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FEASIBILITY STUDY FOR ROCKET OZONE
MEASUREMENTS IN THE 50 TO 80 KM REGION
USING A CHEMILUMINESCENT TECHNIQUE

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Prepared for

GODDARD SPACE FLIGHT CENTER
Greenbelt, Maryland 20771

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i

## Abstract

A study has been conducted to determine the feasibility of increasing sensitivity for ozone detection. The detection technique employed is the chemiluminescent reaction of ozone with a rhoda-mine-B impregnated disk. Previously achieved sensitivites are required to be increased by a factor of about 20 to permit measurements at altitudes of 80 km. Sensitivity was increased by using a more sensitive photomultiplier tube, by increasing the gas velocity past the disk, by different disk preparation techniques, and by using reflective coatings in the disk chamber and on the uncoated side of the glass disk. Reflective coatings provided the largest sensitivity increase. The sum of all these changes was a sensitivity increased by an estimated factor of 70, more than sufficient to permit measurement of ambient ozone concentrations at altitudes of 80 km.

TABLE OF CONTENTS

# LIST OF ILLUSTRATIONS

# I. INTRODUCTION

Panametrics has been concerned with measurement of stratospheric and mesospheric ozone profiles for approximately a decade. Initial feasibility studies[1] on chemiluminescent measurement of atmospheric ozone programs were conducted. Based upon these studies a sonde designed for measurement of profiles up to altitudes of approximately 65 km was constructed and flown. Results obtained were recorded in Refs. 2 and 3. In addition to this work Panametrics has conducted a study to elucidate the kinetics and mechanisms of the ozone-chemiluminescent disk interaction. The results of this initial study were reported in Ref. 4 wherein it was determined that the kinetics of reaction apparently involved at least two different steps, the first being the reaction of ozone to produce energy, and the second being the transfer of this energy from the reaction site to the rhodamine-B molecule impregnated in the disk. The rhodamine-B molecule then fluoresces with its characteristic emission spectrum yielding light of intensity proportional to the amount of energy released by the ozone-disk interaction.

Extension of in situ measurements such as are provided by the chemiluminescent ozone sonde to higher altitudes is desirable. Such measurements would provide a cross check for absorption measurements such as are made by satellites and by rocket borne absorption spectrometers and would provide a firmer basis for the assessment of the validity of the models currently being used to describe the photochemical dynamics of the mesosphere with regard to ozone production. The kinetic study (Ref. 4) suggested avenues whereby increased sensitivity for the detection of ozone might be achieved. These avenues were threefold:

a) Use of a more sensitive photomultiplier tube,

b) Use of higher flux rates to achieve a concentration dependent signal, and

c) Development of more sensitive chemiluminescent disks.

The present study was undertaken to assess the potential increases that could be achieved by these avenues of approach and to determine whether sensitivities compatible with an 80 km ozone sonde could be attained. An approximate value for the maximum sensitivity which existed in the previous ozone sonde is $2 \times 10^9$ molecules per cc. Since ozone concentrations at 80 km altitudes are expected to be in the vicinity of $10^8$ molecules per cc, an increase in sensitivity of a factor 20 is required and two orders of magnitude increased sensitivity would be desirable.

## II. TECHNICAL DISCUSSION

Measurements of low ozone concentrations, particularly at low pressures as well, are fraught with all sorts of problems. The most frequent problem encountered is the requirement for complete passivation of the gas handling and measurements system. This was a serious problem during the previous kinetic studies and, because this present study was conducted at lower pressure still, the problem became more difficult. As a result, sensitivity during the course of the program conducted here appeared to decrease. This decrease was not steady since measures were taken to retain passivation, but an overall decreased sensitivity was encountered. Since the total ozone sensitivity results from a number of factors including the photomultiplier sensitivity, the chemiluminescence disk sensitivity, and the degrees of passivation of the gas handling system, it is not possible to ascribe the general decay in sensitivity during the course of the program to a single one of these causes. It is probable that all three contributed to some degree.

### A. Photomultiplier

The previous sonde designed and constructed at Panametrics used an RCA 8644 PM tube which has S-20 response characteristics. A new PM tube, RCA 4526, which has 111 response characteristics, has become available and was used for this study. According to the published specifications for this later tube, the rated output at 600 nm is approximately twice as great as that for the 8644 tube. The rated output is reported to be conservative. The tube purchased and utilized for this study was selected by RCA to have a high sensitivity. However, no comparative measurements with other PM tubes were made.

During the course of this program the PM tube unexplainedly lost apparent sensitivity. In one case it is possible that the apparent loss of sensitivity was a result of a lack of passivation in our test system. In a second case, however, the tube was returned to the manufacturer who reported that the tube was still functioning satisfactorily. Upon return to us, the tube did show much greater sensitivity than it had before return to the manufacturer but our gas handling system had not been altered in the interim and therefore the recovery of PM response was unexplained.

## B. Cell Geometry

The previous kinetic study[4] had shown that, at pressures higher than approximately 100 torr the kinetics of the reaction could be described by the two constants in the equation

$$S = kC_o F [1 - \exp(-q/F)] \tag{1}$$

where S is the chemiluminescent light intensity resulting from an ozone stream of concentration, $C_o$, passing by the disk at a flow rate of F ambient cc/min. The first of these constants, k, was characteristic of the disk sensitivity. The second of the constants, q, described the efficiency of ozone destruction in the particular cell geometry that was chosen. The second constant caused a diminution in the signal at high flow rates from that which would be predicted had the sensitivity continued to remain the same over the entire flow regime. It was postulated that this effect resulted from the fact that the residence time over the disk at high flow rates was decreased. Consequently, the signal measured should become, in the limit of very high flow rates, dependent upon concentration and not upon flux.

Although the light intensity at high flow rates was decreased from that which would be predicted by extrapolation of data, the total light intensity at high flow rates was higher than at lower ones. It was therefore thought that if the same mechanisms were to prevail at low pressures, and if the residence time could be decreased by decreasing the channel width through which the gas stream flowed, then a high signal could be achieved which would be concentration and not flux dependent. One caveat to this thinking existed, however. The data obtained indicated that the constant, q, which describes the efficiency of ozone destruction, increased with decreasing pressure. Although this was not totally understood in terms of its mechanism, the effect of this might prevent the predicted concentration dependent regime from being achieved.

Accordingly, the same flow system as was utilized in the previous study,[4] was refitted with a new cell holder shown schematically in Fig. 1. This cell holder had provision for causing the gas stream to flow over the surface of the disk and also had provision whereby the disk-window separation could be varied. In this manner the residence time over the surface of the disk could be changed. At the same total flow rate through the system a decrease in disk-window separation results in faster flow past the surface of the disk.
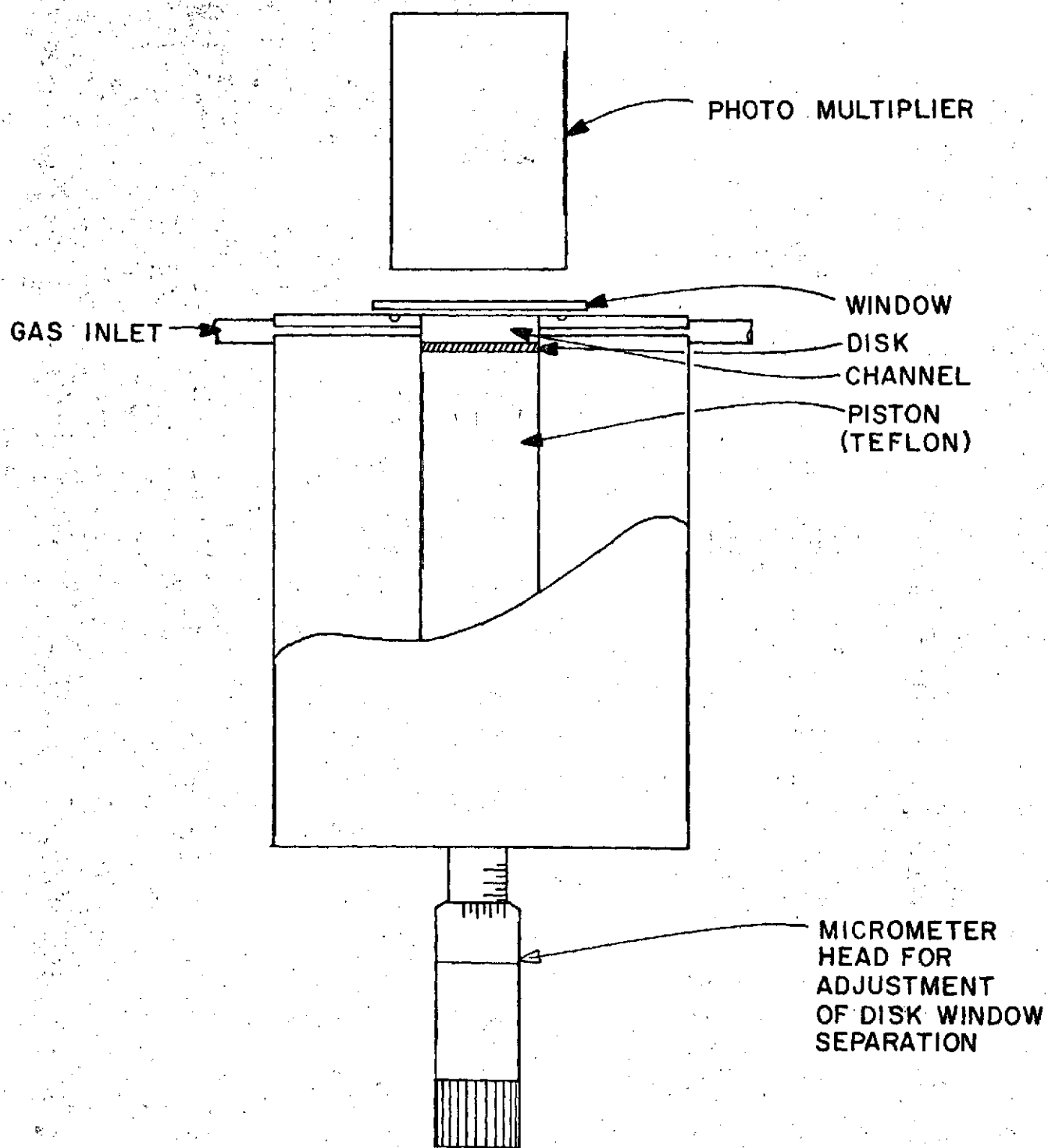
3

PHOTO MULTIPLIER

WINDOW

GAS INLET

DISK

CHANNEL

PISTON
(TEFLON)

MICROMETER
HEAD FOR
ADJUSTMENT
OF DISK WINDOW
SEPARATION

Fig. 1. Schematic Drawing of Cell Holder.

4

A series of measurements were made at a constant ozone composition of 1 ppm, and at constant pressures of 1.9, 4, 7, 50 and 100 torr. For each series, flows were varied over an appropriate range and the disk-window separation was varied from approximately 0.13 to 13 mm. The general character of the results obtained, shown as light intensity versus disk-window separation, is shown in Fig. 2. It is seen that a peak signal is obtained at approximately 1 to 1.3 mm, that at larger separations the signal decreases and that the signal decreases much more sharply at very small separations. Similar results were obtained for all pressures and all total flow rates that were studied. The decrease at larger separations, which are semi-exponential in character, was to be expected from Eq. (1). The decrease at small separations is apparently the result of geometrical factors.

Shown in Figs. 3 and 4 are the disk-window separations corresponding to maximum signal plotted as a function of flow rate for the five pressures that were studied. It can be seen that, although variation exists over the flow regime covered, the vast majority of the data at low pressures, i.e., below 50 mm, show that peak signals are obtained at approximately 1.1 mm. At 50 torr, maxima were broad and flat indicating that the light intensity was not greatly sensitive to the disk-window separation. At 100 torr, however, peaks became sharper again and maxima were back in the vicinity of 1.1 mm. These maxima at 100 torr were observed for higher flow rates. However, for lower flow rates, maxima were observed at much larger separations. Shown in both Figs. 3 and 4 are results obtained for two different disks. Since, within the scatter of the data obtained, these results are in agreement, it may be concluded that the disk-window separation is independent of the particular disk that was used.

In view of the postulates discussed earlier in this section it is of interest to determine how the signal varied with flow rate at constant pressure. Accordingly, in Figs. 5 and 6 there are shown the values obtained for maximum signal as a function of flow rate at the various pressures studied. These data are not necessarily for the same disk-window separation nor were they obtained with the same disks. The scatter shown in Figs. 5 and 6 is, therefore, understandable in terms of the variations in experimental conditions that existed. Nevertheless, it is reasonably clear that at very low flow rates the signal is flux dependent. At somewhat higher flow rates the signal becomes substantially flux independent as long as the pressure remains at 50 torr or less. At 100 torr, however, the signal is flux dependent over the entire flow regime covered.
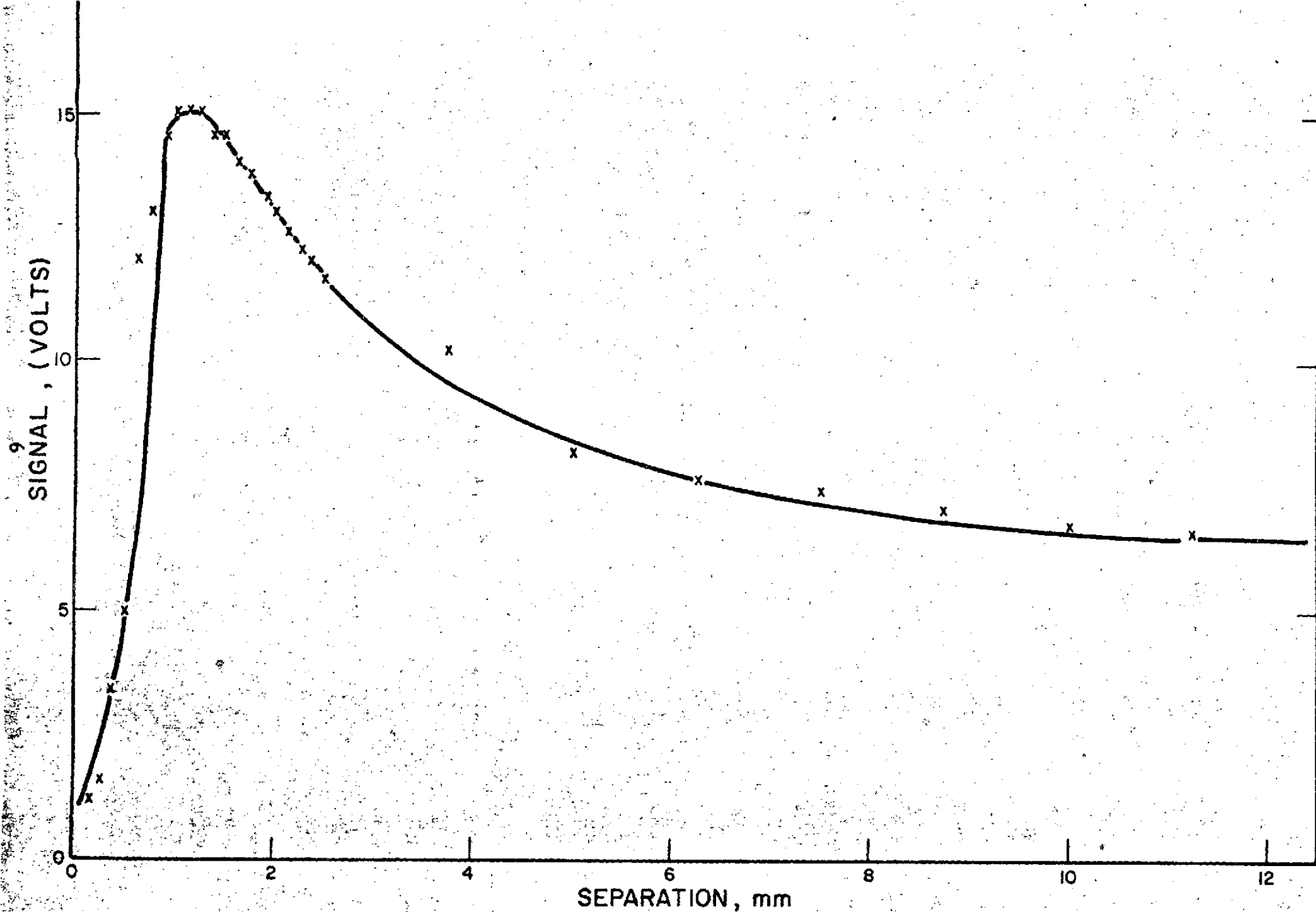
Fig. 2. Signal vs. Disk-Window Separation at 100 Torr and 95 cc/min of 7 ppm $O_3$ Stream.
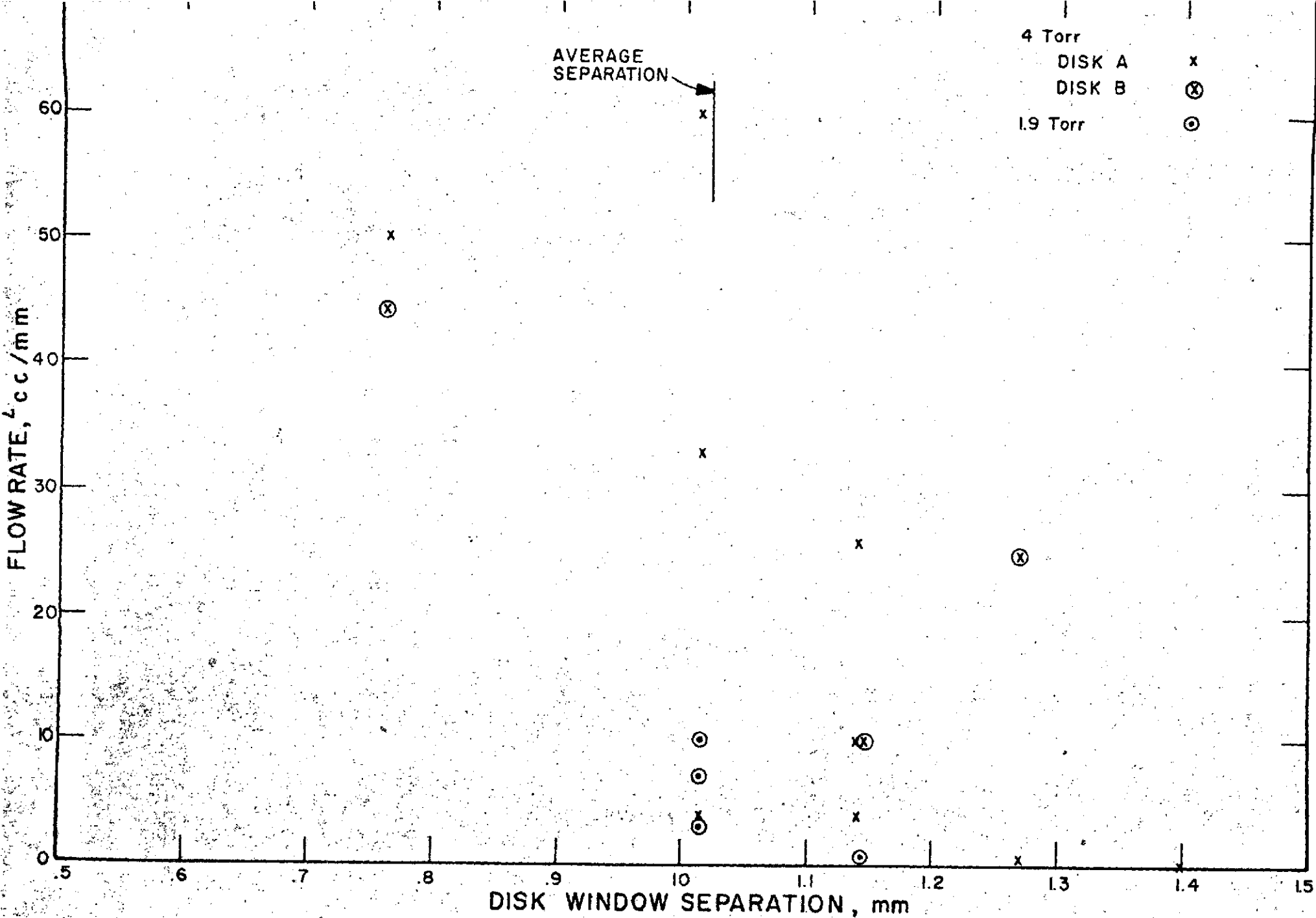
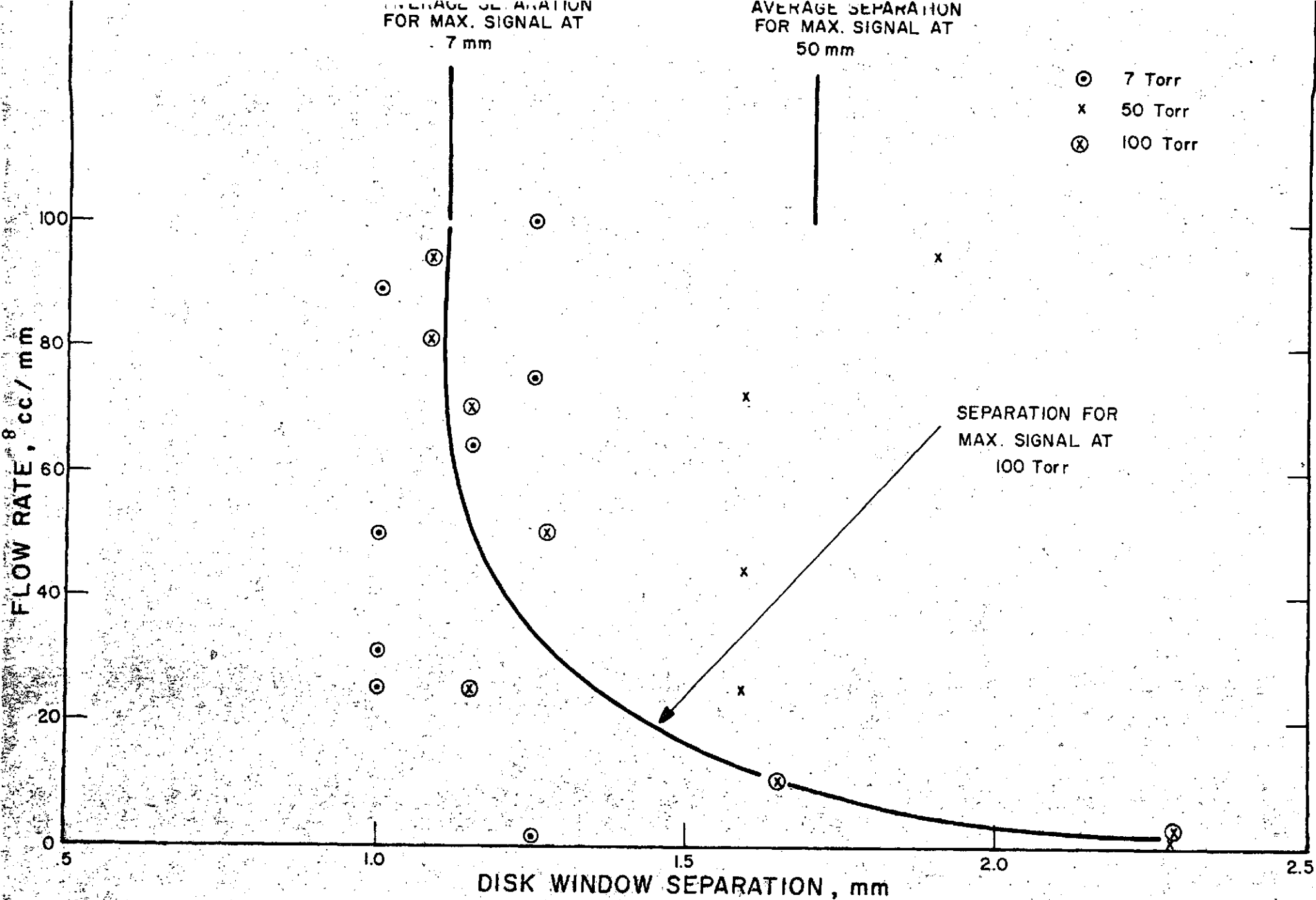Fig. 3. Disk-Window Separation for Maximum Signal as Function of Flow Rate.

Fig. 4. Disk-Window Separations for Maximum Signal as Function of Flow Rate
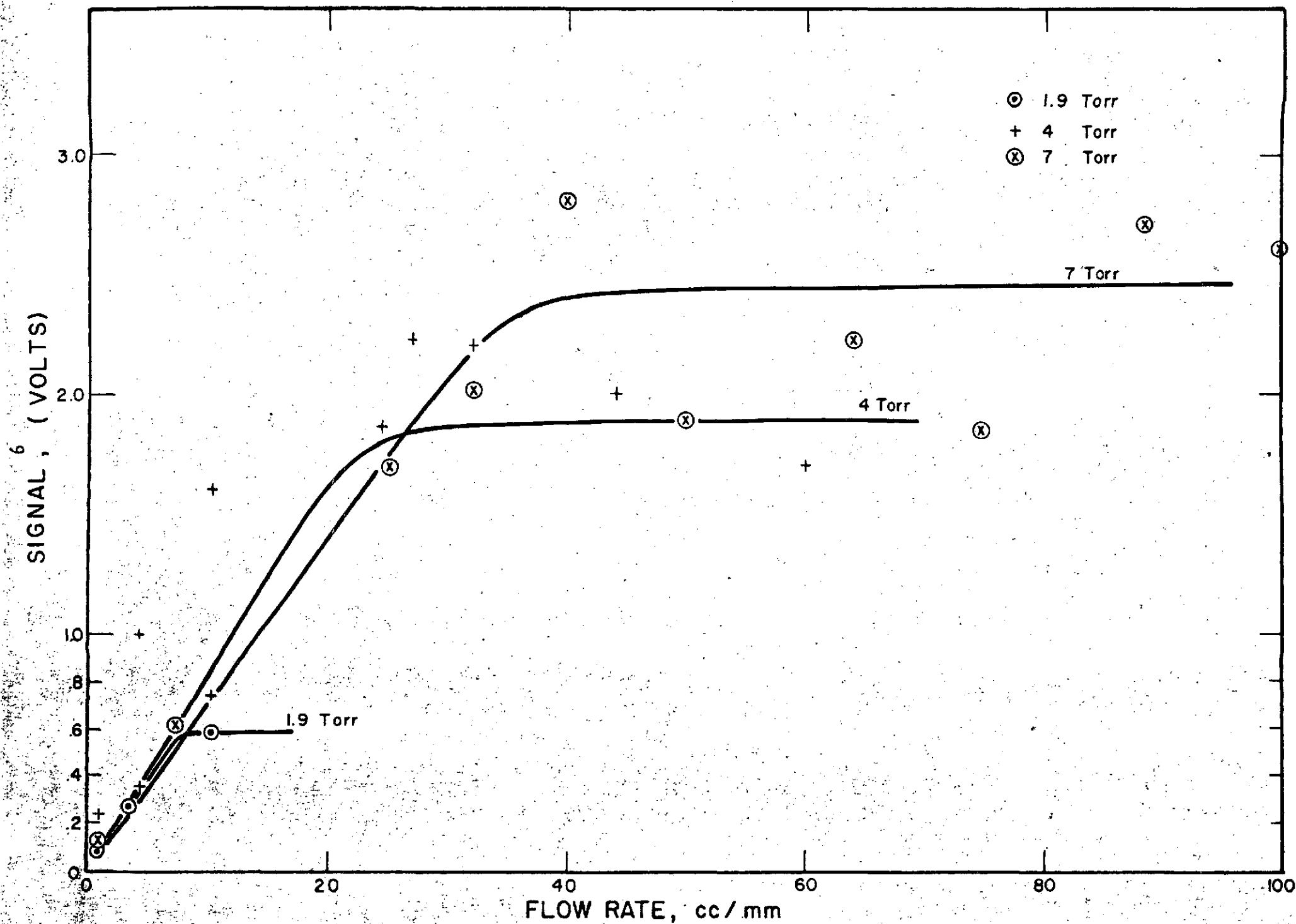
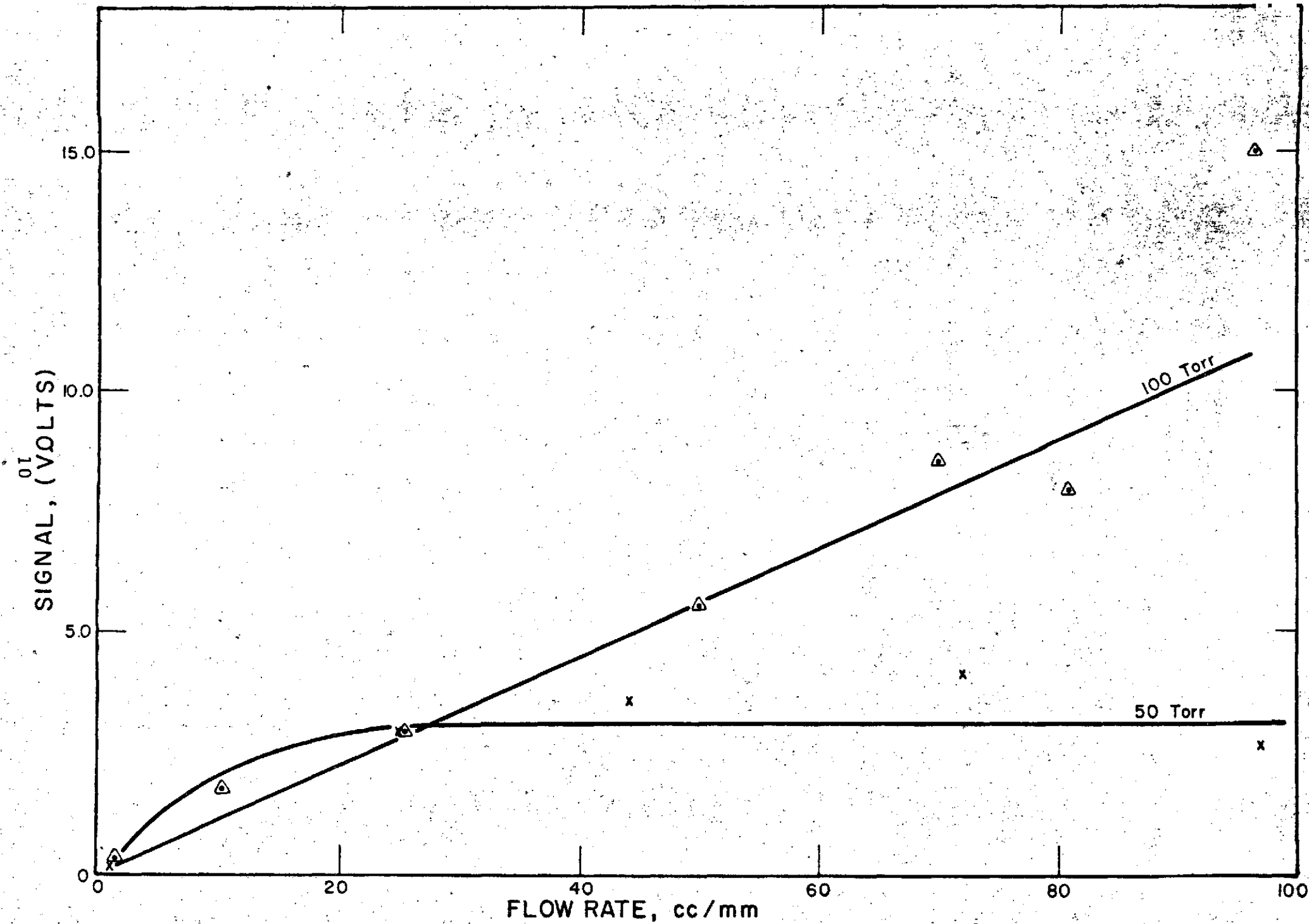Fig. 5.  Maximum Signal vs. Flow Rate at Various Pressures.

Fig. 6. Maximum Signal vs. Flow Rate at Various Pressures

These data are thus in accord with Eq. (1) and with the predictions derived therefrom. At high flow velocities such as are achieved for lower pressures at the same $F_a$ (flow ratio in cc/min at atmospheric pressure) the velocity past the disk is greater. The signal, therefore, becomes concentration dependent as indicated in Eq. (1) and in Figs. 5 and 6. However, at the higher pressures and the same flow rates, the velocity past the disk is smaller. Consequently, the signal remains flux dependent. Taking 50 torr as being the maximum pressure at which a concentration dependent signal is obtained for $F_a$ greater than 25 cc/min, we may calculate the minimum velocity required for concentration dependent signal. This is approximately 25 cm/sec.

The model used to describe the kinetics is not complete and this minimum velocity must be taken as approximate. Other data, not reproduced in this report, were obtained at pressures of 0.6, 4, 25, 50, and 100 torr, for disk-window separations of 1.1 mm, and over a range of both $F_a$ and $O_3$ concentration. Concentration dependent signals were observed at all P and $F_a$. However, at 50 torr, the data were nonlinear and showed augmented intensity for high concentrations at the same $F_a$. The model used would not predict this.

Further features of the data shown in Fig. 4 may now be understood in terms of Eq. (1). At relatively low fluxes but at velocities which are approaching the minimum velocity required for concentration dependent behavior, the exponential term in Eq. (1), q/F, is largest for lowest velocities, i. e., q increases with increasing disk-window separation. Therefore, at low flow rates and 100 torr, maximum signal is obtained at larger separations. As the flow rate increases q cannot increase as rapidly as does F and therefore the exponential term in Eq. (1) comes to predominate yielding a maximum signal at separations that are the same as at lower pressures. Maximum values of q are undoubtedly determined by geometrical and flow parameters that were not varied in these experiments. They result in a decrease in signal for separations smaller than approximately 1 mm as shown in Fig. 2. By this reasoning, the conditions prevailing at 50 torr represent those for which q is substantially invariant with disk-window separation. Hence, the broad maxima that were obtained for data at 50 torr as a function of separation. In Fig. 4 the midpoint of this broad maximum is plotted. However, maximum signal was also achieved at separations as small as about 1 mm. It is to be noted that, for the 100 torr data, maximum signal was observed at separations of about 1 mm when the flow rate was 50 cc/min. This corresponds closely

11

with the onset of concentration dependent behavior at 50 torr for flow rates that are in excess of 25 cc/min, i. e. , the residence time over the disk is the same for these two conditions. The model developed would predict concentration dependent behavior at 100 torr for $F_a > 50$ cc/min but the data shown in Fig. 6 indicates flux dependent behavior for this regime. Obviously, the model requires further refinement. The above discussion suggests that q is a function of the disk-window separations and may be a more complicated function of pressure as well. The present data do not permit a more detailed assessment of these dependencies.

Since measurements of greatest interest are expected to be made at pressures less than 50 torr the average separation for maximum signal was chosen to be 1.1 mm. It was this separation that was used in all subsequent studies.

C. Disk Preparation

Following the developments reported in the previous study[4], a number of different substrates of the thin layer chromatography (TLC) type were investigated. These included Merck Nos. 5763, 5538 and 5524, as well as Corning 7230. All these substrates were silica gel coatings on either glass or aluminum backings. Application of rhodamine-B was investigated using Merck sprays containing 0.5, 0.25 and 0.025% rhodamine-B. The combination of Merck No. 5763 substrate with Merck 0.5% rhodamine-B reagent provided a disk with a significantly greater sensitivity than any other combination tested. However, it was also found, in accord with previous observations, that thin, light coatings provided better sensitivity than did thicker rhodamine-B coatings on the TLC substrate. It was also found that improved sensitivity could be attained by heating the prepared disk to approximately 200°C for about 10 minutes.

By far the greatest improvement in sensitivity was achieved by painting the back of the glass substrate with a white reflective coating manufactured by Pilot Chemical Company, Inc. , Watertown, Mass. Following this observation the interior of the disk holding cell was also coated with this reflective coating. The coatings were air-dried and disks so coated stored in black desiccated boxes.

Comparison of the results obtained with and without coatings are shown in Fig. 7. These results were obtained for a 2 ppm ozone stream at 4 torr. Under these conditions the flow is sufficiently low
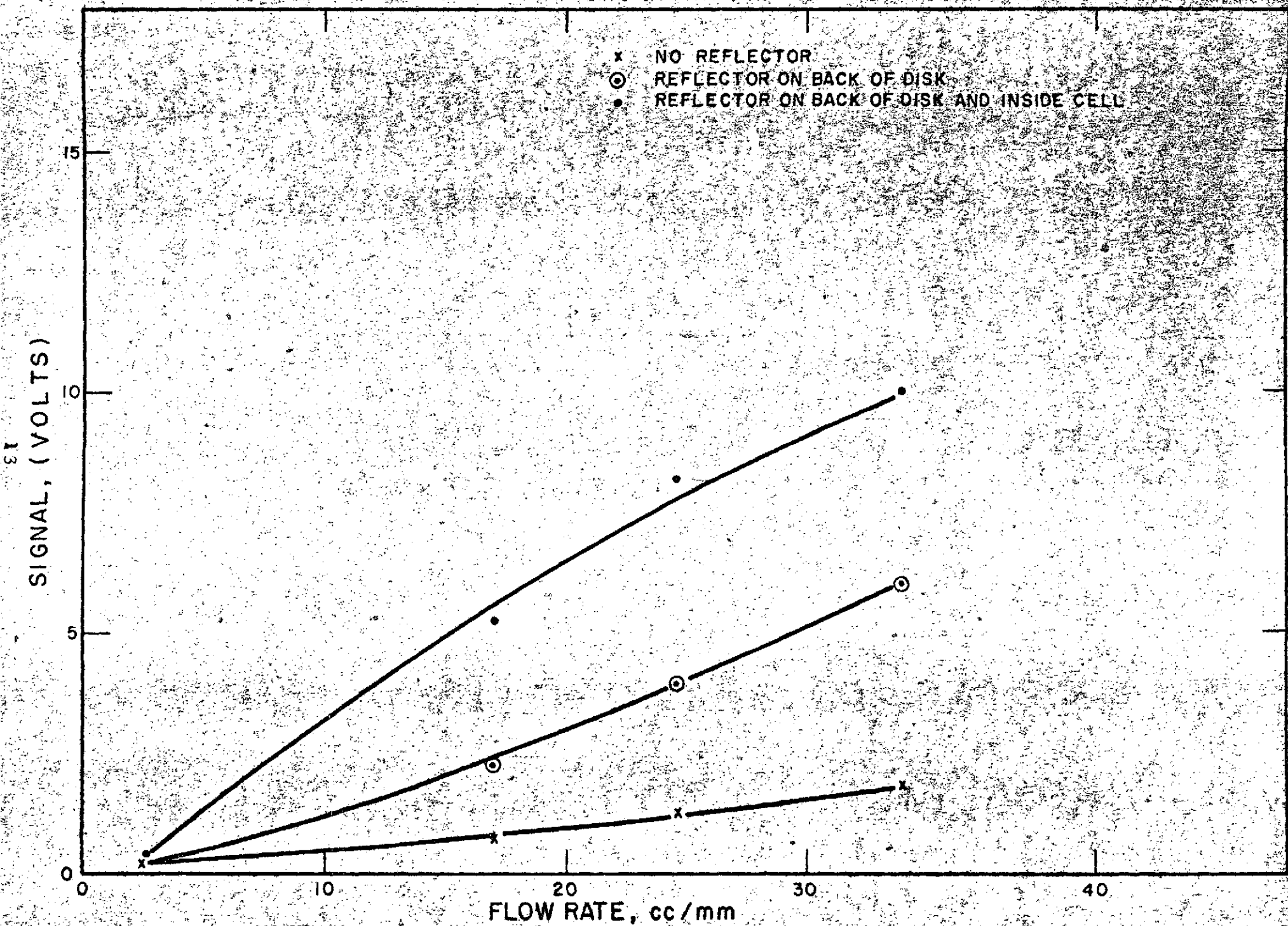
Fig. 7. Effect of Reflective Coating on Signal Strength.

that the output is still in the flux dependent regime.  It is seen that the application of a coating to the back of the disk increased the sensitivity by a factor of 3.1 as compared to the same disk without a coating.  The disk with coating and operated in a disk holder which was also coated with the reflective coating provided a sensitivity which was greater than 6 times as large as that for the disk and holder in the uncoated condition.

Disks prepared as described above were tested for stability and for sensitivity decay during operation as well as during storage following the initial preparation.  Such tests are influenced by the passivation problems of the system which have been encountered earlier and which were particularly troublesome during these studies conducted at lower pressures and hence at lower ozone concentrations per unit volume. Nevertheless, the conclusions reached appear to be independent of the passivation of the system and to be characteristic of the disk preparation itself.  It was found that if a disk, freshly prepared, were to be operated at a pressure of about 2 torr and an ozone concentration of 2 ppm, the initial signal increases to approximately three times its initial value in the period of 5 to 12 hours.  The sensitivity then remains constant for at least another 20 hours of operation of the disk after which time sensitivity starts to decay in a manner consistent with bleaching of the disk. Disks stored in desiccated dark enclosures for periods up to three days showed an initial decreased sensitivity upon reinsertion into the test system.  However, less than 10 minutes exposure to ozone streams restored the initial sensitivity to the same value as was measured prior to storage.

D.  Atomic Oxygen Sensitivity

The possibility that atomic oxygen might generate a light signal in the same way that ozone does was considered and explored.  Atomic oxygen was generated from an oxygen stream using a microwave generator.  At total pressures less than 3.3 torr no light signal was detectable.  At higher pressures a light signal approximately 25% as large as that which would have resulted from a 2 ppm ozone stream was observed.  Because NO formation and luminescence accompany atomic oxygen generation, this signal observed at higher pressures is attributed to NO luminescence rather than atomic O-disk interaction largely because it occurs in a pressure regime wherein previous studies have shown that atomic oxygen does not provide a signal.

14

## III. DISCUSSION OF CONCLUSIONS

The primary objective of the program described was to ascertain whether or not a significant improvement in sensitivity could be achieved which would permit measurement of ozone concentrations at approximately 80 km altitude. It was estimated that an increase in sensitivity over that which had previously existed, by a factor of approximately 20, would be required. The data obtained provide a qualified answer that such sensitivity increases can be achieved in a flyable ozone sonde. Direct comparisons were attempted late in the program but passivation problems and PM tube sensitivity decreases prevented such comparisons from being valid. It has been mentioned above that overall sensitivity decreased during the course of the program. The extent of this decrease is indicated in Fig. 8 wherein duplicate data are shown which were obtained approximately seven months apart. Values of k, as determined from the initial slopes at low $F_a$, are 3500 and 350 mv min/cc ppm for the earlier and later data, respectively, indicating an order of magnitude decrease in sensitivity.

The best estimate that can be made involves comparison of the results reported in Ref. 4 with the data shown in Fig. 6, both for 100 torr. The later data were obtained about July 1971, relatively early in the program and before significant sensitivity decreases are thought to have occurred. The latter data indicate a flux dependent sensitivity of about 140 mv min/cc ppm whereas Ref. 4 gives sensitivities for two Vycor disks of 11.8 and 4.75 mv min/cc ppm for 98 and 100 torr measurements, respectively. To be conservative comparison will be made with the higher Vycor disk sensitivity yielding sensitivity increased by a factor of about 12. This includes the increase associated with a decreased disk-window separation, earlier estimated as 25%, and that associated with an increased PM tube sensitivity which we will assume to be by a factor of 3 to account for selection of PM tubes. This yields an estimate for the increased sensitivity of the TLC substrate disk of a factor of 3.2 as compared to a Vycor substrate disk.

The other significant increased sensitivity achieved in this program is that obtained by using reflective coatings on the back of the disk and on the interior surfaces of the disk holding cell. Possible effects attributable to $O_3$ destruction by the reflective coating were searched for but not found. The sensitivity increase achieved was earlier estimated as a factor of 6.
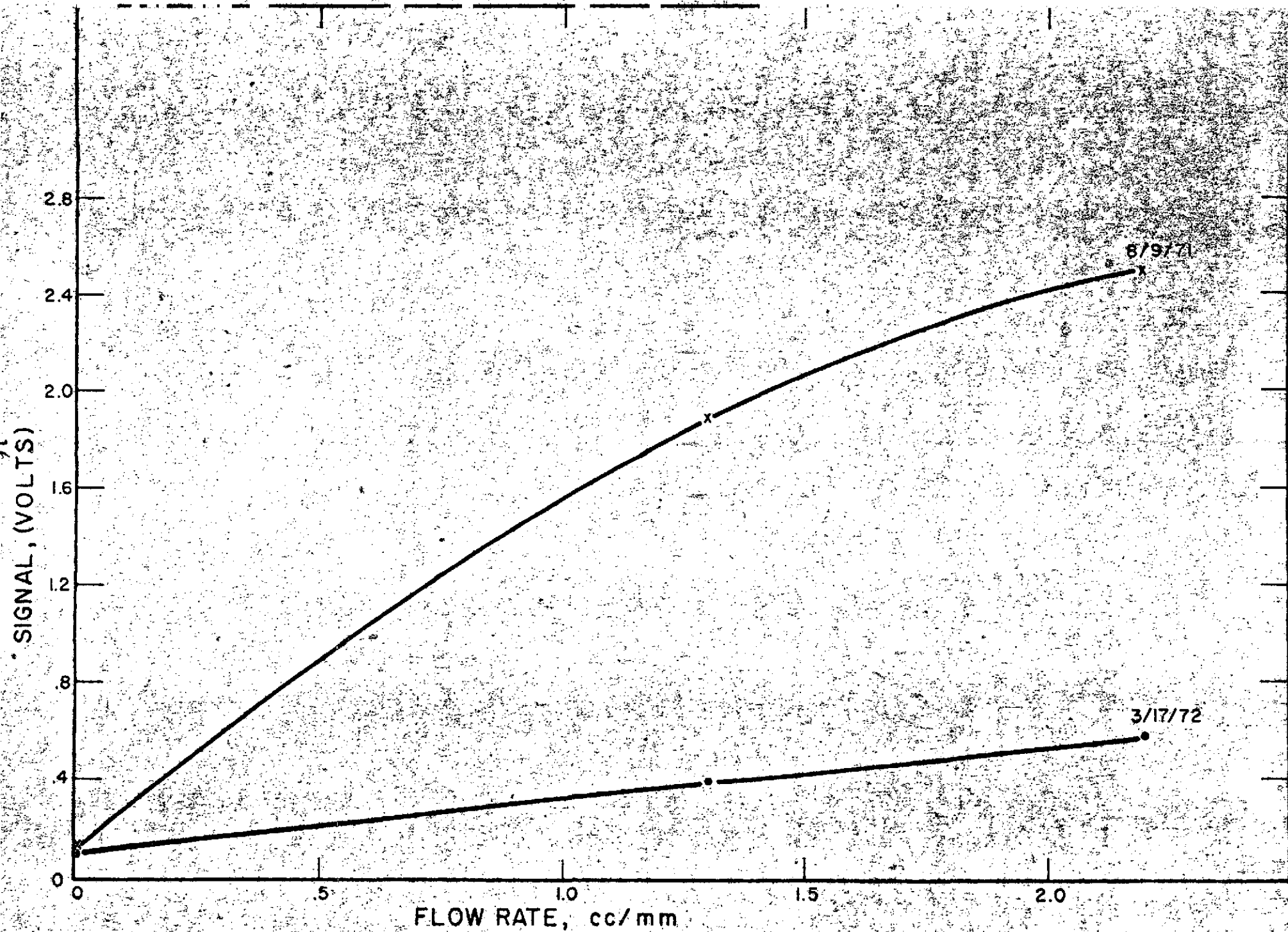
15

Fig. 8. Decrease in Signal Showing Loss in Sensitivity to 2 ppm O₃ Stream at 1 Torr.

Combination of these factors yields a sensitivity increase demonstrated in this program by a factor of 72 (= 6 x 12). This is considerably greater than the minimum required, a factor of 20, and closely approaches the goal established at the inception of the program, a factor of 100.

The major disappointment in the program was that the sensitivity was increased by only 25% by optimizing the disk-window separation. It is believed that still further increases could be achieved by altering the geometry of the gas stream passage past the disk surface. Time and funds available did not permit this additional effort. The model used for the kinetics of the interaction has held quite well, although indicating the need for some refinement. This model would not predict a decreased signal for separations smaller than about 1 mm. The fact that they did occur suggests that at small separations, some significant portion of the gas stream passed around or under the disk rather than over its surface. If this is indeed true, it is probable that an appreciable fraction of the stream was thus diverted even at disk-window separations of 1.1 mm. Reduction of this bypassing stream might yield a sensitivity increased by another 25-50% or even more.

Nevertheless, it does appear feasible to achieve a sufficient increase in chemiluminescent sensitivity to consider construction of an ozone sonde for measurement of expected $O_3$ concentrations at altitudes of 80 km. Such a sonde might be very similar to the previous 65 km sonde developed by Panametrics [2] using the self-pumping concept. A qualitative exploration of this possibility was conducted using the calibration system described in Ref. 2 and the cell developed for these studies. A one liter flask served as the ballast volume and a diaphragm-type pressure gage, of the same type as was used in the 65 km sonde, monitored the pressure. It is capable of measuring pressures as low as about $1\mu$. Following pump-down to about $1\mu$, ozonized air was admitted to the calibrator and, indeed, a measurable signal was observed before the pressure detectably increased. Since this experiment was conducted late in the program, after the PM tube sensitivity had apparently decreased, it was concluded that such a sonde is feasible.

Two major concerns exist with regard to utilization of such a sonde. The first is related to the increased molecular mean free path at higher altitudes and the consequent possibility that $O_3$ might not have a sufficient opportunity to interact with the disk. Actually, the probability of interaction with the disk is decreased by only a factor of about 3.8 both because a) the mean free path does not increase by a complete order

17

of magnitude since the ambient temperature is lower at the higher altitudes for which the pressure is an order of magnitude lower and because b) the disk-window separation has been decreased by a factor of 2.3 thereby increasing the probability of interaction. The second major concern is that the sampling inlet used in the 65 km sonde might not prove adequate. Detailed evaluation of this question has been considered outside the scope of the present program but it is considered that a satisfactory sampling inlet could be designed should such prove necessary.

One caution should be emphasized, however. Careful calibration will be required both because the low pressure regime may suffer from a somewhat diminished number of $O_3$-disk interactions, but also because the anomalies observed in the pressure regime around 50 torr will be present during operation of the sonde. Therefore, calibration in this regime, and at flow rates appropriate to the expected descent velocity, will be necessary.

In conclusion, therefore, this program has shown that sensitivity more than adequate for a 80-km $O_3$-sonde can be achieved. Moreover, initial consideration indicates that the same type of sampling concept can be used as was employed for the 65 km sonde.

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