher concentrations of carbon monoxide in the test gas. The results of the first set of experiments is described in the following section; the results obtained with higher carbon monoxide concentrations are described in a later paragraph entitled: Tests with Higher Concentrations of Carbon Monoxide (Page 18).

Benzene-Porapak Q Experiments.- The Benzene-Porapak Q sorbate-sorbent system was chosen for experiments to check on the system performance for several reasons. The desorption temperature of Benzene on Porapak Q established in the Laboratory Contaminant Sensor development program is roughly comparable to the carbon monoxide palladium-charcoal system. Benzene is a compound for which the mass spectrometer has a relatively high sensitivity and the background at the parent mass,  $m/e$  78, is not detectable in the existing instrument. Also, there is considerable data available for Benzene sorption on Porapak Q, both from the earlier programs and from gas chromatographic literature.

A Porapak Q cell, consisting of a three inch section of stainless steel tubing one-eighth inch OD x 0.010 inch wall, containing 130 milligrams of Porapak Q, was prepared and conditioned by passing helium through it at a temperature of 230 degrees centigrade for six hours. This cell was attached to the valve unit in place of the palladium-charcoal cell. Samples ranging from 100 to 550 cubic centimeters of a test gas mixture containing Benzene at a reported concentration of 109 parts per million were passed through the cell. The stopped flow-rapid heating regime was followed during desorption. The schedule of operations is shown in Table 7.

After about one and one-half minutes with argon flowing through the cell, Benzene is detected in the effluent gas; the Benzene concentration increases to a maximum and decreases to near zero in about five minutes. Desorption curves are shown in Figure 12 and the response of the system to various amounts of Benzene are shown in Figure 13. The cell was not saturated with Benzene at the highest sample volume tested. In one experiment, an argon flow of four cubic centimeters per minute was used during the heating interval; the Benzene  $m/e$  78 intensity in this experiment was sixty percent of that observed in a stopped flow experiment with the same amount

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\*The actual background level in the instrument is not much higher than that present in the vacuum desorption experiments, but because the leak conductance is low, the effective background level is much higher.

of sample. The data demonstrated that the stopped flow technique could operate successfully in situations where the variations in background levels are not a factor and that the system using the atmospheric leak is capable of a fair degree of sensitivity.

TABLE 7.- BENZENE DESORPTION OPERATION

| <u>Time (min)</u> | <u>Operation</u>   |
|-------------------|--|
| 0-5               | Sample   |
| 5-12              | Sweep bulk gas from system with argon                                      |
| 12                | Close gas exit, stop argon flow, start heating                             |
| 15.5              | Cell temperature at 230°C  |
| 15.5 - 20         | Monitor for benzene  |
| 20                | Open gas exit, start argon flow at approximately 4 cc/min. Monitor m/e 78. |

The amount of Benzene recovered was calculated from the area (area calculated as the product of peak height by the half-height width) under the desorption curve and the flow rate of carrier gas, using an estimate of the sensitivity of the mass spectrometer to Benzene derived from published data. These calculations indicate that the sample contained about seventy percent more Benzene than shown in the analysis. Furthermore, on calculating the relative Benzene peak pressure produced per microliter of Benzene sorbed, note that the peak pressure is increased by a factor of 800 over that observed with the vacuum technique used in the Laboratory Contaminant Sensor studies. For example, in earlier work, an average peak value of 335 high sensitivity divisions were observed per microliter of Benzene vapor when the instrument sensitivity yielded a signal of 1000 high sensitivity divisions per micron of nitrogen in air. This is equivalent to a peak pressure of 0.21 microns per microliter of Benzene sorbed. In contrast, in the small cell system a value of 22.2 high sensitivity divisions per microliter of Benzene sorbed is observed when the instrument sensitivity is 55,000 divisions per atmosphere (740,000 microns ambient pressure) of argon. This is equivalent to 300 microns per microliter of Benzene sorbed or a factor of  $300/0.21$ , or 1430 increase in the peak pressure. If allowance is made for the difference between the amount of Benzene calculated from the desorption curve and that indicated by the test sample vendor, this factor is reduced to 800. This represents a significant increase in the pressure at the peak of the desorption curve.



An estimate of the expected carbon monoxide sensitivity in this operation mode can be made by comparing the earlier measurements of sensitivities for Benzene and carbon monoxide. Calculating the peak pressure for carbon monoxide from the earlier (NAS1-8258) data,\* a value of 0.064 microns per microliter is obtained. Assuming the same peak enhancement factor of 800 in the slow flow desorption technique, the calculated peak pressure is 51.2 microns per microliter of carbon monoxide sorbed and, taking into account the difference in source sensitivity for argon and carbon monoxide, the calculated peak signal for carbon monoxide in the test system is approximately three and three-tenths divisions per microliter. At saturation at 100 parts per million carbon monoxide, the three inch accumulator cell has approximately 28 microliters of carbon monoxide, which should yield a signal of 92 divisions at the peak. This is about a factor of three higher than the signal observed in initial experiments. One difference between the two cases, is the fact that the data for Benzene is obtained at less than saturation level. The estimate for carbon monoxide is for a saturated cell and neglects losses that may occur in the prepurge, which will be greater for saturation samples than for less than saturation level. A reasonable conclusion therefore, is that the failure to obtain positive results in the initial tests is the result of the low amounts of carbon monoxide in the test cell.

At the conclusion of these experiments, the palladium-charcoal cell was replaced on the system and tests with carbon monoxide in nitrogen at 123 parts per million were repeated using the technique employed in the Benzene experiments. Again, there was no signal which could definitely be attributed to carbon monoxide; the m/e 28 intensity was variable for blank air samples and, also, for samples containing carbon monoxide.

One sample of pure carbon monoxide was tested and this gave a very large signal which appeared as soon as the argon flow was started. This conformed the conclusion that the difficulties in detecting carbon monoxide were due to too low a sample concentration.

Tests With Higher Concentrations of Carbon Monoxide.- A larger accumulator cell containing a 0.425 gram of Batch 4 palladium-charcoal was made from a six inch section of one-eighth inch x 0.010 inch wall stainless steel tubing and installed in the test device after preliminary conditioning. This cell was tested with gas samples containing higher concentrations of carbon monoxide; the test gas samples are listed in Table 8.

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\*NASA CR-66826. Final Report Laboratory Contaminant Sensor System

TABLE 8.- TEST GAS SAMPLES

| <u>Carbon Monoxide<br/>Concentration (ppm)</u> | <u>Bulk<br/>Gas</u> |
|--|---------------------|
| 123  | Nitrogen            |
| 1020   | Nitrogen            |
| 5150   | Argon               |

For the experiments described in this section the test gas mixtures were diluted with argon or nitrogen in the Matheson Gas Proportioner to yield the desired concentration level. Sample volumes which would saturate the cell were determined by monitoring the effluent gas with the Carbon Monoxor for carbon monoxide. The time period and the flow rate were the basis for calculating the volume required to saturate the cell at a given concentration.

Equilibrium constants calculated from the measured saturation values in these experiments are shown for comparison in Figure 23 on the line labeled "small cell data". The saturation level in the small six inch cell appears to be approximately forty percent lower than observed with the Laboratory Contaminant Sensor type cells. While this difference in capacity might be due to real differences in sorbent conditioning, it is more likely due to measurement inaccuracy resulting from the relatively fast linear velocity of gas through the small cell.

Initial experiments were performed in the stopped flow, rapid heating mode of operation. After an initial prepurge, the argon flow is stopped by closing the needle valve, the exit from the leak flange capped, and the cell rapidly (about 3 minutes) heated to 270 degrees centigrade. The exit line is opened and argon flow started immediately. With the cell saturated with carbon monoxide at concentrations of about 550 parts per million (in argon), a response to carbon monoxide was detected, which started as soon as the argon flow was started. In this mode of operation, however, establishing a base line for m/e 28 was difficult, because of what appeared to be a pressure increase in the system due to cell heating. Accordingly, the mode of operation was switched to a continuous slow flow of argon during the heating cycle.

An attempt was made to maximize the response by varying the flow rate and the heating rate. Both peak area and peak height correlations were examined, but the results were too erratic to permit a choice of optimum

conditions. Therefore, a set of operating conditions was selected somewhat arbitrarily and a series of determinations performed to evaluate the sensitivity. The results of this set of experiments is shown in Figure 14 (peak height) and Figure 15 (area).

Some experiments were performed using helium as a carrier gas with the cell saturated with carbon monoxide at a concentration of either 1020 or 123 parts per million. The peak height and the area are doubled. Apparently greater sensitivity can be obtained using helium as a carrier gas.

Typical desorption curves for the carrier gas (helium) mode of operation are shown in Figures 16, 17, and 18. These curves were derived from a series of individual runs for each mass number monitored, since elution of the various components occurs too rapidly to permit scanning in this system of operation. The double-topped m/e 28 peak, which is frequently observed in the vacuum experiments, was noted (Figure 18) and, in addition, a third peak was noted at about 120 degrees Centigrade in tests with the mixture containing 123 parts per million carbon monoxide in nitrogen. Monitoring m/e 12 and 14 during desorption shows that the third peak (120°C) was due to nitrogen.

The desorption characteristics of carbon dioxide and water are quite different in the carrier gas mode compared to vacuum operation. Carbon dioxide desorbs after carbon monoxide and water desorbs after both of these compounds. In vacuum operation carbon dioxide comes off immediately, usually during precut, and water peaks at about 100 degrees Centigrade, depending on the concentration.

Table 9 shows the peak maximum intensity observed in this series of experiments. These experiments were performed with an ionizing current of sixty microamperes instead of the usual twenty microamperes, so that the peak intensity values are a factor of three larger than in the carbon monoxide detection experiments.

Carbon dioxide values for these experiments are invariably higher in the samples containing carbon monoxide, which raises the question of whether carbon monoxide is being oxidized to carbon dioxide on the sorbent. Comparisons of the amounts of carbon dioxide (as estimated from peak area) with the amount of carbon monoxide not recovered (CO recovered by area) do not yield convincing evidence for carbon monoxide conversion, although the possibility is not ruled out. The highest carbon dioxide values are always obtained for the first samples analyzed. Subsequent runs are lower. On three successive runs on argon samples containing 5,150 parts per million carbon monoxide, the carbon dioxide values ranged from 1,550 to 620

divisions at the peak. The source of oxygen for the oxidation for these argon samples is debatable. When the cell is not in use, it is generally left under helium, but it may be possible that intermittent exposure to air during sampling is sufficient to replenish a carbon oxide layer on the surface of the sorbent. It is also possible that carbon dioxide is contained in the test gas mixtures that have not been analyzed for this component.

TABLE 9.- DESORPTION PEAK-MAXIMUM FOR OTHER COMPOUNDS PRESENT IN THE SYSTEM

| Sample                                 | Nitrogen          | Component       |                    | Water |
|--|-------------------|-----------------|--------------------|-------|
|  |                   | Carbon Monoxide | Carbon Dioxide     |       |
| <u>Nitrogen</u>                        | 555               | 0               | 445                | 850   |
| 123 ppm CO in nitrogen                 | 510               | 80              | 210<br>1384        | 1236  |
| <u>Argon</u>                           | 200               | --              | 250                | --    |
| 5150 ppm CO in Argon                   | not<br>observable | 4750            | 1550<br>950<br>620 | 240   |
| 1000 ppm CO in Argon                   | 150               | 1600            | 3250<br>2580       | 2000  |
| <u>Air</u>                             | 450               | 0               | 960                | 170   |
|  | 530               | 0               | 1280               |       |
| 207 ppm CO in Air/N <sub>2</sub> (4:1) | 520               | 1260            | 2150               |       |
| 190 ppm CO in Air/N <sub>2</sub> (4:1) | 490               | 790             | 2170               |       |
| 87 ppm CO in Air/N <sub>2</sub> (8:1)  | 570               | 250             | 1690               |       |
| 415 ppm CO in Air/N <sub>2</sub> (2:1) | 560 (sh)          | 1320            | 1900               |       |

The apparently greater sensitivity resulting from operation with helium as a carrier gas in comparison with argon is somewhat difficult to understand. In gas chromatography using charcoal sorbents, it is reported in the literature\* that argon causes retention times on charcoal to decrease relative to helium. This should lead to a sharpening of the peaks and increased peak height during desorption. The result obtained here is just

\*Greene, S.A. and H.E. Roy, Anal. Chem. 29, 569 (1957)

the opposite. The fact that the carbon monoxide peak does not change desorption temperature very much under the variety of desorption conditions tested argues for some different type of sorption process.

The conclusions from these experiments are that operation under carrier gas flow does not afford sufficient sensitivity for monitoring carbon monoxide at low concentrations.

## SORBENT EXPERIMENTS

In the initial phase of this program some experiments were performed to adapt a chemical method for determination of carbon monoxide to the accumulator cell system to verify the mass spectrometer results. A description of these experiments is included in Appendix A. The results obtained were inconclusive mainly because of difficulties with the Carbon Monoxide Accumulator Cell after its initial test with the system and, since the chemical method was not functioning in an optimum manner, this part of the experimental program was discontinued in order to pursue the mass spectrometer studies.

### Sorbent Preparation Experiments

Two new batches of palladium-charcoal were prepared to test the reproducibility of this sorbent preparation, since experience was limited to the two samples prepared in the Laboratory Contaminant Sensor development programs. One batch was prepared in the same way as the earlier batches and one was prepared omitting nitric acid. A Laboratory Contaminant Sensor type cell was made from each batch of sorbent and the carbon monoxide sorption characteristics were studied. A description of the preparations and the cells is presented in the following paragraphs. The tests conducted with these cells are reported in the Carbon Monoxide Sorbent Experiments subsection on Page 23.

#### Sorbent Preparation.-

Batch 3 Sorbent: Palladium chloride (0.68 g, Research Inorganic Chemicals Pd-08, 99.5% PdCl<sub>2</sub>) was dissolved in 0.2 N hydrochloric acid with heating. The solution was cooled to room temperature and six and eight-tenths grams of activated coconut charcoal (Coast Engineering Corp., MI-1) added with stirring. The mixture was allowed to stand over night and filtered through a porous glass filter. The charcoal was washed with distilled water until a filtrate was neutral and air dried. A sample of the resulting

sorbent was packed in a glass tube and heated slowly under a slow flow of helium to 375 degrees centigrade (temperature measured on the outside of the tube). The sample was maintained at 375 degrees centigrade for fifteen minutes and allowed to cool under the helium flow.

**Batch 4 Sorbent:** This sorbent was prepared from hydrated palladium chloride (Research Inorganic Chemical PD-21). A sample of one and two-tenths grams was dissolved with heating in seventy milliliters of water with the addition of seven-tenths of a cubic centimeter of aqua regia. (This preparation was similar to that employed for the original test sorbent.) The solution was filtered and ten grams of MI-1 charcoal was added to the filtrate. The sorbent was separated by filtration and air dried. A sample of this sorbent was conditioned by heating rapidly to 375 degrees centigrade under helium flow and maintaining this temperature for twenty minutes. The sample was allowed to cool under helium flow.

During conditioning of the sorbents, hydrochloric acid is evolved, and at 375 degrees centigrade carbon monoxide is also evolved. The evolution of carbon monoxide is not detectable at temperatures below 250 degrees centigrade.

Cell Description.- The cells were prepared from five inch sections of 0.25 inch OD x 0.025 inch wall stainless steel tubing. One was packed with one and two-tenths grams of Batch 3 sorbent and the other with one and three-tenths grams of Batch 4 sorbent. The sorbent was retained by a 150 mesh stainless steel screen inserted in the Gyrolok fitting on the Hoke valves (4112 G 4Y), which were used for end closures. The cells were equipped with Cajon VCR vacuum couplers for connection to the Laboratory Contaminant Sensor inlet system. A thermocouple was attached to the center of the packed section and the entire cell, including the valves, was wrapped with insulated nichrome heater wire, and glass wool and asbestos insulation. After an initial heating to 250 degrees centigrade, the Gyrolok fittings were retightened and the cells appeared to be leak-free in all subsequent operations. The cells are shown in Figure 19.

### Carbon Monoxide Sorption Experiments

Carbon monoxide mixtures in air were prepared by diluting a purchased mixture of carbon monoxide (115 ppm) in nitrogen with air using a Matheson gas proportioner unit. Three concentrations in the range from eight to fifty parts per million were tested. Three liter samples of these mixtures were passed through the cell and sorption of carbon monoxide was verified by monitoring the effluent gas with a Monoxor, a carbon monoxide test device employing a colorimetric reaction. The charged cells were attached

to the inlet system of the mass spectrometer (see Figure 20) and residual air was precut from the sample in the usual manner. Cells were heated and the desorbed gas pumped past the inlet leak of the mass spectrometer in the manner described in earlier reports.

In initial experiments, a heating rate of six and four tenths degrees centigrade per minute was employed. The carbon monoxide peak for both test cells occurred at temperatures in excess of 230 degrees centigrade, or some fifty to seventy degrees centigrade higher than previously noted with the original cell. Using a slower heating rate, four degrees centigrade per minute, the peak desorption temperature for the Batch 4 sorbent cell was shifted to about 200 degrees centigrade and that for Batch 3 to 215 degrees centigrade for samples containing thirty parts per million carbon monoxide. The desorption temperatures are comparable at the slower heating rate to those observed in the Laboratory Contaminant Sensor study program at a heating rate of six and four-tenths degrees centigrade per minute.

The response of the system to carbon monoxide content for Batch 3 and Batch 4 sorbents is shown in Figure 21. The response is higher for the Batch 3 sorbent, which was prepared without nitric acid. Calculated in terms of peak pressure per microliter of carbon monoxide sorbed, the Batch 3 sorbent has a sensitivity of 0.092 microns per microliter and Batch 4, 0.08 microns per microliter. The earlier cell had a carbon monoxide sensitivity of 0.11 microns per microliter. The apparent lower sensitivity of the new sorbent preparation is due, at least in part, to the slower heating rate. The sensitivity is directly related to the heating rate; slower heating rates result in lower sensitivity. At the heating rate employed in these experiments (4°C/minute), the sensitivity estimated for the earlier cell is 0.07 microns per microliter.

#### Sorbent Saturation Studies

The amount of carbon monoxide sorbed at saturation was determined as a function of carbon monoxide concentration to obtain an estimate of the equilibrium constant for sorption and its variation with concentration. The equilibrium constant is defined by the following equation:

$$K = \frac{C_g}{C_s}$$

where  $C_g$  = concentration in the gas phase, microliters per milliliter  
 $C_s$  = concentration on the sorbed phase, microliters per gram

This constant was determined by passing a gas mixture containing a known concentration of carbon monoxide in air or in nitrogen through the sorbent cell at a measured flow rate. The effluent gas was monitored with the Monoxor detector to determine the time, and hence the volume required to saturate the cell. The equilibrium constant is calculated from this data:

$$C_s = \frac{FtC}{w} \text{ g}$$

$$K = \frac{w}{Ft}$$

where F = flow rate

t = time

w = weight of sorbent

Carbon monoxide concentrations in the range from eight to 115 parts per million were used. The amount of carbon monoxide sorbed is shown in Figure 22 as a function of concentration and the equilibrium constants calculated from the data are shown in Figure 23. Desorption curves for the saturated sorbent are shown in Figure 24. The peak maximum response to carbon monoxide from the saturation experiments is shown in Figure 25. Variations in the amount of carbon monoxide lost on precut probably account for some of the spread in the data.

An estimate of the heat of sorption was obtained by measuring the saturation volume of two temperatures above room temperature. The gas emerging from the flowmeters was heated by passing it through three feet of stainless steel hose, which was maintained at an elevated temperature. The cell that was attached to the hose was heated to the same temperature and the volume of gas required to saturate the cell was determined. The carbon monoxide concentration used in these experiments was eighteen parts per million. The results are presented in Figure 26, which shows the variation in the equilibrium constant with reciprocal temperature. The heat of sorption calculated from these data is 3.4 kcal/gm-mole.

The saturation experiments show, that within the limitations of the technique used, Batch 3 and Batch 4 palladium-charcoal have the same capacity for carbon monoxide. There are some differences in the desorption characteristics. It was mentioned earlier that Batch 3 sorbent had higher desorption temperatures for the standard samples. Desorption curves for



saturated samples show that Batch 3 sorbent yields higher desorption pressure than Batch 4 for the same amounts of carbon monoxide sorbed. Desorption curves are shown for comparison in Figures 27, 28, and 29. The observed differences might result from differences in packing of the two cells, or may represent real differences in the sorbents. The main purpose of these experiments was to demonstrate that the sorption capacities of the sorbent could be reproduced reasonably well, and this was demonstrated. Nevertheless, these data suggest that obtaining greater sensitivity may be possible by changes in the method of sorbent preparation.

The data on the variation in the amount of carbon monoxide sorbed with concentration is at variance with the assumption made in developing a model to describe the desorption characteristics of the system. In the model it was assumed that the equilibrium constant was independent of concentration over the concentration range of interest. The data show this is not the case and that the equilibrium constant increases with concentration over the entire range tested. At higher concentrations, a proportionately smaller amount of carbon monoxide is sorbed. In consequence, if sample volumes are used which saturate the sorbent, the system response as a function of concentration will be nonlinear, and the response will be less sensitive to changes in concentration than for samples which do not saturate the sorbent.

One other interesting aspect of the desorption curves for the saturation experiments is the shoulder that appears on the high temperature side of the desorption peak. This suggests that there may be two sorption sites, one having higher heat of sorption than the other. One may be due to palladium chloride and the other to metallic palladium. The proportions of these two sites would be affected by the method of preparation.

The performance of the sorbent appears to be satisfactory for detection of carbon monoxide, although additional experimental work might lead to improved performance. Such work might reasonably be considered after evaluation of the total system reliability with the Mass Spectrometer Atmospheric Sensor.

#### CONCEPTUAL DESIGN OF A FLIGHT PROTOTYPE CARBON MONOXIDE ACCUMULATOR CELL

The Flight Prototype Accumulator Cell System for carbon monoxide detection with the Mass Spectrometer Atmospheric Sensor will employ the vacuum mode of operation in order to attain a high degree of sensitivity for low concentrations of carbon monoxide. Based on results obtained in the study

program concentrations of five parts per million carbon monoxide in air should be readily detectable; the design range for detection will be five to 100 parts per million (5.7 to 114 mg per cubic meter).

The cell system will interface with the Mass Spectrometer Atmosphere Sensor type of instrument through a high conductance leak and will be operated in parallel with the atmospheric sensor sample line, which interfaces the mass spectrometer through a low conductance leak. At intervals to be determined by application requirements, monitoring of major atmospheric components will be interrupted for approximately ten minutes for determination of carbon monoxide.

The cell system will include, in addition to the palladium-charcoal cell, a scrubber cell for removal of water. Provision for removing organics will also be included if it appears that this is required. Using small two-way automatic valves from Energy Research and Generation, Inc. is recommended to accomplish the required flow switching functions. The sequence of valve operations will be controlled with a clock motor for laboratory evaluation; an electronic timing device will be considered for the flight system.

Power required for the cell heaters is estimated to be ten watts based on thermal analysis and the experimental results presented in Project Note No. 2 in Appendix B. The ER and G valves are magnetically latched valves with a response time of two milliseconds. The power required for actuation is one-tenth to two-tenths of a joule, which is supplied by a capacitor discharge system. The total power demand on the twenty-eight volt supply for a firing rate of once per second is one-tenth of a watt for each valve. Since rapid firing action is not a system requirement, the peak demand for the valve operation will not exceed one-tenth of a watt.

#### Analysis of Signal Requirements

The maximum total pressure from the sample is controlled by several factors; the most important factors are the leak rate from the valves, the amount of water sorbed and the amount of carbon monoxide in the sample. In the test system, the valve leakage rate combined with the pumping speed of the system yielded a relatively constant background pressure of about thirty microns at atmospheric pressure on the valves. The valves recommended for use in the flight system are reported to have a leakage rate which is a factor of ten lower than the laboratory type valve; this, combined with the lower ambient pressure in the spacecraft, will have a significant effect on the leak sizing and selection of the electrometer range change.

Estimating the total pressure developed at the leak for a 100 parts per million carbon monoxide sample at twenty microns, the leak conductance which yields an ion source pressure of  $1 \times 10^{-4}$  torr for the total sample is:

$$C_L = \frac{C_s P_s}{P_L} = \frac{50 \times 1 \times 10^{-4}}{0.020} = 0.240 \text{ cc/sec}$$

The partial pressure of carbon monoxide in the source, with this leak conductance, for maximum concentration, minimum detectable concentration, cell background and ion currents for a source sensitivity of  $1.5 \times 10^{-6}$  amperes per torr are:

|                      | $p_s$ (torr)          | $I_{28}^+$ (amps)     | V (volts) |
|----------------------|-----------------------|-----------------------|-----------|
| Maximum CO (100 ppm) | $0.72 \times 10^{-4}$ | $1.1 \times 10^{-10}$ | 2.2       |
| Minimum CO (5 ppm)   | $2.9 \times 10^{-6}$  | $4.3 \times 10^{-12}$ | 0.086     |
| Cell Background      | $3.8 \times 10^{-6}$  | $5.7 \times 10^{-12}$ | 0.114     |

With the nitrogen feedback resistor,  $2 \times 10^{10}$  ohms, the output signal is given in the last column above. The background nitrogen signal is 0.002 volts which is below the noise and drift level of 0.010 volts. Therefore, electrometer range switching will be unnecessary for the flight system assuming that the reported valve leak rates are actually achieved and that the water content is satisfactorily reduced.

The signal-to-noise and drift level at the minimum sample level is:

$$\frac{S}{N} = \frac{0.086}{0.010} = 8.6$$

The estimated variation in cell background values is on the order of twenty percent of the background value. The ratio of the minimum sample signal to this variation is three and eight-tenths. Since the apparent cell background level is affected by the analyzer background level, the absolute value of the background level may be different in the Mass Spectrometer Atmospheric Sensor. However, the more important analytical consideration is the stability of the cell blank value, since corrections might be applied for the blank value in any event.

## Description of the Mass Spectrometer System

The Mass Spectrometer Atmospheric Sensor as developed on NAS9-9799 will be used in its present configuration with the four liter per second ion pump. The inlet leak manifold will be modified as described in the following section to accommodate the dual leak system. The leak rate will be sized to develop maximum pressure in the ion source for the anticipated maximum total sample pressure from the cell. Electrometer range change provision will be included on the m/e 28 channel as required for maximum carbon monoxide sensitivity.

A block diagram of the mass spectrometer system is shown in Figure 30, and a brief description of the various subsystems is presented in the following paragraphs. More detailed descriptions of the system are available in other reports.

Analyzer .- The analyzer is the basic element of the system; it consists of the ion source, the magnet sector and the collector flange. Gas samples enter the ion source through the inlet leak and are ionized by electron bombardment. The positive ions produced are directed from the ion source into the magnetic sector, where they are separated according to their mass-to-charge (m/e) ratio. The separated ion beams are measured on collectors, positioned on the collector flange to intercept the ion beam at or near their focal point. The analyzer is operated under vacuum supplied by a support vacuum system.

The ion source is a nonmagnetic, electron bombardment type which has dual filament and anode assemblies for reliability. The filament assemblies are mounted at right angles to each other and to the direction of gas entry. Gas samples enter the source from the leak through a ceramic tube in the repeller electrode. Gas flow from the source is restricted by the electrodes and the filament assemblies, so that the pressure in the source is higher than that in the surrounding analyzer region.

This "differentially pumped" ion source provides higher sensitivity than is available for an open ion source and also minimizes sample distortion due to reaction with the filament, which is located in a relatively low pressure region outside the ionizing region.

The filaments mounted at right angles to each other, are made of a tungsten-rhenium alloy (97 percent W - 3 percent rhenium) and have been operated for 5000 hours without failure. The other components of the ion source are fabricated from nonmagnetic stainless steel. Electrodes are separated by ceramic or ruby insulation. Electrical connections are made by means of nichrome lead wires, which are spot welded to the electrodes.

Power to the electrodes is supplied through headers in the vacuum envelope. A separate set of electron beam-focussing electrodes and slits for each filament serve to control the shape of the electron beam in the ion source. The electron beam current is regulated from the anode by the emission regulator.

The ion beam is extracted from the source by the repeller and accelerator and ion focussing electrodes and is shaped by the object slit. The ion beam enters the magnetic sector from this object slit and is bent through a nominal angle of ninety degrees and dispersed according to the mass-to-charge ( $m/e$ ) ratio of the ion species. The magnetic sector focuses the ion beam on the collectors, which are positioned on the flange at the focal point of the dispersed beams. This single focusing sector focuses ions which have an angular spread as they leave the object slit. This is necessary to achieve good resolution in the image plane.

The ion beams are collected on individual shielded buckets located at or near the focal points of the beams. These collectors are connected (through headers in the vacuum envelope) to individual electrometer amplifiers which amplify the ion current and convert it to a voltage analog of the partial pressure of the components of the gas mixture.

Analyzer Vacuum System.- The analyzer and collector assemblies are mounted within a vacuum envelope, which is equipped with a four liter per second ion pump. The system is initially roughed down to the operating pressure of the ion pump with a cryosorption pump. The ion pump maintains the flow of gas through the inlet leak and the necessary low pressure in the analyzer. An internal pressure monitor is provided as a safety device to turn off the ion pump and the analyzer electronics in the event of excessive pressures in the analyzer.

Electronics Subsystem.- The electronics subsystem derives its power from a switching input voltage regulator which is used to supply a regulated 28 volts dc to the power supply system.

The power supply system consists of a single inverter with multiple secondary windings that drive voltage regulators, which in turn supply regulated voltages for the electrode bias voltage divider network, the electrometer amplifiers and buffer amplifiers, the telemetry isolation circuitry, the total pressure transducer, the feedback and comparator network, the filament current, and ionizing or emission current regulators. The low voltage regulators are all of a similar type. They are modified as required for the particular voltage and regulation requirements of the circuit or device which they drive. The three voltage regulators, which must deliver higher voltages to the electrode bias voltage divider, utilize a unique technique in which a relatively low voltage regulator is utilized to regulate a higher voltage.

Six separate electrometer amplifiers are connected to the ion current collectors through header pins located in the collector flange. These electrometer amplifiers consist of a high impedance MOSFET input device followed by an integrated circuit operational amplifier and have feedback resistors ranging from  $10^{10}$  to  $3 \times 10^{12}$  ohms, depending on the expected ion current level at a particular collector. The time response adjustment, temperature compensation, and the requisite filtering and scaling are obtained at the output. The linear signal from each electrometer, zero to five volts full scale, is supplied as a meter output through buffer amplifiers and isolation circuits. In addition to performing the necessary output isolation and protection, these circuits invert the electrometer signals to provide positive outputs.

The electrometer outputs are also connected to a summing amplifier, through scaling input resistors that normalize the mass spectrometer gains for all channels. This provides a total pressure signal which consists of the sum of the partial pressure outputs. This total pressure signal is compared with the output of a total pressure transducer and the difference signal drives the emission regulator. The emission regulator circuit performs the function of adjusting the ion source filament drive, which in turn, controls the level of the ionizing or emission current, which in turn, controls the ion current output of the mass spectrometer. Utilizing this closed loop approach, the gain of the mass spectrometer transfer function is maintained at a constant level, which eliminates any common-mode errors, such as those arising due to inlet, ion pump or ion source sensitivity changes. This makes a substantial improvement in the accuracy of the mass spectrometer. This system is operated open loop, that is, the summing circuitry is not utilized during the carbon monoxide analytical cycle, since the inlet system is operated under vacuum during this portion of the analytical cycle.

The emission regulator circuit is set up to operate the electron gun system at a nominal level of about ten microamperes of anode current. In closed loop, this level is corrected based upon the difference signal obtained from the comparison of the total pressure summation and the total pressure transducer. The filament control part of the circuit allows the filament power to be supplied unrectified for maximum efficiency. The emission regulator also acts to inhibit the filament when the ion pump current is too high, indicating an excessive pressure in the analyzer, which would be harmful to the filaments if analyzer operation were maintained.

The voltages required for the operation of the ion source are derived from an electrode bias voltage divider network, which is nothing more than a resistor network with three low impedance points supplied by the electrode bias voltage regulators which correspond to the electron accelerator, anode

and filament reference potentials. These points receive the majority of the total emission current and must, therefore, be regulated in order to avoid voltage variations due to changing currents being injected into the high impedance electrode bias string.

The ion pump is powered by a high voltage power supply (about 4 kV) which supplies a nominal current of less than 150 microamperes. The ion pump supply must also deliver sufficient current to start the pump at  $10^{-4}$  torr. In order to avoid excessive power requirements during the starting period, the supply must be able to deliver a lower voltage when the load current is high. This necessitates the use of a separate inverter for the ion pump supply. This also allows the ion pump to be operated independent of the rest of the Mass Spectrometer System.

The operator is assisted at startup by the indicator signals that are provided by the system. When input power is applied to the system an internal thermistor temperature sensor is activated which determines if the internal pressure is sufficiently low ( $\sim 10^{-3}$  torr) to safely turn on the ion pump. The sensor will automatically inhibit the ion pump if input power is applied to the pump when the pressure is too high; also, an output signal suitable for an indicator light is also provided.

When the light indicates that the pressure is low enough, the ion pump can be turned on, or the pump will turn on automatically if power has been previously applied. At this point the valve on the roughing line is closed and the pumpdown proceeds. When the pressure reaches  $1 \times 10^{-5}$  torr an indicator signal indicates that a safe pressure for mass spectrometer operation has been reached, and the inhibit on the mass spectrometer electronics is removed, which allows the electronics to be turned on when external power is applied.

In the event of a loss of vacuum for any reason, the indicators and inhibit functions perform as protective devices turning off first the mass spectrometer electronics and then the ion pump.

### Inlet System

The inlet system for the carbon monoxide and atmospheric sensor unit includes a dual leak manifold, two sample lines, a Carbon Monoxide Accumulator Cell and a water scrubber cell. A schematic diagram of the inlet system is shown in Figure 31.

The dual leak manifold consists of a thick flange, which contains the Mott low conductance leak and a Siemens high conductance leak, mounted at right angles to each other. The manifold is mounted on the analyzer housing to interface with the ion source. The Mott leak is equipped with a shutoff valve similar to that used on the Mass Spectrometer Atmospheric Sensor. All sample lines terminate in a common vacuum manifold which utilizes a single rough pump or a line to outer space to provide the required sample gas flow.

During operation, in monitoring the major components of the atmosphere, the sample valve (Figure 31) is open, permitting flow past the Mott leak; all other valves are closed. The flow rate, nominally 100 cubic centimeters per minute is controlled by a critical orifice located well downstream of the leak near the entrance to the manifold. At selected intervals, the sample valve is closed to stop flow past the Mott leak for the carbon monoxide analysis part of the cycle. The closed loop emission control, which ratios the sum of the partial pressures to the total atmospheric pressure, is inactivated and filament emission control is returned to open loop operation.

The scrubber cell, carbon monoxide and orifice valves are opened to sample the atmosphere for carbon monoxide. The gas sample passes first through a scrubber cell to remove water from the cell, and then through the carbon monoxide cell containing the palladium-charcoal sorbent for sorption of carbon monoxide. Sample flow rate is controlled by a critical orifice between the orifice valve and the vacuum manifold. At the conclusion of the sampling period the scrubber cell valve is closed and residual air is pumped from the carbon monoxide sample line. The pressure at the Mott leak, the low conductance leak, will be reduced to a low value at this time so that interference due to residual nitrogen in the atmospheric sample line will be negligible. When this pre-cut operation is completed, the carbon monoxide valve is closed and the leak valve and bypass valve are opened.

The carbon monoxide cell is heated rapidly to 180 degrees centigrade and the desorbed gases flow past the high conductance Siemens leak through the leak valve and the orifice valve. When the cell temperature is 180 degrees centigrade, the mass spectrometer signal at  $m/e$  28 is read and displayed on the carbon monoxide output meter. The leak valve is closed at this point, the orifice valve is opened and the carbon monoxide valve is opened. The scrubber cell and the carbon monoxide cell are heated to 260 degrees centigrade for regeneration for a period of five minutes. The heat is turned off and the valves in the carbon monoxide sample lines are closed. The sample line valve is opened, closed loop operation is reinstated and monitoring of the major atmospheric components is resumed.



For the prototype system, the sample lines will be one-eighth inch stainless steel tubing. The Carbon Monoxide Accumulator Cell will consist of a three inch section of one-eighth inch stainless steel tubing containing two tenths of a gram of palladium-charcoal sorbent. The scrubber cell will be a six inch section of one-eighth inch O.D. stainless steel tubing containing a section of high capacity water sorbent, such as calcium sulfate or Molecular Sieve 4-A. A laboratory vacuum system will be used for the pump out lines in the test program. For the flight instrument, a vacuum line to space vacuum will be furnished.

A time schedule of events is set up on the basis of the required frequency of analysis for carbon monoxide. Approximately a ten minute interval is required for carbon monoxide analysis, and the analysis is repeatable at approximately twenty minute intervals. For analysis of carbon monoxide on a once an hour basis, the following time schedule is typical:

| <u>Time (min)</u> | <u>Operation</u>  |
|-------------------|---|
| 0-45              | Normal atmospheric monitor  |
| 45-47             | Sample for carbon monoxide  |
| 47-49             | Precut air from cells   |
| 49-50             | Heat CO accumulator cell to 180°C   |
| 50                | Readout CO content  |
| 50-52             | Heat both cells to 270°C for regeneration   |
| 57                | Turn off heaters, close CO sample line valves, resume normal component monitoring |

#### Electronic Subsystem for the Dual Leak Inlet System

The central part of this electronic subsystem is a sequencer timer that controls the series of events required to perform the analysis. A block diagram of this system is shown in Figure 32. The sequencer unit provides the master clock, counter unit and gating circuitry to activate the various elements of the system according to the predetermined schedule.

Valves are actuated by a trigger pulse furnished by the sequencer. The trigger pulse causes discharge of a capacitor to furnish power to the electromechanical valve and resets the logic circuitry so that the next pulse reverses the direction of the valve action. Since the system operation is relatively slow, a single capacitor can probably be used for all the valves. Two temperature controllers are utilized to control the cell

temperatures at 180 and 260 degrees centigrade. During carbon monoxide desorption the 180 degree centigrade controller is in operation; during the regeneration cycle the 260 degree centigrade controller is operated. A time delay circuit activated by this temperature sensor will also insure that the cells are at the regeneration temperature for a predetermined time interval. The master clock also controls power to the Carbon Monoxide Accumulator Cell to initially heat the cell to 180 degrees centigrade. Both cells are heated to 270 degrees centigrade for the regeneration of the sorbent.

Three other functions are also controlled by the sequencer. At the start of the carbon monoxide analysis, the summing circuit-transducer circuit will be inactivated. This circuit acts to control the filament power by comparing the sum of the outputs of the electrometers with a pressure sensor to yield partial pressure data for the major atmospheric components. This circuit must be inactivated at or before valve A is closed; stopping sample flow through major components sample line, in order to avoid damage to the ion source filament.

#### Packaging and Weight and Power Summary

The packaging developed for the Mass Spectrometer Atmospheric Sensor, (NAS9-9799) will be utilized as much as possible. The Carbon Monoxide Accumulator Cell System will be mounted in a separate package, which will be located under the mass spectrometer. One of the salient factors in such a design will be the length of the sample lines intersecting the two packages. The lines will be rerouted through the side of the container to minimize this length.

The weight estimated for the dual leak inlet system and the electronics subsystem is five and one-half pounds. During the carbon monoxide part of the analysis cycle, the peak power requirement is estimated at twelve and one-half watts.

#### CONCLUSIONS

The results obtained with the small cell system operating in the vacuum mode, show that this approach can be used to monitor carbon monoxide at low concentrations. The increase in sensitivity resulting from the stepped temperature program operation shows that the time period for a complete analysis cycle can be reduced to a reasonable value with no sacrifice in sensitivity. The nonlinearity of the results in the low concentration range

requires further study, but does not present a serious impediment to the use of this mode of operation, since calibration will be required in any event. The results of this phase of the test program confirmed in a qualitative way the conclusions derived on the basis of the desorption model.

The results obtained with the carrier flow gas mode of operation were generally unsatisfactory. This technique appears to be lacking in both sensitivity and in reproducibility. The lack of reproducibility can probably be overcome by more careful control of the experimental variables, but the lack of sensitivity appears to be inherent in the physical properties of the sorbent.

The sorbent studies show that the isotherm for sorption of carbon monoxide is nonlinear. The amount of carbon monoxide sorbed at saturation increases very slowly with concentration. In the initial studies with the laboratory contaminant sensor type cells, it appeared as if there was a plateau in the sorption curve; that is the total amount of carbon monoxide sorbed did not increase on increasing the concentration from seventeen to thirty parts per million. The desorption curves for those samples confirmed this. However, at higher concentrations, the amount of carbon monoxide sorbed increased and the experiments with the small cell show that it continues to increase slowly with concentration over the range tested. Thus, if the sample size is such that the saturation level is exceeded, the analysis will be less sensitive to changes in concentration than if a sample is chosen which does not saturate the sorbent. In considering the isotherm data, some attempt was made to devise a physical mechanism that would account for the observed results. The best model appeared to be one in which it was assumed there were a small number of sites that could absorb a fixed amount of carbon monoxide regardless of the concentration in the gas phase, and another group of sites that absorb carbon monoxide in proportion to the concentration in the gas phase. Such a mechanism could account for the appearance of double topped peaks in the desorption curves which are frequently observed. With the limited data available, the sorption mechanism cannot be identified more definitely.

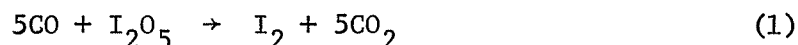
The sorption characteristics of carbon monoxide on this palladium-charcoal sorbent are quantitatively different for the Benzene-Porapak Q system, for example. Although the saturation levels of Benzene were not specifically investigated, the amount absorbed at saturation on Porapak Q is considerably larger than the amount of carbon monoxide sorbed, and the heat of desorption from gas chromatographic data is higher. Both of these factors are reflected in the greater sensitivity of the technique to Benzene. In the experiment the Batch 3 sorbent provided higher desorption pressures than Batch 4; this suggests that the heat of desorption may be higher for this material.

Additional studies of the effect of preparation on the physical properties of the sorbent might yield greater sensitivity in desorption. Where the sorbent and the vacuum technique are satisfactory for determination of carbon monoxide, improvements might result from additional studies.

## APPENDIX A

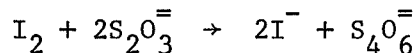
Contract #30006  
Project Note #4SUMMARY OF EXPERIMENTS WITH IODINE PENTOXIDE  
DETERMINATION OF CARBON MONOXIDE

Carbon monoxide reacts with iodine pentoxide to yield carbon dioxide and iodine according to the following equation (reaction):



This reaction is used to determine carbon monoxide in gases evolved in the Schutz method for direct determination of oxygen in organic compounds. It was proposed to use this reaction to determine carbon monoxide evolution from the palladium-charcoal cell after sorption of a known quantity of gas in the usual manner.

Reaction (1) occurs in the temperature range from 60°C to 150°C. At higher temperatures, > 195°C, iodine pentoxide begins to evolve iodine by thermal decomposition. The iodine liberated from iodine pentoxide is trapped in potassium iodide solution and determined by titration with standardized sodium thiosulfate.



Variations on this analytical technique include

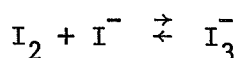
- a. Determination of carbon dioxide by precipitation with  $\text{BaCl}_2$
- b. Oxidation of iodine to iodate with sodium formate, decomposition of excess formate with bromine, removal of bromine and reaction of iodate with iodide to yield iodine.
- c. Trapping iodine in concentrated sodium hydroxide, followed by neutralization and determination of the iodine.

The method used in Perkin-Elmer Aerospace Division's experiment, trapping iodine in potassium iodide, and direct titration was chosen because it appeared to be the simplest method that could be readily undertaken in the laboratory.

The apparatus shown in Figure 33 was used for these experiments. It consists of a glass tube containing the iodine pentoxide which is connected to a U-shaped bubble chamber containing potassium iodide solution. The tube

is connected to a gas stream through a Kovar glass-to-metal seal and a 1/4 inch Swagelok fitting. The design of the bubble chamber evolved from a series of earlier designs, which were unsatisfactory because it appeared there were losses of iodine due to incomplete trapping in some instances or because of iodine deposited on the cold surfaces between the hot iodine pentoxide zone and the cold area containing the potassium iodide solution. The apparatus was somewhat awkward to use, but there was no evidence of iodine lost from the potassium iodide solution with this apparatus.

In preliminary experiments, the iodine pentoxide apparatus was connected through the Swagelok fitting to a stainless steel tube which contained a Swagelok tee, one end of which was fitted with a silicone rubber system for injection of carbon monoxide gas and the other end of which was connected through a flow meter to an argon tank. Known amounts of carbon monoxide (50-200  $\mu\text{l}$  NTP) were injected through the system and carried through the iodine pentoxide tube for reaction. The liberated iodine was carried to the potassium iodide solution in the U-tube where it was trapped by reaction with potassium iodide.



In initial experiments the recovery of iodine ranged from 60 to 80% with various versions of the apparatus. With the system finally used, the recovery was approximately 80% of theoretical. Further attempts to improve the yield were unsuccessful and it was decided to accept the 80% recovery rather than expend additional effort trying to improve this result.

A measured quantity of a purchased mixture of carbon monoxide and nitrous oxide in argon was analyzed and results based on an 80% recovery level agreed with reported analysis for carbon monoxide, 475 ppm.

The palladium charcoal cell was tested with a sample of carbon monoxide at a concentration of 100 ppm in argon. The cell saturated with 2 liters of gas (425 cc/min), corresponding to an equilibrium constant of  $7 \times 10^{-4}$  gm/cc. The cell was purged with argon at a flow rate of 138 cc/min for 1 minute. It was connected to the iodine pentoxide tube and heated with argon carrier gas flowing at a rate of 50 cc/min. The iodine yield corresponded to 85% recovery of the calculated amount of carbon monoxide (uncorrected for the 80% of theoretical recovery with known carbon monoxide samples). A blank value had been previously run with the cell and no carbon monoxide had been recovered.

The cell was tested with a sample of carbon monoxide in air at a concentration of 25 ppm. A 3-liter sample was used and there was no sign of carbon monoxide on the Monoxor detector, indicating that the sample was completely

sorbed. The cell was heated under argon at a flow rate of 20 cc/min to desorb carbon monoxide but only 5% of the theoretical amount was recovered at temperatures up to 275°C.

Another sample of carbon monoxide in air was tested at a concentration of 100 ppm. The cell was run to saturation which occurred at the same value as previously noted for the sample at 100 ppm in argon. The cell was purged with argon at a flow rate of 400 cc/min for 1 minute and heated in argon at a flow rate of 65 cc/min. Less than 10% of the theoretical amount of carbon monoxide was recovered at temperatures below 310°C. At temperatures above 325°C, copious amounts of carbon monoxide were desorbed. This was determined by the iodine pentoxide method and verified by a test with the Carbon Monoxor unit, although this detector indicated a lower evolution rate than the iodine pentoxide method.

After this experiment, the palladium-charcoal was heated in an argon stream for 24 hours at 325°C. The sorption of carbon monoxide was retested with the Carbon Monoxor, and it was found that essentially none sorbed. The cell was transferred to a vacuum system and heated for 48 hours at temperatures in the range 275°C to 300°C. Sorption of carbon monoxide at the end of this interval was questionable and the cell was returned to the vacuum system for further conditioning. After 140 hours at 275°C the cell was detached from the vacuum system and tested for carbon monoxide retention, but this again appeared equivocal. There was an apparent sorption of about 130  $\mu$ l of CO, but when the cell was purged with argon carbon monoxide was observed (with the Monoxor) in the effluent gas.

It was decided at this point to examine the performance of the cell on the mass spectrometer. However, during this test, it was discovered that the pumping speed through the bypass valve on the mass spectrometer inlet system had decreased by a factor of two from previously measured values and, accordingly, values for water and carbon dioxide were higher than normal. Consequently, no valid conclusions about the CO cell performance could be obtained from this approach until the pumping speed problem could be corrected. At this point experiments with the palladium charcoal cell were terminated.

#### Experiments with Other Sorbents

Two new palladium sorbents were prepared and tested during the course of the experiments described above. These were 10% palladium chloride on Porasil A and 10% palladium chloride on Davisison Silica Gel-08.

Method of Preparation.- Two grams of  $\text{PdCl}_2$  from Research Inorganic Chemicals were dissolved in dilute hydrochloric acid. The solution was filtered and one-half was added to 10 grams of Porasil A and one-half to 10 grams of silica gel. The slurries were allowed to stand overnight, and were evaporated to dryness with low head under a slow stream of helium.

The palladium-chloride-Porasil A sorbent (2 to 6g) was packed in a 4 inch section of 3/8 inch x 0.065 inch stainless steel tubing. It was heated under helium slowly to a final temperature of 375°C. Evolution of hydrogen chloride was noted; heating was continued until no more HCl was evolved. The capability for retention of carbon monoxide was tested at a concentration of 100 ppm; approximately 500 microliters of carbon monoxide were sorbed. Carbon monoxide did not desorb from this cell at temperatures below 400°C.

The sorbent was heated with hydrogen at temperatures between 190 to 200°C for 25 minutes to reduce the palladium chloride. Retention of carbon monoxide increased to 3500 microliters. However, the desorption temperatures were still higher than 400°C. In the next experiment the sorbent saturated at about 900 microliters of CO, and again CO recovery only occurred at temperatures in excess of 400°C. It was suspected at this point that the apparent evolution of carbon monoxide at temperatures above 400°C was due to decomposition of the iodine pentoxide by the hot argon coming from the cell. When the experiment was repeated with a longer tube between the cell and the iodine pentoxide tube, only small amounts of carbon monoxide were recovered.

In these experiments, it was observed that each time carbon monoxide was sorbed less was taken up than in the previous experiment. However, with the limited data and the fact that carbon monoxide apparently cannot be desorbed from this sorbent, it is not certain that this is a significant observation.

Palladium Chloride on Silica Gel.- A cell containing 3.73 grams of this sorbent was prepared from a 4 inch section of stainless steel tubing (3/8 inch x 0.042 inch). Conditioning was carried out slowly with helium and sorption of carbon monoxide checked after conditioning at increasing temperatures. No sorption of CO was noted after conditioning up to temperatures of 325°C. After further conditioning at temperatures up to 415°C, the sorbent took up approximately 300 microliters of carbon monoxide. However, this CO was not desorbed up to temperatures of 450°C. The experiment was repeated with essentially the same result. Work with this sorbent was discontinued at this point.



## APPENDIX B

HEAT TRANSFER CALCULATIONS  
AND EXPERIMENTAL TESTS

The power required to heat the CO Accumulator Cell is calculated from the heat loss at steady state at the maximum temperature required for desorption. In these calculations that temperature is assumed to be 250°C. Various cell geometries are considered.

Heat losses from the cell occur in three ways: 1) radiation and convection from the cell; 2) conduction through and radiation and convection from the connecting sample lines; and 3) by carrier gas flow through the cell. The latter two mechanisms are assumed to be independent of the cell geometry.

The equation used to calculate the heat losses for cells of cylindrical geometry is:

$$Q = \frac{2\pi (T_c - T_a)}{\frac{1}{r_2 h} + \frac{1}{K} \log n \frac{r_2}{r_1}} \times L$$

Q = Total power required (cal/sec)

T<sub>c</sub> = Temperature of the cell (250°C)

T<sub>a</sub> = Ambient temperature 25°C

r<sub>2</sub> = Radius of the insulation (cm)

r<sub>1</sub> = Radius of the cell

h = Heat transfer coefficient from the surface of the insulation  
(cal/cm<sup>2</sup> sec °C)

K = Thermal conductivity of the insulation (cal/cm °C sec)

L = Length of the cell.

Heater power requirements calculated for various assumed values of the parameters are summarized in Table 10. These power requirements are for a cell of 1 cc volume. Two heat transfer coefficients were used in these calculations. The lower value, 1 x 10<sup>-3</sup> cal/cm<sup>2</sup> sec °C, is that measured for a 1/8 inch electropolished stainless steel tube; it compares relatively well with a value calculated for nichrome wire of the same diameter.

TABLE 10.- HEATER POWER REQUIREMENTS FOR ACCUMULATOR CELLS

| Cell Radius<br>(inches)              | Insulation<br>(inches) | <u>Tubes</u><br>Heater Power (watts/cm <sup>3</sup> ) |       |        |
|--------------------------------------|------------------------|---|-------|--------|
|                                      |                        | H = 5 x 10 <sup>-3</sup> cal/cm <sup>2</sup> sec      |       |        |
|                                      |                        | K = 0.001   | 0.002 | 0.0002 |
| 0.0625<br>(.056 cm <sup>3</sup> /cm) | 0.0725                 | 85.5  | 91.5  | 58     |
|                                      | 0.09                   | 85.5  | 100   | 39     |
|                                      | 0.125                  | 80  | 108   | 26     |
| 0.125<br>(.23 cm <sup>3</sup> /cm)   | 0.135                  | 38.6  | 41    | 26.2   |
|                                      | 0.180                  | 31.6  | 41    | 11.2   |
|                                      | 0.250                  | 25.6  | 38.4  | 6.55   |
| 0.1875<br>(.50 cm <sup>3</sup> /cm)  | 0.1975                 | 26.2  | 27.8  | 18.3   |
|                                      | 0.250                  | 19.6  | 25.7  | 6.75   |
|                                      | 0.375                  | 12.9  | 21.1  | 3.2    |

|        | Insulation<br>(inches) | <u>Tubes</u><br>Heater Power (watts/cm <sup>3</sup> ) |       |        |
|--------|------------------------|---|-------|--------|
|        |                        | H = 1 x 10 <sup>-3</sup> cal/cm <sup>2</sup> sec      |       |        |
|        |                        | K = 0.001   | 0.002 | 0.0002 |
| 0.0625 | 0.0725                 | 19  | 19.3  | 17.2   |
|        | 0.09                   | 22.3  | 23.2  | 17.7   |
|        | 0.125                  | 27.4  | 30.0  | 16.0   |
| 0.1875 | 0.1975                 | 5.65  | 5.85  | 5.3    |
|        | 0.250                  | 6.30  | 6.85  | 3.9    |
|        | 0.375                  | 6.80  | 8.3   | 2.6    |

TABLE 10. (Cont)

Flat Spiral (25 cm<sup>2</sup> surface area)

$$H = 1 \times 10^{-3} \text{ cal/cm}^2 \text{ sec}$$

|           |  |        |
|-----------|--|--------|
| K = 0.001 |  | 0.0002 |
| 11.8      |  | 3.92   |

Coiled Tube

$$H = 1 \times 10^{-3} \text{ cal/cm}^2 \text{ sec}$$

|           |  |        |
|-----------|--|--------|
| K = 0.001 |  | 0.0002 |
| 7.4       |  | 1.8    |

Calculations were also performed for a higher value of  $h$  to examine the effect of the magnitude of this parameter on power requirements. Several thermal conductivity values were used to test the effect of this parameter on heat losses quantitatively. The lowest value of thermal conductivity is that for glass wool at a density of 0.064 gm/cc.

Two other geometries were considered in these calculations. One cell was a 1/8 inch tube coiled in a flat spiral of 1 inch radius, which is heated between two plates insulated on the outside. The other cell was a coil of 1/8 inch tubing with a 0.75 inch inside diameter. Heat is supplied by heater wire wrapped around the coil. The coil is insulated by various thicknesses of insulation. The center of the coil is packed with glass wool and it is assumed that heat losses occur only over the outside surface.

The results in Table 10 show that, as expected, heater power requirements are lowest for the geometry which has minimum surface area per unit volume. It is interesting to note, from Table 10, that for  $h = 1 \times 10^{-3}$  cal/cm<sup>2</sup> sec, in cases where  $K$  is high (0.001, 0.002), the heat loss actually increases as the thickness of the insulation increases. For the 1/8 inch OD tube, heating powers are lower with no insulation, unless the insulation has very low conductivity. This arises from the fact that: if  $r_1 \frac{h}{K} < 1$ , the heat flow has a maximum at  $r_2 = \frac{h}{K}$ ; if  $r_1 \frac{h}{K} > 1$ , the heat

flow steadily decreases as  $r_2$  increases. The smaller the diameter of the tubing, therefore, the lower must be the thermal conductivity of the insulation in order to decrease the heat losses by insulating the tube<sup>1</sup>.

The cooling time increases as the insulation increases. Calculated curves are shown in Figure 34a for two different cells and test results are shown in Figure 34b through 34g.

The power required to heat argon carrier gas is calculated to be  $3.0 \times 10^{-3}$  watts/cc/min. At a flow rate of 5 cc/min, this is equivalent to 0.015 watts, which is small in comparison to that required for the cell.

Heat losses by conduction through the gas sample tubes were calculated to be 0.73 watts for two tubes 1/16 inch in diameter. This value is calculated on the basis that the temperature will drop to the ambient value (25°C) in a 1 centimeter length. (This is estimated on the basis of a heat transfer coefficient of  $12 \times 10^{-3}$  cal/cm<sup>2</sup> sec; for a heat transfer coefficient lower by a factor of 10, the length to cool to 25°C increases but the net heat loss decreases by a factor of three.)

From these calculations, it is apparent that the power requirements are least for shorter cells.

#### Experimental Evaluation of Heater Power Requirements

Some experiments were performed to evaluate the power requirements for heating the cell; these are summarized as follows:

- a. The power required to heat an uninsulated stainless steel tube six inches in length (1/8 inch OD x 0.010 inch wall) containing palladium charcoal sorbent to 255°C at the center point of the tube is 14.2 watts. A temperature gradient of about 100°C exists between the ends of the tube and the center.
- b. Using an aluminum reflector reduces the power requirements to 11.2 watts.
- c. With glass wool insulation between the cell and the aluminum sheath reduces the power required to 8.1 watts. The temperature gradient between the center and the ends of the tube is about 70°C.

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<sup>1</sup> Ref: Carslaw and Jaeger, Conduction of Heat in Solids, Oxford University Press, 2nd Edition 1959.

- d. With argon flowing through the cell, there is an increase in power required to 9.5 watts to maintain a temperature of 255°C at the center of the tube. This power requirement is independent of the flow rate of argon, and since there is a substantial temperature gradient on the end of the tube to which the argon supply is attached, it is concluded that the increased power required is due to losses to the argon supply lines and Swagelok connections. The end losses to these lines appears to be higher than simple heat transfer calculations indicate.
- e. One further test was performed on a spiral coiled tube of the same dimensions. This tube was wrapped with glasswool to an outside diameter of 1.4 inches. Power required to heat the packed section to 250°C was 4.7 watts. Nine minutes are required to heat the cell from room temperature to 250°C. The temperature gradient in the packed section was about 10°C; the cooling time was approximately 20 minutes.

The coiled geometry which minimizes the surface heat losses obviously represents the minimum power requirement. The experimentally measured value is within the range anticipated from the calculations described earlier. Further reduction in power requirements must come from minimizing the thermal conductivity of the insulation and losses from the surface of the insulation.

## APPENDIX C

DESIGN OF A TEST MODEL  
CARBON MONOXIDE ACCUMULATOR CELL

## Introduction

Carbon monoxide is to be determined using an accumulator cell to increase its effective concentration in the gas sample analyzed by the mass spectrometer. This project note contains a discussion of the factors involved in the determination of carbon monoxide by this technique and a description of two systems to be evaluated by experimental tests.

The original accumulator cell for carbon monoxide was developed during the Laboratory Contaminant Sensor studies. This unit was operated under vacuum desorption conditions. Subsequently, the possibility of operating the cell in conjunction with Two Gas Sensor was considered in order to permit the major components of the atmosphere and carbon monoxide to be determined with a single system. This change in the mode of operation affects the sensitivity with which carbon monoxide can be determined. The extent of this effect cannot be evaluated from the existing data on the sorbent characteristics. Therefore, in this design note both vacuum and non-vacuum modes of operation are considered and two system designs are proposed for test.

The end objective of this program is to develop an automated instrument which can meet the weight and power constraints imposed for space instrumentation and provide adequate sensitivity for the detection of carbon monoxide. To meet this objective, it is necessary to obtain additional information about the physical-chemical characteristics of the sorbent and to evaluate whether the desired sensitivity can be achieved in a system designed also to monitor major components of the atmosphere. The test system to be described is designed to give more information about the characteristics of the sorbent by observing its performance under a change of variables and at the same time to move in the direction of reducing the system size to a value which is in the range of that which may be considered for flight instrumentation. The translation of the system from vacuum operation to atmospheric pressure operation is considered in the analysis, and an alternate system design based on atmospheric operation is described.

## System Function

The CO accumulator cell system must perform the following functions:

- a. Sample the air for carbon monoxide.
- b. Separate organics from the sample prior to sorption of carbon monoxide.

- c. Remove residual air from the system prior to heating the carbon monoxide sorbent.
- d. Heat the sorbent to desorb carbon monoxide.
- e. Provide a means to detect the carbon monoxide and quantitatively relate the detector signal to the concentration of carbon monoxide in the sample.
- f. Repeat the analysis at stated intervals.

Sampling the air on a sorbent which is to sorb carbon monoxide requires that the air come into good contact with the sorbent. This is generally most effectively accomplished by forcing the air to flow through a packed bed of the sorbent.

The sorbent which is used to retain carbon monoxide also has good retention properties for many organics and these must be removed from the sample prior to sorption of carbon monoxide to avoid interference in mass spectra at  $m/e$  28. This is accomplished by first passing the air through a scrubber sorbent, which will selectively remove organics, and then through the carbon monoxide sorption cell.

Since the carbon monoxide is to be detected with mass spectrometers, it is essential to remove most of the air from the system before desorbing the carbon monoxide. This can be accomplished by either pumping air off with a vacuum pump or by flushing the system with some other inert gas. Neither of these techniques affords a perfect separation - but it is only necessary to reduce the nitrogen content to a low level above which the carbon monoxide can be detected. The oxygen content should also be reduced to avoid interfering reactions between oxygen and carbon which may occur at higher temperatures in the range of the desorptive temperature.

The sorbent is heated to desorb the carbon monoxide. The pressure of carbon monoxide which results in heating the system is determined by the physical-chemical properties of the sorbent, by the amount of sorbent in the system and the volume of the system, and also by the mode of operation of the system. The effects of these factors on system sensitivity are evaluated in the following section on system analysis. The power requirements for heating the cell are an important consideration in the design of a flight system. Until more experience is obtained with the smaller systems, the tradeoffs in sensitivity versus power requirements cannot be realistically evaluated.

The mass spectrometer is used to measure the pressure of carbon monoxide on desorption, and this pressure must be related to the concentration of carbon monoxide in the original sample. In the Laboratory Contaminant Sensor

study, the pressure at the peak of the desorption curve was used as a measure of the original carbon monoxide concentration. Background levels due to residual nitrogen were subtracted for this purpose. For a flight system, it will be simpler to use the pressure measured at some predetermined temperature during desorption. If the nitrogen level is relatively stable from one analysis to another, the predetermined level can be simply subtracted from the m/e 28 peak at the selected temperature. Such a measurement would also simplify the electronics involved in presenting the analytical result for a flight system.

The analysis of carbon monoxide and determination of the major atmospheric components is scheduled to take place on a definite cycle. The system tentatively assumed would measure the major atmospheric components continuously for a given time period during which carbon monoxide is sampled from the air. At the end of that interval, the carbon monoxide measurement would start with either purge gas flow through the cell or vacuum pump to remove the residual air. Next, the sorbent cell would be heated and, at some temperature, the carbon monoxide pressure would be recorded as an indication of the concentration in the atmosphere. Then the cell would be allowed to cool and the cycle would be repeated. The flight system design must repeat this cycle continuously. The test system design has as one of its objectives the evaluation of components and the simplification of operations to the point where automation of the device can be undertaken in the next design phase.

#### Analysis of the System

The analysis of the system begins with consideration of the pressures required at the mass spectrometer inlet leak to yield a detectable signal for the minimum concentration of carbon monoxide. The design of a system to furnish the required pressure is considered, and equations are derived to relate the variables which control the desorption pressure. Unfortunately, the available quantitative data is limited and the effects of some of the parameters can only be estimated at present. The test system for this program is designed on the basis of assumptions for some of these quantities.

Background Factors.- Signal requirements are considered for two systems: the cycloidal focusing mass spectrometer which will be used in the actual test program, and the Mass Spectrometer Atmosphere Sensor which will be used in the flight system.

The primary consideration involved in evaluating signal requirements is the background in the instrument or system used to detect carbon monoxide. This can be regarded as the signal which would result from an air sample



which does not contain any carbon monoxide. This background consists of three elements:

- 1) The noise or drift level in the detector,
- 2) The instrument background at m/e 28, and
- 3) The system background at m/e 28.

In the cycloidal focussing instrument these components are readily identified. The noise level is about six divisions equivalent to an inlet system pressure of 0.006 microns. (One division corresponds to an ion current of  $10^{-16}$  amperes. With the leak used for contaminant analysis, the instrument has a sensitivity of 1000 divisions/micron of nitrogen in the inlet system.) The background in the analyzer is of the order of 300 divisions or 0.3 micron. When the Laboratory Contaminant System (LCS) is operated in the usual desorption mode, the background from the cell and the inlet system from a sample of air containing no carbon monoxide is of the order of 1000 divisions. This corresponds to a pressure of 1.0 micron at m/e 28 and represents the background which the carbon monoxide signal must exceed in order to be detectable in the existing LCS instrumentation. When the desorption mode or system geometry is changed, the background level will change and should be evaluated for that system. Anticipated levels of nitrogen are calculated for the test system in a later section.

For the Atmospheric Sensor Mass Spectrometer, the noise level is less significant than the drift level, which is assumed to be of the order of 10 mV for the highest feedback resistor,  $1 \times 10^{12}$  ohms. This corresponds to an ion current of  $10^{-14}$  amperes. At a source sensitivity of  $2.5 \times 10^{-6}$  amps/torr with an inlet leak conductance of  $1 \times 10^{-5}$  cc/sec and a nominal source conductance of 40 cc/sec; this is equivalent to an inlet pressure of 16 microns which is negligible in comparison with the background. The background at m/e 28 is of the order of  $2.5 \times 10^{-13}$  amperes, which is equivalent to 0.4 torr at the leak for a leak conductance of  $10^{-5}$  cc/sec. If a lower leak conductance is used, of the same order as that used in the cycloidal instrument, this background value will correspond to a lower inlet system pressure. For a 0.2 cc/sec leak, this pressure is 0.2 micron.

Thus, if the Two Gas Sensor were used with the existing operating system, the background would be predominantly that due to the sorbent cell. However, if it is a requirement to measure the partial pressure of the atmospheric components with the same instrument, it will be necessary to establish from the mode of operation whether the cell background or the instrument background is the limiting factor. The same considerations apply to the cycloidal instrument. If the leak conductance is decreased, so that the instrument can sample at atmospheric pressure, the background pressure

of nitrogen in the analyzer will correspond to a higher inlet system pressure. Assuming that the cell background of 1 micron remains constant, the pressure of carbon monoxide that can just be detected would increase to a value about equivalent to that of the Two Gas Sensor.

One further consideration is involved in establishing the desorption pressure of carbon monoxide necessary to detect a minimum concentration: this is the stability of the controlling or predominant background level. Thus, if the mass spectrometer background of 0.4 torr is the major background component and it is stable within +10%, a carbon monoxide pressure equivalent to about 30% of background or 0.15 torr would be detectable, with some uncertainty in the actual value. If both the MS background and the cell background contribute to the overall background, the total variation in the two will be the determining factor for the carbon monoxide level. Thus, it is not only the background level, but also the variation in the background that will affect the minimum detectable concentration of carbon monoxide.

In summary, if a high conductance leak is used, it appears that the limiting factor in determining the detectable limits for carbon monoxide will be the cell background that can be achieved in the test system. If a low conductance leak ( $10^{-5}$  cc/sec) is used, the limiting factor may be the mass spectrometer background. At present, it appears that the desorption pressure from the system must exceed approximately 0.5 torr in order to be detectable with the low conductance or atmospheric leak.

Pressure in Relation to Cell Operation.- The CO accumulator cell system and its mode of operation must be capable of delivering a partial pressure in excess of the background. From the preceding discussion minimum background levels for the instruments are:

- 1) Cycloidal instrument with 0.2 cc/sec leak 0.3  $\mu$
- 2) Cycloidal instrument with  $10^{-5}$  cc/sec leak 0.6 torr
- 3) Two Gas Sensor with  $10^{-5}$  cc/sec leak 0.4 torr

The background levels of nitrogen from the cell must be evaluated and compared to the mass spectrometer background to determine the actual carbon monoxide pressure required to be detectable. Before evaluation of these background levels, the calculation of the pressure that will result from a given sample of carbon monoxide will be considered.

An equation for the pressure of carbon monoxide on desorption can be derived in the following manner. Assuming a linear adsorption isotherm, an equilibrium constant is defined according to the following equation:

$$K = \frac{P}{c_s}$$

in which  $K$  is the equilibrium constant defined in units of grams/cc.

$p$  is the partial pressure of carbon monoxide (units of atm.-cc/cc of volume)

$c_s$  is the concentration on the sorbent (units of atm.-cc/gm)

The total amount of carbon monoxide in the system is given by:

$$N_o = p_o V + C_s W \quad V_s = \text{volume of the system}$$

$$N_o = \text{atm. cc of CO} \quad W_s = \text{weight of sorbent in the system}$$

Substituting for  $C_s$

$$N_o = p_o \left( V + \frac{W}{K} \right).$$

If no carbon monoxide is removed from the system, the pressure at some higher temperature is given by

$$p_T = \frac{p_o \left( V + \frac{W}{K_o} \right) \frac{T}{T_o}}{\left( V + \frac{W}{K_T} \right)}$$

in which

$K_o$  = equilibrium constant for the temperature,  $T_o$ , at which CO was sorbed

$K_T$  = equilibrium constant at the temperature  $T$ . The term,  $W/K$ , can be regarded as a volume term, but this volume is a variable with temperature.

$K_T$  is related to  $K_o$  by the following expression:

$$K_T = K_o \exp \left[ \frac{-\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_o} \right) \right]$$

$\Delta H$  = heat of desorption (cal/gm-mole)

$R$  = gas constant (cal/gm-mole °K)

If the volume of the system is small relative to  $W/K$ , the expression above can be simplified to give:

$$p_T = p_o \frac{K_T}{K_o} \left( \frac{T}{T_o} \right) = p_o \frac{T}{T_o} \exp \left[ \frac{-\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_o} \right) \right]$$

For example  $\Delta H$  is taken as 10 kcal mole, this expression yields at 180°C

$$\frac{p_{180}}{p_o} = \left( \frac{453}{298} \right) \exp \left[ \frac{-10,000}{1.986} \left( \frac{1}{453} - \frac{1}{298} \right) \right] = 466$$

If  $p_o = 1 \times 10^{-6}$  atm, corresponding to the equilibrium pressure for sorbent saturated with CO at 1 ppm concentration

$$p_{180} = 466 \times 1 \times 10^{-6} \text{ atm} = 354 \text{ microns}$$

Ignoring for the moment the background due to residual nitrogen in the cell, it is fairly obvious, that the one part per million level would be detectable in system (1), the cycloidal instrument with the high conductance leak, but would be marginal in the other two systems with atmospheric leaks of low conductance.

If  $\Delta H$  is lower by 20%, or  $\Delta H = 8$  kcal/mole, the pressure ratio decreases from 466 to 129, and the pressure for  $p_o = 1 \times 10^{-6}$  atm is 98 microns, which should be detectable in system (1) but is well below the background levels for the instruments with low conductance leaks. The uncertainty in the value of heat of desorption,  $\Delta H$ , is one reason for preferring the vacuum operated system, which has high sensitivity for the sorbed gases.

This relationship above holds independent of the actual value of  $K_o$  as long as the assumption that  $V$  is negligible with respect to  $W/K$  is valid. For an idealized system, the smallest volume that can be obtained is just that which is associated with the packed bed of sorbent. For charcoal this may be as high as 2 cc/gm if the pore volume is considered, or as low as 1 cc/gm if only the free gas volume is included.

Rearranging the equation above, gives

$$p_T = p_o \frac{\left( \frac{V}{W} + \frac{1}{K_o} \right) \frac{T}{T_{180}}}{\left( \frac{V}{W} + \frac{1}{K_T} \right)}$$

If the limiting value of  $V/W$  is taken as 2, the assumption will be valid as long as

$$\frac{1}{K_T} \gg 2 \quad \text{or} \quad K_T \ll 0.5$$

In the actual system to be tested, there will be additional free gas volume associated with the valves and the leak. The ratio of desorption pressure to initial pressure is given by

$$\frac{P_T}{P_o} = \frac{\left(V + \frac{W}{K_o}\right) \frac{1}{T_o}}{\left(V + \frac{W}{K_T}\right) \frac{1}{T} + \frac{V_S}{T_o}} = \frac{\left(\frac{V}{W} + \frac{1}{K_o}\right)}{\left(\frac{V}{W} + \frac{1}{K_T}\right) \frac{T_o}{T} + \frac{V_S}{W}}$$

( $V_S$  = volume associated with system other than the sorbent.)

assuming that only the cell volume is heated.

Using the values cited above for  $K_o$ , and assuming

$$\frac{V}{W} = 2$$

$$\frac{V_S}{W} = 2$$

$$\frac{P_T}{P_o} = \frac{(2 + 10^{+5})}{(2 + 322) \left(\frac{298}{453}\right) + 2} = 466$$

which is the same as the values cited above. As long as  $\frac{V_S}{W}$  is small in comparison to  $\left(\frac{V}{W} + \frac{1}{K_T}\right) \left(\frac{T_o}{T}\right)$ , the effect of  $V_S$  on the final pressure will be negligible.

The term  $V_S/W$  will become important if either the value of  $K_T$  is larger than has been assumed in these examples or the weight of sorbent is reduced. For example if  $K_T$  is higher by a factor of 100 or the weight

of sorbent is lower by a factor of 100 and  $\Delta H$  is assumed to have the same value

$$\frac{P_T}{P_O} = \frac{(2 + 10^3)}{(2 + 3.22) \left(\frac{298}{453}\right) + 2} = 184$$

In summary, it should be emphasized that at present, the values of the equilibrium constant are not known. The equation indicates, therefore, that conservative design would allow for the possibility that the K values may be small and the maximum desorption pressure will be obtained by increasing the weight of the sorbent in the system while minimizing the volume associated with the system. The weight of sorbent in the system will be a factor in the heating power requirements, and therefore it cannot be increased indefinitely. The ratio of the desorption pressure to the initial pressure can also be increased by measuring desorption at a higher temperature. There is a limit to this temperature, however, because the reaction of residual oxygen with charcoal begins to be significant at temperatures of about 240°C. On the basis of present knowledge, the desorption temperature should be restricted to about 200°C.

Removal of Nitrogen from the Cell.- Residual air in the system must be removed prior to measurement of the carbon monoxide pressure to avoid interference from nitrogen and to minimize oxygen reactions with the sorbent to produce carbon monoxide. Two methods are considered: one, to be used with an atmospheric (low-conductance) leak, involves purging the system with argon; the other, to be used for vacuum operation, involves a vacuum pre-cut, which also serves to reduce the total pressure in front of the leak. Two factors need to be determined: one is the amount of purge gas or pre-cut time necessary to reduce the nitrogen level to a value comparable with the mass spectrometer background level, and the other is the loss of carbon monoxide which may result from the removal of nitrogen.

For example, in the Atmospheric Sensor Mass Spectrometer, there is an existing background which is approximately equivalent to 0.4 torr of nitrogen. The sorbent nitrogen background should be maintained at or below this level at the desorption temperature of carbon monoxide. The background level of nitrogen for the cycloid instrument is equivalent to 0.3 micron; but since the sensitivity is high for this instrument, it may be possible to tolerate a higher nitrogen background from the cell as long as it is only a small fraction of the anticipated CO level.

The nitrogen pressure in the system is determined by the residual nitrogen content after the precut or purge operation. Assuming that all the nitrogen is in the gas phase at the carbon monoxide desorption temperature, its pressure at 180°C is related to the residual pressure at room temperature by

$$P_{N_2}(180) = \frac{450}{300} P_{N_2} (25) \left( \frac{V + \frac{W}{K_{N_2}}}{V} \right)$$

Data in Dushman\*, indicates that  $K_{N_2}$  is of the order of 0.125 gm/cc at 15°C.

In order to have a final nitrogen pressure of 0.4 torr, the pressure of nitrogen in the system must be reduced to

$$P_{N_2,25} = 0.4 \text{ torr} \left( \frac{300}{450} \right) \frac{2}{2 + \frac{1}{.125}} = 0.053 \text{ torr at room temperature.}$$

For the purge gas system, the removal rate is given by

$$\frac{dp}{dt} = \frac{-F p_c}{V + \frac{W}{K_c}}$$

where:  $F$  is the flow rate of purge gas through the cell,

$K_c$  is the equilibrium constant for the component at ambient temperature, and  $p_c$  is the partial pressure due to that component.

Integrating

$$\ln \frac{p_c}{p_{o,c}} = \frac{-Ft}{V + \frac{W}{K_c}}$$

---

\*Saul Dushman and J.M. Lafferty, Scientific Foundation of Vacuum Technique, 2nd Edition, John Wiley and Sons, Inc. New York 1962

Taking the value of  $K_C$  for nitrogen on charcoal,  $K_C = 0.125$ , the amount of purge gas (Ft) required to reduce the partial pressure from 1 atm to 0.053 torr

$$\begin{aligned} Ft &= \left( 2 + \frac{1}{0.125} \right) \ln \frac{760}{.053} \\ &= 96 \text{ cc (per gram of sorbent)} \end{aligned}$$

The amount of carbon monoxide lost is given by

$$N_{CO \text{ lost}} \text{ (atm-cc)} = p_o \left[ v + \frac{W}{K_{CO}} \right] \left[ 1 - \exp \left( \frac{-Ft}{v + \frac{W}{K_{CO}}} \right) \right]$$

The percentage lost is in this example

$$1 - \exp \left[ \frac{-96}{2 + \frac{1}{10^{-5}}} \right] \sim 0 \text{ if } K_W \text{ is again}$$

assumed to be  $10^{-5}$  gm/cc. For  $K_{CO}$  a factor of 100 higher, the loss increases to about 10%. The amount of carbon monoxide lost from the sorbent is not dependent on the design of the system, but is mainly a function of the relative retention of air and carbon monoxide on the sorbent.

For a vacuum precut, which would be used for system (1) operating with the high conductance leak, the nitrogen level does not necessarily have to be reduced to a level comparable to the effective background level of  $0.3 \mu$ . Since the anticipated signal is much larger, if none of the gas is pumped out during heating the sorbent, the nitrogen level could be reasonably set at 10% of the anticipated signal level, or about  $35 \mu$  for  $\Delta H$  assumed 10 Kcal/mole. Under this assumption the level required for the final nitrogen pressure after precut is

$$P_{N_2} = 35 \mu \left( \frac{300}{450} \right) \cdot \left( \frac{2}{2 + \frac{1}{0.125}} \right) = 4.7 \mu$$

For viscous flow out of the system,

$$\left( v + \frac{W}{K} \right) \frac{dp}{dt} = C_S \left( p^2 - p_o^2 \right)$$



Or if  $p_o^2 \ll p^2$

$$\frac{1}{p_f} - \frac{1}{p_i} = \frac{C_S t}{V + \frac{W}{K}}$$

If  $C_S$  is of the order of  $12 \times 10^{-3}$  cc/min- $\mu$ , as may be the case for the proposed system, it would require three hours to reduce the pressure to this level at room temperature. An estimate of the loss of carbon monoxide during this period is made by first calculating the loss during an initial pressure drop when the effective conductance is high and then during the second interval when the conductance is relatively low. Thus, for the system pressure to drop from 1 atmosphere to 200 microns requires about 4 minutes. The carbon monoxide loss is calculated from

$$-\frac{d p_{CO}}{dt} = \frac{c p_{ave} p_{CO}}{V + \frac{W}{K_{CO}}}$$

where  $p_{ave}$  represents the average total pressure in the system.

In a 4 minute interval, approximately 20% of the carbon monoxide would be lost. During the next 176 minutes, the average conductance is much lower, and the total amount of carbon monoxide lost is less than 1 percent of that remaining.

One other factor which may affect the rate at which nitrogen is removed during the precut is the water content of the gas sample. Assuming a relatively high water content comparable to that which has been observed in the LCS studies, the final conductance out of the system is controlled more by the water desorption rate. Typically in precutting samples for the LCS studies, a final pressure of about 100 to 300 microns was obtained. Using this pressure, the precut operation for air may be controlled by the total pressure down to about 100 microns.

$$\left(V + \frac{W}{K}\right) \frac{dp_{N_2}}{dt} = -C P_T P_{N_2}$$

where  $C$  is the usual geometric factor.

Assuming a pressure of 200  $\mu$  for illustration, the time required to reach this pressure would be

$$\frac{1}{200} - \frac{1}{76000} = \frac{12 \times 10^{-3}}{10} t$$

or  $t = 4$  minutes.

With a constant pressure of 200  $\mu$  from the water desorption rate, the time to reduce the nitrogen from 200 microns to 4.7 microns is

$$t = 12 \times 10^{-3} \times 200 \ln \frac{200}{4.7}$$

$t = 9$  minutes

The total time in this case is much lower than that expected for pure viscous conductance of the single component. In actual practice the transition pressure may occur at some other value, either higher or lower depending on the water content and other factors such as the system leakage rate and the flow characteristics through the sorbent. The important feature for the test system design is that the conductance for the precut flow pattern should be as high as possible in order to minimize this time.

System Operation.- The test system to be fabricated for this contract is basically designed to be operated under vacuum with a precut operation. The selection of this system is governed by the consideration that it affords a higher sensitivity for studying the system parameters which affect the carbon monoxide pressure on desorption. In effect, the mass spectrometer will see more of the gases retained on the sorbent in a vacuum system, as compared to one operated with a high dilution of argon purge gas. If the results of the test program with a vacuum system indicate that nitrogen levels can be reduced low enough and that relatively high pressures of CO can be obtained on desorption, it should be possible to design a simpler system for purge gas operation.

The analysis presented in a previous section (entitled "Pressure in Relation to Cell Operation") for the desorption pressure of carbon monoxide, was based on two assumptions: 1) that the sorbent was saturated with carbon monoxide; and 2) that no carbon monoxide was removed from the system after the precut (or purge) operation.

The first of the above assumptions is not really necessary. The same result will be obtained if a higher concentration of carbon monoxide is used and the sorbent is not completely saturated with the higher concentration sample. The limiting detectability for carbon monoxide for the system

can only be realized, however, by saturating the sorbent. If the adsorption isotherm is linear as assumed, this is the best approach to operation of the sorbent. If the isotherm is non-linear, this fact will be reflected in the analysis of samples at different concentrations.

The second assumption is not realistic, at least for the vacuum operated test system. In practice, sampling and precutting air from the system must be carried out in a device that will permit stream switching from sample flow to the vacuum system and ultimately to the mass spectrometer system. The cell cannot conveniently be placed directly in series with the mass spectrometer leak, but must be connected to the leak with tubulation. The system must provide for a low flow of gas to transport the desorbed carbon monoxide to the leak. Consequently, the pressure of carbon monoxide will be lower than that attainable if no CO is removed while the sorbent is heated. If the heating rate is rapid compared to the gas flow rate, the loss of carbon monoxide will be minimized. The relationship which determines the loss of carbon monoxide that is lost from the system was derived in an earlier report. An approximate upper limit for the amount of carbon monoxide lost is given by

$$\Delta CO = p^2 C \frac{\Delta T}{\beta}$$

in which  $\Delta T$  is the temperature difference between the temperatures at which desorption pressure of CO is measured and the initial temperature

$\beta$  is the heating rate;

$C$  is a conductance calculated from the total pressure at the desorption temperature;

$p$  is the pressure of carbon monoxide at the desorption temperature.

With values for  $K_T$  assumed earlier and taking the measurement temperature as 180°C, this upper limit loss is estimated to be

$$\begin{aligned} \Delta CO &= (350 \mu)^2 \times 12 \times \frac{10^{-3} \text{ cc}}{\mu \text{ min}} \times \frac{155^\circ \text{C}}{10^\circ \text{C/min}} \\ &= 22.8 \times 10^3 \mu \text{cc.} \end{aligned}$$

The total amount of carbon monoxide sorbed was calculated to be (at 1 ppm)  $76 \times 10^3 \mu \text{cc}$ . This approximate upper limit to the amount lost is roughly one-third of the total sample. The loss can be restricted by reducing the conductance out of the system, but the conductance must be sufficiently high to maintain acceptable pressures at the mass spectrometer leak. A more complete analysis of the total available gas in the system

would permit a better estimate of the loss rate. The test system design and operation characteristics are designed to be flexible. The heating rate will be adjustable and the pumping rate out of the system will be controlled by a needle valve.

### The Test System

The system to be tested is designed to interface with the cycloidal focusing mass spectrometer and to be operated in either the vacuum mode or the argon purge mode. A schematic of the system is shown in Figure 35.

The system consists of two Carle 8-port, 2-position valves - one of which is connected to a flange which interfaces with the leak assembly of the mass spectrometer. The flow pattern for the valves is shown in Figure 1. When the instrument is operated in the vacuum mode the standard 0.15 cc/sec two-hole leak will be employed. A special sintered stainless steel leak with a conductance of  $1 \times 10^{-5}$  cc/sec will be fabricated for operation in the purge gas mode.

The Carle valves are chosen for this application because they are believed to have the smallest volume associated with the valving mechanism, they are best for leak-free operation under vacuum, and the material used in their construction should present the lowest background from outgassing. The sealing surfaces in the valves are optically flat, carbon-filled Teflon surfaces on stainless steel. The valve surfaces are held in contact by a spring-loaded ball; a torque of 0.4 ft-lbs is required to turn the valve 90°. American Electronics has a stepping motor which is adapted to actuate this valve through a 90:1 gear ratio. This motor requires 8 watts to operate.

The valves are equipped with 1/16 inch O.D. x 0.023 inch I.D. stainless steel tubes through which connections to the valve ports are made. For this system, the connection to the leak flange will be welded. Connections to the cell and to the tubes for the various lines will be made with Swagelok fittings.

In order to minimize the volume of the system, the cell to be tested will consist of a 4-turn coil of 1/8 inch x 0.010 inch wall stainless steel tubing which will contain 0.5 gm of the sorbent. This approach is taken because it will permit connections to the cell to be made with a minimum volume and flexibility in changing the cell size, if this should prove necessary. The heater power necessary to reach a final temperature of 250°C is estimated to be 5 watts. Heating power requirements for selected geometries are described in Appendix B.

Initial tests with this system will be performed in the vacuum mode of operation. This will permit a more direct comparison of the results with those obtained on the Laboratory Contaminant Sensor System and study of the sorbent performance. For these tests, connections will be made to the vacuum system through a 1/16 inch needle valve to restrict the gas flow past the mass spectrometer leak. This is required because the estimated conductance of the lines connecting the cell to the leak is relatively low - 16 cc/min. It may prove necessary to use a slower heating rate in order to simulate the results obtained on the earlier system. These tests, in conjunction with observations with the Monoxor, will furnish a basis for developing confidence that the sorbent is performing as required. It is planned, at the conclusion of these tests, to examine results obtained with the faster heating rate that would result from direct application of the power required to achieve a final temperature of 250°C. The results of these tests will serve to define the heater power requirements and the sensitivity to carbon monoxide under these conditions. They will also serve to establish leak rate for the valves.

System operation with argon purge gas will be performed after the vacuum study. The leaks will be interchanged and the necessary changes in the valve flow pattern effected. The first tests will be carried out with blank air samples (not containing carbon monoxide) to establish the background as m/e 28 for the system. If necessary, changes in the variables of operation, mainly the argon flow rate, will be investigated to minimize the nitrogen background. Once a minimum value is established, tests with carbon monoxide samples will be performed to establish the detectable limit in this mode of operation.

## ADDENDUM 1 TO APPENDIX C

## Valve Survey

Principal contacts in searching for valves for this purpose were with companies listed as manufacturing valves for gas chromatographs. Companies from whom literature was obtained are listed.

## Ideal Aerosmith, Chenenne, Wyoming

Makes a directional control valve of poppet design and "O" ring seals. Roller cam operated pushbutton actuator. These valves are available in 2-way, 2-port; 5-way, 2-port; 3-way, 3-port; and 4-way, 4-port design. They are available in aluminum, brass, and stainless steel at about \$20.00 for the most expensive (stainless steel) with actuators.

## Carle Valves, Fullerton, California

Directional Control Valves for gas chromatography. Sliding seals of ceramic filled Teflon. 8-port, 2-position valve. Many other porting arrangements available. Valves have reported leakage rates of  $10^{-4}$  cc per minute across 60 psia. These valves are highly recommended by most of the people, including vendors with whom the requirements were discussed. They are expensive - approximately \$300.00 each. Available with air actuation. Torque required for single valve is 0.4 ft. lb. (1.35 watts per ft. lb. per sec.)

## Energy Research and Generation, Inc.

This company has designed and presumably patented a small 2-position valve with a fluid actuation mechanism as well as some other normal types. These valves were proposed for the flight gas chromatograph-mass spectrometer combination. They are lightweight; the 2-position valve - the heaviest of the ones proposed - weighs less than 100 gms and requires 6 watts for 1 sec to operate. They can withstand operating temperatures to 200°C and have reported leakage rate of  $10^{-6}$  cc/sec He. Costs on these valves are high - last estimate \$2000 each.

## Perkin-Elmer

Perkin-Elmer, Norwalk, has a Precision Gas Sampling Valve for injection of gas samples into a gas chromo stream. This valve is a 6-port, 2-position valve. In the first position sample gas flows through a sample loop, whereas the carrier gas flows directly

to the column. In the second position, the carrier gas flows through the sample loop, carrying the sample gas into the column for analysis. Little information is available about this valve. It is an "O" ring sealed valve.

Perkin-Elmer, Norwalk, was - up until sometime last year - the sole agent for Biotron Gas Chromatograph valves. These SS valves have Rulon (cone-expanded Teflon) seals. Various flow switching patterns are available. Recent conversations with Dick Conden of P-E Norwalk indicate some distrust of the Biotron valves, and P-E, Norwalk, is no longer engaged in the licensing agreement with Biotron. In discussing our valves requirements, Mr. Conden strongly urges the use of Carle valves if we could afford the price. He said they were too expensive for P-E gas chromos, but they are the best available. They are currently negotiating with a German firm for valves. Mr. Conden knows of no other valve that he would recommend.

#### ASCO Solenoid Operated Valves

These valves, in general, do not have flow patterns suitable for the CO cell application. One model permits flow to be switched so that it goes through two ports instead of one but this will not answer our problem.

#### Circle Seal Valves, Anaheim, California

Circle Seal makes a valve to channel flow in two directions. This is a typical gas chromatograph flow pattern. These valves have an "O" ring seal on a cylindrical surface to prevent leakage between ports. A 2-stage valve is available that has acceptable flow patterns for this application. Although these valves are reported to be leak tight, it is questionable that they would be satisfactory for operation in an, MS inlet system. The valves are fairly large.

#### Norgren Fluidics, Littleton, Colorado

Flow selection valve which directs flow into one of three channels is unsuitable for application.

#### Veriflow

Flow control valves only.

## Republic Manufacturing Co., Cleveland, Ohio

This company manufactures a chromatography selector valve, a valve with a tapered Teflon plug which provides the sealing surface. No data on vacuum leakage was available from the local representative. (He recommended Carle valves for our application.) The stainless steel version weighs 2 1/2 pounds. "O" ring seals are utilized to eliminate leakage where tubular connections are made and at the ends of the Teflon plug. The double 4-way valves, which have the flow pattern necessary for the CO cell, cost \$108.00.

Hoke, Inc., Cresskill, N.J.

Flow control valve only.

Loenco, Mountain View, California.

Loenco employs a sliding plunger valve for their gas chromo gas sampling valves. These are, in general, 2-position multiport valves. Seals between ports and at the end of the valves are made with "O" rings. Loenco reports that the valves were vacuum tested with the helium leak detector for one application, and he says they did not leak; however, he cannot recall what the ultimate sensitivity of the leak detector was. While these valves could be adapted to the CO accumulator cell, the required plumbing is more complex and several separate valves are required.

Fluorocarbon Company, Anaheim, Calif.

Fluorocarbon makes a Teflon 3-way valve with either manual or solenoid operation. The valve body is made entirely of Teflon and is isolated from the solenoid actuator. Port seals are made with a Teflon diaphragm. The available 3-way valve weighs 2 pounds 13 ounces.

A number of companies manufacture flow switching valves for gas chromatographs. These are slider valves, similar to the Loenco valve; or rotary valves, like the Perkin-Elmer Biotron valve. In general, these valves have not the number of switching modes which are available with the Carle valve.



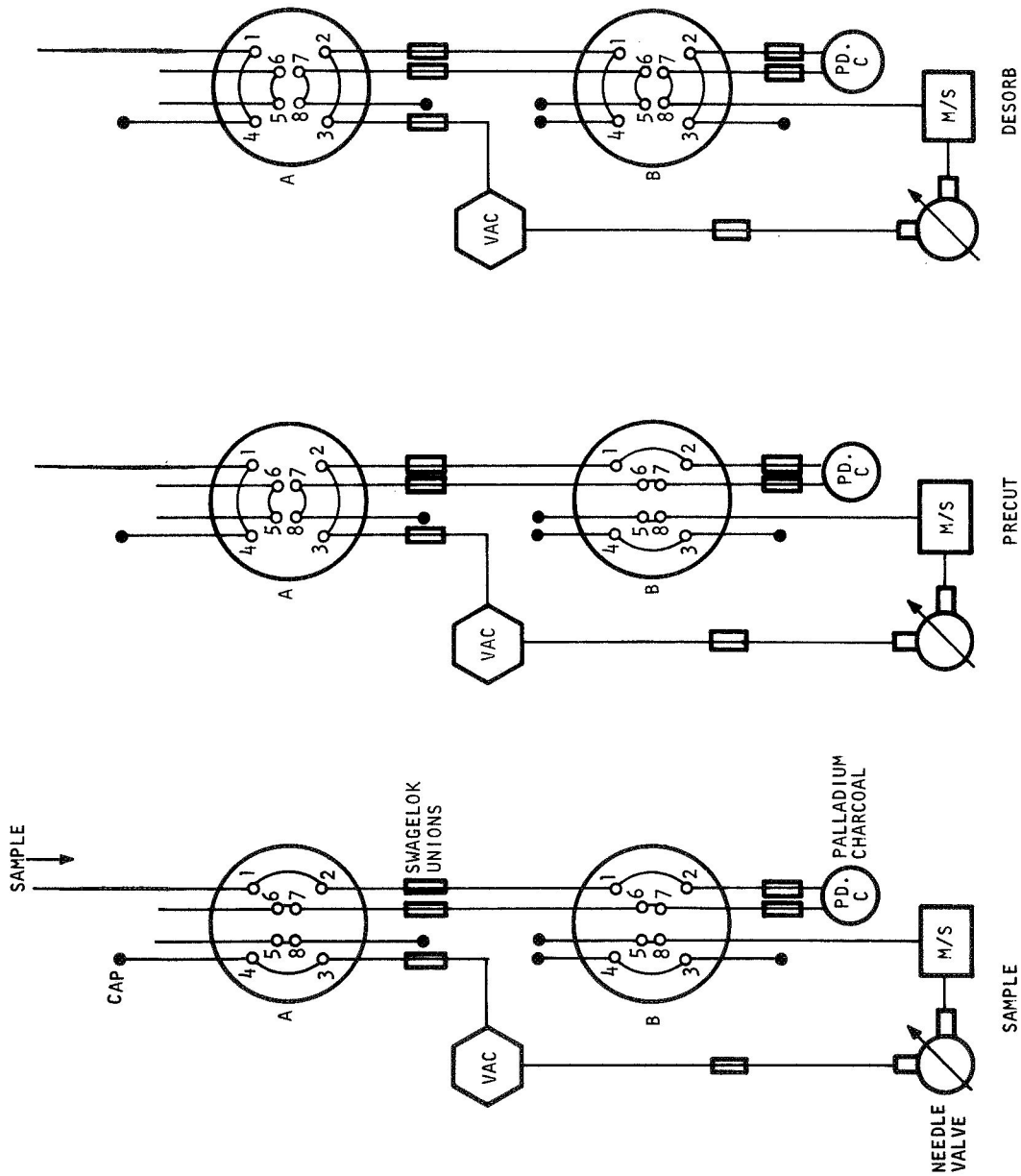


FIGURE 1.- Flow Diagram for Vacuum Operation

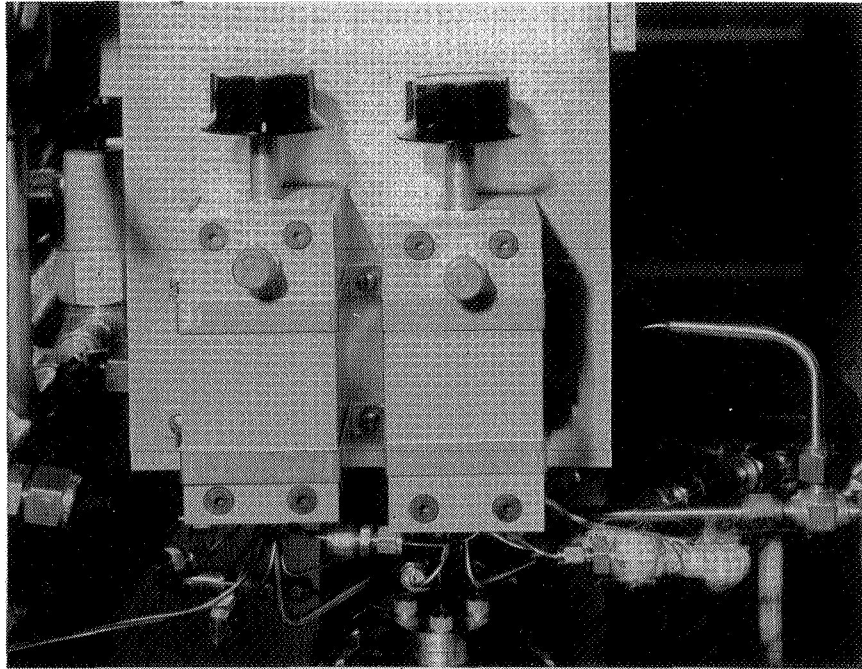


FIGURE 2.- Test Model

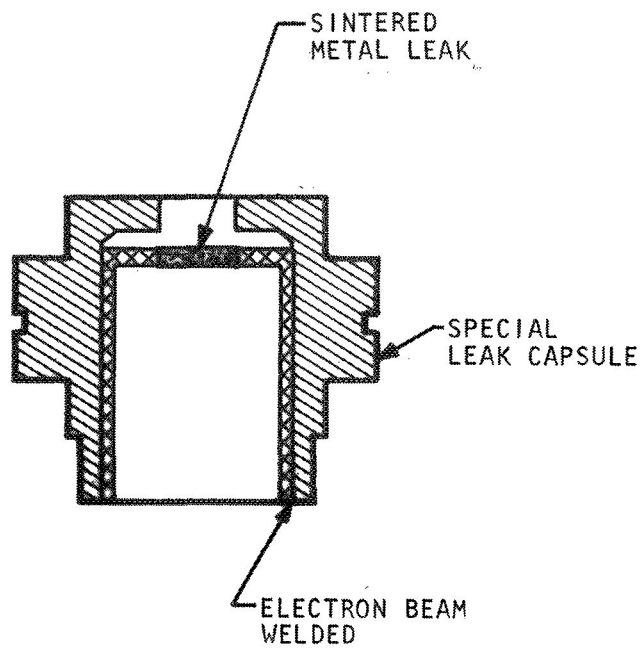


FIGURE 3.- Sintered Metal Low Conductance Leak and Assembly

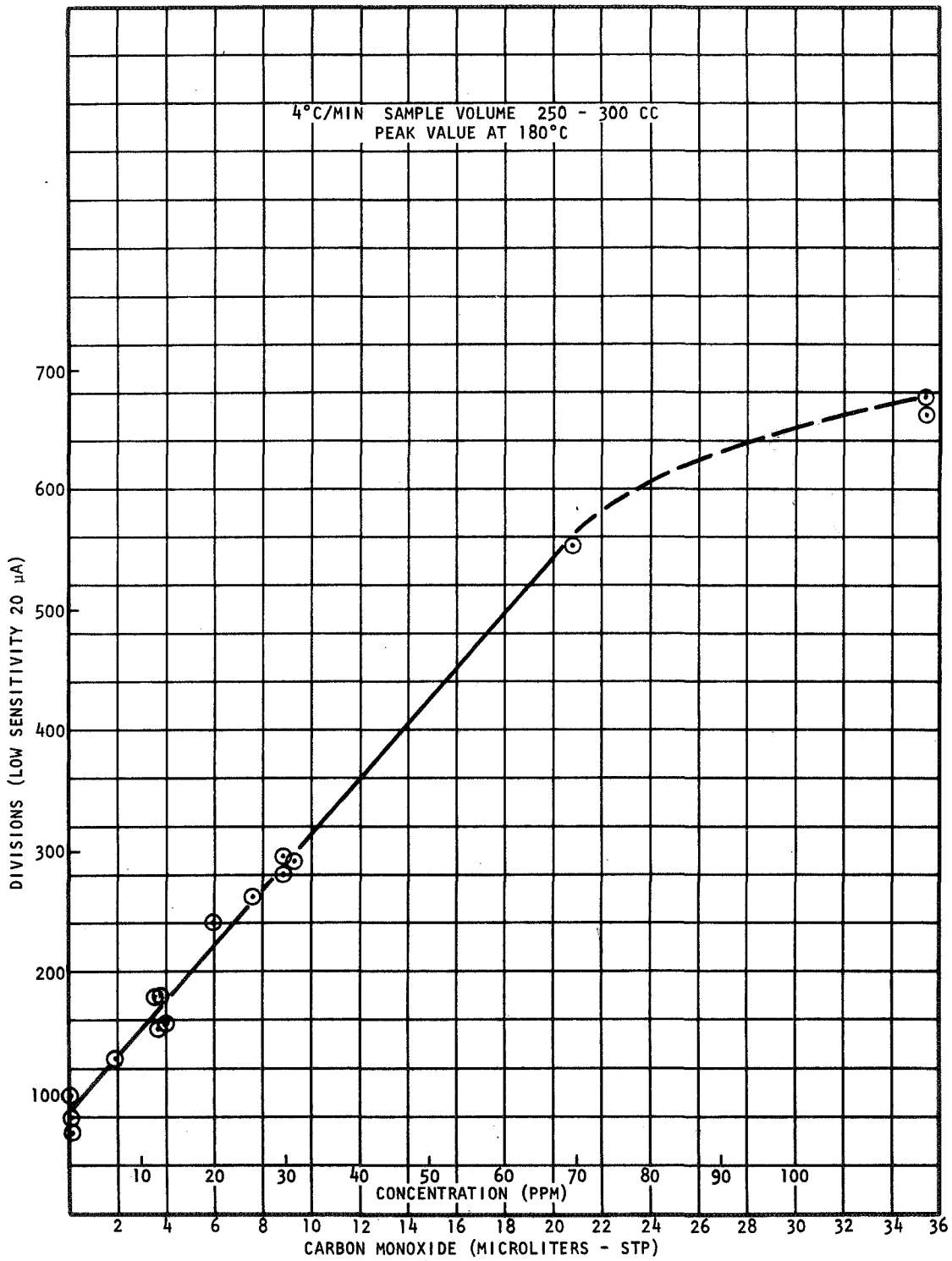


FIGURE 4.- Vacuum Desorption Results - Linear Temperature Program

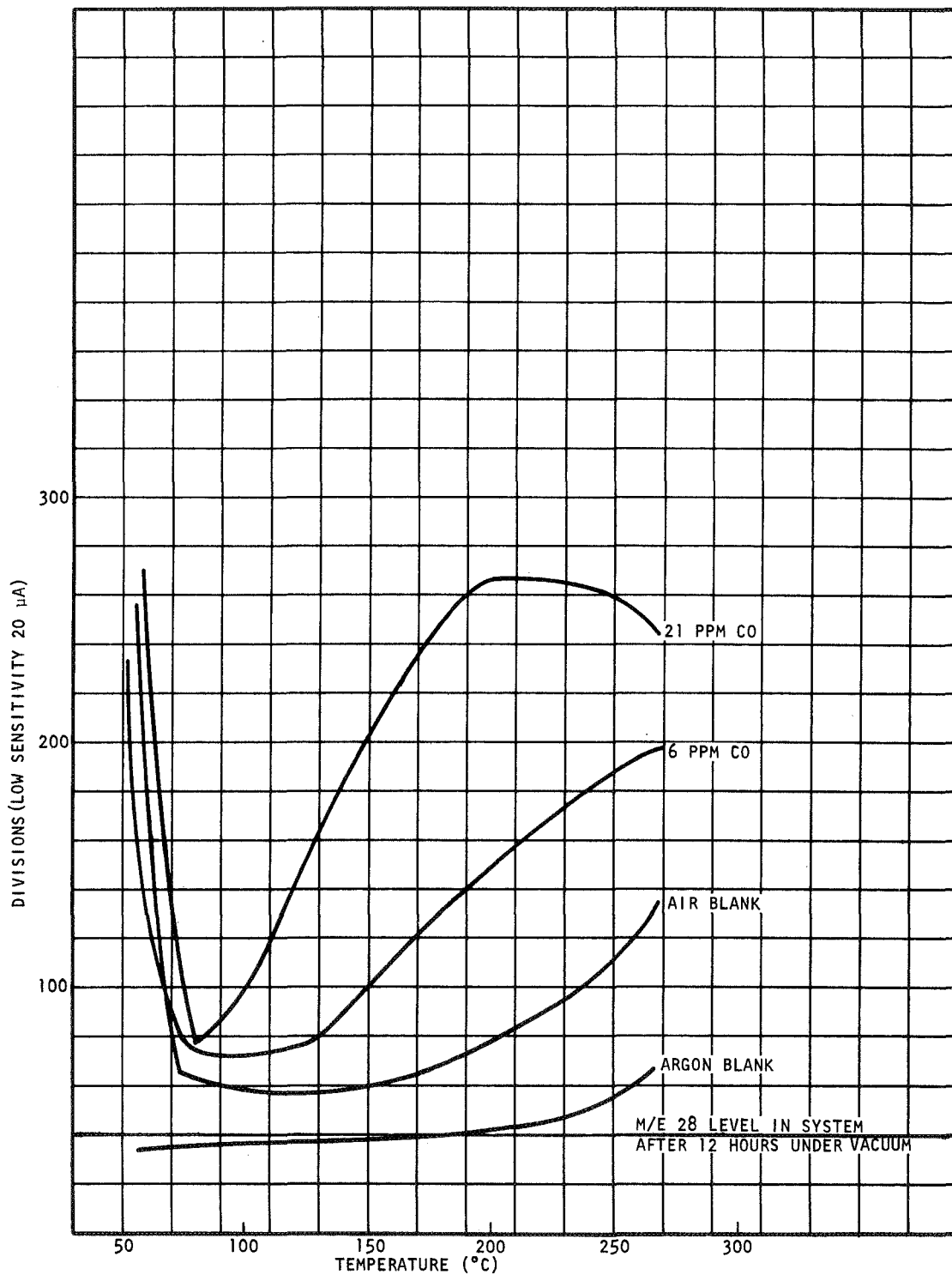


FIGURE 5.- Typical Desorption Curves - Linear Temperature Mode

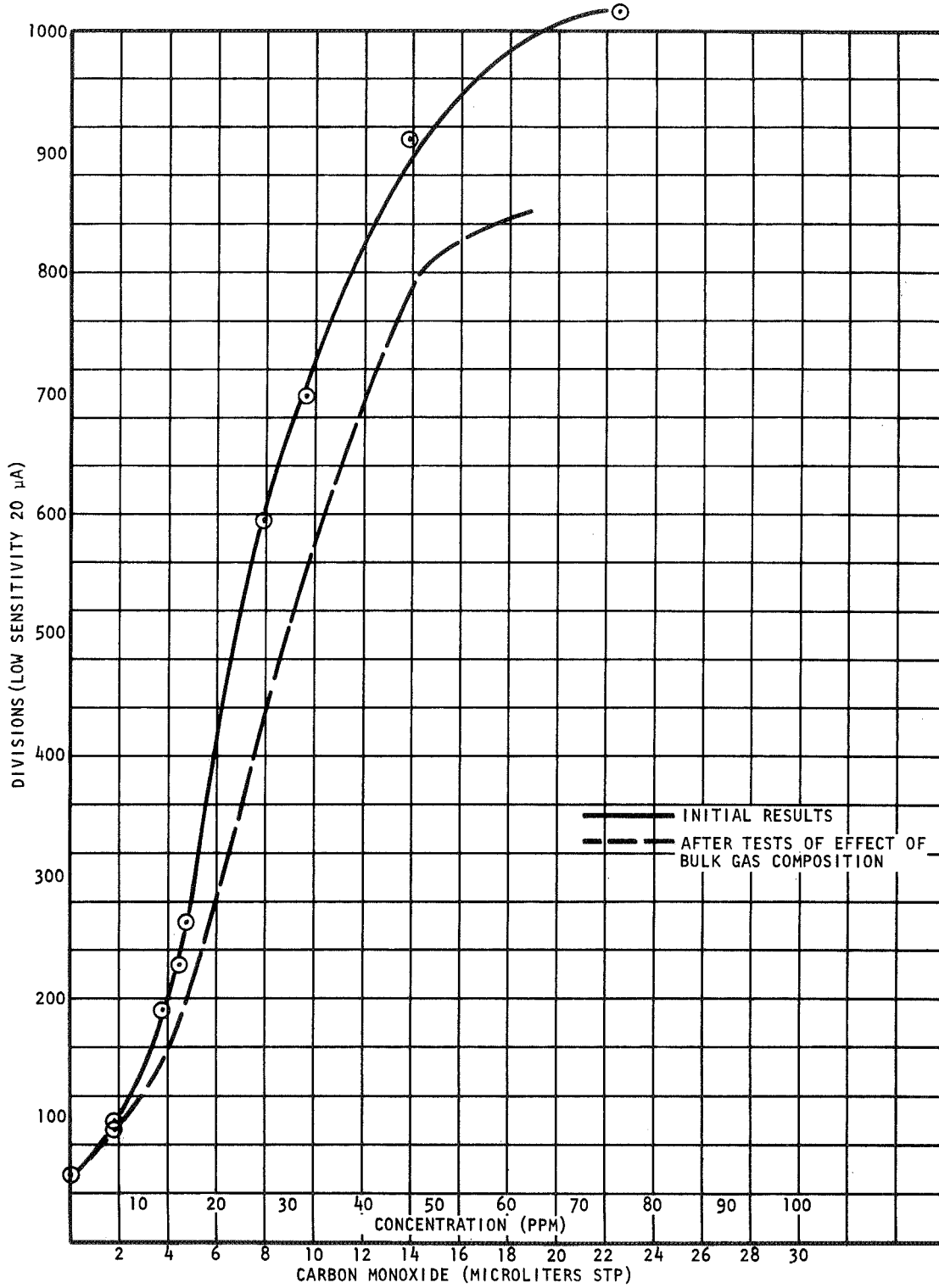


FIGURE 6.- Vacuum Desorption Results - Stepped Temperature Program

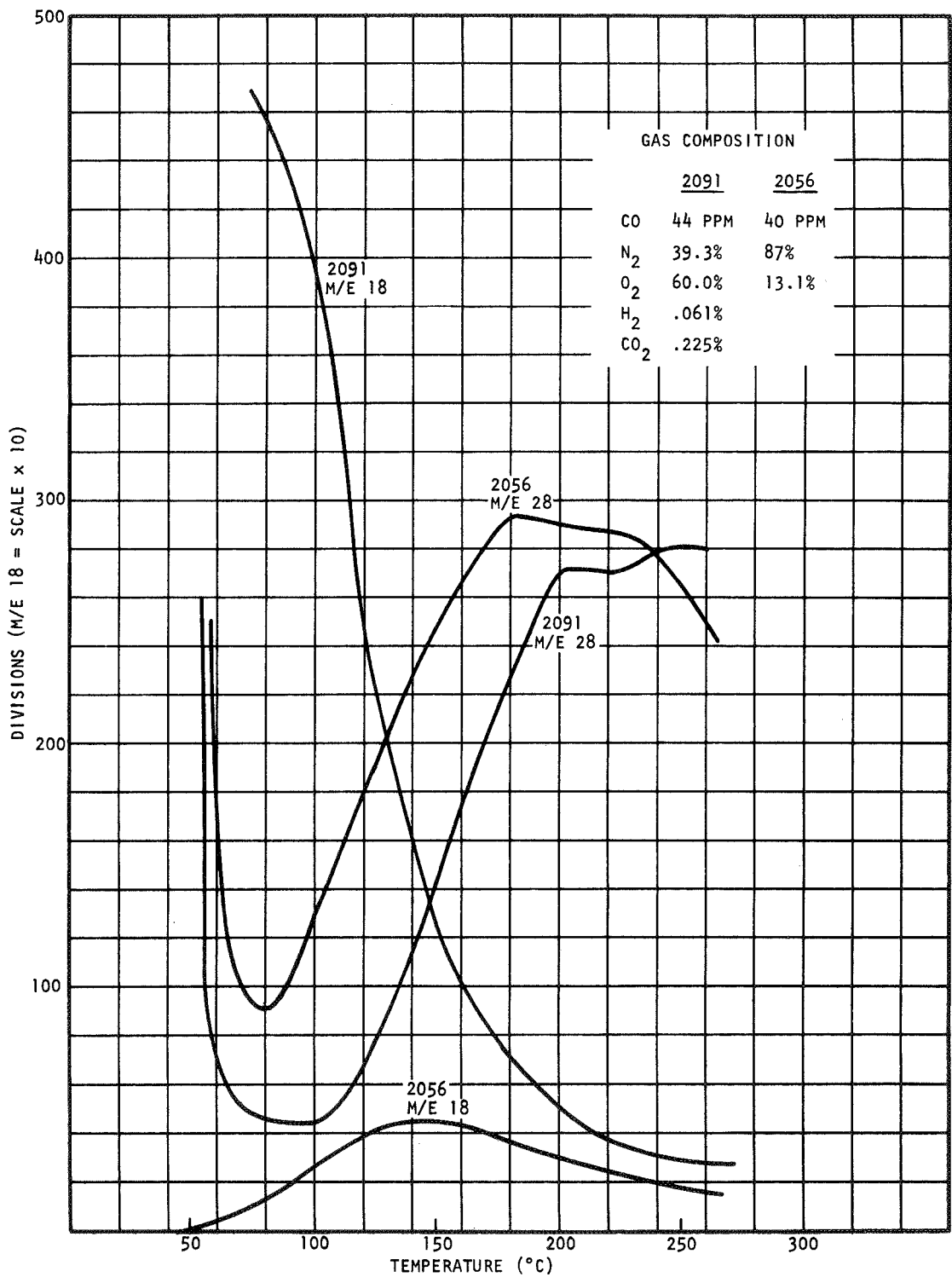


FIGURE 7.- Effect of Bulk Gas Composition on Desorption Curve for Carbon Monoxide

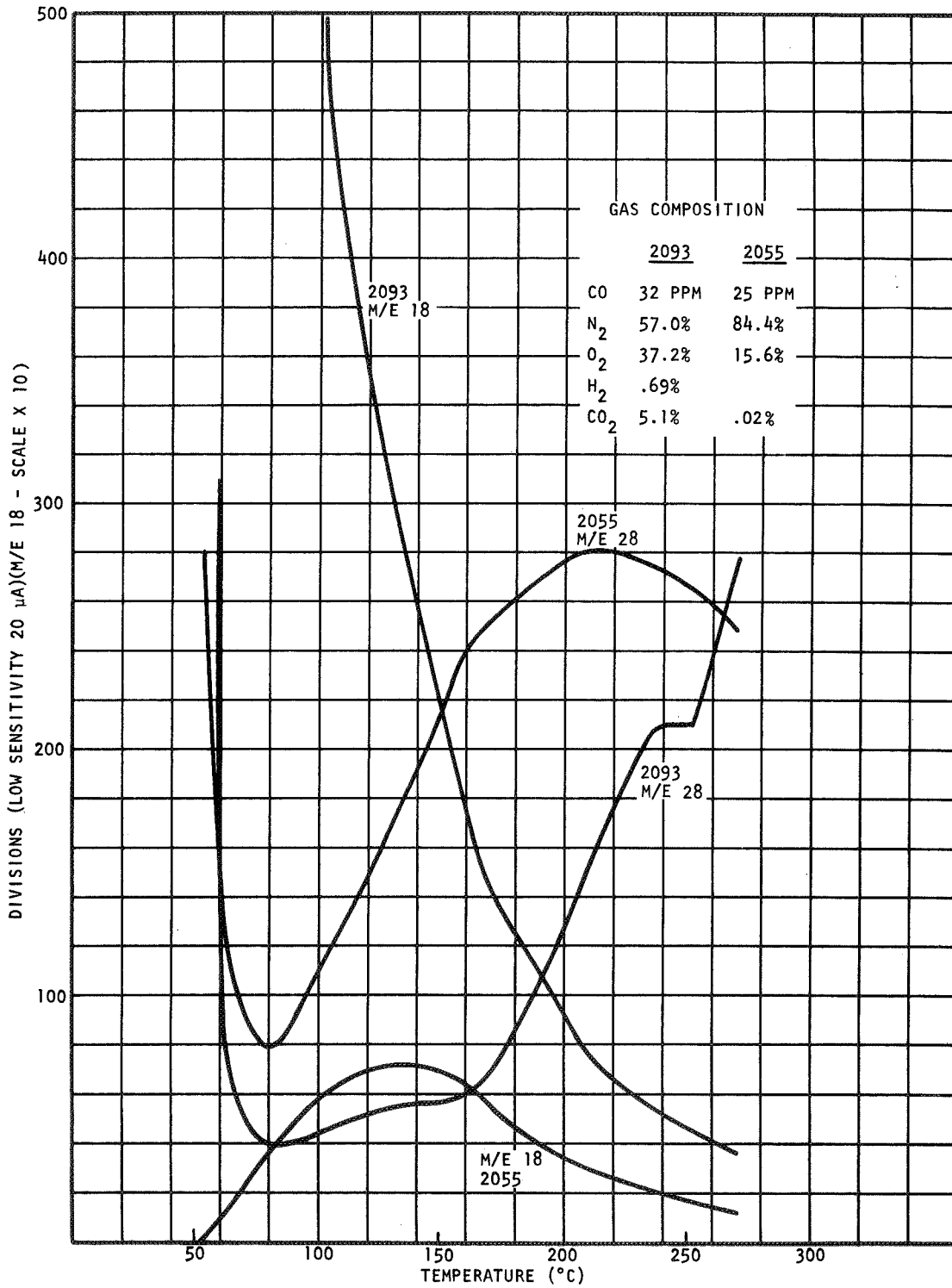


FIGURE 8.- Effect of Bulk Gas Composition On Desorption Curve for Carbon Monoxide

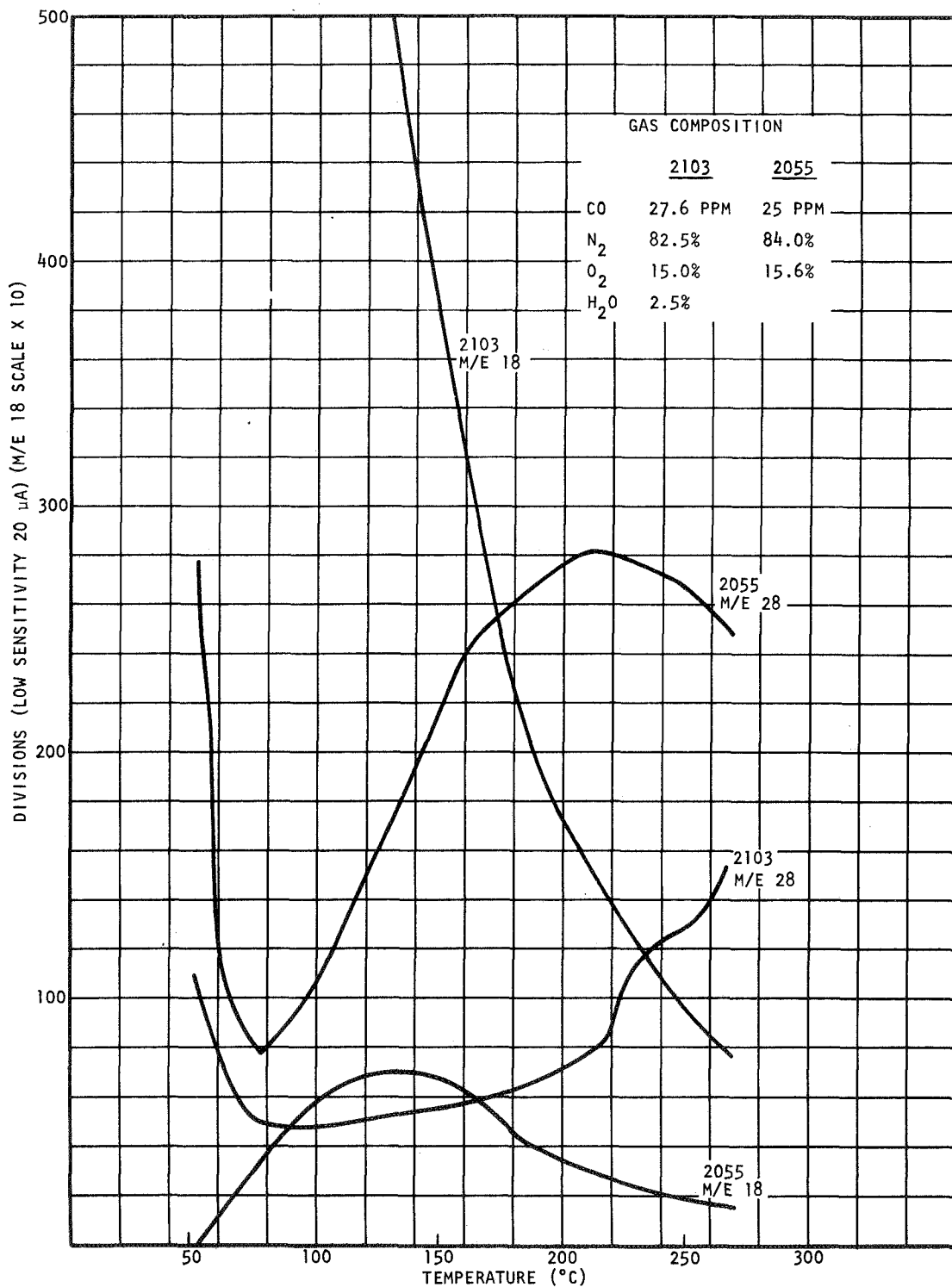


FIGURE 9.- Effect of Water on Carbon Monoxide Desorption Curve



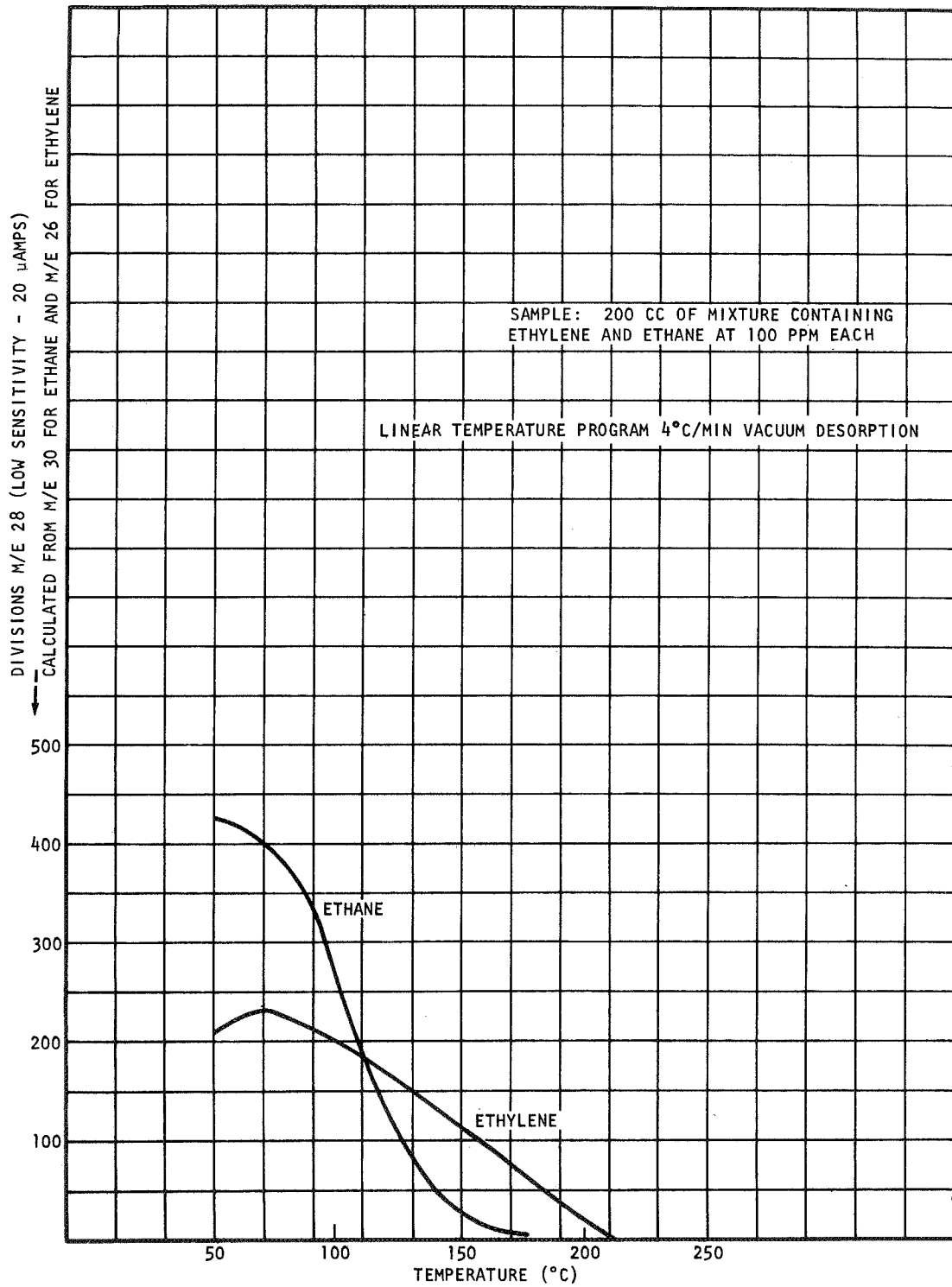


FIGURE 10.- Desorption of Ethylene and Ethane From Palladium-Charcoal

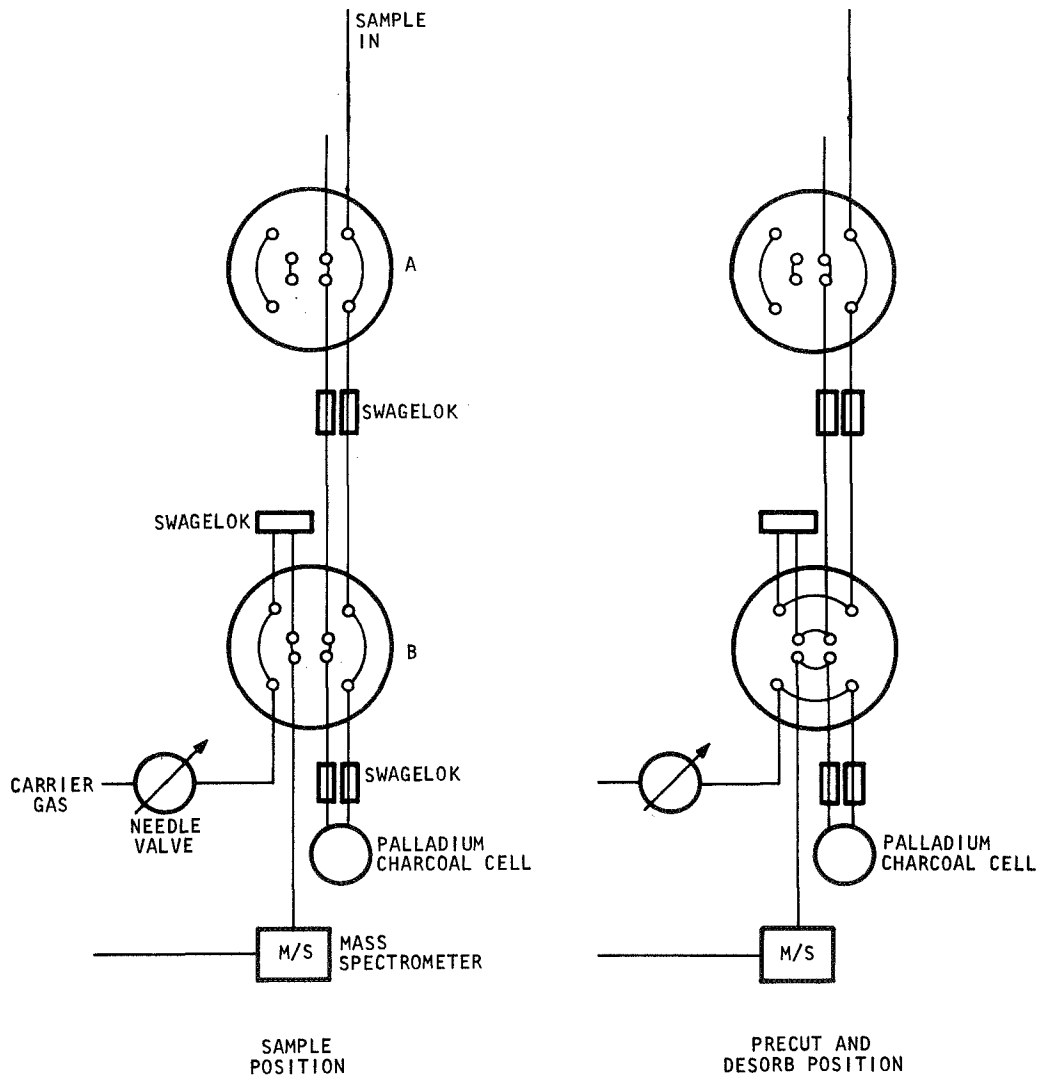


FIGURE 11.- Flow Diagram for Carrier Gas Operation

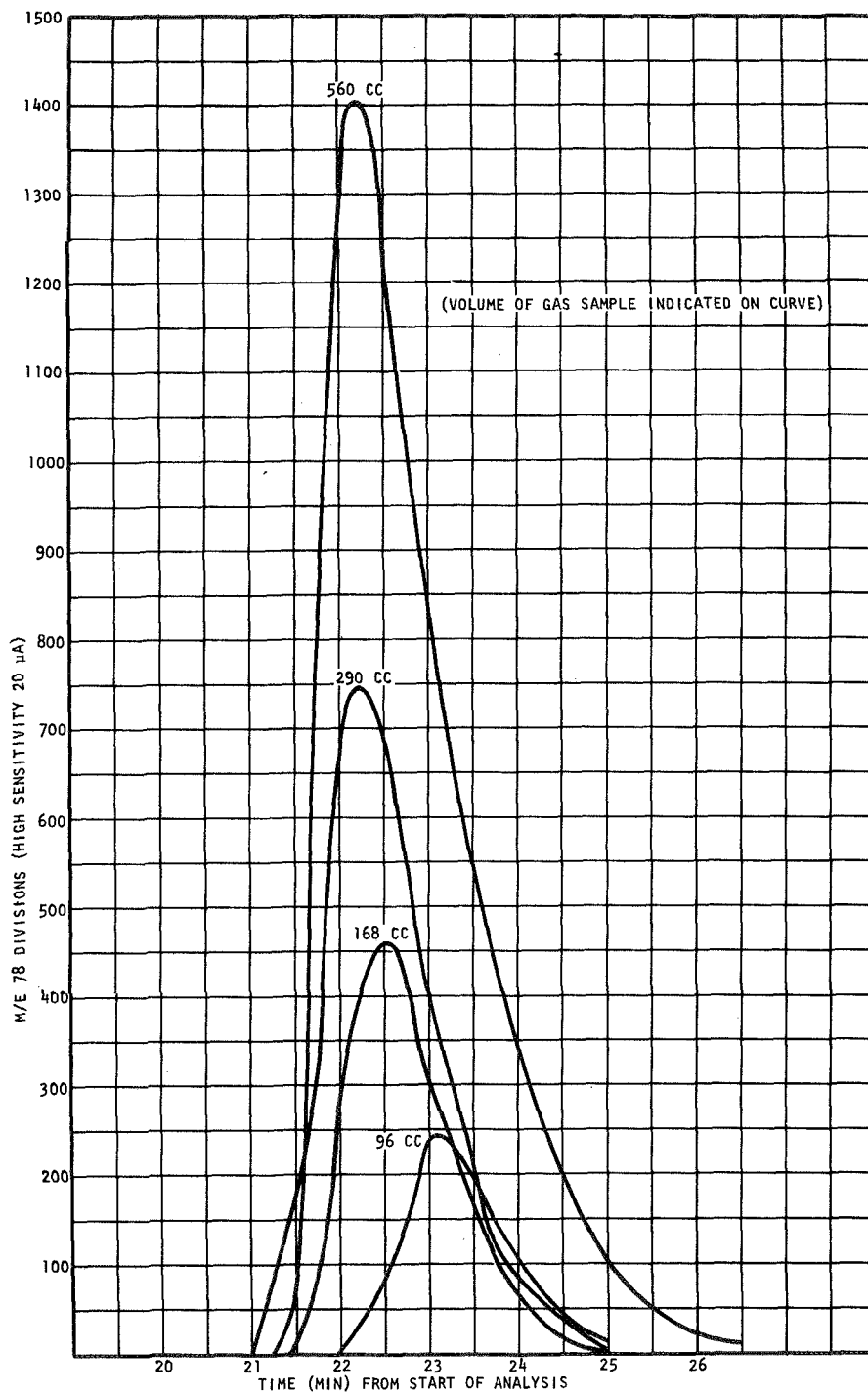


FIGURE 12.- Benzene Desorption Using Argon in Carrier Gas Mode of Operation

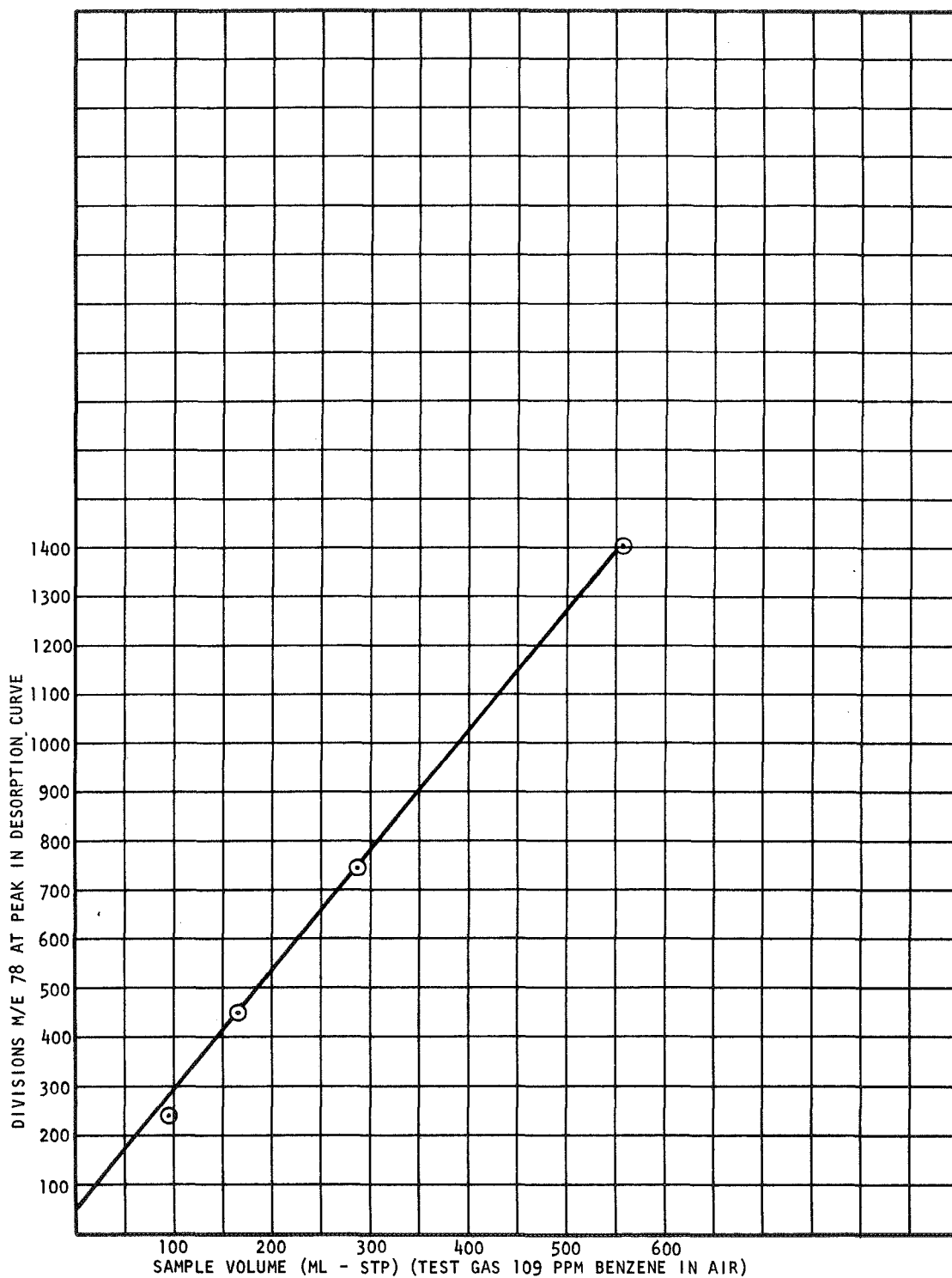


FIGURE 13.- Response of System to Benzene During Desorption

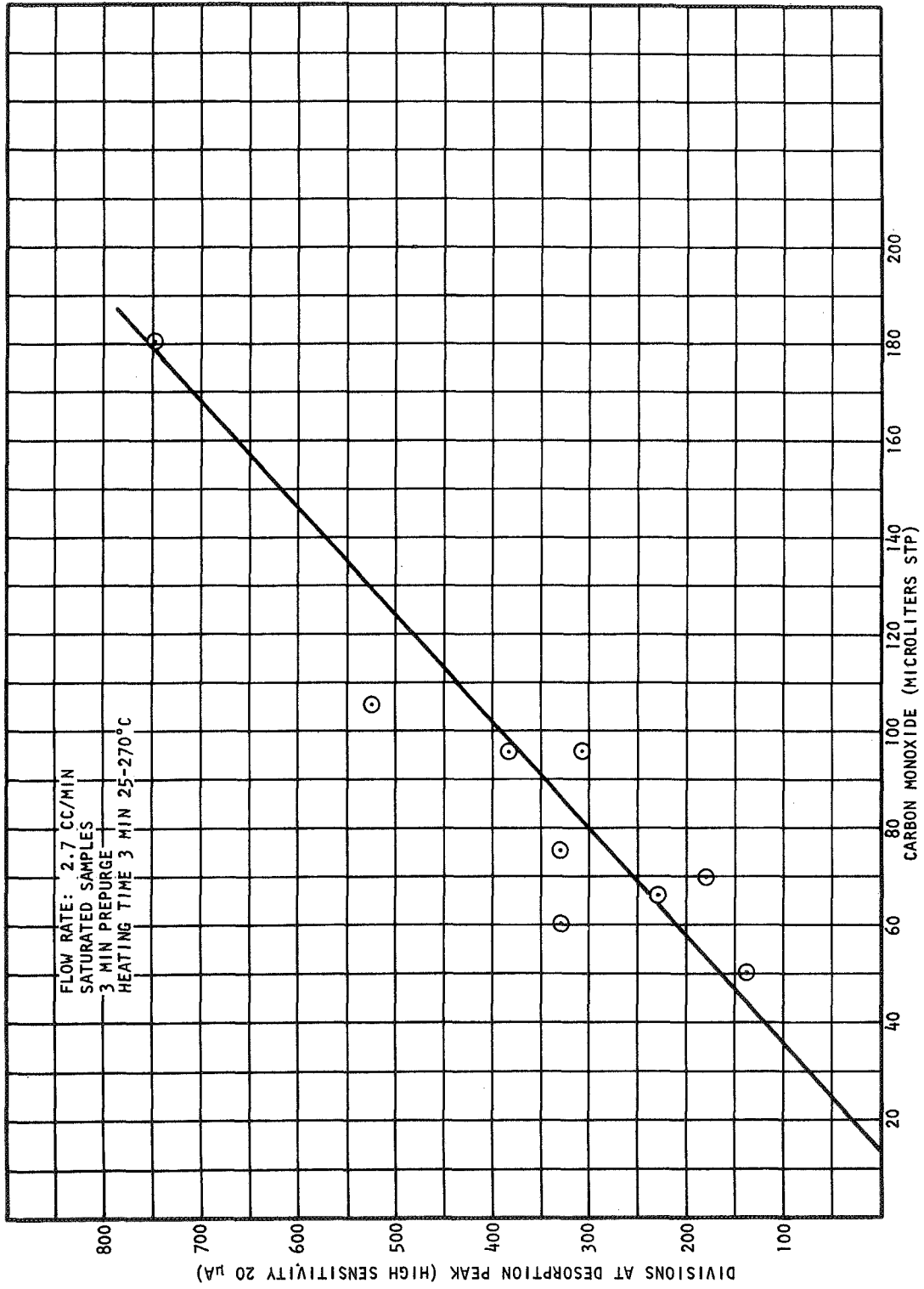


FIGURE 14.- Mass Spectrometer Signal as a Function of Carbon Monoxide Sorbed - Carrier Gas Operation

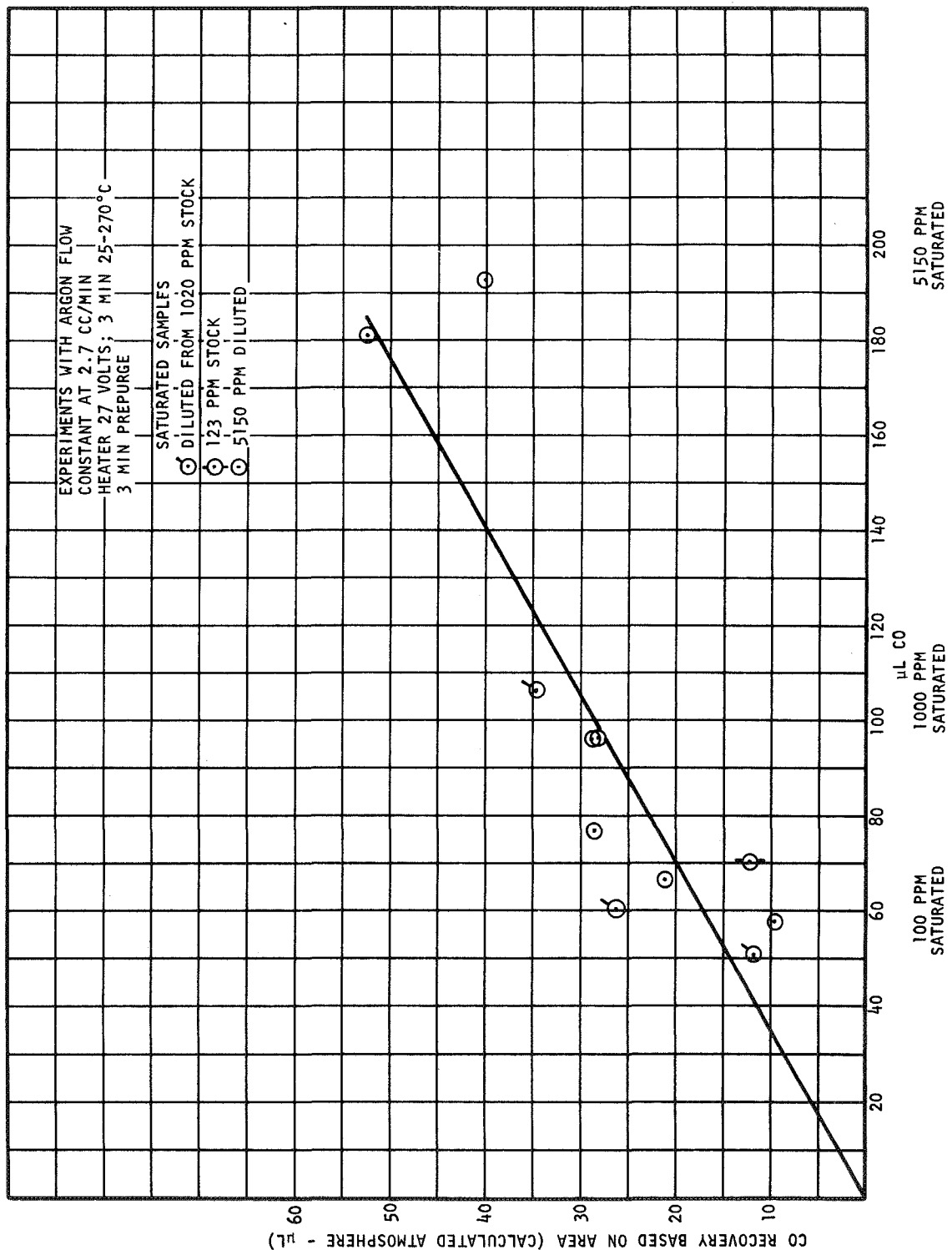


FIGURE 15.- Area Under Desorption Curve as a Function of Carbon Monoxide Sorbed - Carrier Gas Operation

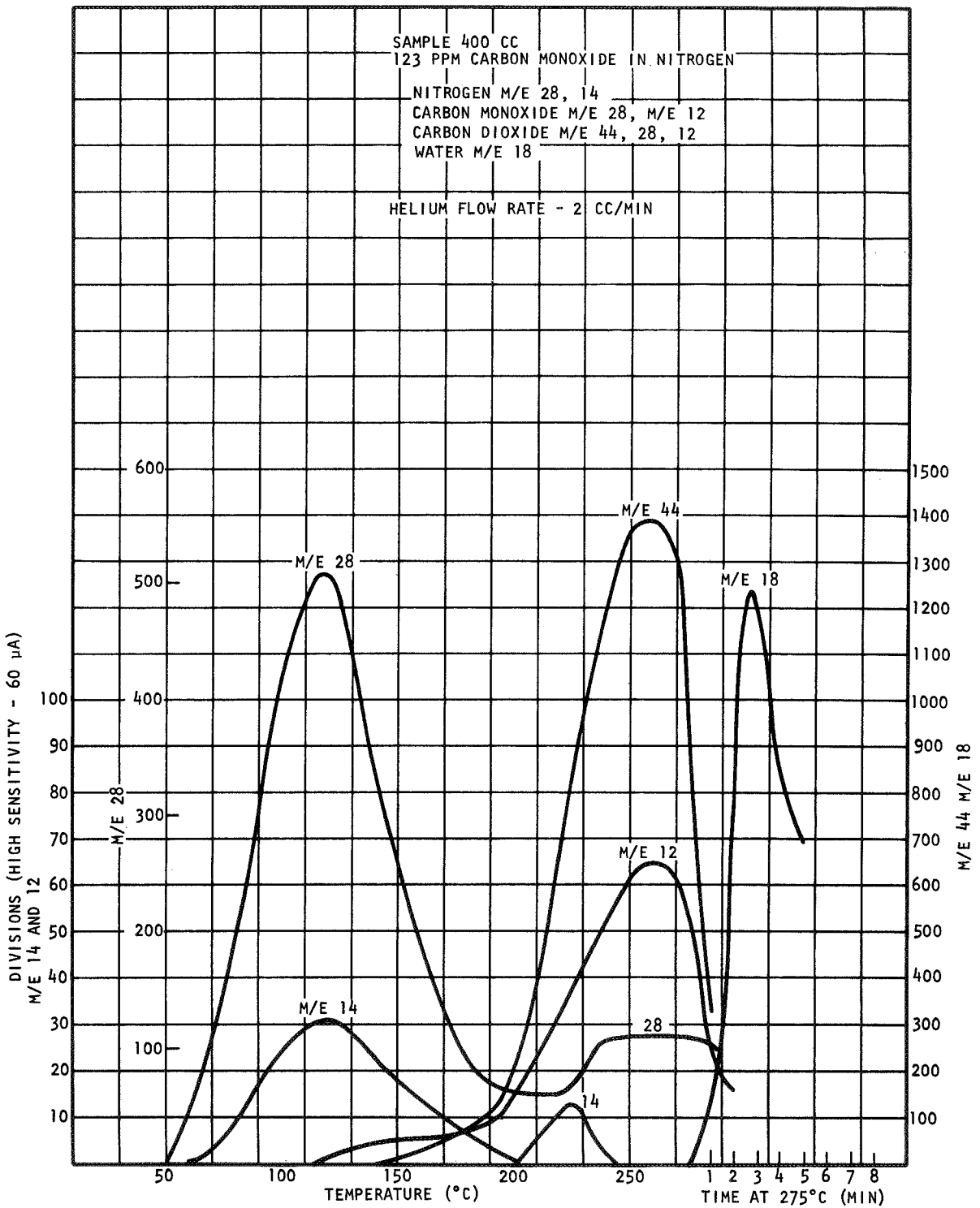


FIGURE 16.- Desorption Curves Under Helium Flow

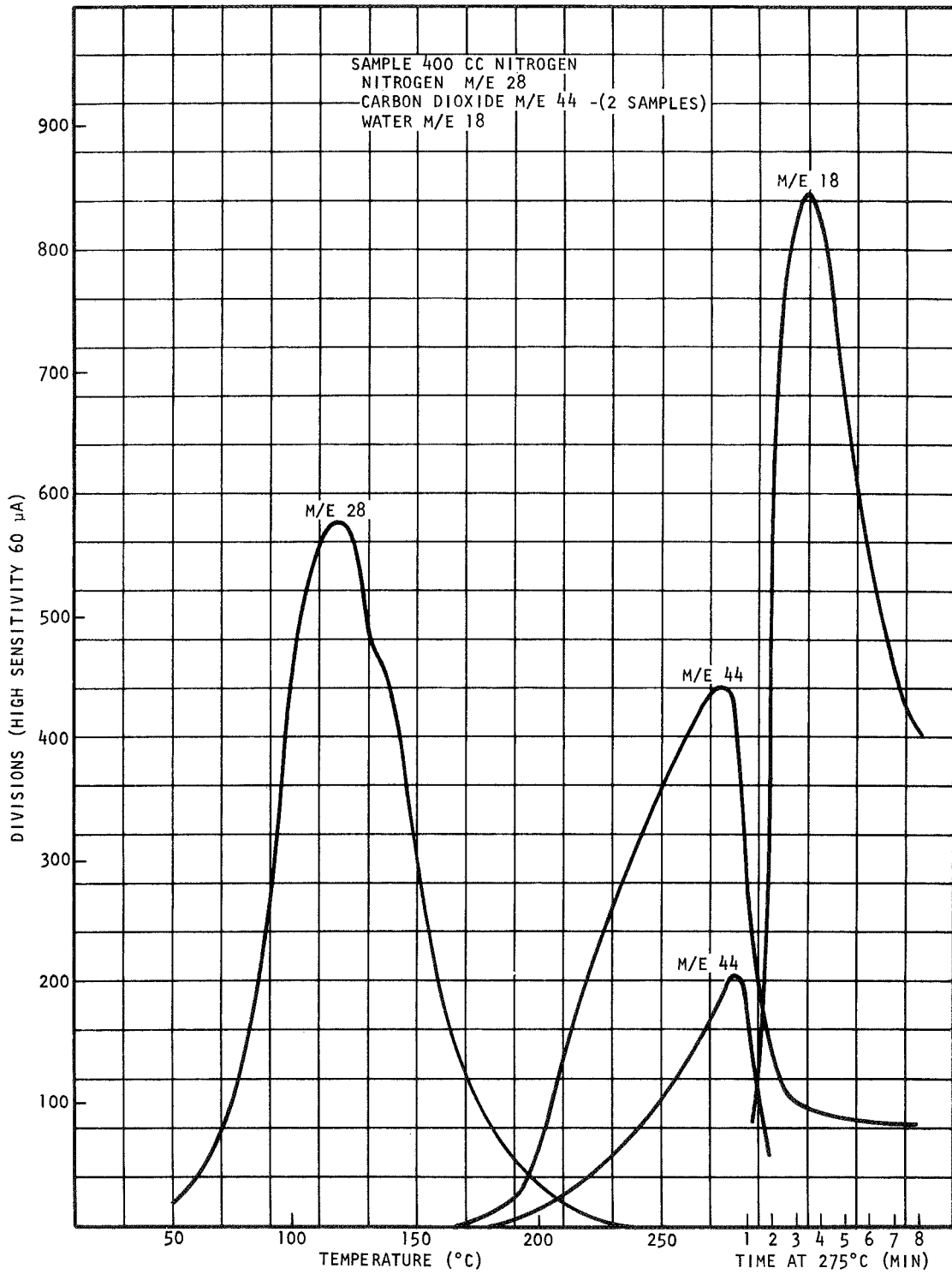


FIGURE 17.- Desorption Curves Under Helium Flow



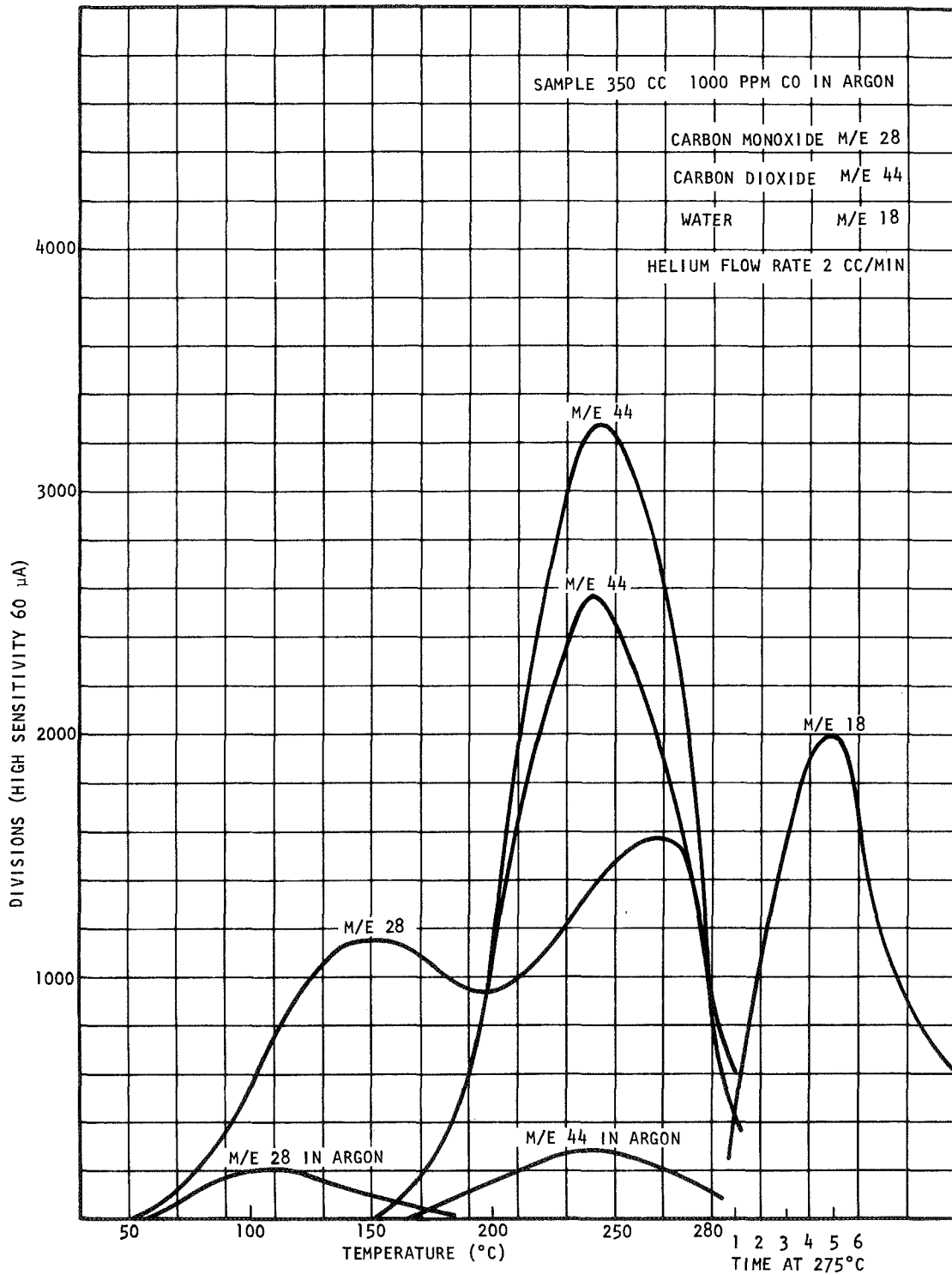


FIGURE 18.- Desorption Curves Under Helium Flow

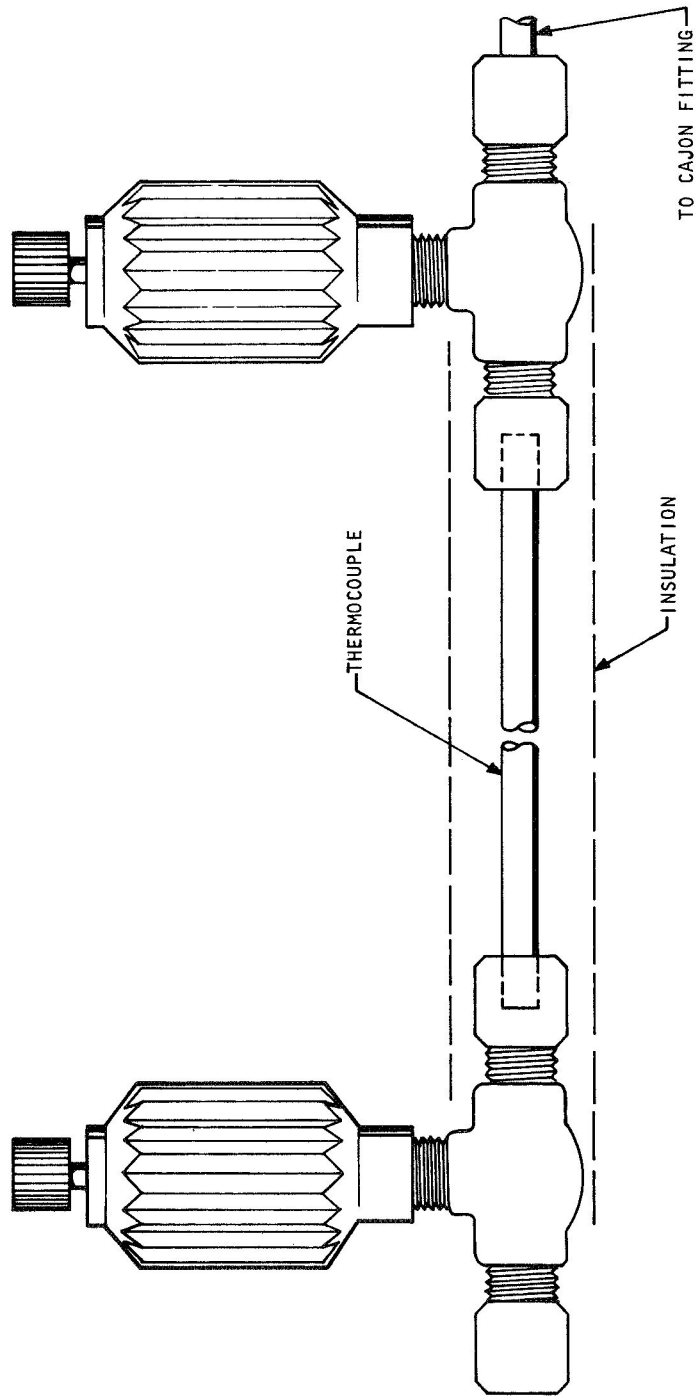


FIGURE 19.- Sorbent Test Cells

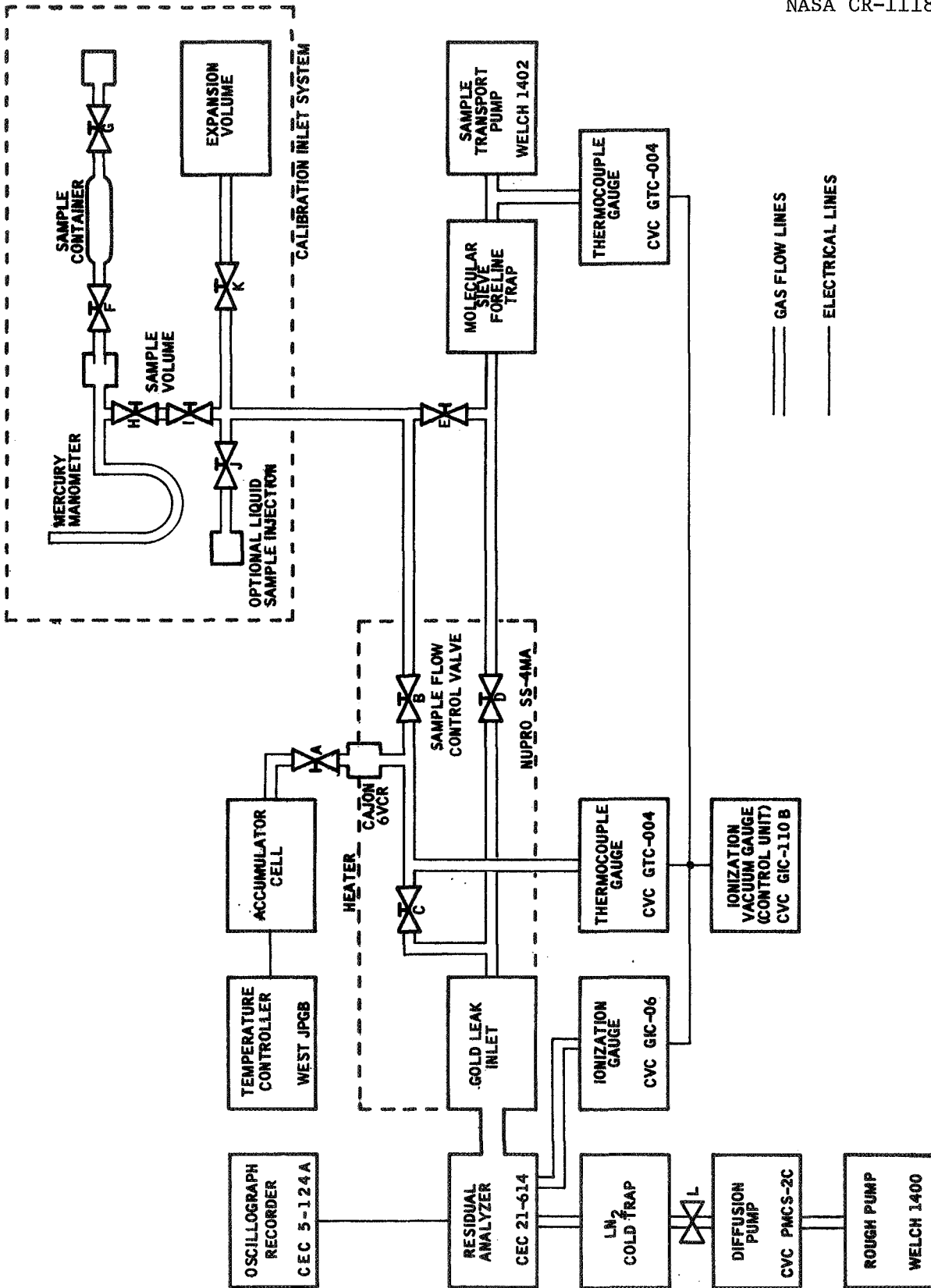


FIGURE 20.- Laboratory Contaminant Sensor Inlet System

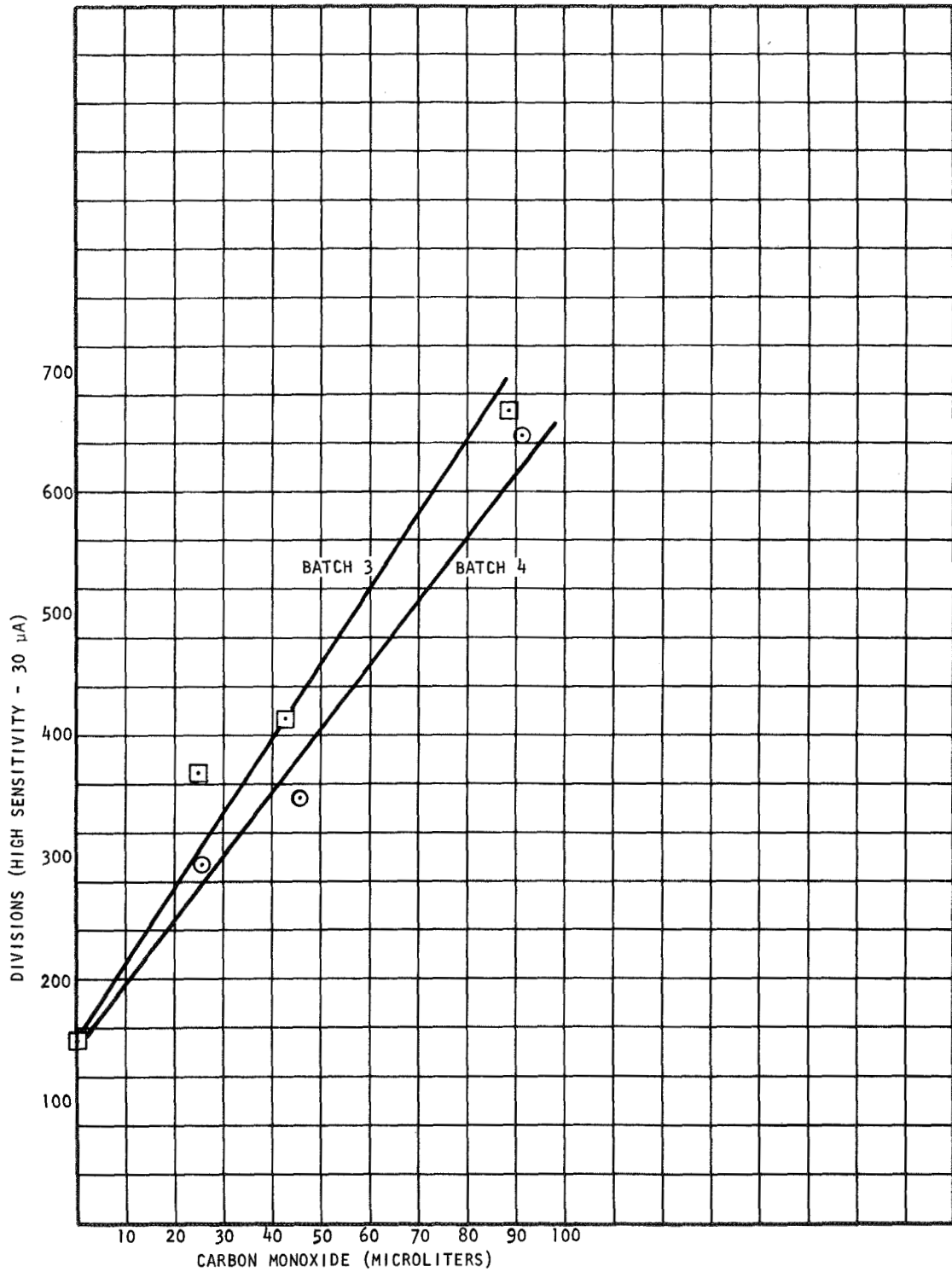


FIGURE 21.- Response of System With Batch 3 and Batch 4 Sorbents to Carbon Monoxide

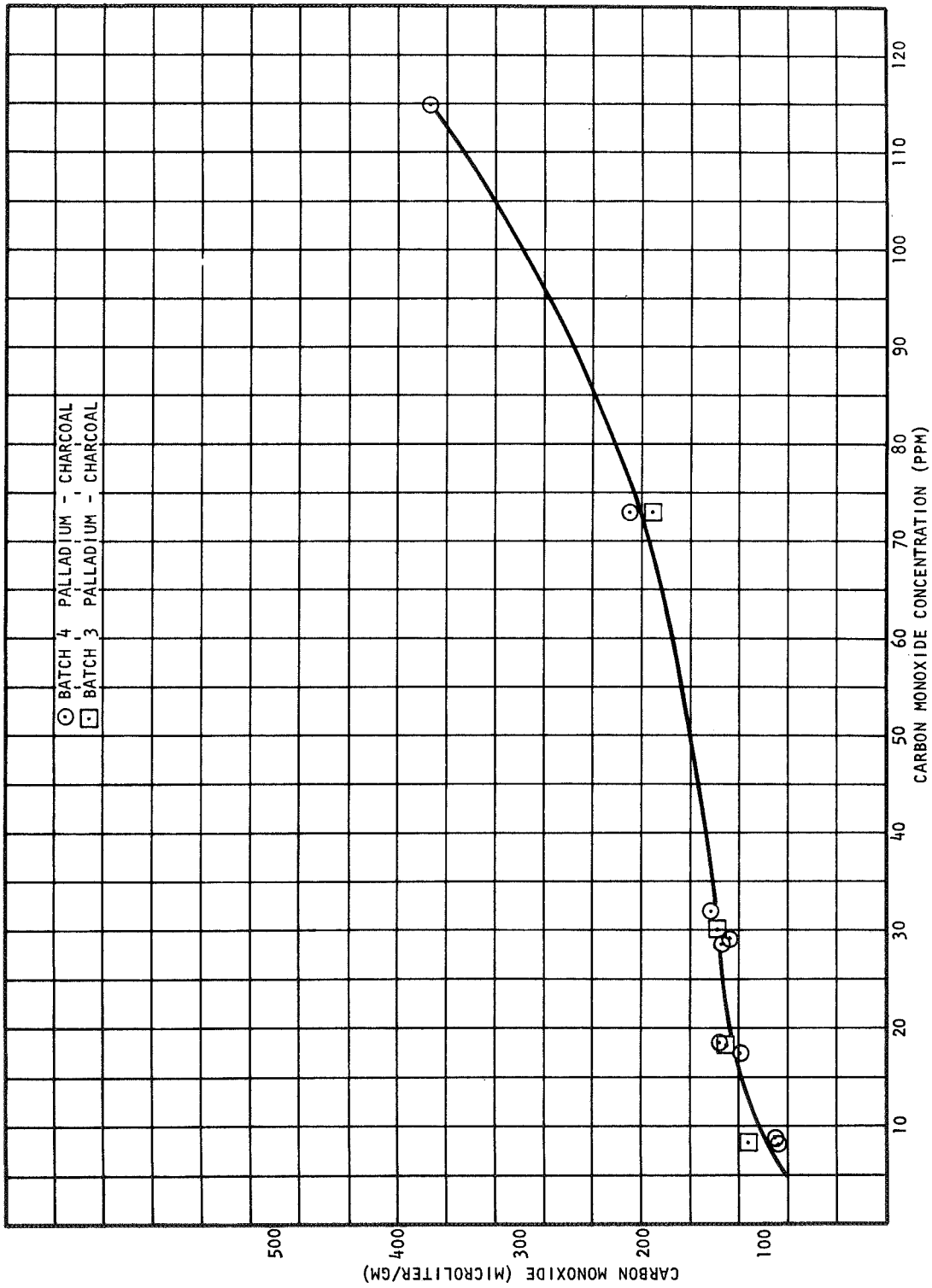


FIGURE 22.- Carbon Monoxide Sorbed at Saturation as a Function of Concentration

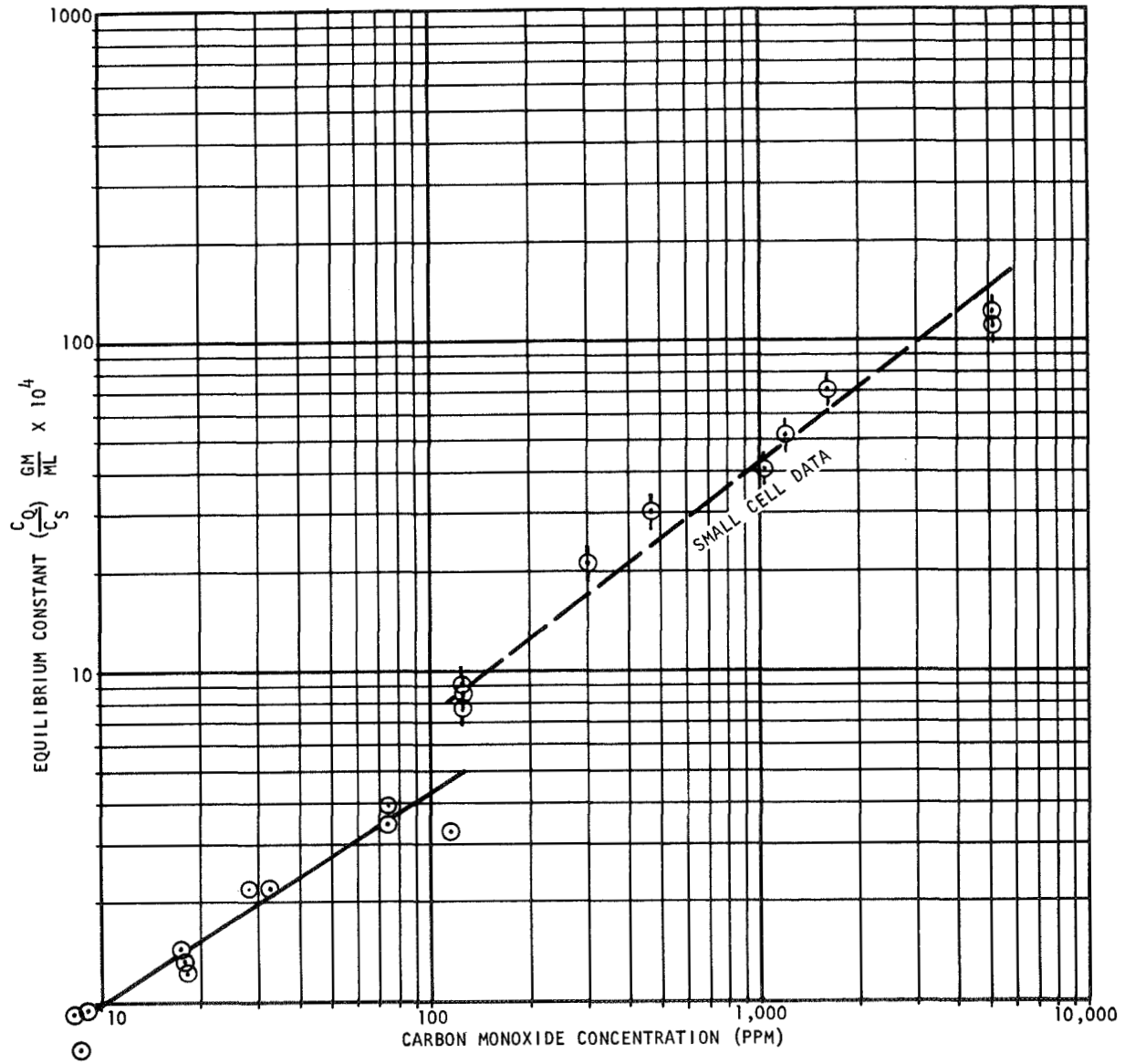


FIGURE 23.- Equilibrium Constants as a Function of Concentration

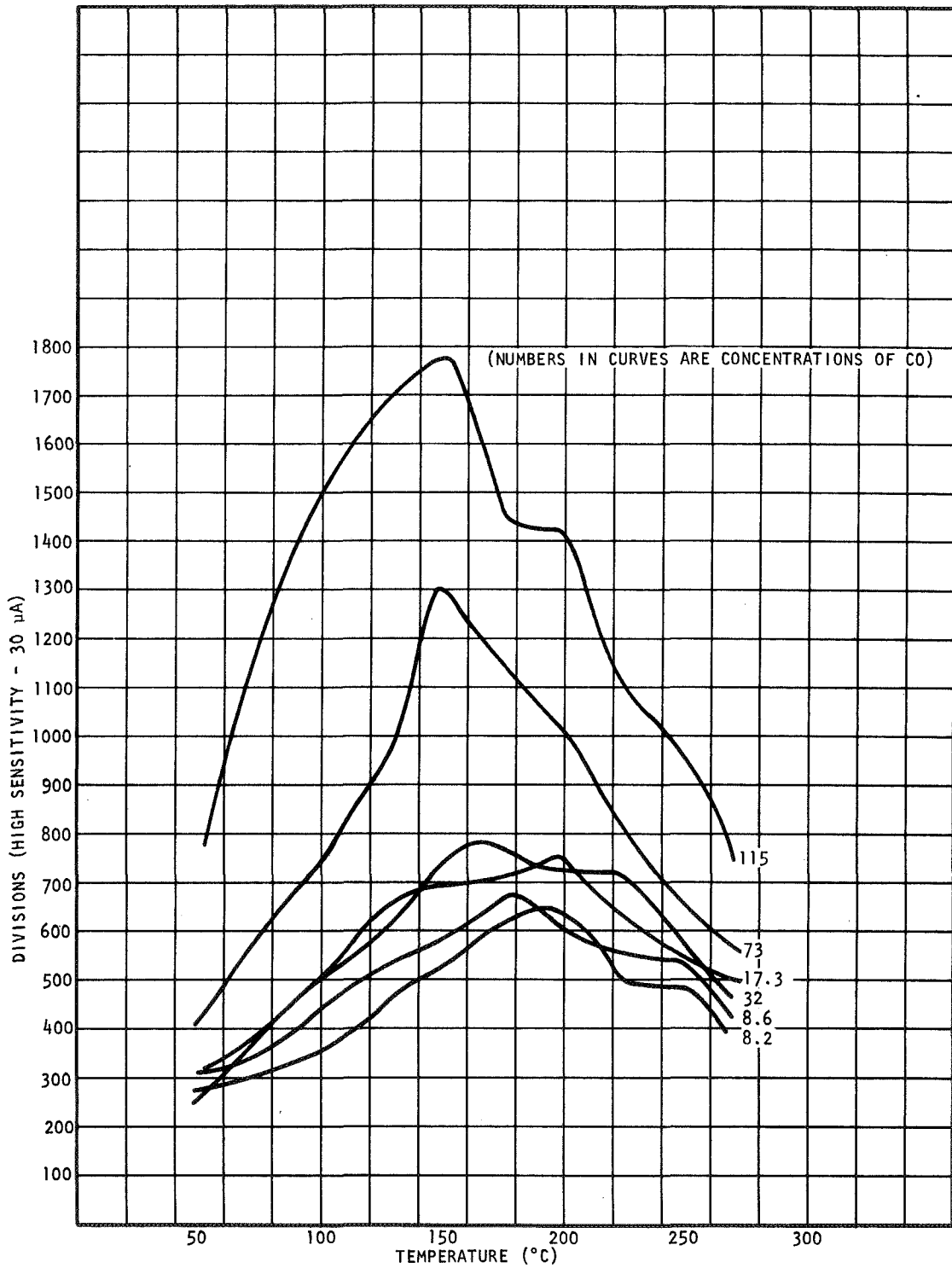


FIGURE 24.- Desorption Curves for Saturated Cells

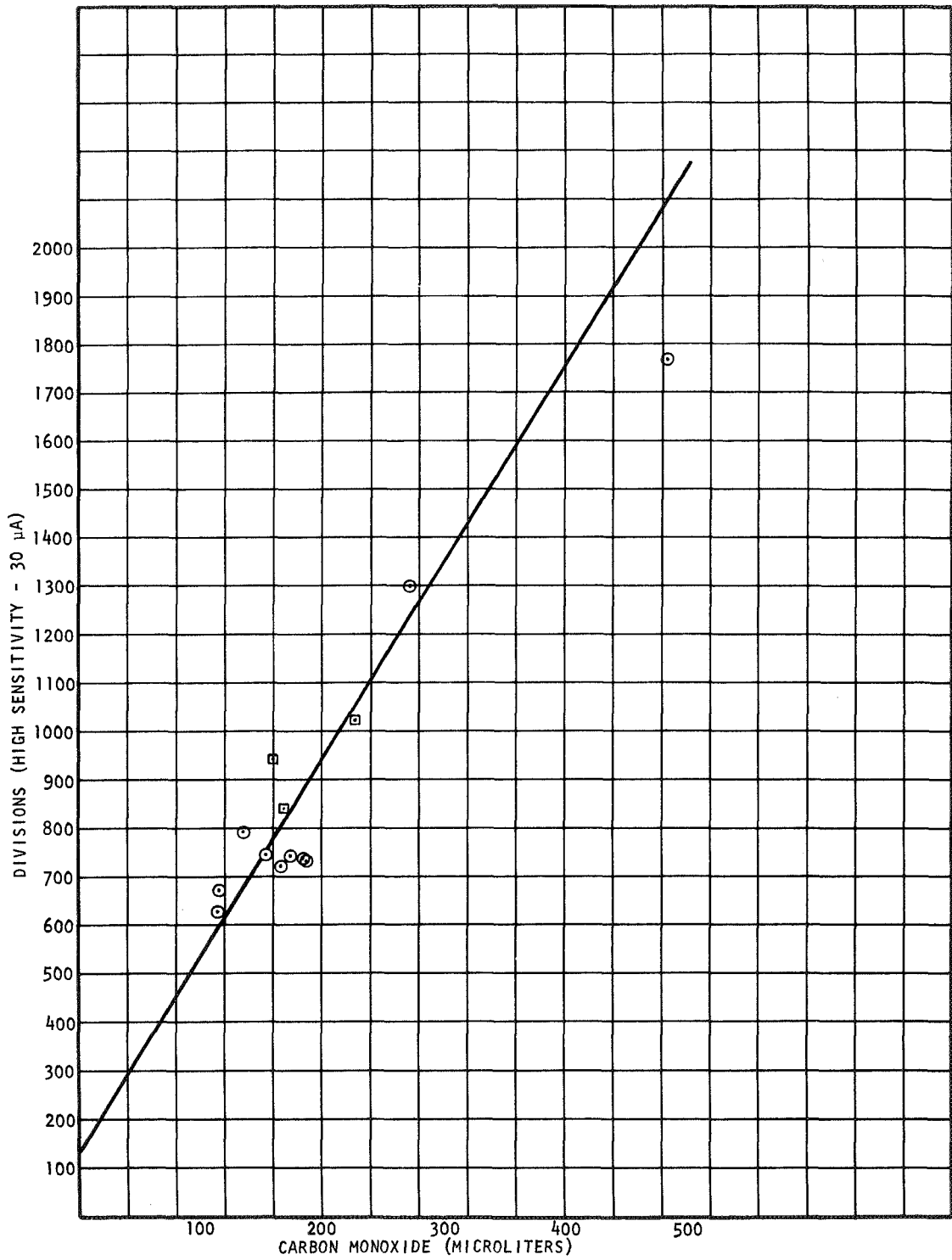


FIGURE 25.- Response as a Function of Amount of Carbon Monoxide Sorbed at Saturation



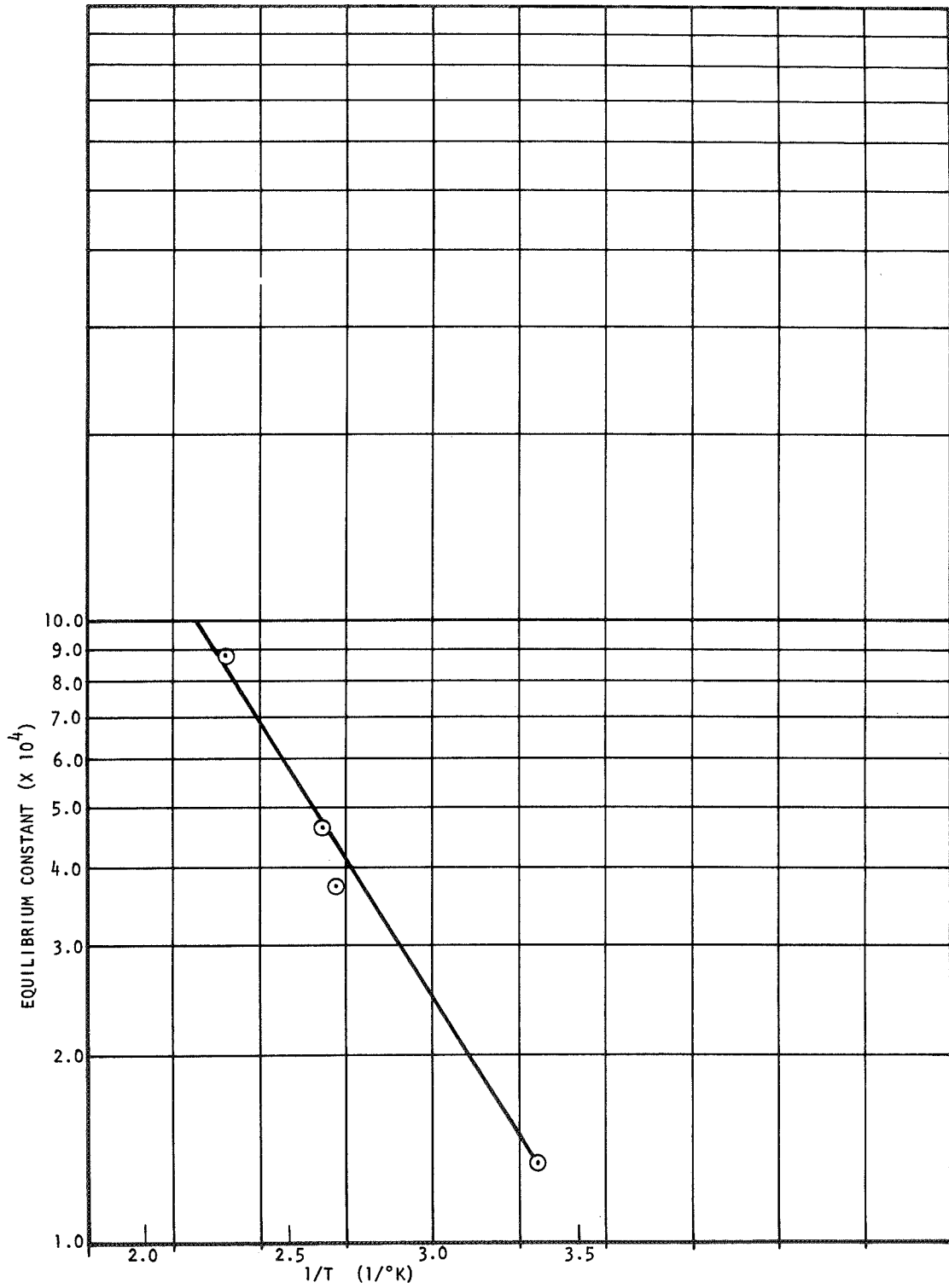


FIGURE 26.- Variation in Equilibrium Constant With Temperature

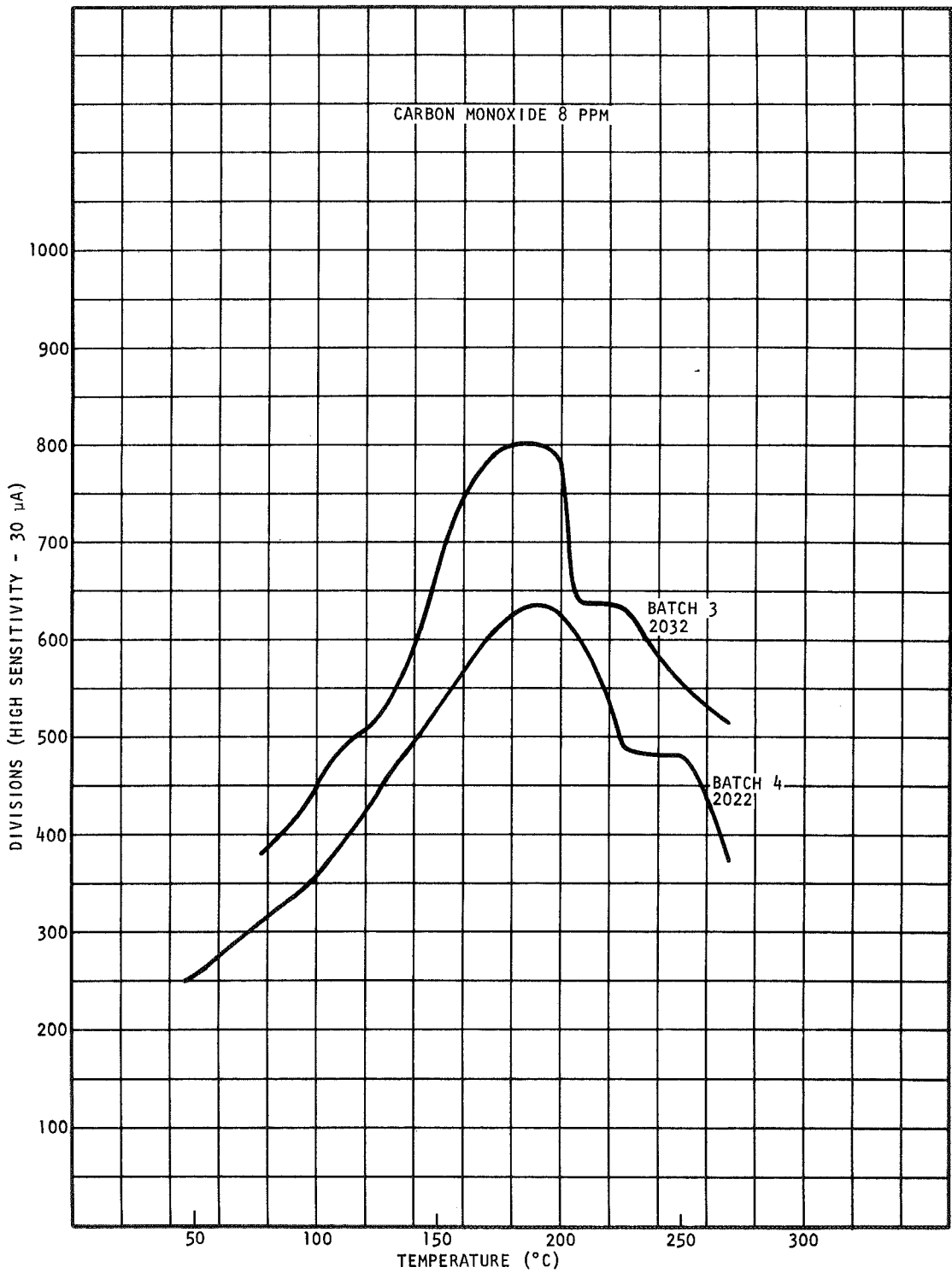


FIGURE 27.- Comparison of Desorption Curves For Batch 3 and Batch 4 Sorbents

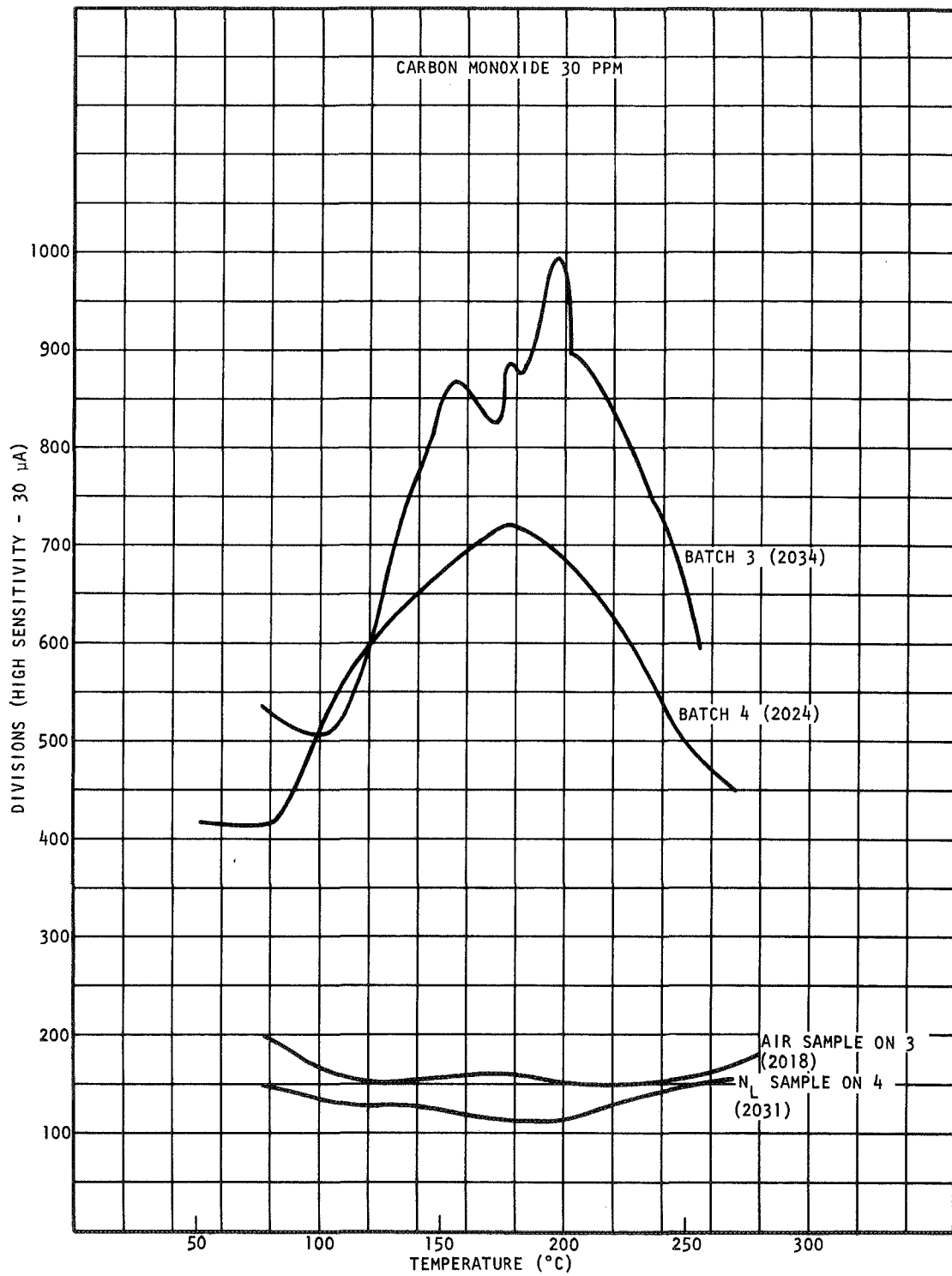


FIGURE 28.- Comparison of Desorption Curves For Batch 3 and Batch 4 Sorbents

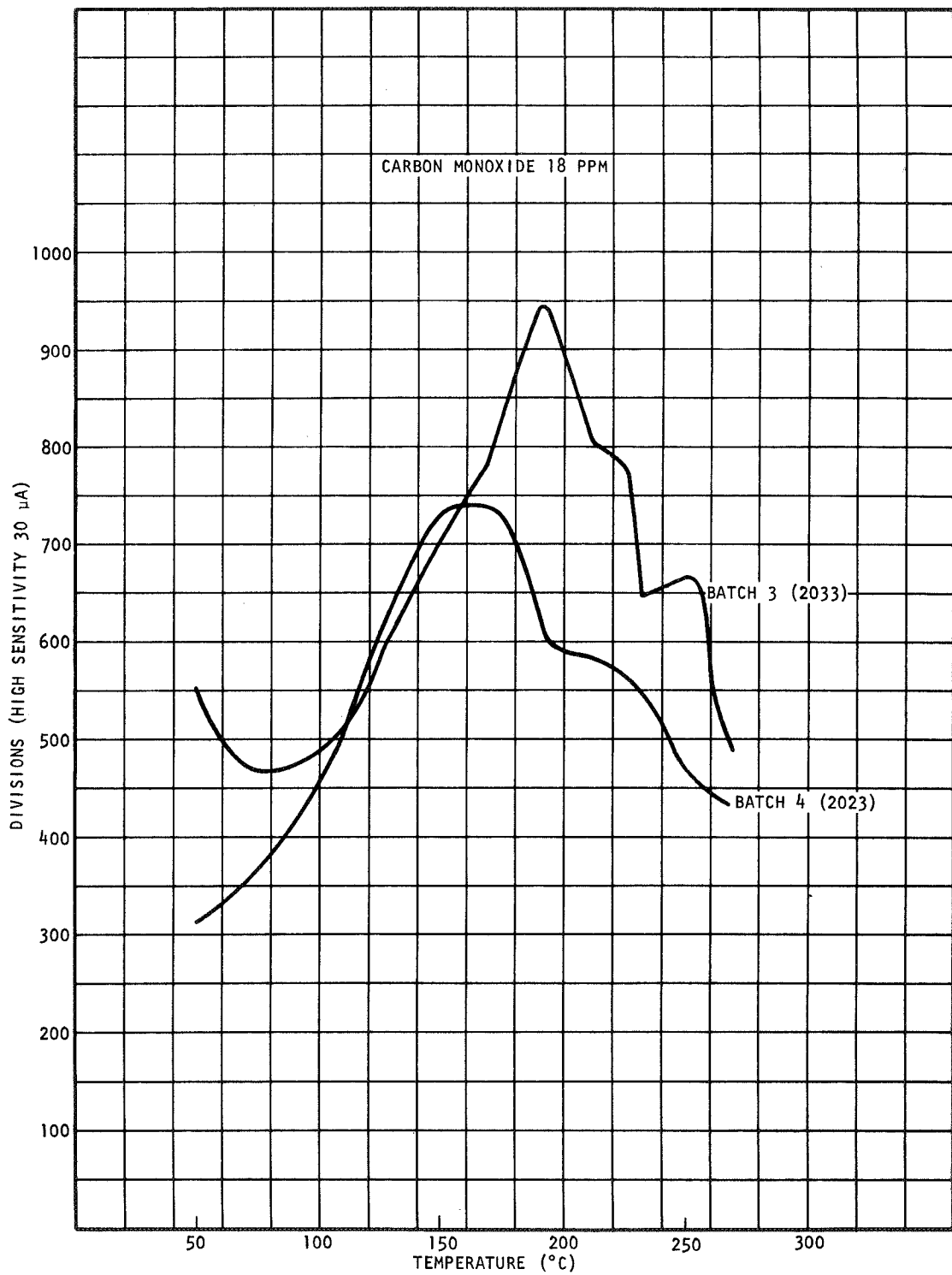


FIGURE 29.- Comparison of Desorption Curves For Batch 3 and Batch 4 Sorbents

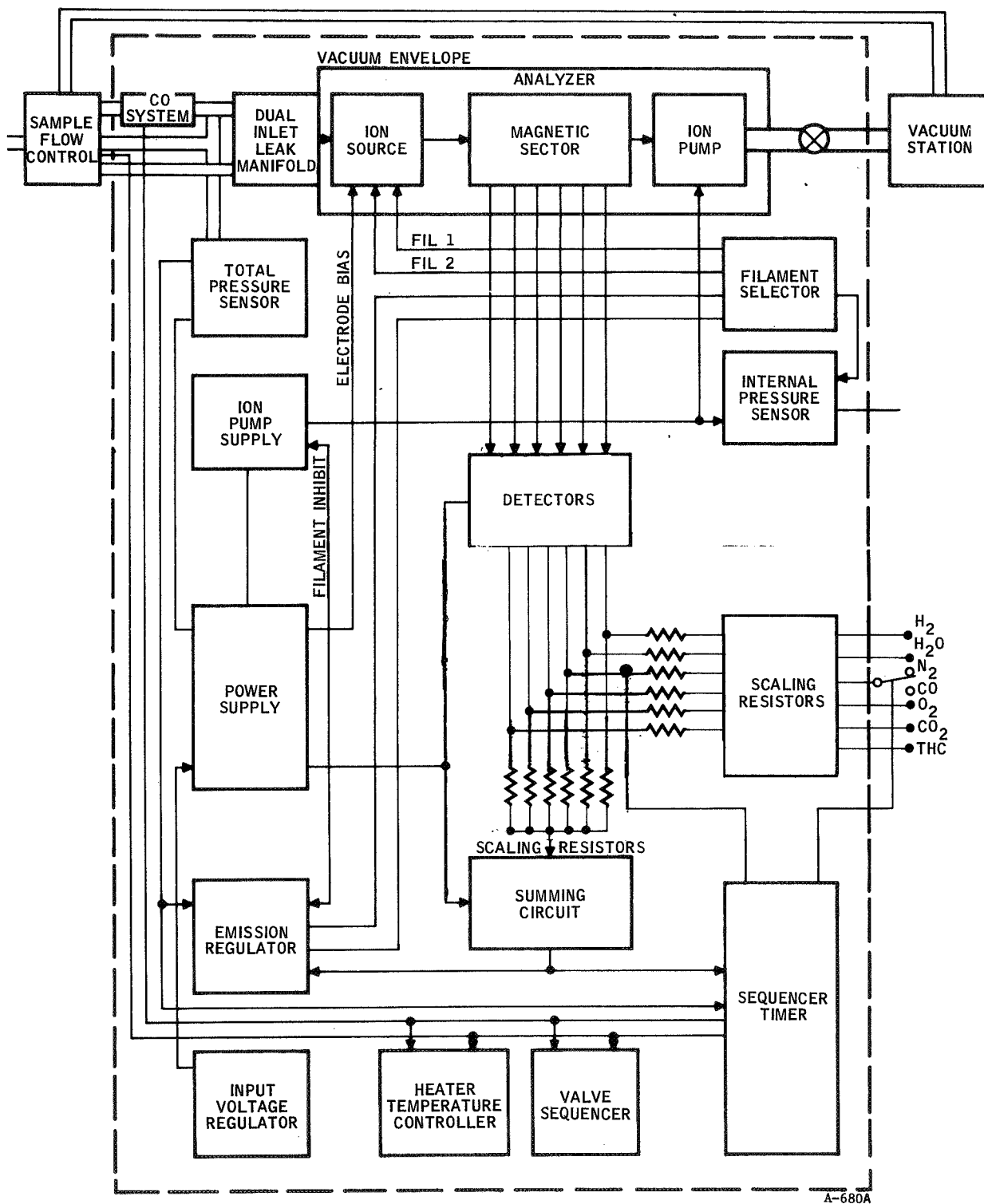


FIGURE 30.- Block Diagram of Mass Spectrometer And CO Accumulator Cell

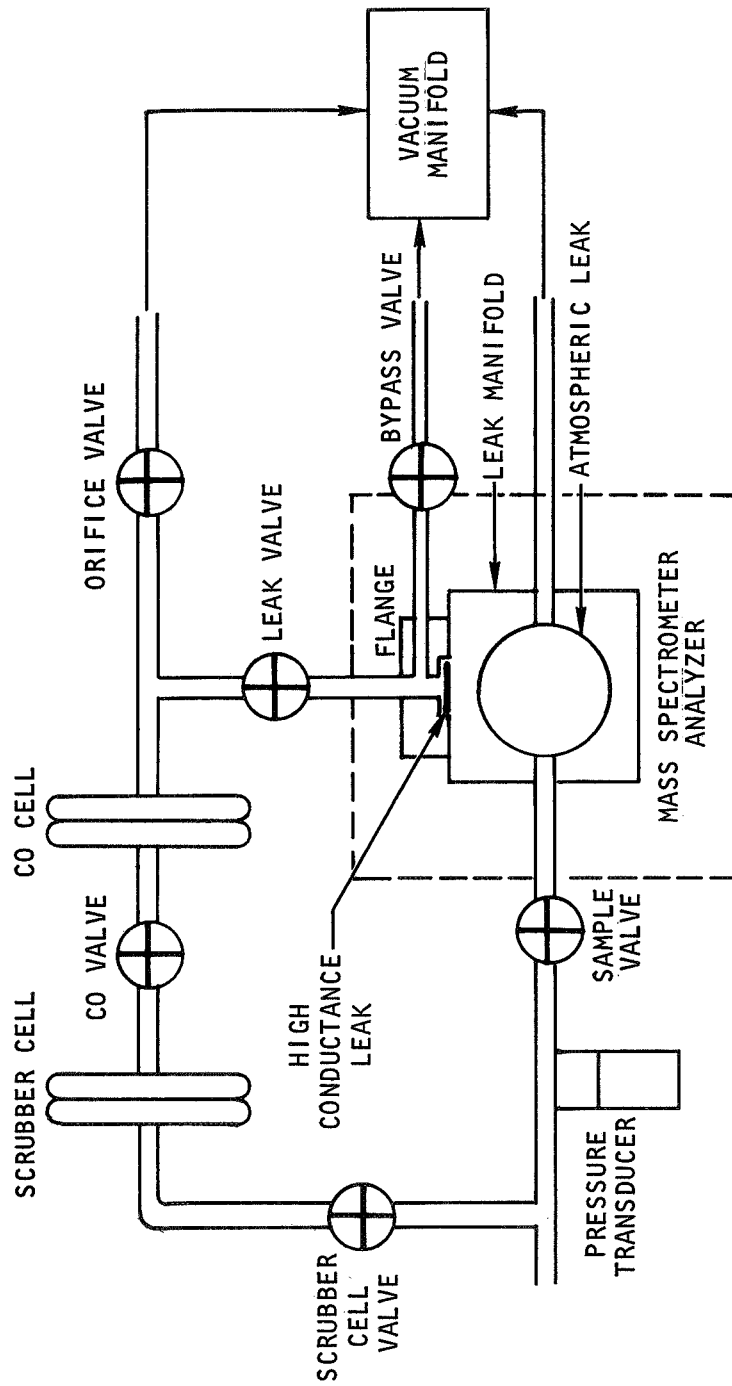


FIGURE 31.- Dual Leak CO Accumulator Cell Inlet System

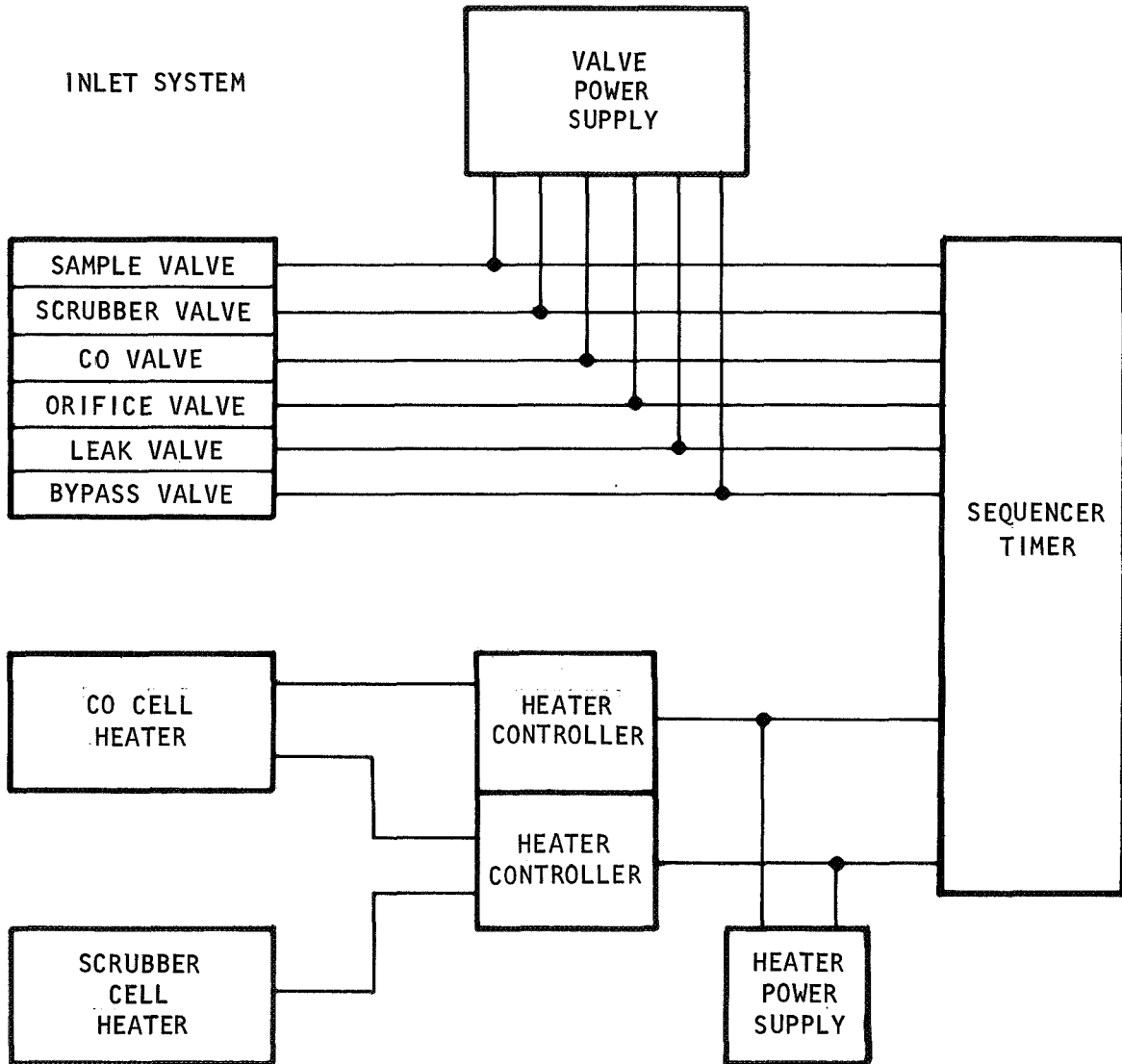


FIGURE 32.- Electronic Subsystem Schematic Diagram

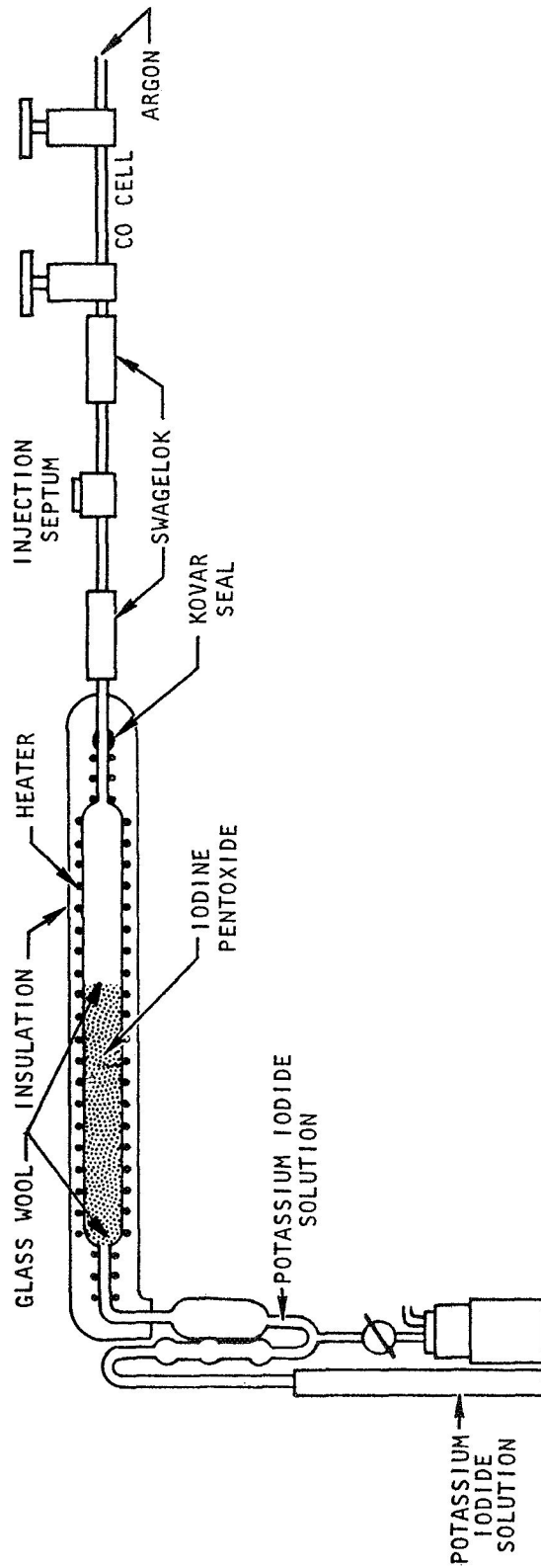
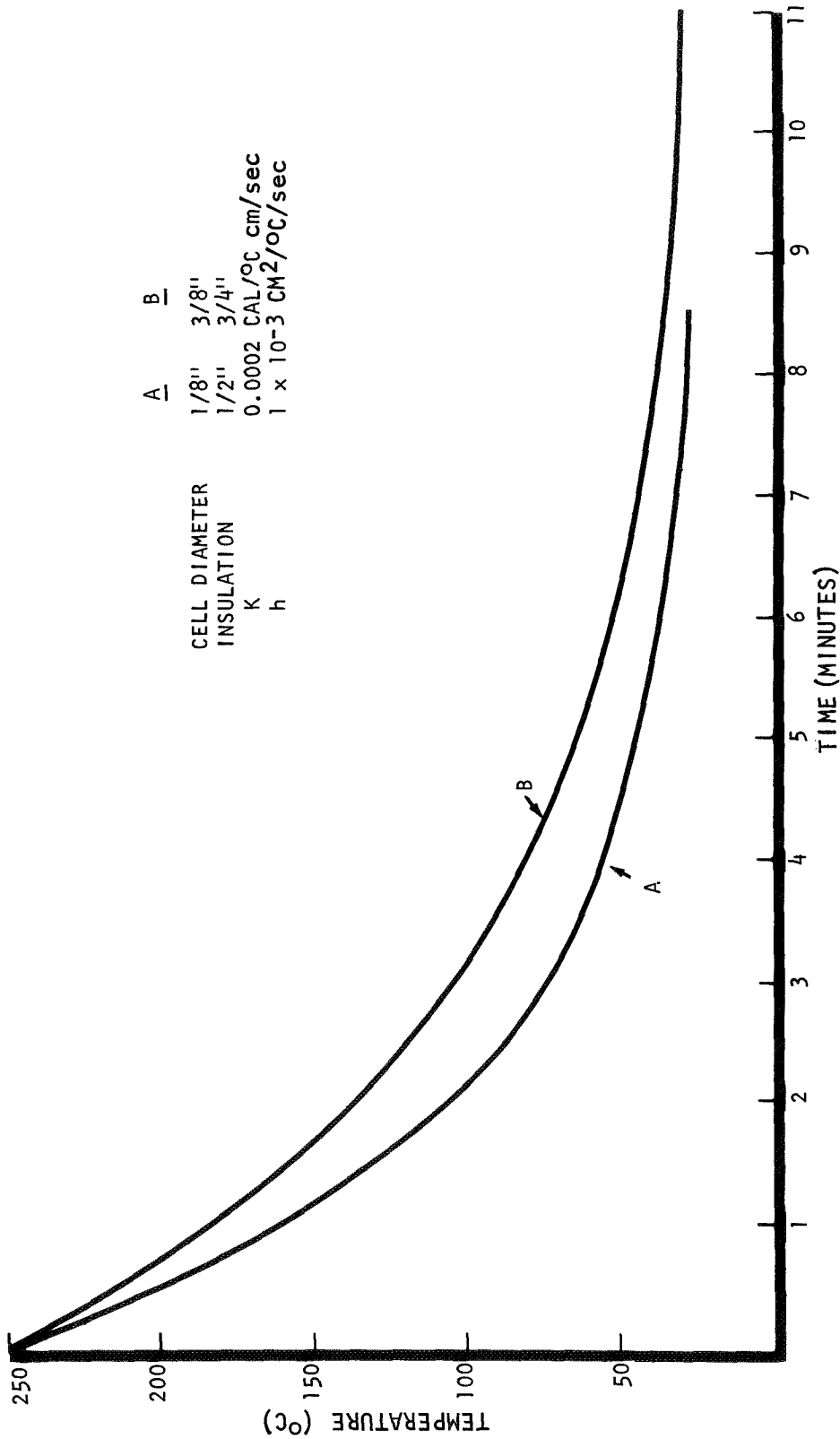


FIGURE 33.- Apparatus for CO Determination





|               |                      |                         |
|---------------|----------------------|-------------------------|
|               | <u>A</u>             | <u>B</u>                |
| CELL DIAMETER | 1/8"                 | 3/8"                    |
| INSULATION    | 1/2"                 | 3/4"                    |
| K             | 0.0002               | CAL/°C CM/sec           |
| h             | 1 x 10 <sup>-3</sup> | CM <sup>2</sup> /°C/sec |

FIGURE 34a.- Cooling Curves - Calculated

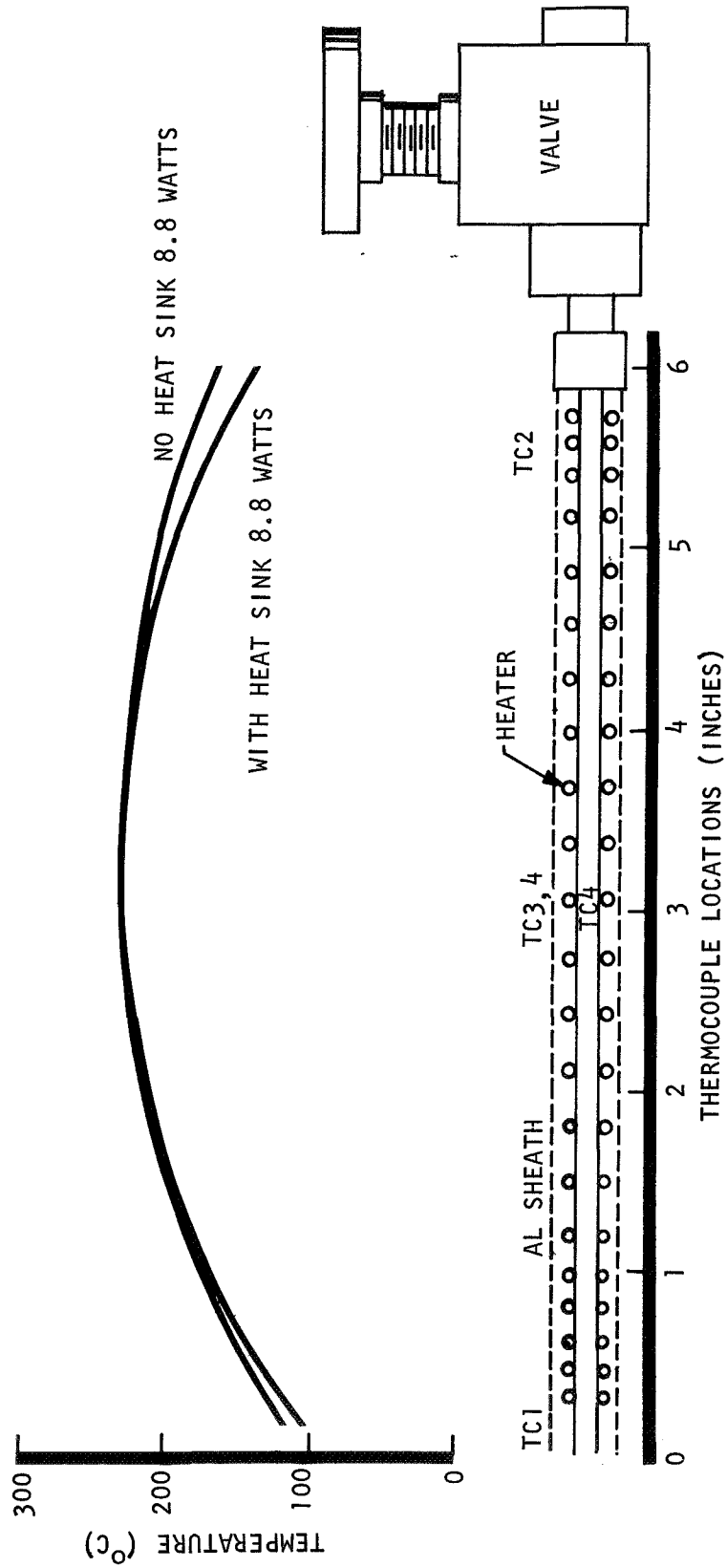


FIGURE 34b.- Test Results

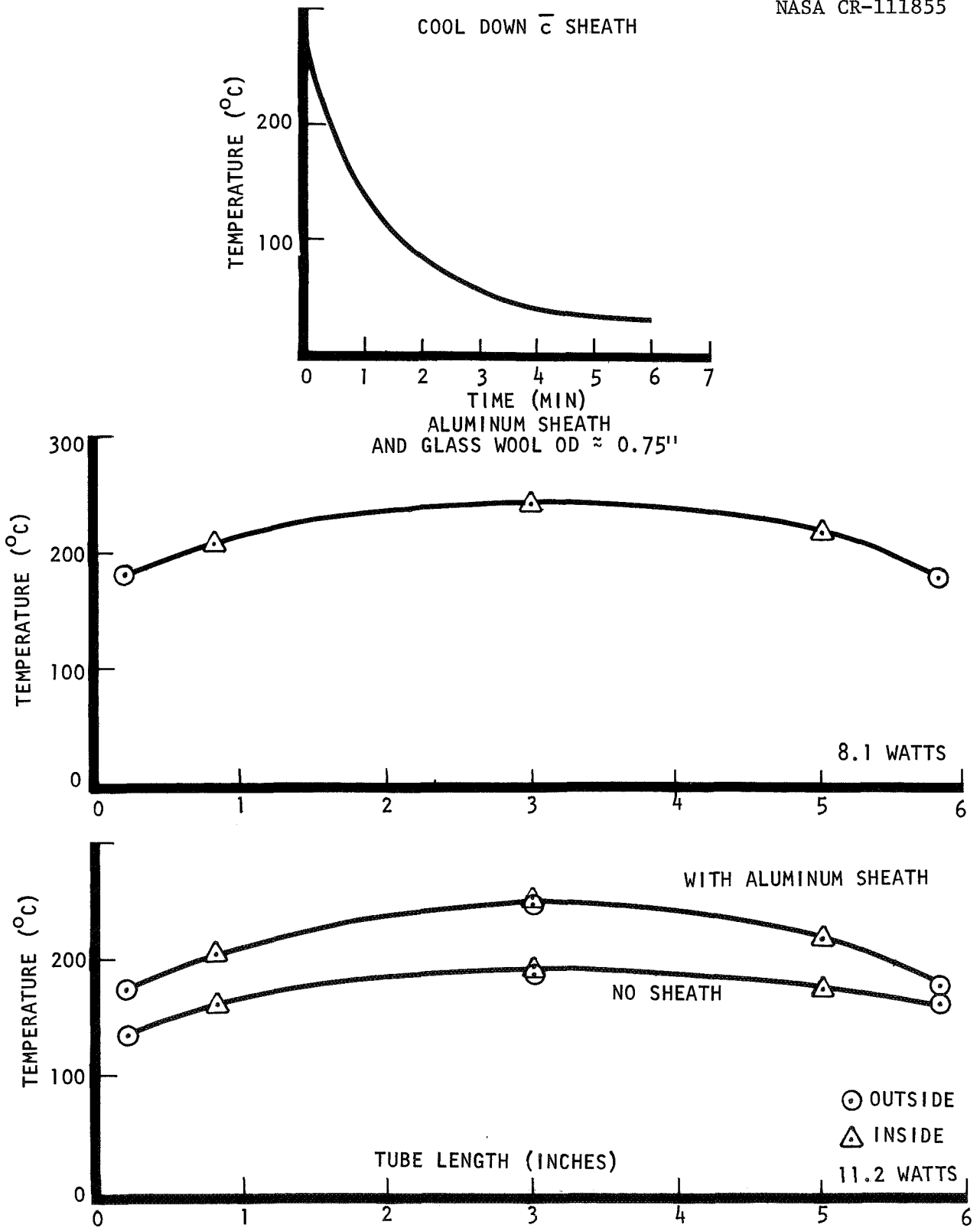


FIGURE 34c.- Test Results

ALUMINUM SHEATH  
THERMOCOUPLES SPOT WELDED ON  
11.2 WATTS

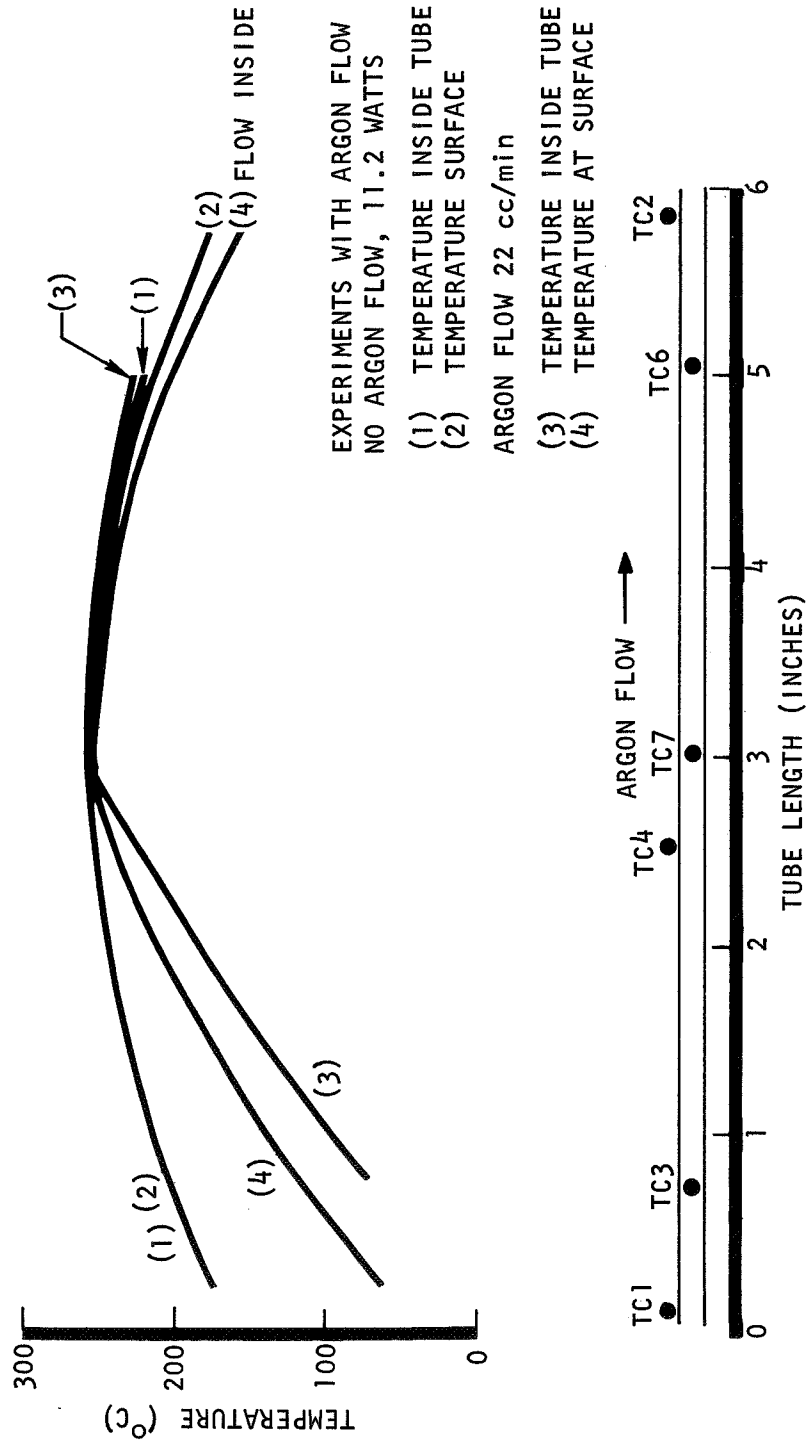


FIGURE 34d.- Test Results - Temperature Distribution

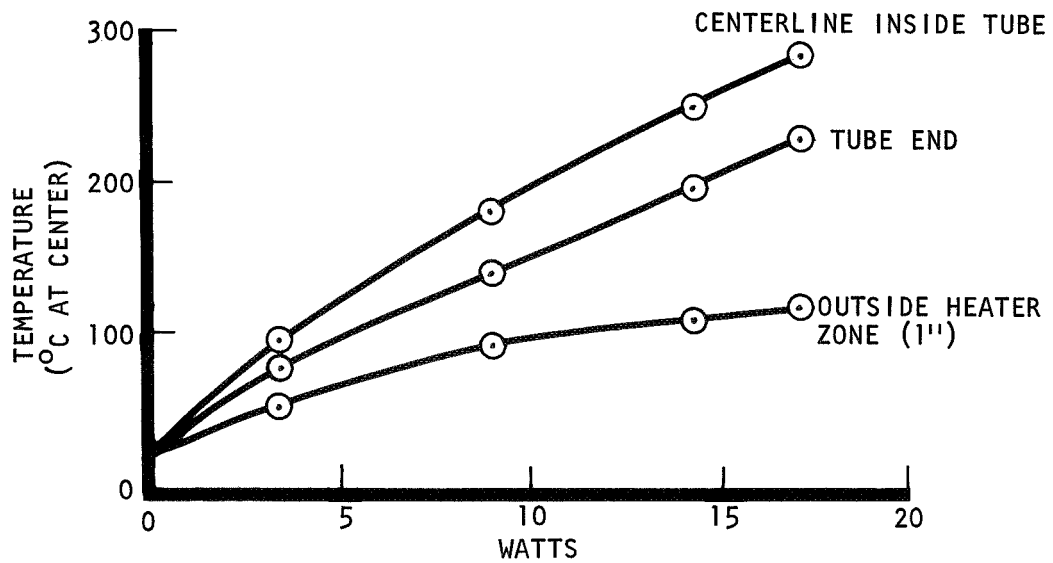
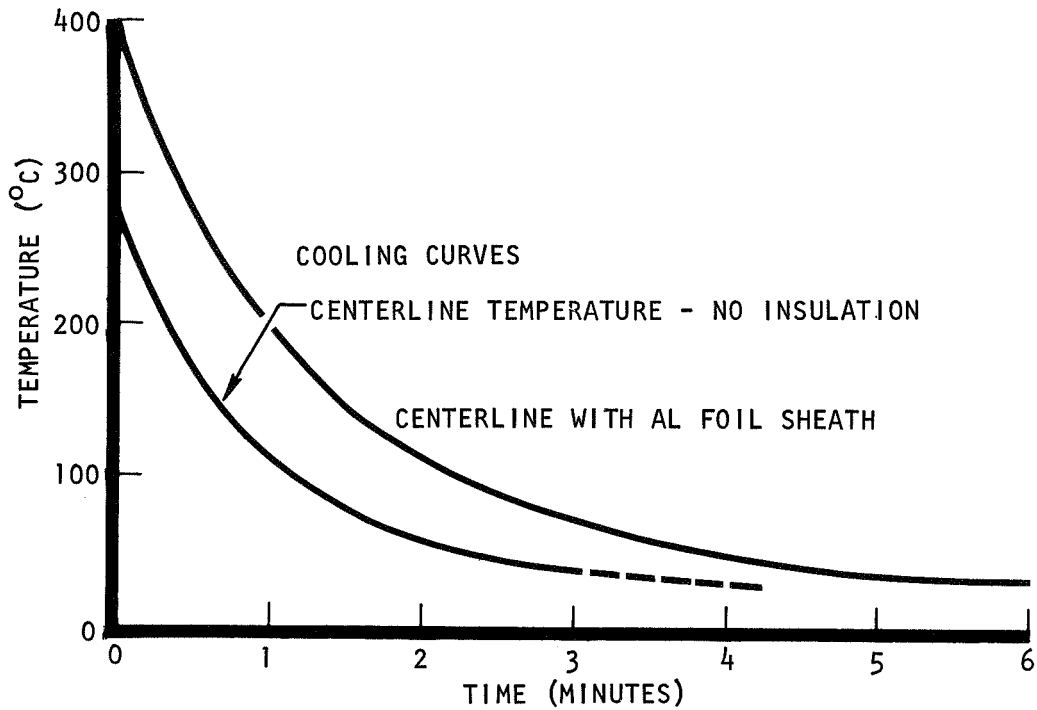


FIGURE 34e.- Test Results - 6" x 1/8" x 10 MIL Stainless Steel With 0.39 g PD Charcoal No Insulation

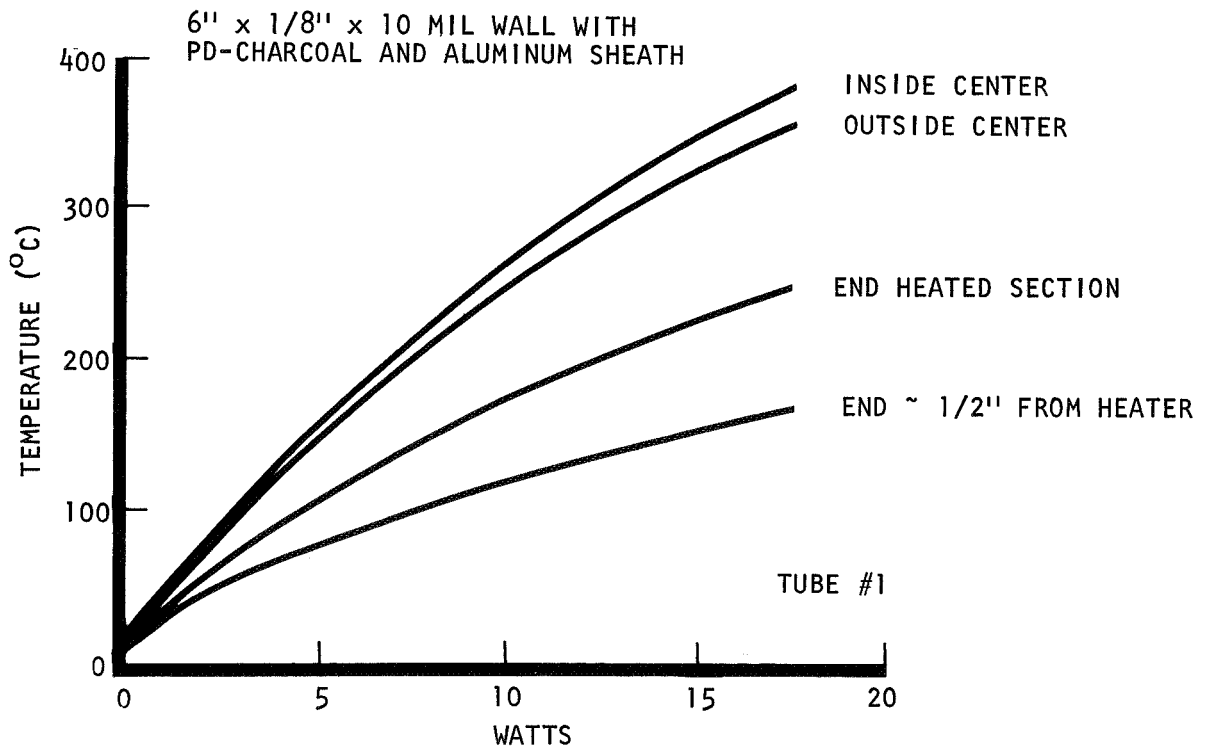
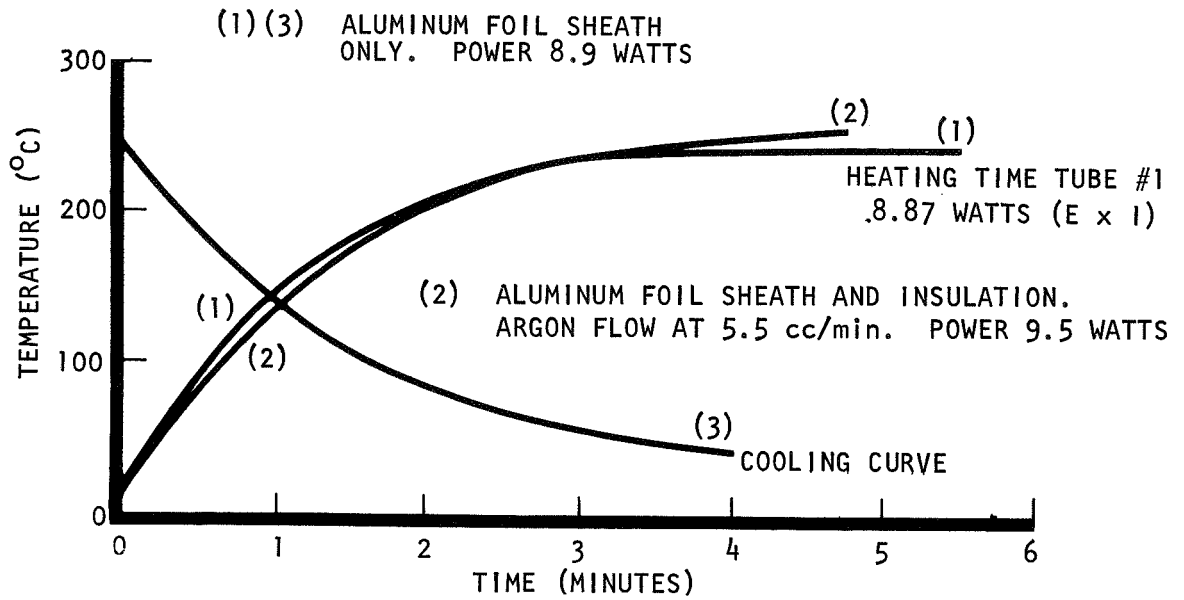


FIGURE 34f.- Test Results

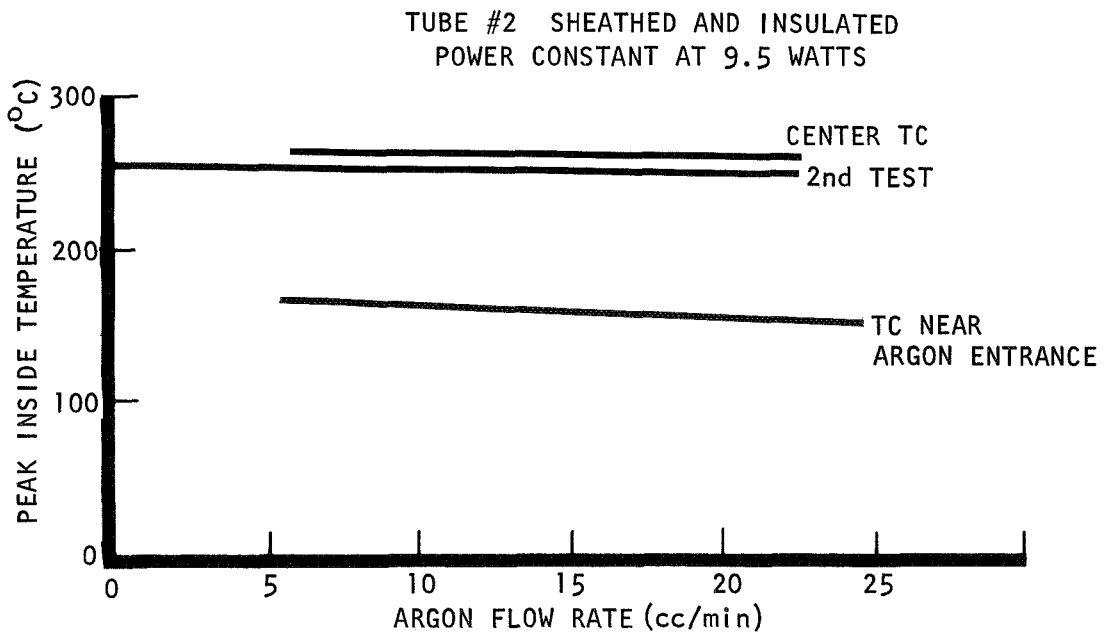
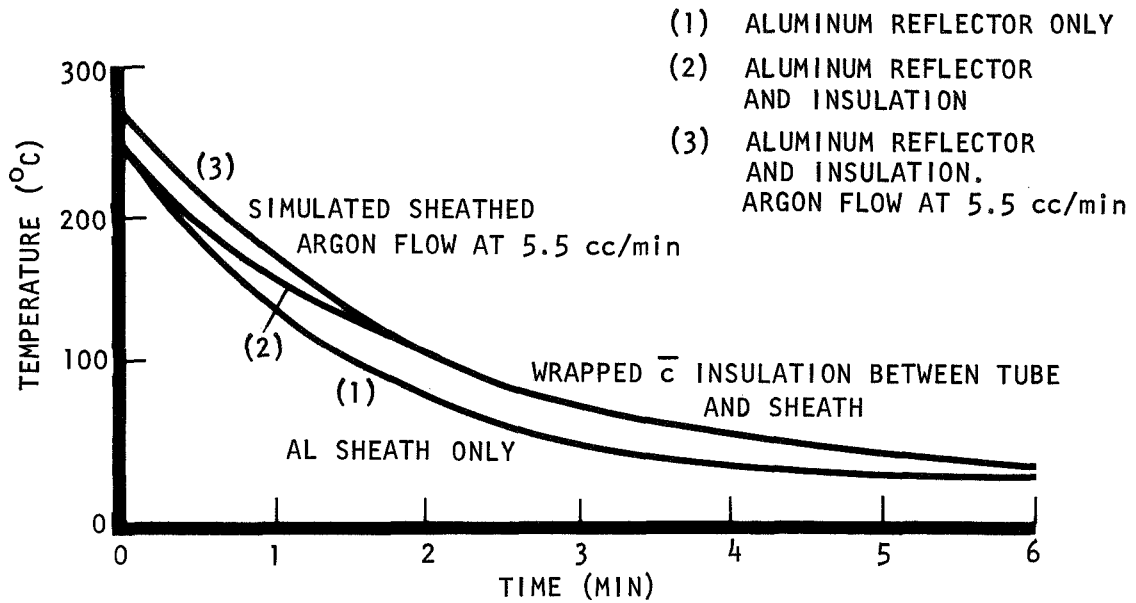


FIGURE 34g.- Test Results

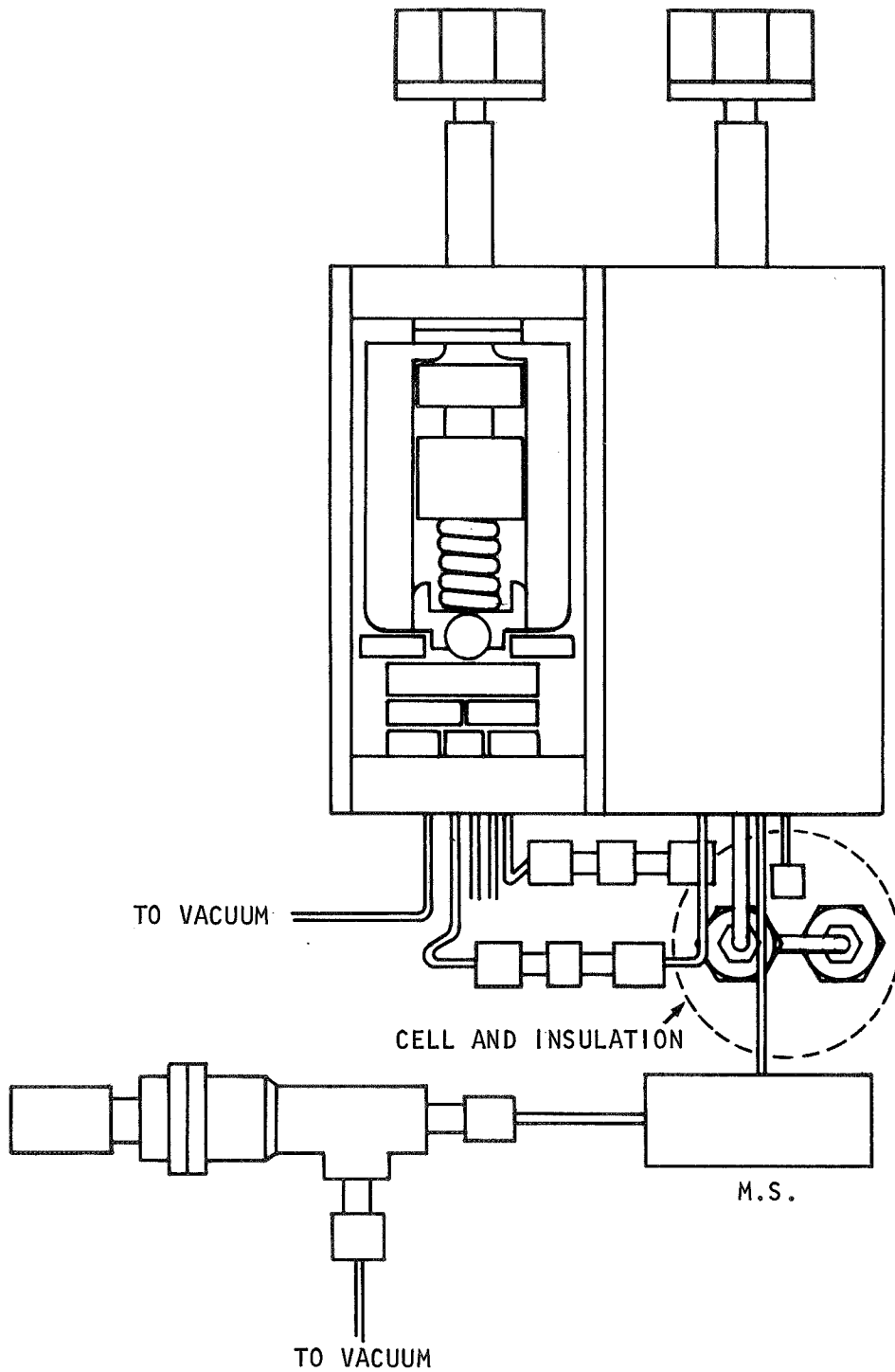


FIGURE 35.- CO Accumulator Cell System