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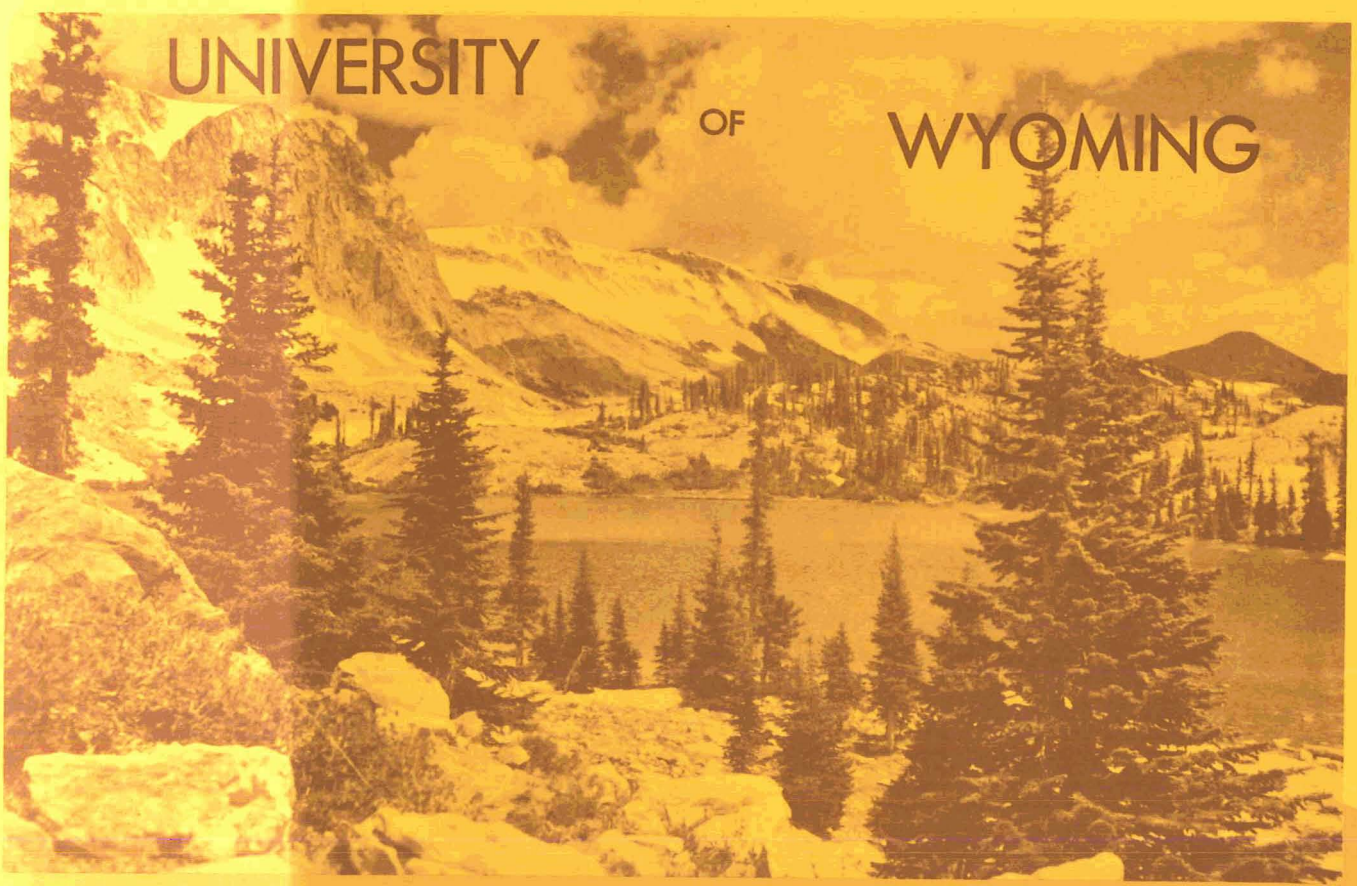

LAKE MARIE IN THE SNOWY RANGE—A SHORT DRIVE FROM CAMPUS

UNIVERSITY OF WYOMING

DEPARTMENT OF PHYSICS

Status Report
on
NASA Grant NGR 51-001-020
for the period 1 January 1967 to 1 January 1969

submitted by
Edgar A. Rinehart

Introduction

It was originally proposed that an experimental investigation be made of Harrington's theory of Intensity measurements, and a critical study be undertaken to determine the sources of possible instrumental errors. The ultimate aim of such studies being that of determining the necessary procedures required to perform quantitative analyses of polar gases in gaseous mixtures.

Experimental Methods and Results

In Figure 1 is shown a block diagram of the Hewlett-Packard R-8400 B Microwave Spectrometer purchased under this grant. The spectrometer is an in-line type rather than a bridge type. A calibration arm is included for accurate measurements of ΔP_g, the power absorbed by the gas due to a transition. This allows the accurate determination of either the Γ defined by Harrington[1] as:

$$\Gamma = \Delta P_g / L(P_o)^{\frac{1}{2}}$$

or the Beers Law intensity coefficient, γ defined (for small γL) as:

$$\gamma = \Delta P_g / L P_o$$

In the theory of saturated intensity coefficients developed by Harrington[1,2], the coefficient Γ is expressed as the product of two functions, $\Gamma = \eta\phi$, in which only the function η contains molecular information, and the value of

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[1]Harrington, H. W., J. Chem. Phys. 46, 3698 (1967)

[2]Harrington, H. W., J. Chem. Phys. 49, 3023 (1968)

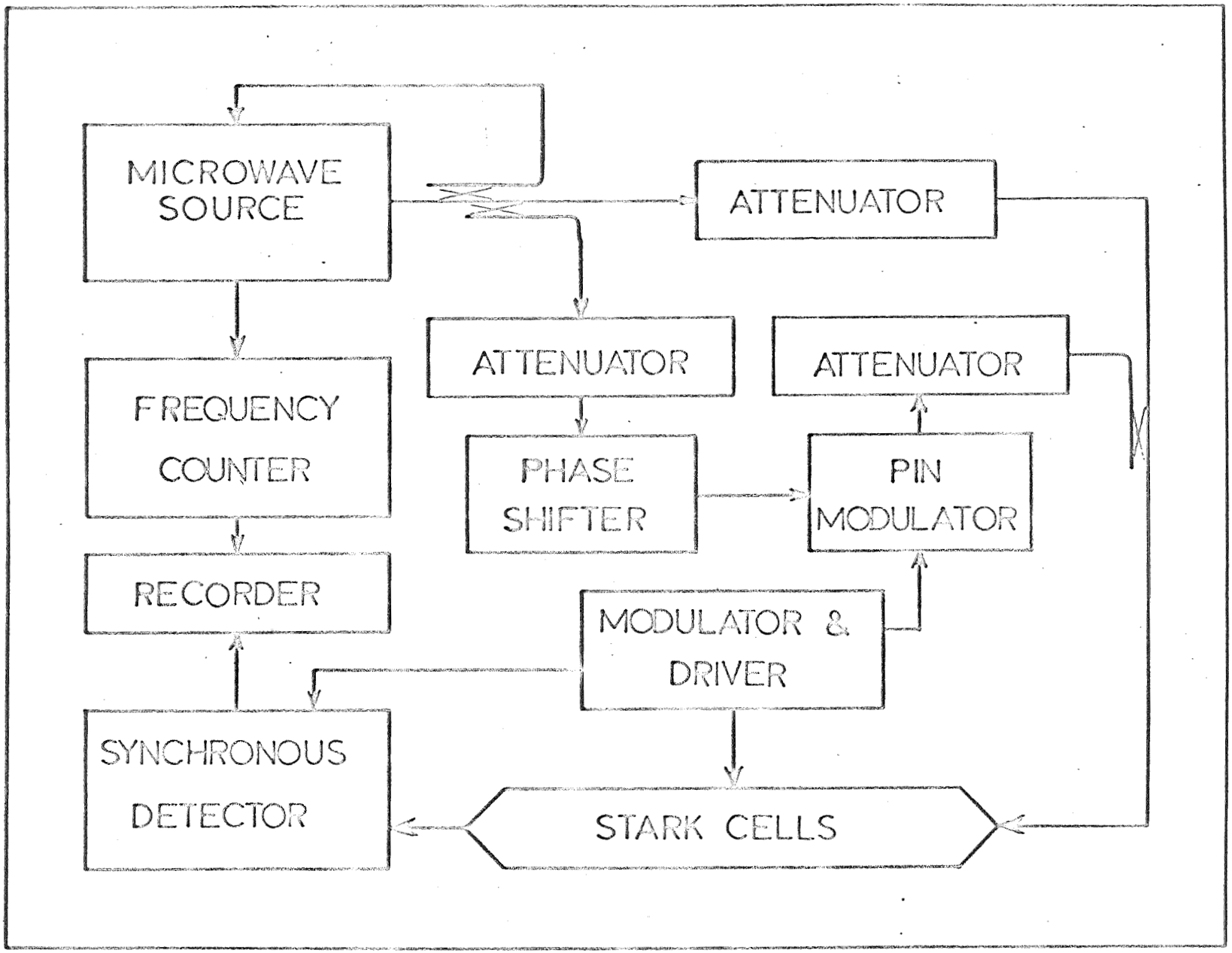
MICROWAVE SOURCE
ATTENUATOR
ATTENUATOR
ATTENUATOR
FREQUENCY COUNTER
PHASE SHIFTER
PIN MODULATOR
RECORDER
MODULATOR & DRIVER
SYNCHRONOUS DETECTOR
STARK CELLS

FIGURE 1

ϕ may be varied by the variation of incident power, P_o. The conclusion reached by Harrington[2] is that a curve of "Intensity" (here defined as spectrometer signal) vs incident power will have the same shape independent of molecular species or specific transition. That this is indeed the case is shown in Figure 2. Such curves are shown for three transitions in methanol. One may see that although the curves are shifted in both maximum signals available, and in the power at which maximum signal is obtained, their shapes are the same.

A comparison was then made of the saturation method and "constant crystal current" method of the variation of signal with pressure of the absorbing gas. The results are shown in Figure 3 for the strong transition in methanol at 37703.72 MHg. The constant crystal current curve was made under conditions of partial saturation. At higher pressures, in accordance with the Van Vleck-Weiskopf line shape theory, the signal will become constant with pressure. The data represented by the curve was obtained by saturating the transition to maximum signal for each pressure. The pressures for this and all subsequent experiments were measured with an MKS Barytron manometer. The linearity of signal vs pressure is evident from the figure, although the graph does not pass through the origin as predicted by Harrington's theory.

A detailed examination of the spectrometer signal at very low pressures was then made. These results for two transitions in methanol are shown in Figure 4. Both curves approach linearity below 1 millitorr and above 3.5 mtorr. The curvature in the region between 1.0 and 3.5 mtorr is believed to be due to the transition between molecule-wall collision relaxation, and molecule-molecule relaxation processes. Further study of this phenomenon is in progress.

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[2]Harrington, H. W., J. Chem. Phys. 49 3023 (1968)

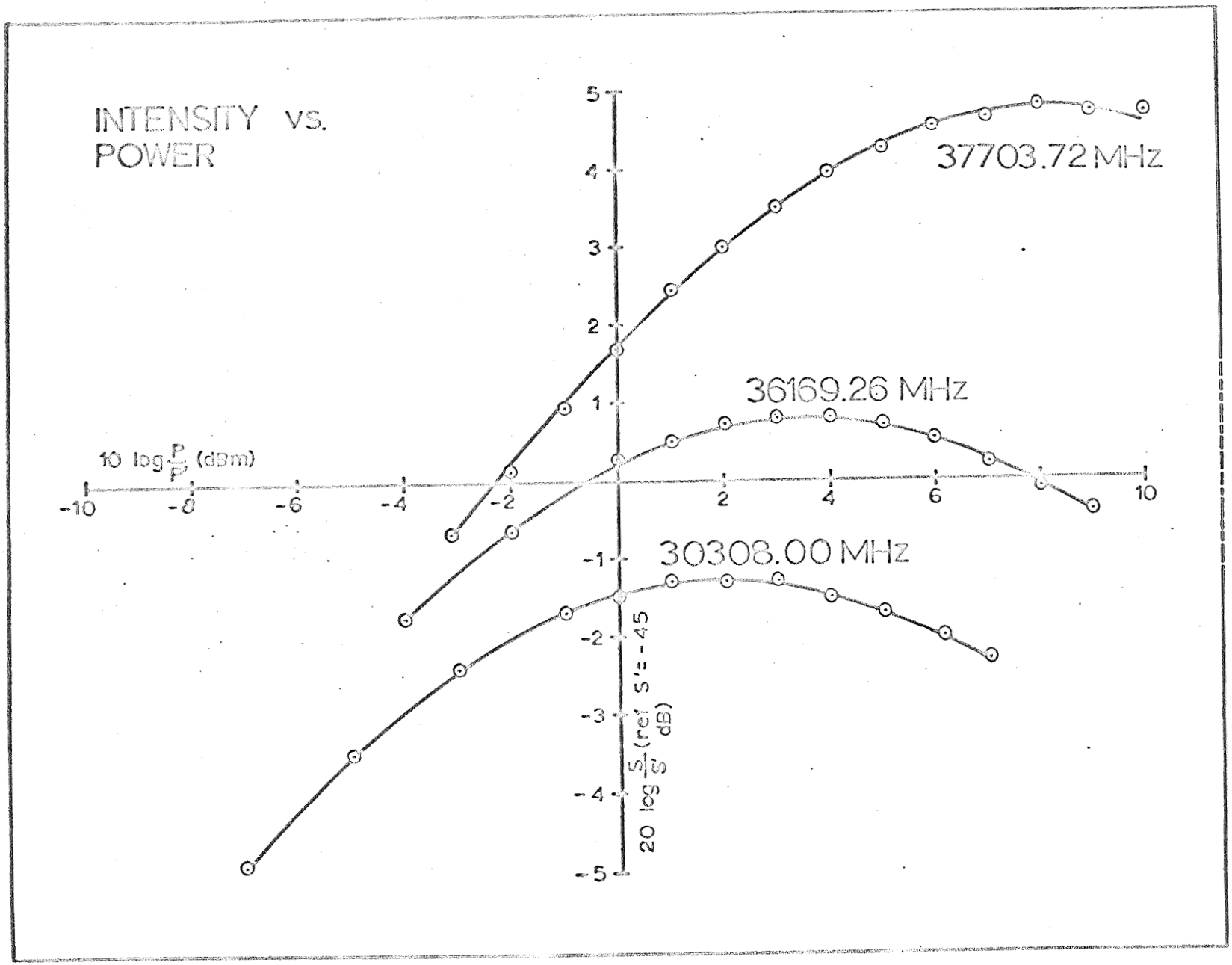

INTENSITY vs.
POWER
37703.72 MHz
36169.26 MHz
30308.00 MHz
10 log P/P' (dBm)
-10
-8
-6
-4
-2
2
4
6
10
5
4
3
2
1
-1
-2
-3
-4
-5
20 log S/S' (ref S'= -45 dB)

FIGURE II

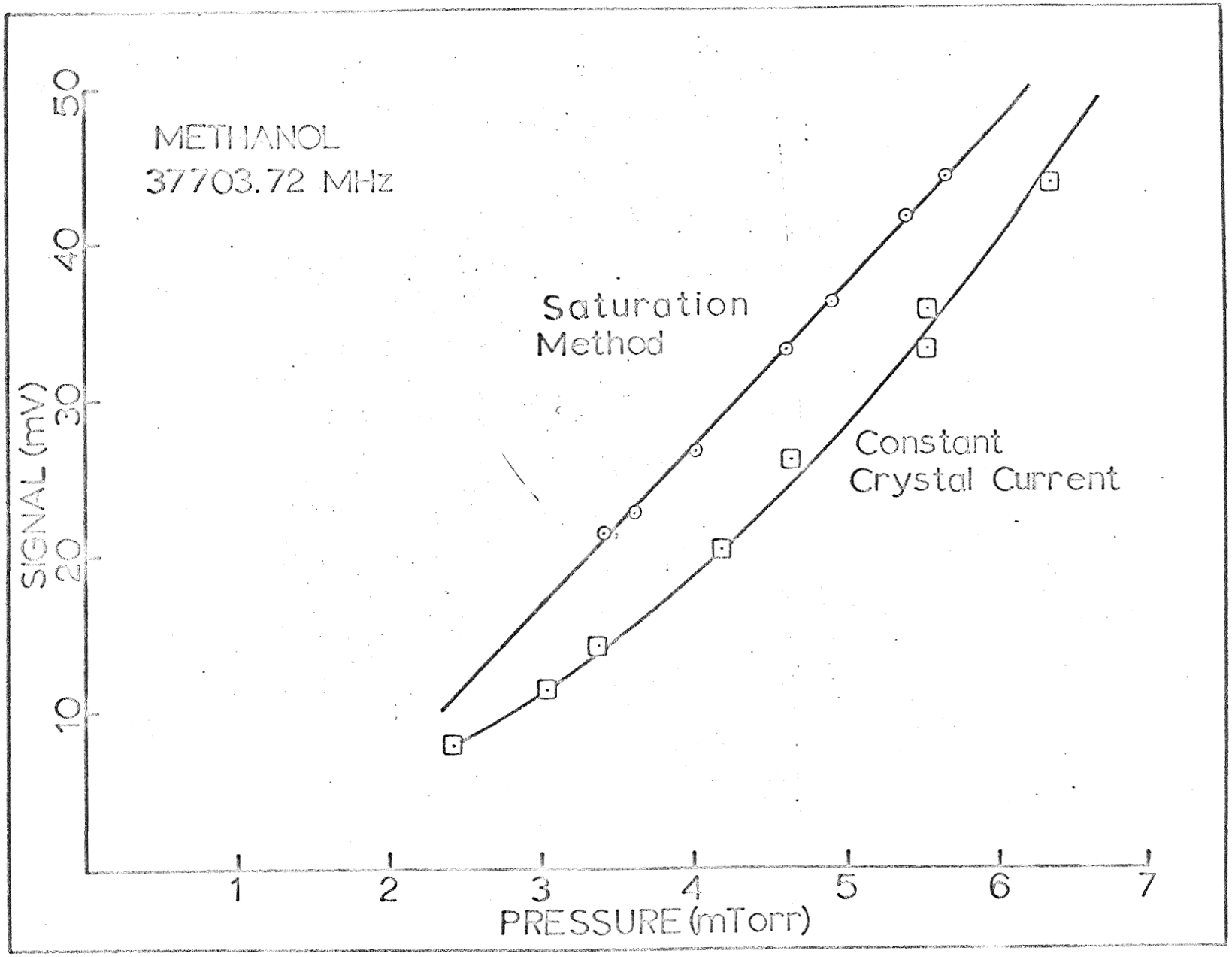

METHANOL
37703.72 MHz
Saturation
Method
Constant
Crystal Current
SIGNAL (mV)
10
20
30
40
50
1
2
3
4
5
6
7
PRESSURE (mTorr)

FIGURE III

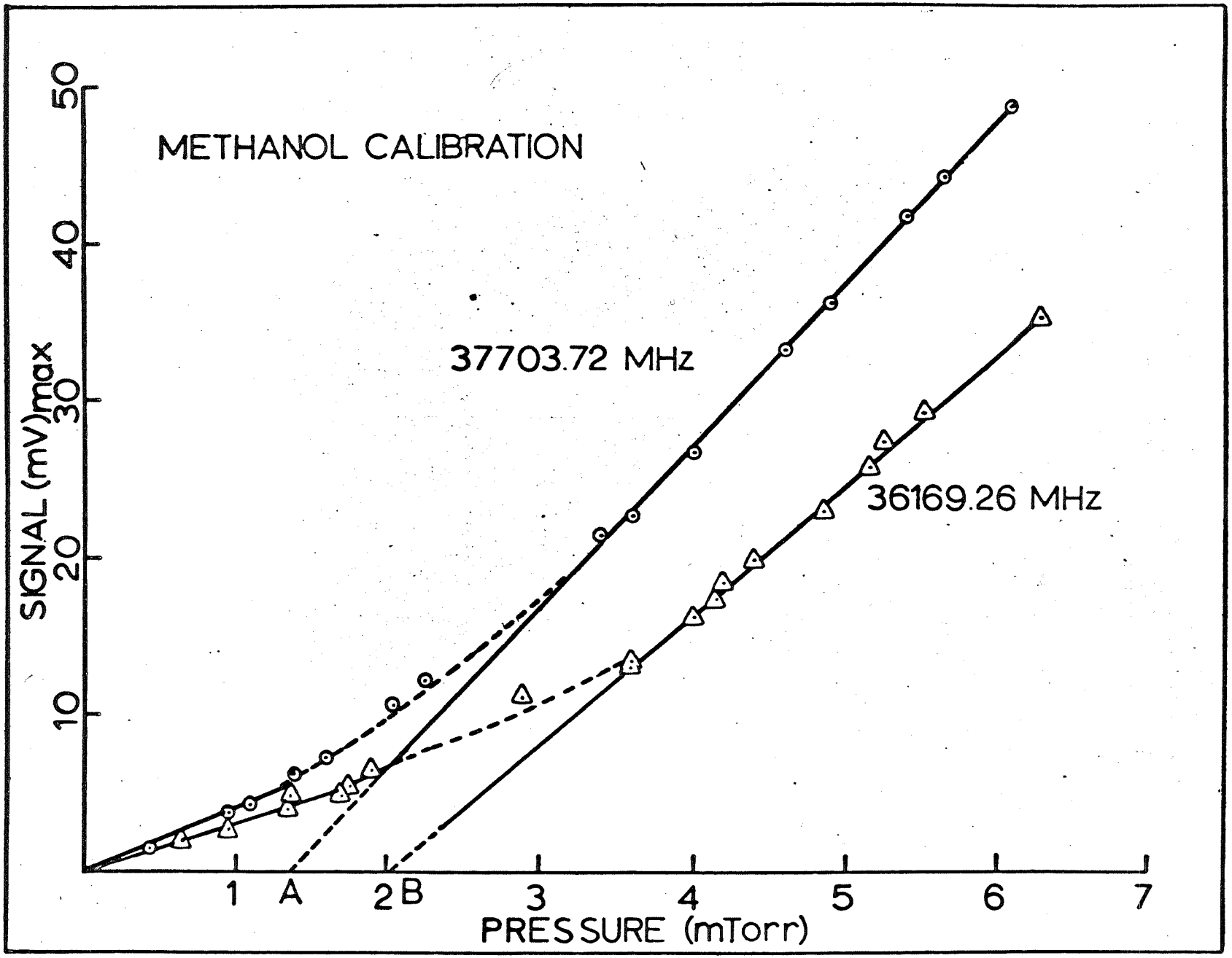

METHANOL CALIBRATION
37703.72 MHz
36169.26 MHz
SIGNAL (mV)max
10
20
30
40
50
1
A
2
B
3
4
5
6
7
PRESSURE (mTorr)

FIGURE IV

Utilization of the linearity of signal vs pressure of the absorber to determine quantity of absorbing species present was attempted using these calibration graphs. A small quantity of methanol was admitted to the absorption cells, and was then diluted with air. A measurement of the signal for two transitions should then produce a measure of the partial pressure of methanol. This is depicted in Figure 5, where a remarkably close agreement is shown. For partial pressures lower than 5 mtorr, however, the agreement was poor. It was noted emperically, that the apparent intercept of the graph with the x-axis for a dilute gas varied as $B = N^2 B_o$ where B_o was the intercept of the extended graph for a pure absorber, and N is the mole fraction. This emperical rule was used in further dilution experiments. The results, in Table I, demonstrate that this rule does give self-consistent results.

TABLE I

METHANOL DILUTION EXPERIMENT

PARTIAL PRESSURES (mTorr)

	From Calib. Graph			Calculated ($B=N^2B_o$)			Total Press (mtorr)
RUN	36169	37703	Δ	36169	37703	Δ	
1	4.22	4.09	-.13	3.71	3.73	+.02	7.45
2	4.10	3.93	-.17	3.55	3.54	-.01	7.60
3	3.31	3.02	-.29	2.25	2.27	+.02	14.00
4	3.90	3.71	-.19	3.23	3.24	+.01	8.60
5	4.46	4.29	-.17	3.83	3.83	.00	9.60
6	4.47	4.21	-.26	3.75	3.70	-.05	12.60
6'	ITERATED			3.56	3.56	.00	

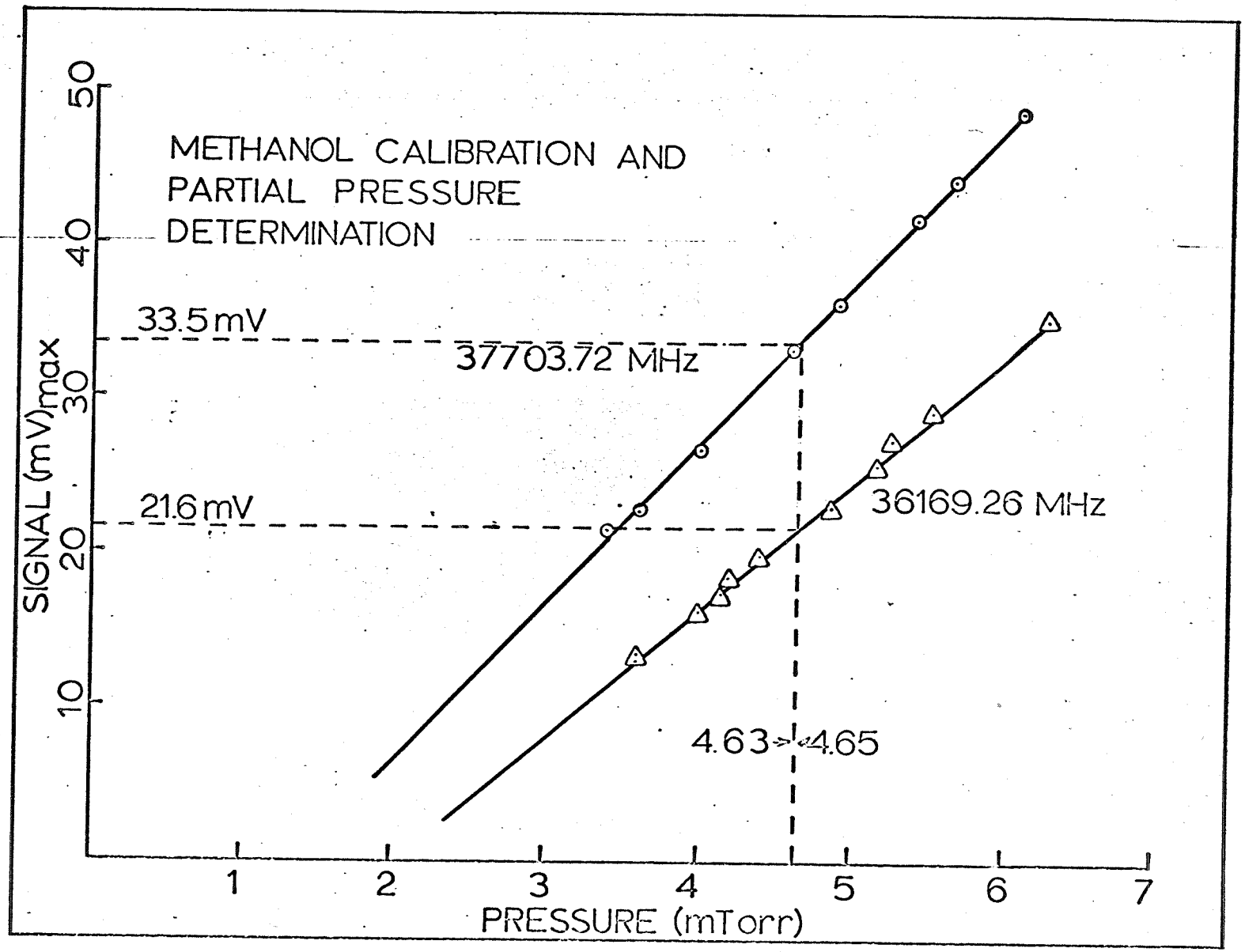

METHANOL CALIBRATION AND
PARTIAL PRESSURE
DETERMINATION
33.5 mV
37703.72 MHz
21.6 mV
36169.26 MHz
4.63 → 4.65
SIGNAL (mV)max
10
20
30
40
50
1
2
3
4
5
6
7
PRESSURE (mTorr)

FIGURE V

However, since no solid theoretical reasons have been developed as yet for this behavior, such a procedure cannot be considered reliable. In spite of this lack of solid theoretical results, an attempt was made to determine mole fractions of methanol in ethanol. Considerable time was spent in providing exceptional cleanliness of the vacuum system, and it was found that the concentration of methanol varied with time within the absorption cell. This is apparently a problem of differential adsorption of the molecules on the walls of the cells and vacuum system, and differential absorption into materials within the vacuum system. The concentration of methanol was, therefore, measured as a function of time for several runs. For most of these runs, the cell was "seasoned" at a pressure slightly higher than the operating pressure. Pumping time between runs, except for one run, was just sufficient to reduce current in the Ion pump to below 100 μA, corresponding to a pressure of the order of 10^{-5} torr. In the exception, the pumping time was longer, but the cell was seasoned in a manner similar to the other runs. The results of this experiment are shown in Figure 6. The exception is Run 1, sample A. The measured mole fraction as a function of time is seen to approach the prepared mole fraction. For sample A, the average of the last measurements for all four runs was .1287 and for sample B the average was .1065. The agreement is believed to be fortuitous.

These results were presented at the 155th National ACS Meeting in San Francisco in April 1968.

In the course of the experiments discussed up to this point, it was noted that the slope of a calibration curve could vary from day to day. A more stable calibration was required, preferrably one which could be made constant from instrument to instrument, as well as for one instrument from day to day. Furthermore, careful consideration of detector crystal response as a function of crystal current dictated a more refined calibration technique.

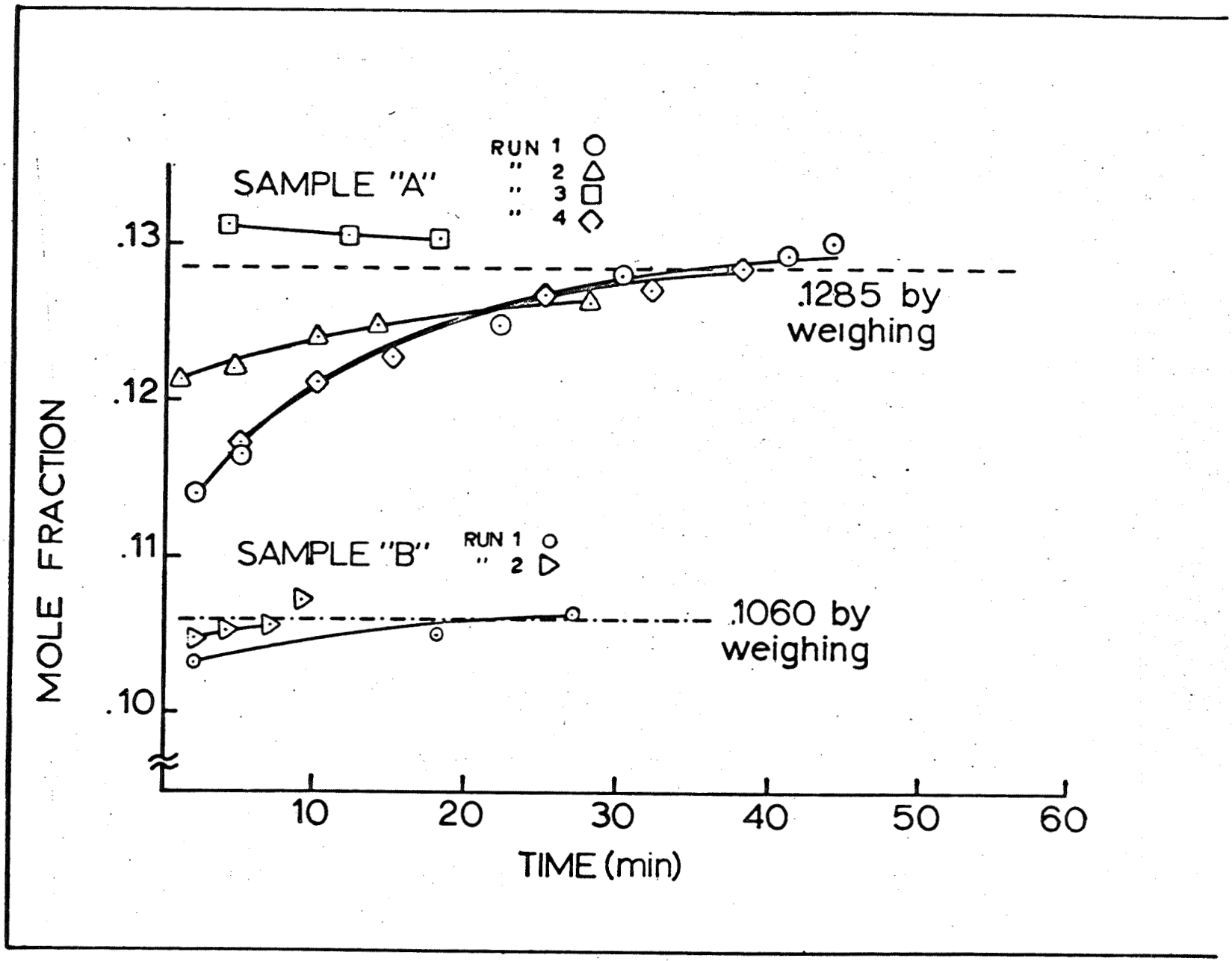

SAMPLE "A"
RUN 1
" 2
" 3
" 4
.13
.12
.11
.10
.1285 by weighing
SAMPLE "B"
RUN 1
" 2
.1060 by weighing
MOLE FRACTION
10
20
30
40
50
60
TIME (min)

FIGURE VI

An examination of the detector crystal sensitivity as a function of current (in Figure 7) reveals that at higher powers, therefore higher pressures, the sensitivity remains almost constant with crystal current. This implies that, although the higher pressure measurements (above 3.5 mtorr) vary little due to this factor, the lower pressure measurements could be in serious error due to reduced sensitivity. To circumvent this difficulty with an in-line spectrometer, the calibration arm was used to provide a constant reference signal with which the molecular absorption signal could be compared.

The experiment then proceeded as follows:

The attenuators in the calibration arm were set so that the signal appearing at the synchronous detector output due to the calibration signal was near the mid range of the molecular signal. The molecular signal is then designated as V_{stark} and the signal from the calibration arm as V_{cal}. For a given absorption by the gas ΔP_g, the ratio of these signals should remain constant despite variations in detection system sensitivity. The "signal" was then redefined as $\frac{V_{stark}}{V_{cal}}$. The improvement in consistency of results was remarkable. Previously, a calibration curve was prepared and used the same day. Afterwards, data from several days' operation could be combined to provide a single calibration curve. Such curves, for the same methanol transitions discussed previously, are shown in Figure 8. The improvement at low pressure (therefore low power and low crystal current) may be seen immediately. It may be seen that the apparent intercept with the x-axis is identical, within experimental error for the two transitions. Insufficent data is available at present to generalize on this particular point. It would seem, however, that since the absorbtion at pressures below 1 mtorr depends almost wholly upon wall collisions for the relaxation process, that this indeed should be the case. Transferring calibration figures from instrument

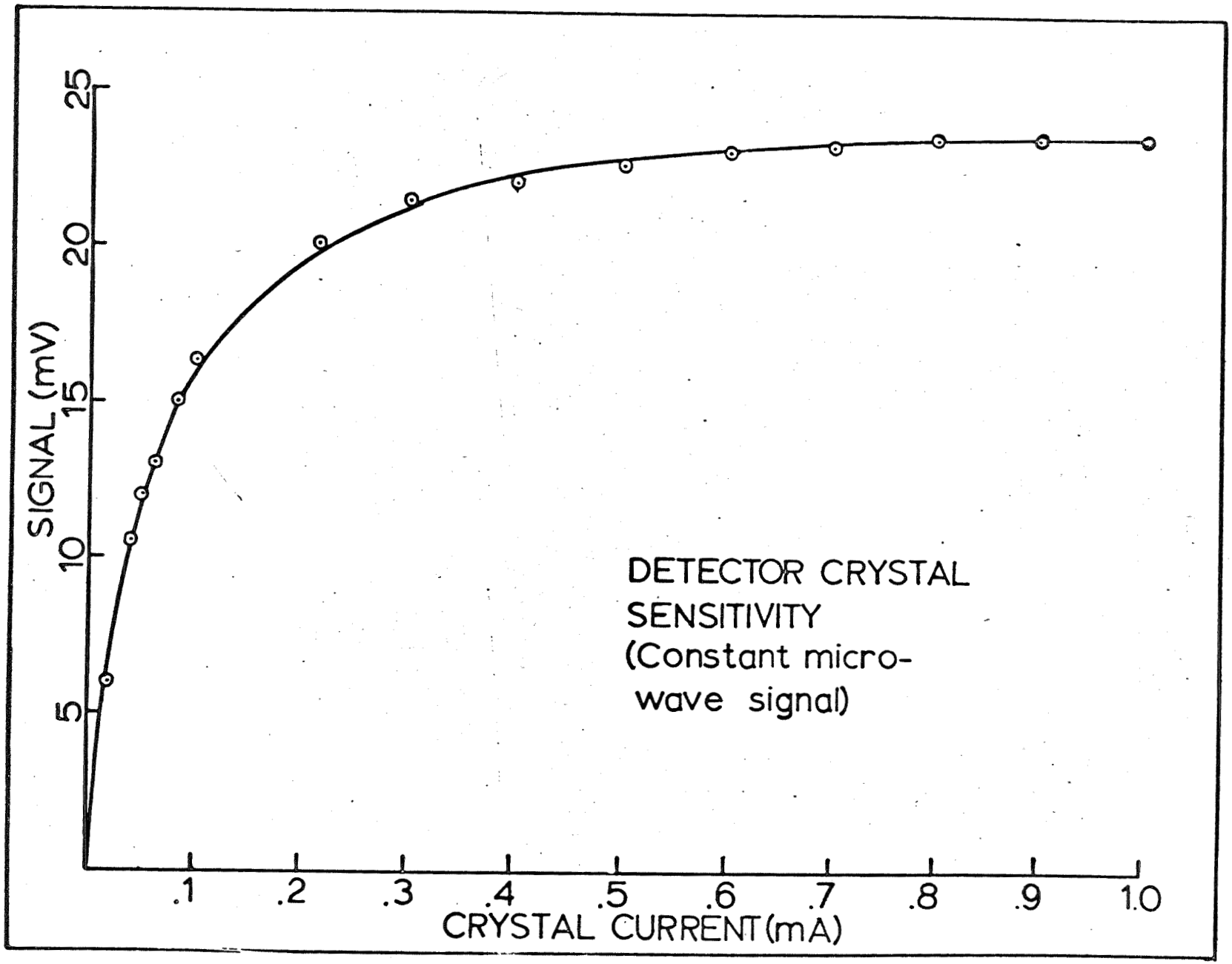

SIGNAL (mV)
5
10
15
20
25
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
CRYSTAL CURRENT (mA)
DETECTOR CRYSTAL
SENSITIVITY
(Constant micro-
wave signal)

FIGURE VII

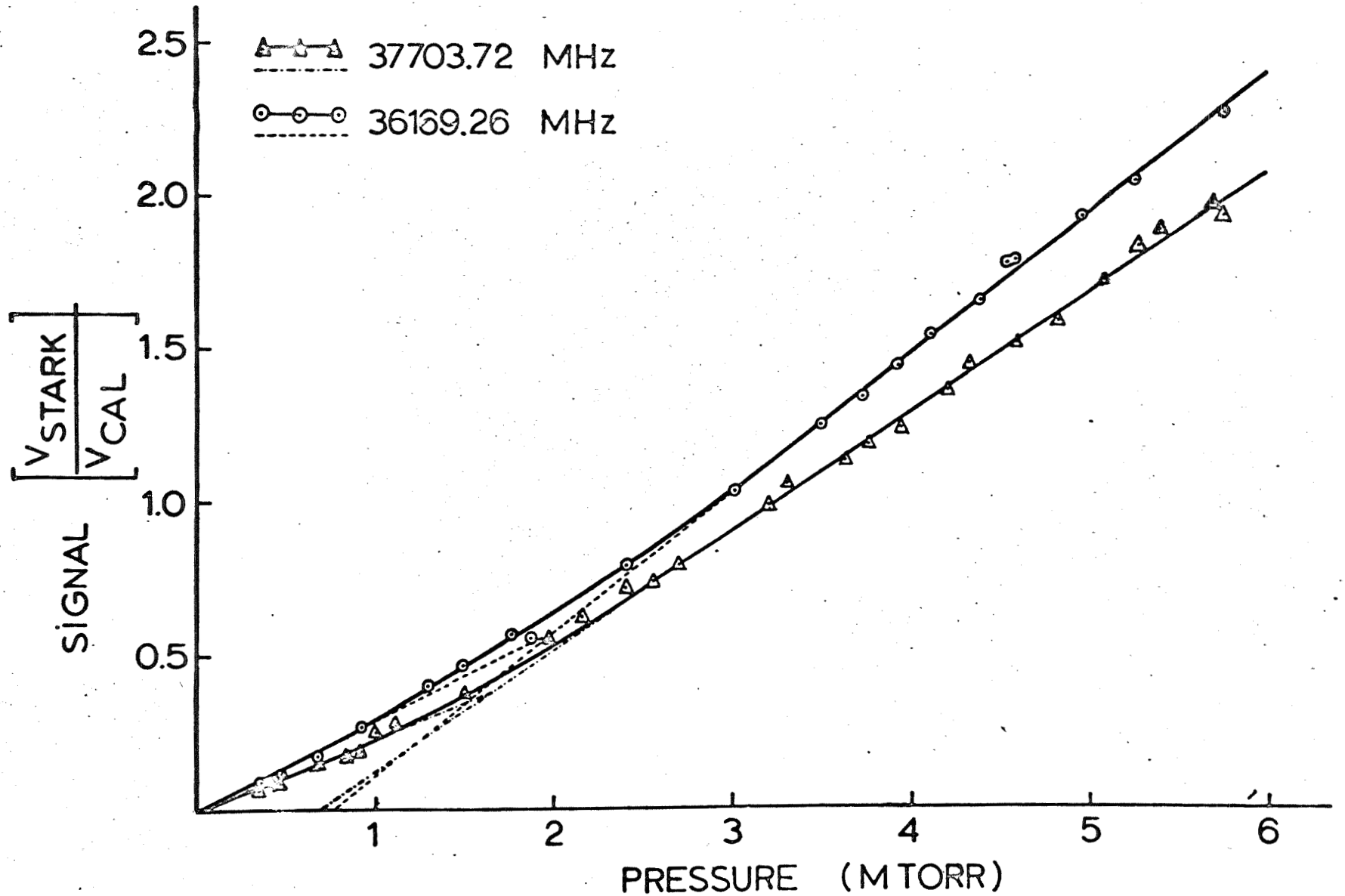

37703.72 MHz
36169.26 MHz
SIGNAL [V_STARK / V_CAL]
2.5
2.0
1.5
1.0
0.5
1
2
3
4
5
6
PRESSURE (M TORR)

FIGURE VIII

to instrument now depends upon accurate absolute calibration factors for each individual instrument, and upon the adoption of suitable standards, by analytical microwave spectroscopists, for a definition of "signal".

The region below 3.5 mtorr is shown, in greater detail, in Figure 9. The data points below 1 mtorr give a fair least squares fit to a straight line passing through the origin. At these pressures, the mean free path is considerably larger than the cell dimensions, reinforcing the conclusion that the relaxation process in largely due to wall collisions. A series of samples of methanol in benzene were then prepared, and measurements were made to determine if the slopes of signal vs partial pressure graphs were constant for dilution. The results are shown in Figure 10. Partial pressures were determined from the measured total pressure and the known, prepared, mole fraction. A least squares fit to the data showed the slopes to be identical, within experimental error. Furthermore, as dilution was increased, the graphs tended to pass closer to the origin. This is reasonable, since, even at low partial pressures, solvent molecules are available for collisions between molecules to produce relaxation. This indicates that the slope of the signal vs partial pressure of absorber is the critical quantity to be determined for analytical purposes, and is the quantity containing molecular density information. A simple technique for determining concentration of absorbing species could be that of measuring the actual signal. If this technique were used, and the assumption made that the curve is linear through the origin, serious errors can result. The data discussed above, for several dilutions, was examined to determine how large these errors might be. A "Relative Signal" was defined as the actual partial pressure divided by the partial pressure using the linear approximation (as if the curve passed linearly through the origin). This was plotted vs the partial pressure, and is shown in Figure 11. The errors from this approximation may be

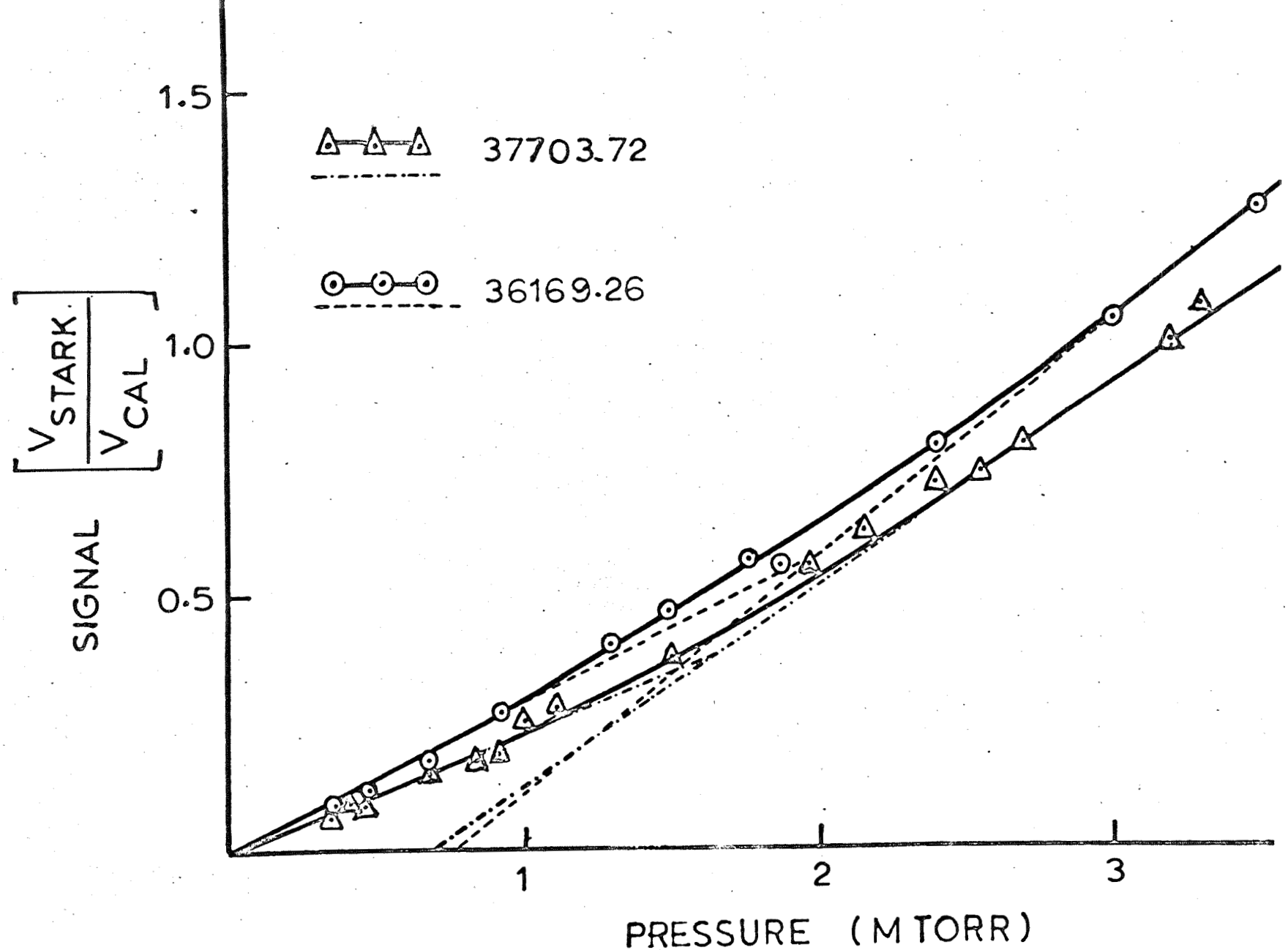
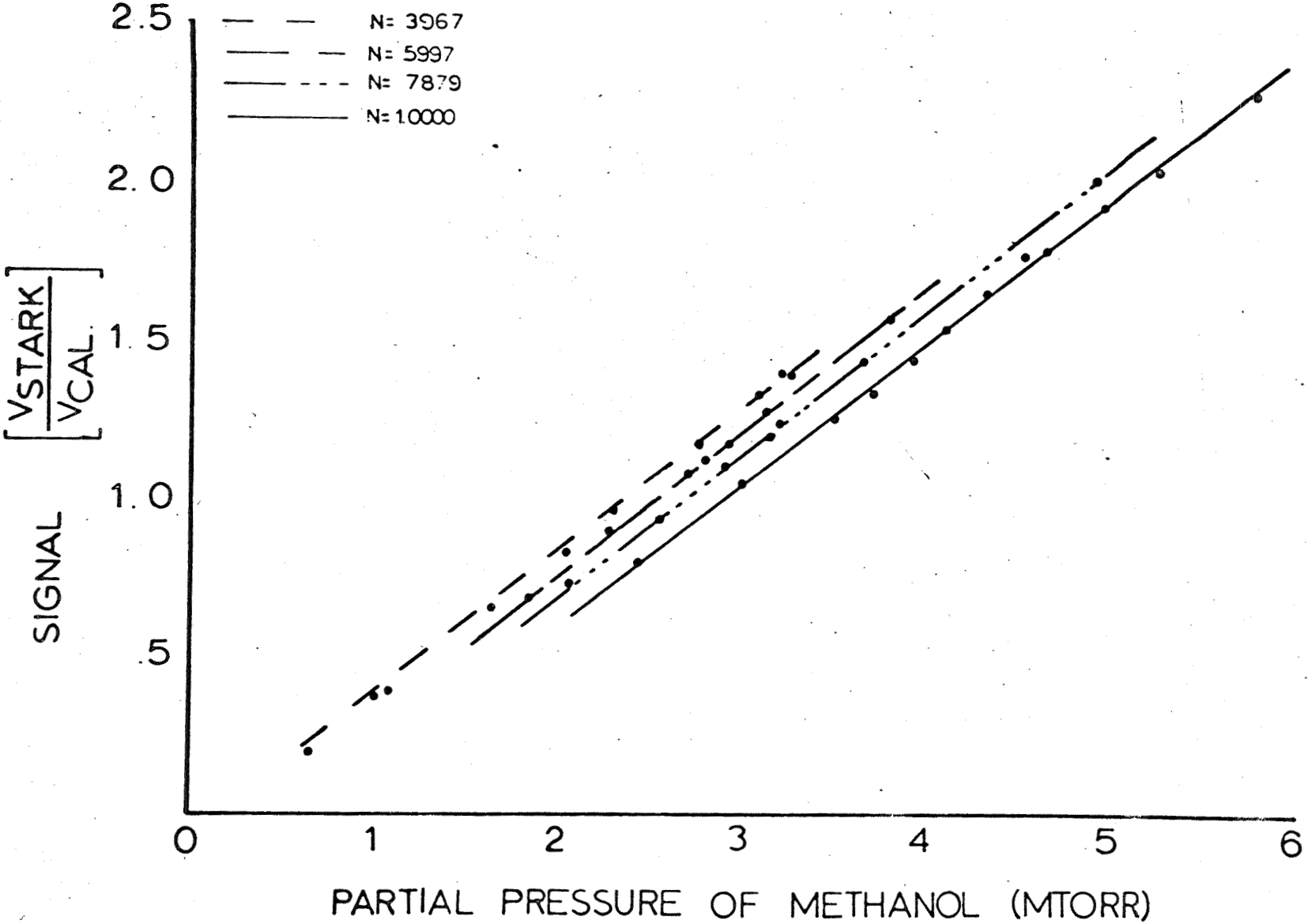

1.5
1.0
0.5
SIGNAL [V_STARK / V_CAL]
37703.72
36169.26
1
2
3
PRESSURE (M TORR)

FIGURE IX

FIGURE X


N= 3967
N= 5997
N= 7879
N= 10000
SIGNAL [VSTARK / VCAL.]
2.5
2.0
1.5
1.0
.5
0
1
2
3
4
5
6
PARTIAL PRESSURE OF METHANOL (MTORR)

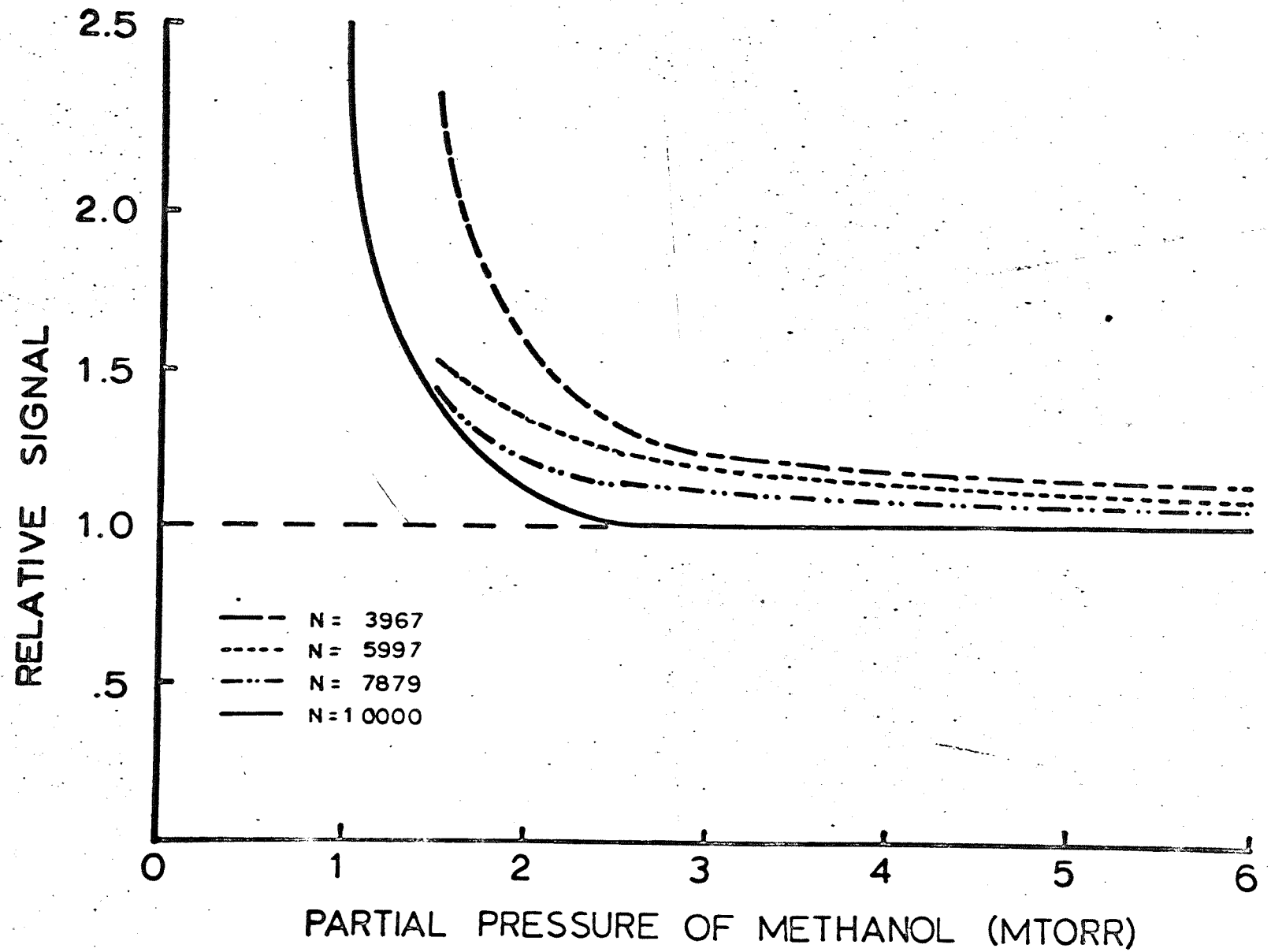

2.5
2.0
1.5
1.0
.5
RELATIVE SIGNAL
N = 3967
N = 5997
N = 7879
N = 10000
0
1
2
3
4
5
6
PARTIAL PRESSURE OF METHANOL (MTORR)

FIGURE XI

seen to become quite large at very low partial pressures. This indicates that a more careful procedure must be followed. If the behavior of the apparent intercept can be confirmed by careful theoretical work, then the previous procedure can be utilized. An alternative procedure is suggested, however, by Figure 12. In this figure, the signal is plotted vs total pressure. Although data points are not shown, the curves are a least squares fit to the data presented in Figure 10. The slopes from this least squares fit were compared, and it was found that the ratio $\frac{\Delta S_N}{\Delta P} / \frac{\Delta S_{N=1}}{\Delta P} = N$ where $\frac{\Delta S_N}{\Delta P}$ is the slope of the curve for mole fraction N. An examination of Harrington's theory shows that this should be the case. These slope ratios are compared with the prepared mole fractions, and with the ratio of signals method in Table II.

TABLE II

METHANOL DILUTION

Prepared N		.788	.600	.397
Slope	N	.791	.593	.396
Ratios	$N_{sl}-N_{prep}$	.003	-.007	-.001
Signal	N	.805	.612	.418
Ratios	$N_{sig}-N_{prep}$	.017	.012	.021

The mole fractions determined by signal ratios are seen to be consistently high, indicating a systematic error. The slope ratio method appears to produce much better results, and further study of this method, particularly for concentrations in the parts per million range, is being undertaken at the present time.

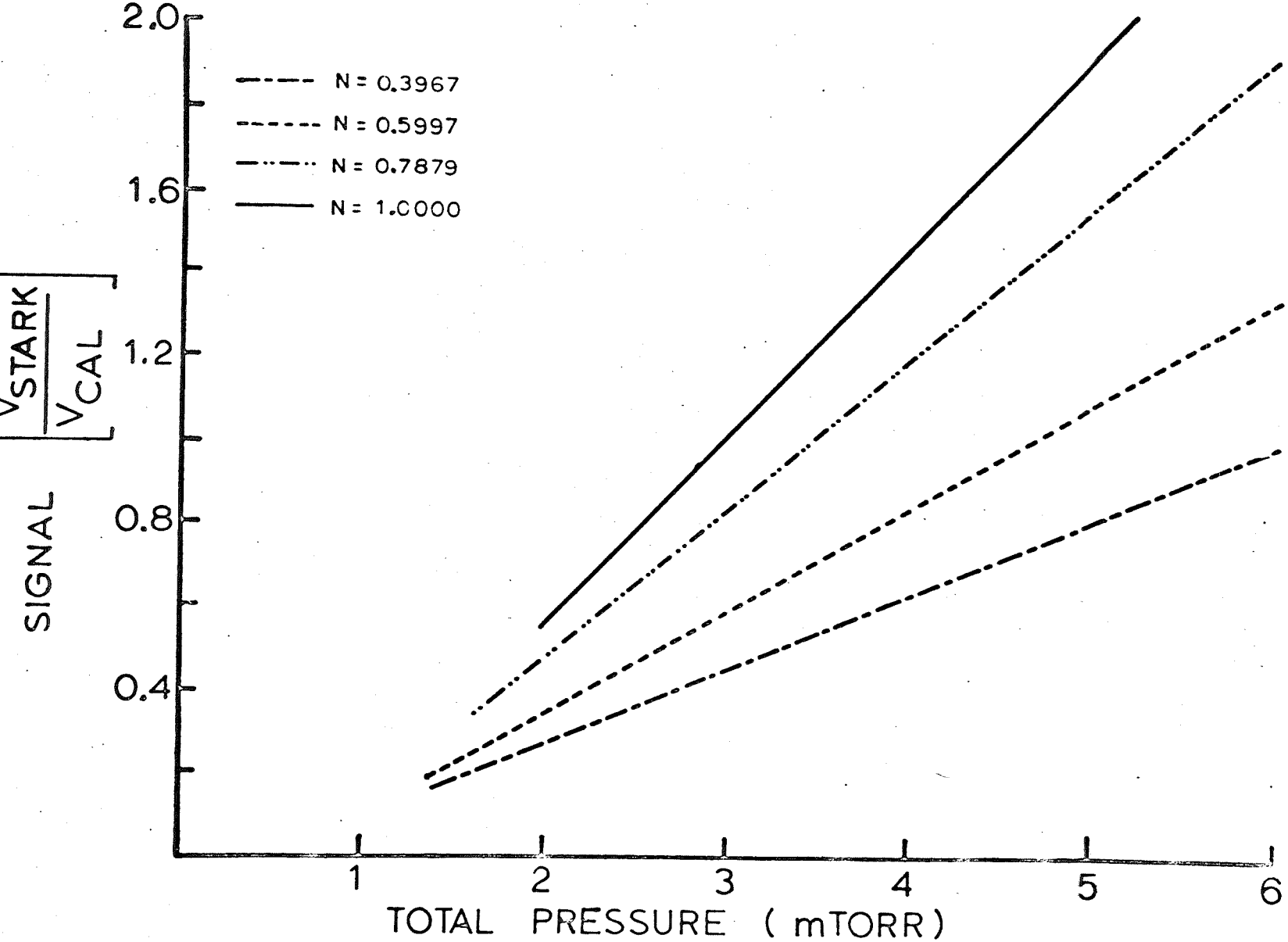

2.0
1.6
1.2
0.8
0.4
SIGNAL [VSTARK/VCAL]
N = 0.3967
N = 0.5997
N = 0.7879
N = 1.0000
1
2
3
4
5
6
TOTAL PRESSURE (mTORR)

FIGURE XII

An examination of the energies of the torsional vibrations in benzaldehyde and related substances has been undertaken also in this laboratory. Since these torsional vibrational energy levels have been studied in the far I-R, their determination for microwave intensity measurements provides a convenient cross-check of the validity of these measurements. In the process of studying both benzaldehyde and deutero-benzaldehyde, the problems of intensity measurements in a very rich, weak spectrum proved to difficult, but not impossible. A typical graph of signal vs pressure for a single rotational transition in two torsional vibrational states is shown in Figure 13. Such measurements for several rotational transitions have resulted in a figure of 110.8 ±2 cm^{-1} for the energy separation of the torsional states. The energy reported[3] from far IR studies[3] is 111 ±1 cm^{-1}. Intensity measurements have also revealed another vibrational mode which is accidentally near degenerate with the second excited torsional state. The benzaldehyde work has also resulted in the assignment of a very large number of rotational transitions. This work is nearing completion, and will be reported in the literature, as well as being a part of a future report.

Discussion

The work reported herein may be considered as experimental verification of the value of Harrington's saturation approach to Intensity measurements, and of the value of this type of measurement in quantitative analytical microwave spectroscopy. It has been demonstrated that spectrometer signal is a linear function of partial pressure of the absorber over a pressure range above 3.5 mtorr for pure gases. For gases of much higher dilution, the linear range extends to much lower pressures. A straight

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[3]Spectrochimica Acta, 23A, 981, (1967)

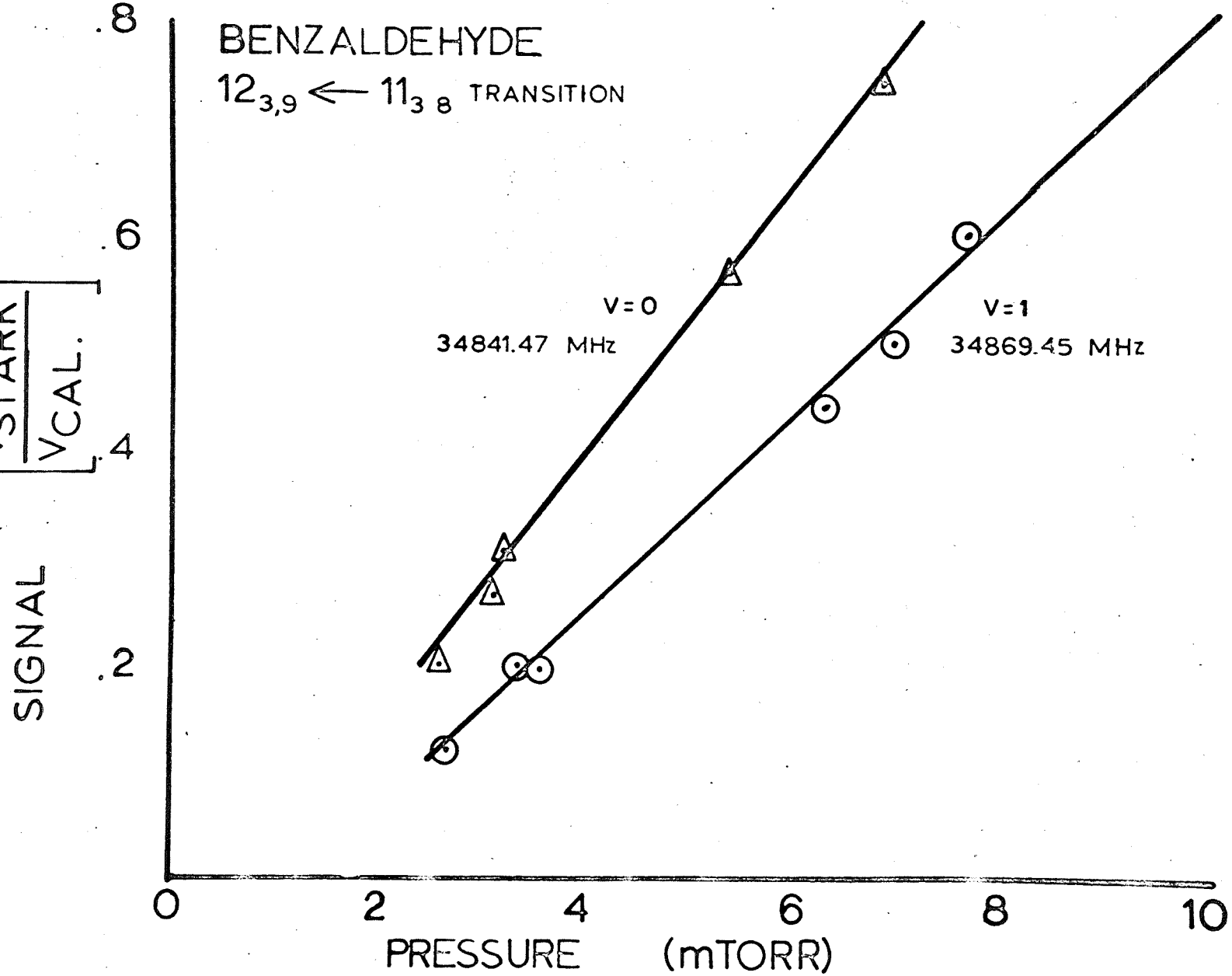
BENZALDEHYDE
$12_{3,9} \leftarrow 11_{3\,8}$ TRANSITION
V=0
34841.47 MHz
V=1
34869.45 MHz
SIGNAL $\left[\frac{V_{STARK}}{V_{CAL.}}\right]$
.8
.6
.4
.2
0
2
4
6
8
10
PRESSURE (mTORR)

FIGURE XIII

forward technique has been developed for the determination of concentrations, based upon the slope ratios. A less straightforward method, based on signal measurements only, has also been demonstrated. Accurate partial pressure measurements of individual components in a gaseous mixture have been shown to be feasible. The tremendous amount of data which could be made available from measurements on many compounds is, however, far to large to colllect with any efficiency under manual operation and recording. Operator errors would also tend to make such data unreliable. Operation under control of a small computer was, therefore, indicated. Such a computer was purchased with funds from this grant and was delivered in March 1969. Specific interfacing and programming methods will be reported in the future.

A program of study of the sulfur dioxide content of selected air samples was commenced near the end of the reporting period. This will provide a test of the methods reported here for very small quantities of polar consitutents of a mixture of gases. Concentrations in the parts per million range are easily determined, and the ultimate sensitivity appears to be several parts per billion. This work will be reported in a future reporting period.

A few inadequacies exist in the present instrumentation. These are:
(1) Low microwave power. Operation at higher pressures would be possible if powers above 50 milliwatts were available to saturate at shorter relaxation times. Backward wave oscillator tubes are now available to produce these powers, and instrument modification should include conversion to these higher power tubes.
(2) Restriction to in-line operation. Conversion of the instrument to bridge operation would allow operation of the detector diode at optimum

current and still allow variation of input power to the cells.
(3) Inadequate sampling system. At the present time the vacuum system contains elastomers which absorb many of the gases of interest. Furthermore, it is somewhat difficult to add a small, precisely known amount of gas to the system. A sampling valve which will alleviate the latter difficulty is being constructed for this instrument and will be installed soon. Some modification of the present vacuum system will be required to correct the first difficulty.

A problem related to number 3 above is that of separating compounds out of a many-component mixture. A large number of components may produce an extremely dense spectrum with overlapping stark lobes, making analysis difficult. Some method of pre-separation would, therefore, be very useful. Separation of polar constituents out of sample highly diluted with non-polar gases would greatly enhance the sensitivity of the system. Two methods are now available in this laboratory. The first amounts to simply freezing out the condensible components and pumping away the N_2 and O_2 in air samples. The second is a small, simplified gas chromatagraph arranged to collect individual peaks and pass the samples into the spectrometer individually. The latter system is nearing the test phase.