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ANALYSIS OF PEROXYBENZOYL NITRATE IN SMOG

Edgar R. Stephens

Principal Investigator

Statewide Air Pollution Research Center

University of California

Riverside, California 92507

Project Participants:

Edgar R. Stephens, Principal Investigator

Monty Price

William H. Snider (from June 1972)

James Beck (to June 1972)

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P. O. BOX 2815
SACRAMENTO, CA 95812

SUMMARY

The overall objective of this project is to develop a gas chromatographic procedure suitable for the detection and estimation of peroxybenzoyl nitrate (PBzN) in the concentration range of 1 to 5 ppb. The successful, automatic, and routine use of this method with electron capture detection for PAN made it appear that this would be a simple method. In addition, PBzN had been detected in laboratory mixtures by Heuss and coworkers at General Motors using this method.

A long path infrared cell was used to prepare PBzN samples in the ppm range by mixing benzaldehyde with nitrogen dioxide and ozone. This provided a mixture whose PBzN content could be rapidly measured by the infrared absorption. These PBzN mixtures could be diluted to ppb levels and injected into an electron capture chromatograph. First trials were very encouraging for these synthetic PBzN mixtures. Difficulties were encountered when the attempt was made to apply this procedure to ambient polluted air samples. Conditions which would separate the PBzN from other components (especially oxygen and water) would not separate adequately from an unknown ambient air peak. Although many combinations of column, temperature and flow rate were tried, none solved all these problems. In addition the instability of PBzN made the peak height not reproducible. Direct tests on the column effluent did show that a powerful eye irritant was present.

To improve the sensitivity of the method freeze-out experiments were begun. This permitted use of larger samples so that bigger peaks were obtained. This in turn permitted a wider choice of chromatographic parameters. But this procedure was also plagued by irreproducibility of peaks.

Samples of ambient air were injected on numerous occasions when smog was present and sometimes a PBzN peak appeared to be present but it was never reproducible enough to support the claim that PBzN had been detected. In the following pages the more recent attempts to use a two column technique are described in detail.

DETAILED REPORT

Since the last report, work centered on the use of an OV-type silicone column with packed trapped freeze-out and thaw. With this technique it was found that 18" x 3/16", 3/4% OV-17/GCQ 80/100 worked the best of the OV columns (OV-17, OV-101, different lengths and diameters), using a flow rate around 200 ml/min at 45°C. This gives a broad peak with some interference from the initial peak, resulting from air, water, and impurities in the synthetic mixture, such as benzaldehyde (Fig. 1). Generally, the first sample of the day showed no peak or a very small peak. The peak increased in size with every shot thereafter until it leveled off. Diluting the PBzN in the flask usually resulted in a larger peak. "Apparent" sensitivity was around 1 ppb. Dilutions were all done in the same flask used to tap the original high concentration PBzN from the LPIR tank, in which the PBzN was made by reacting 7 µl benzaldehyde with 65 ml NO and about 4 liters of 2% O₃ in O₂. Factors affecting the peak, besides column temperature and flow rate, were height of the LOX on the trap; overpressure in the sample flask; number, size, and frequency of previous injections; thaw temperature (ambient to 60°C little change, below ambient-caused broadening). A sample diluted with room air and not nitrogen produced too big an initial (water) peak to see the PBzN at the desired attenuation. Results from the OV-17 column showed the need to remove the water peak in order to see PBzN clearly. Attempts to insert a short column of powdered drying material (drierite, CaC₂P₂O₅) before the main column always resulted in substantial loss of PBzN, although water removal was efficient.

A dual column-dual trapping system was tried next. The first trap and column was used for crude separation of the water and impurities from the PBzN. As the PBzN peak emerged, the first column effluent was switched from the detector to the second trap. Finally, the partially purified PBzN was analyzed on the second column. It was important to be able to connect either column to the detector and, therefore, a system was designed with two columns, two traps, and three hexaport slide valves to accomplish this. A description of this system is included at the end of this report. The OV-17 column described previously was chosen for the precut column. Optimum conditions for this column, experimentally determined, were 49°C, with a flow rate around 150 ml/min (64 psi on the regulator), room temperature thaw, and LOX level about 5/8" below the Swagelok fittings on the trap. The analytical column, chosen for the narrowest peaks and best response among several tried was 12" x 3/16", 1% JXR/GCQ 80/100. Those rejected were other 1/8" and 1/16" 1% and 3% JXR columns of various lengths, also OV-17 and OV-101 columns. This column was used at room temperature, carrier flow about 240 ml/min (56 psi), room temperature thaw, and the same LOX level on the trap. Results with this system were similar to those obtained using a single column: no peak is seen initially until repeated injections have boosted the apparent sensitivity. The advantages were a cleaner, sharper peak with no obliterating water peak (Fig. 2). The biggest new problem was the loss of PBzN in the process of retrapping and chromatographing. The peak obtained from one column chromatography was perhaps 4 to 10 times larger than the same size sample run through the dual trapping system. Blank injections between samples did not eliminate the problem of changing sensitivity. A quantity of PBzN, 1-3 ppb, released in a closet could not be detected. PBzN was never detected in the air on smoggy days.

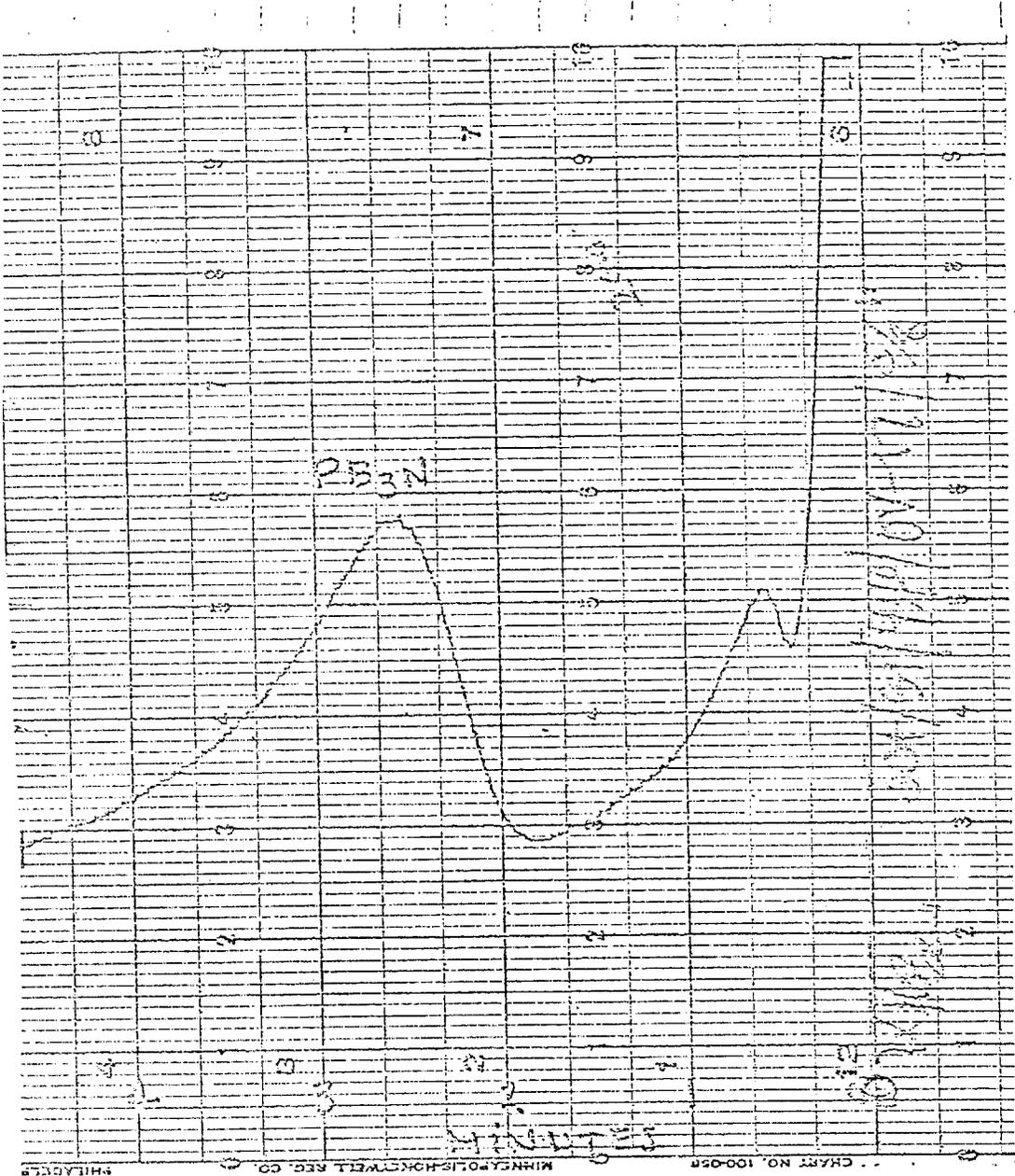


Figure 1

Single column technique
18" x 3/16", 3/4% OV-17/GCQ 80/100
20ml, 39 ppb PBzN
150ml/min, x32

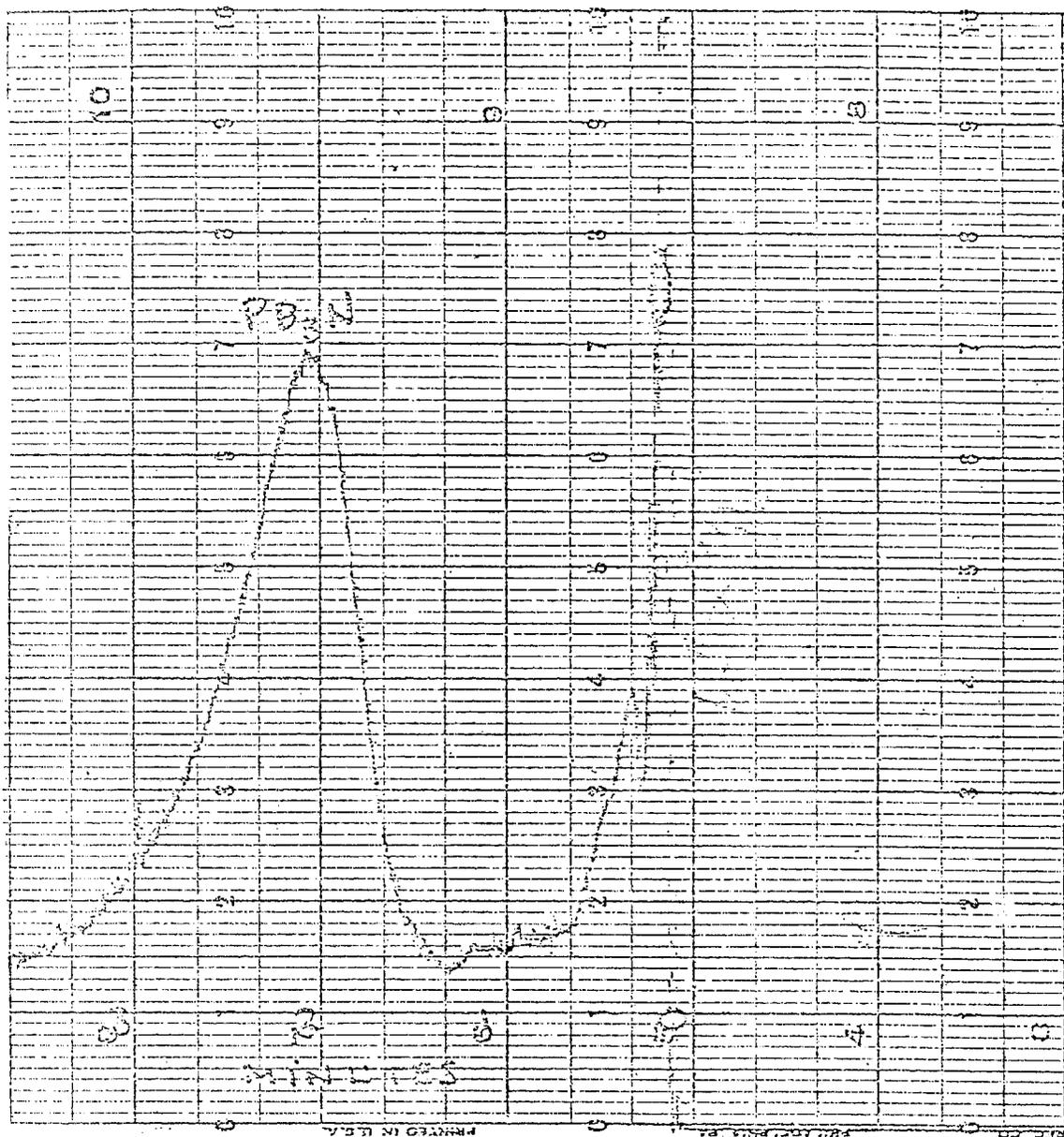


Figure 2

Dual column technique
 18" x 3/16", 3/4% OV-17/GCQ 80/100, 150 ml/min
 12" x 3/16", 1% JXR/GCQ 80/100, 240ml/min
 50ml, 0.14 ppb PBzN, x8
 after a long series of injections

The next series of tests were done using the analytical column only. Small sample size (20 ml) reduced the initial peak sufficiently to clear the PBzN region. The idea was to try a series of carefully timed, low concentration samples, alternated with blank injections, hoping to get reproducible sensitivity. The column would never be exposed to high concentrations of PBzN. At this time it was discovered that one of the transfer valves removed 75% of the PBzN from a sample. The result of the low concentration samples alternated with room air blanks was more stable, reproducible sensitivity, but still showing a tendency toward increasing peak size; however, it was possible to detect 1 ppb on the first injection (Table 1). Once again, no PBzN could be detected in the closet experiment. PBzN in a 20 liter bottle could be detected, but only at much higher concentrations than in the flask. Many of these results suggest that the flask may have had a much higher concentration of PBzN in it than was calculated from the dilutions (the dilution technique, itself, was shown to be reliable).

These findings led us to the conclusion that the only alternative was to go back to a dual trapping system so that a large sample could be used. Assuming that the larger peaks seen after several samples were false, sensitivity was measured from only one sample injection. Working in the 20 liter bottle gave only a moderate peak for 100 ppb at the lowest usable attenuation (x8). Another technique, making the final dilution in a clean flask not exposed to high PBzN concentrations, was tried, but also showed poor sensitivity at 100 ppb (Fig. 4).

The PBzN peak was verified by passing the sample through a 5" column of Cu turnings and making sure that the PBzN peak disappeared.

The following are suggestions for continuation of the project. It may be possible to improve the present dual trapping technique to the point where it is usable. A change in the valving could reduce PBzN losses. Treating the solid support might eliminate the problem of changing sensitivity. Using capillary columns could also end many problems which are possibly due to the solid support. Another approach might be a chemiluminescent technique developed in conjunction with the Chemistry department group at UCR.

Other current studies of PBzN include the method developed by Dr. Bruce Appel of the State Department of Public Health in which PBzN is converted to methyl benzoate and then chromatographed. He has submitted a proposal to further develop this technique and make atmospheric studies at SDPH. The General Motors group has a chromatographic method using a 20" x 1/4", 3% JXR/GCQ 60/80 column with on-column injection of 20 ml air samples capable of detecting PBzN in the ppb range, although they have presently measured PBzN in lab samples only. On this campus, the group studying chemiluminescence is planning a study of PBzN.

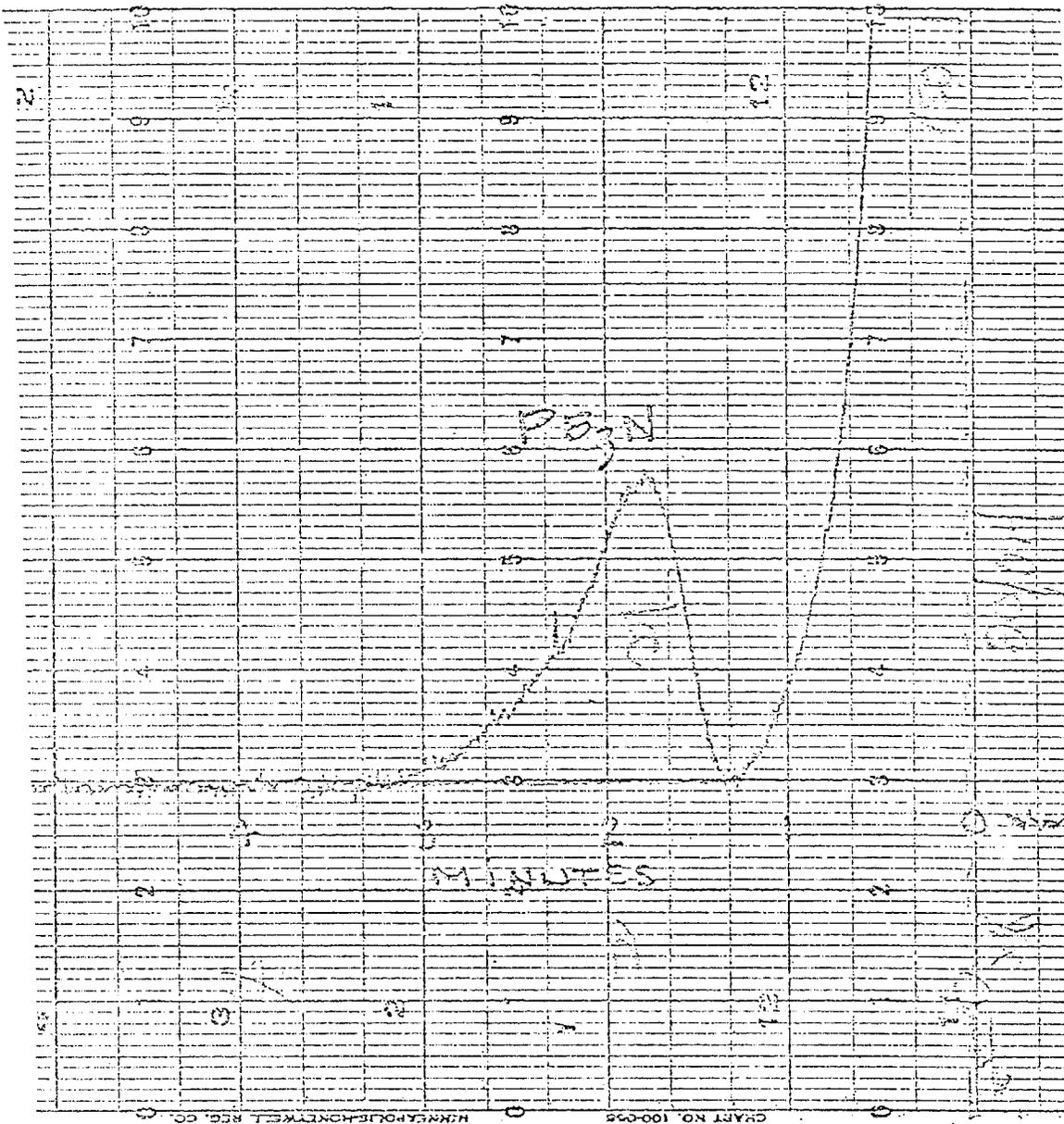


Figure 3

Single column technique
 12" x 3/16", 1% JXR/GCQ 80/100
 20ml, 0.4 ppb PBzN
 240 ml/min, x8

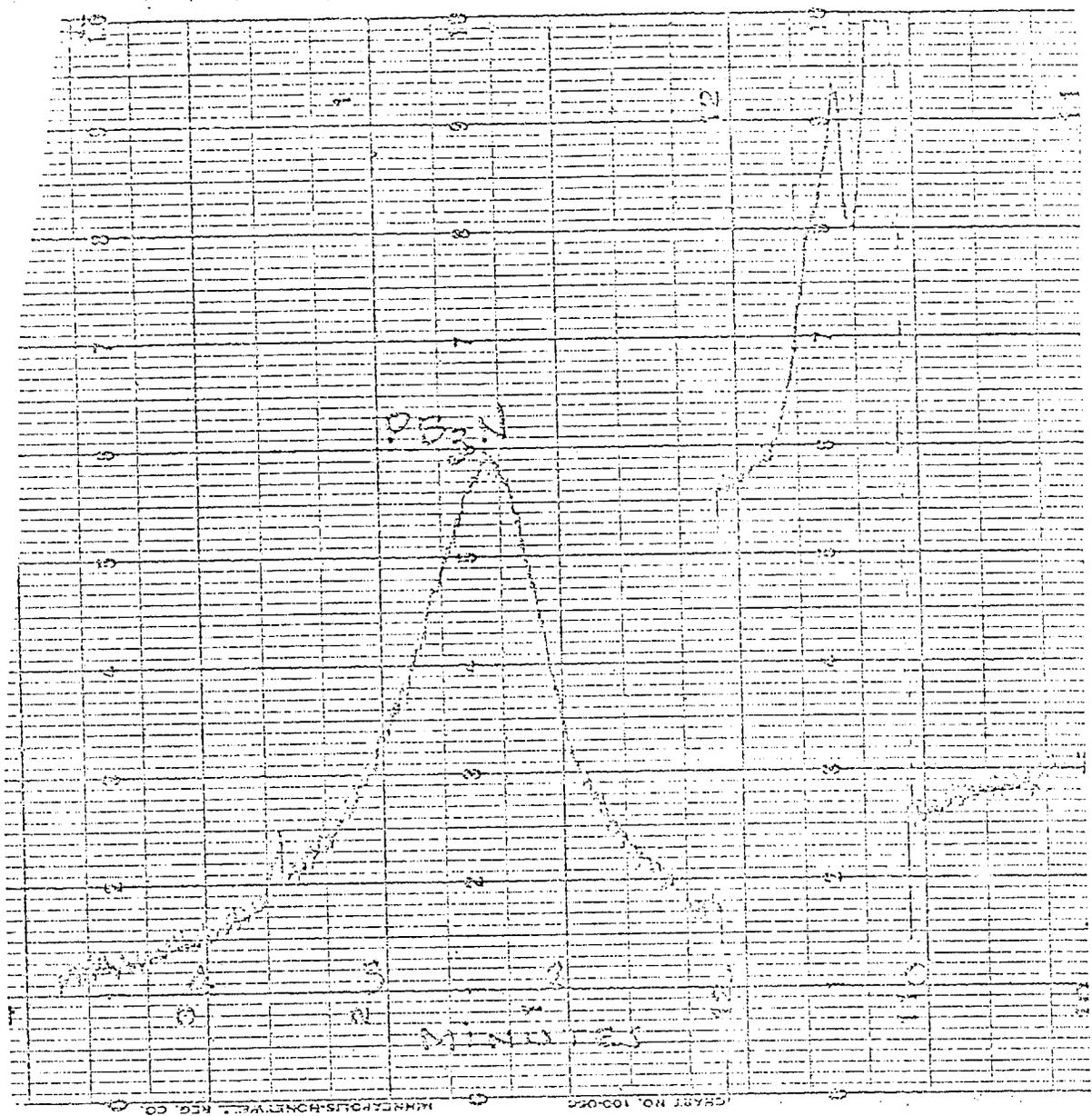
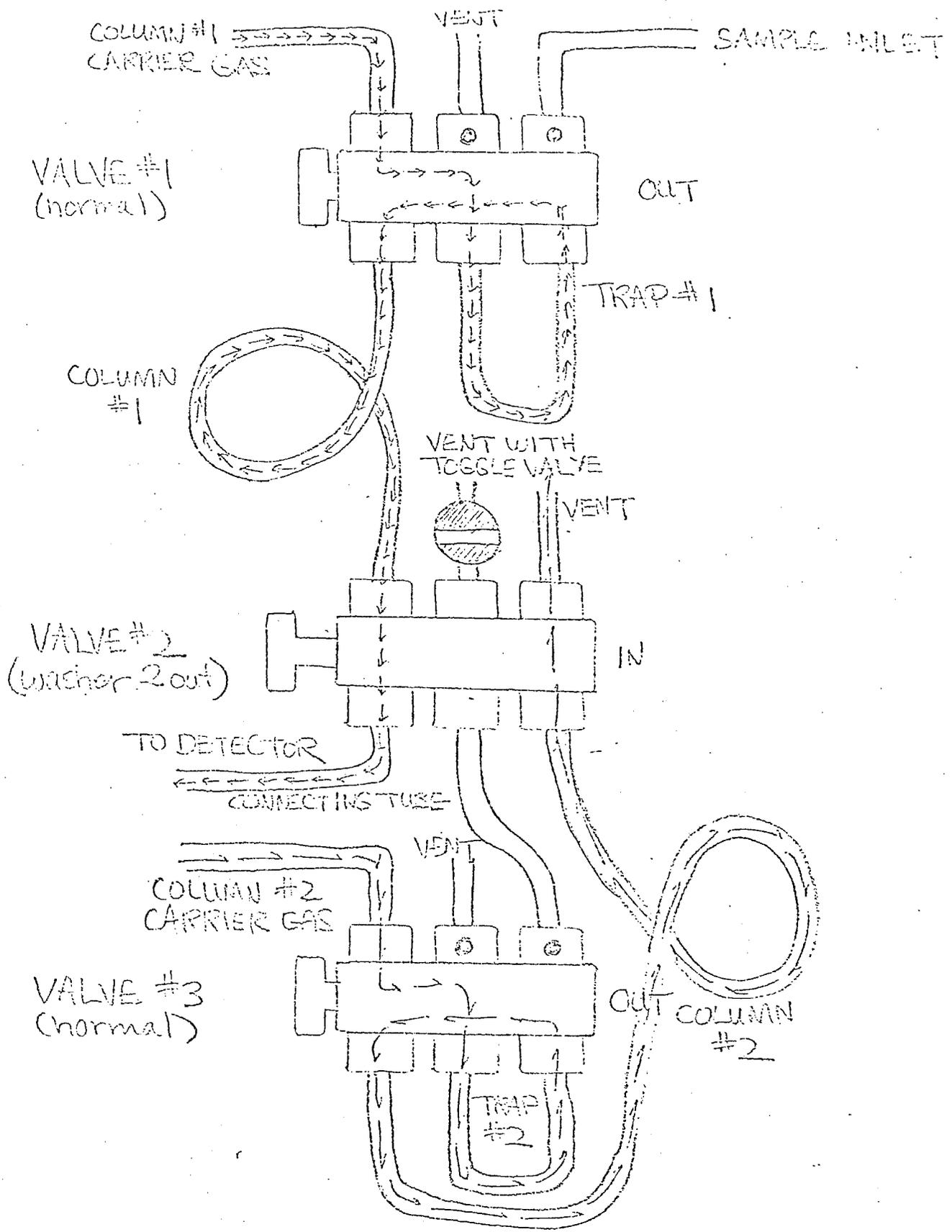
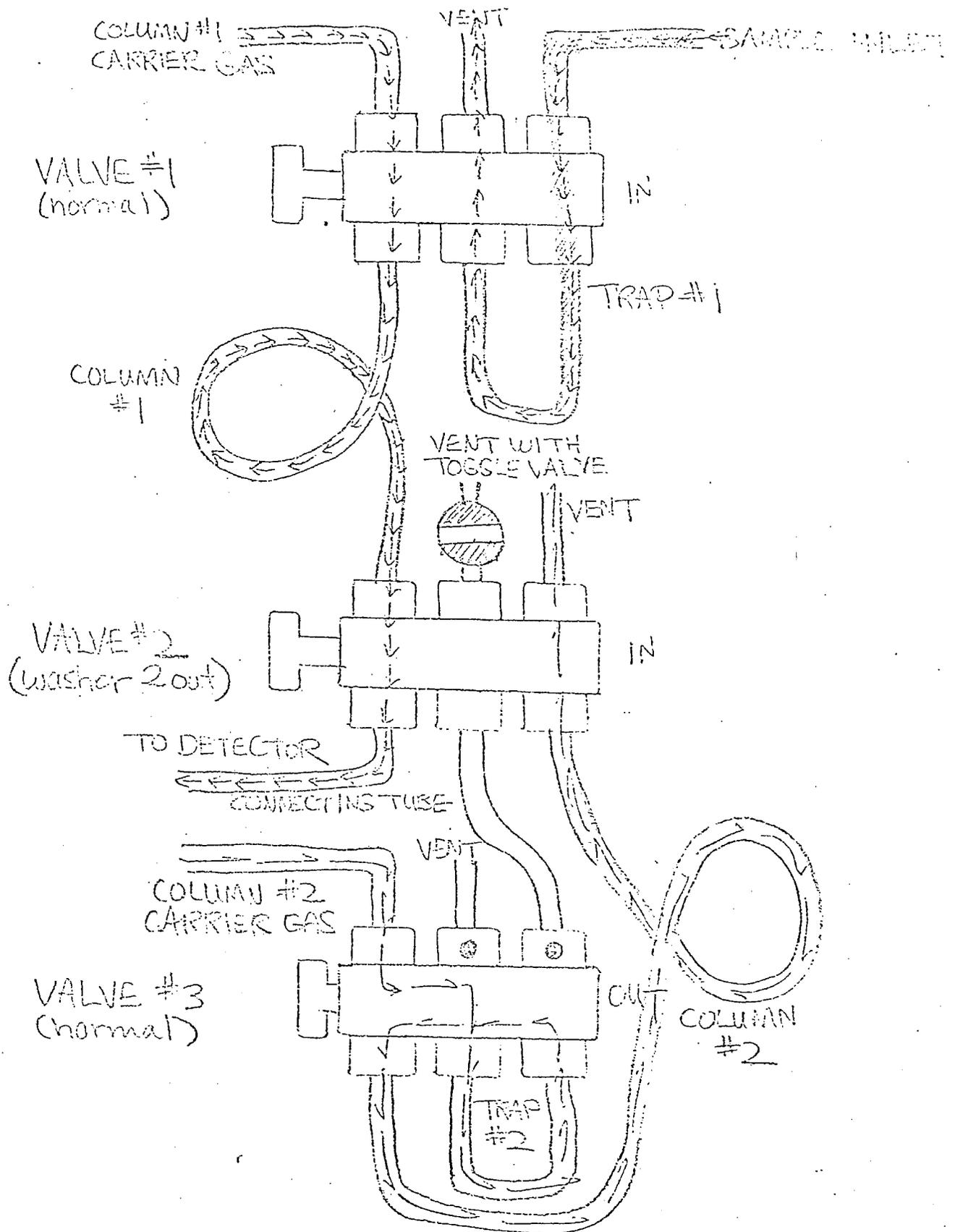


Figure 4

Dual column technique
18" x 3/16", 3/4% OV-17/GCQ 80/100, 150ml/min
12" x 3/16", 1% JXR/GCQ 80/100, 240ml/min
100ml/90ppb PBzN, x8
No previous injections

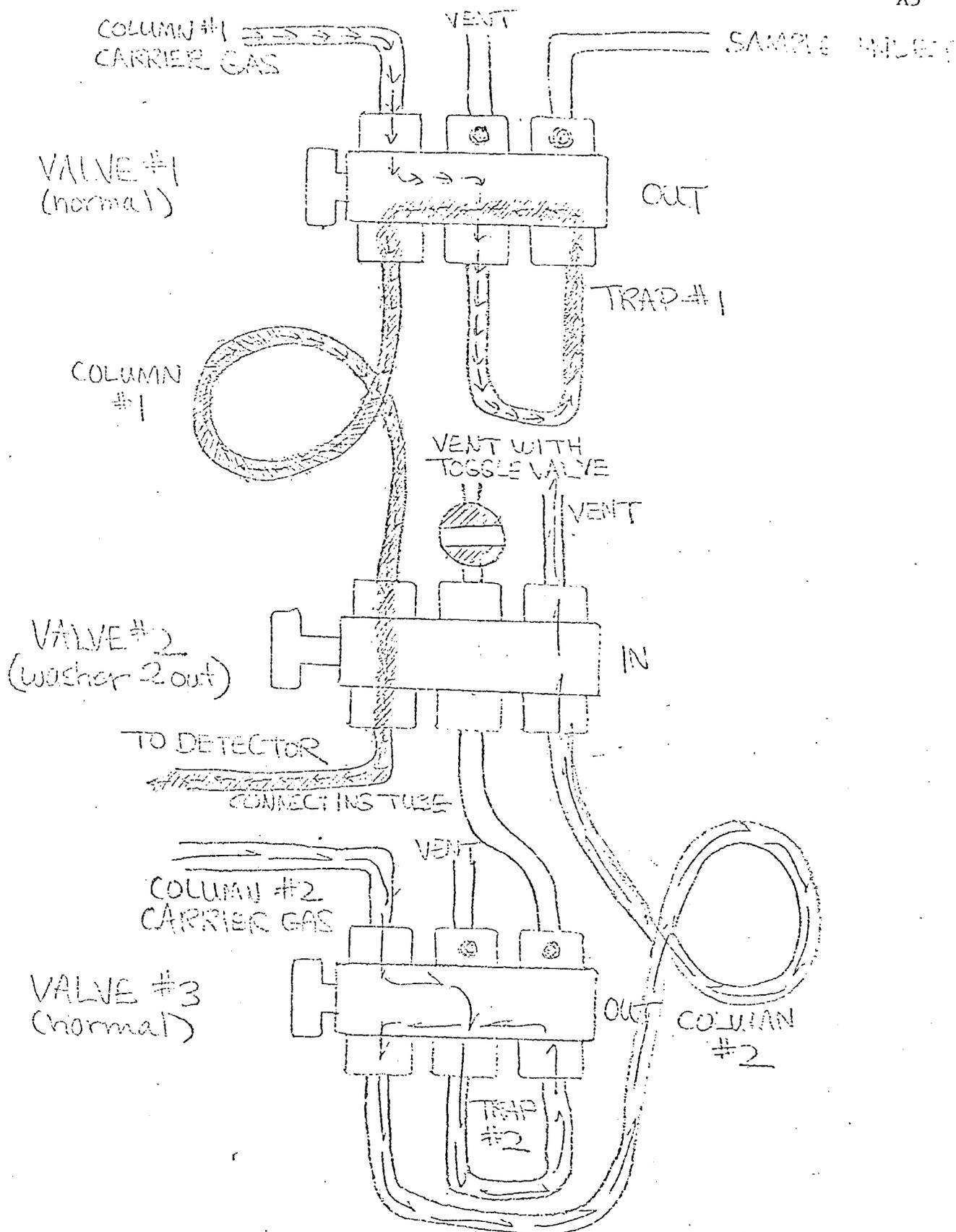


1. idle flushing
 Column #1 on the detector



2. sample frozen out in trap #1

STEPS: PUT LOX ON TRAP #1
 WHEN TRAP IS CHILLED PUSH VALVE #1
 FROM CUT TO IN
 INJECT SAMPLE THROUGH INLET



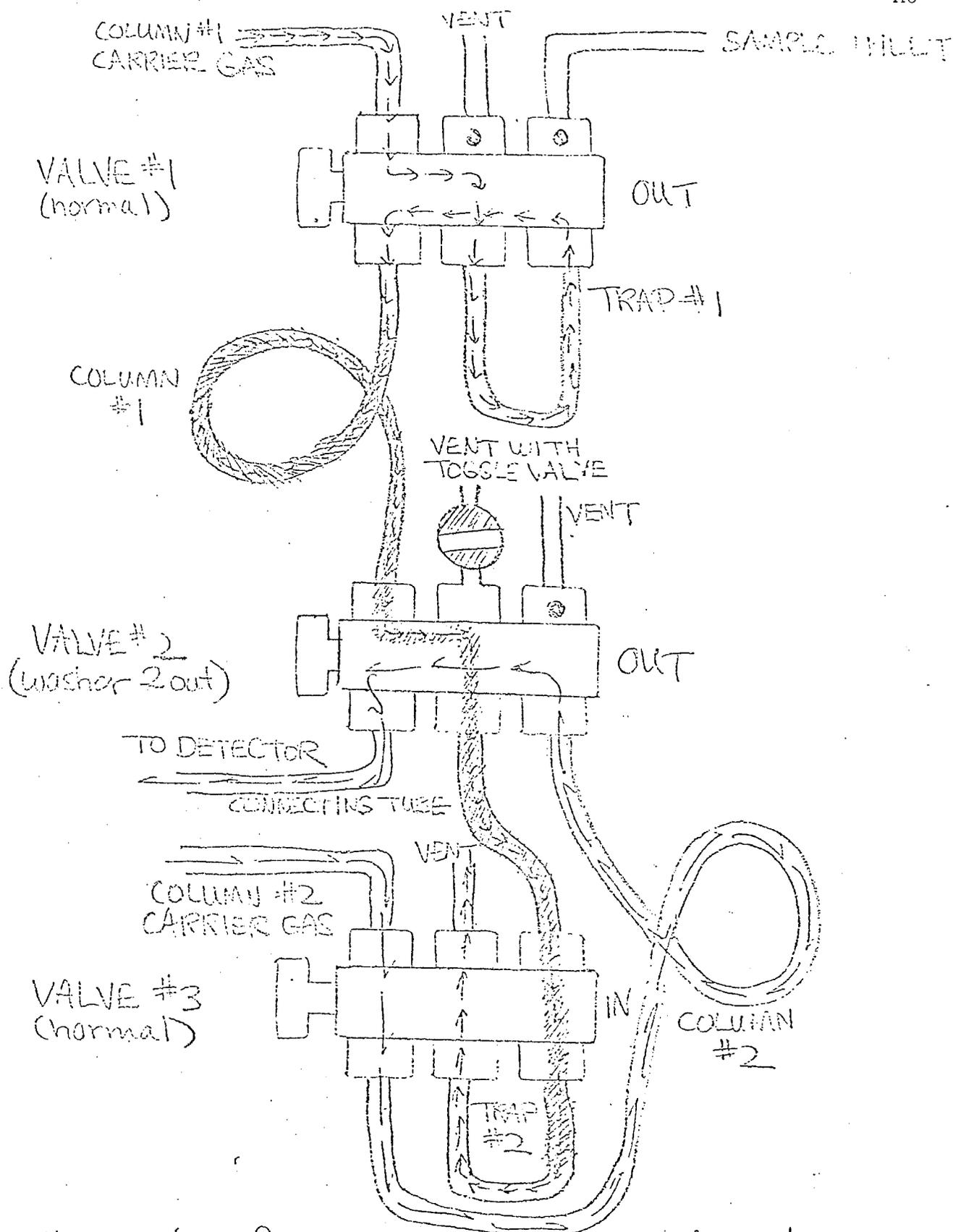
3. Sample thawed and analyzed

STEPS; REMOVE LOX FROM TRAP #1

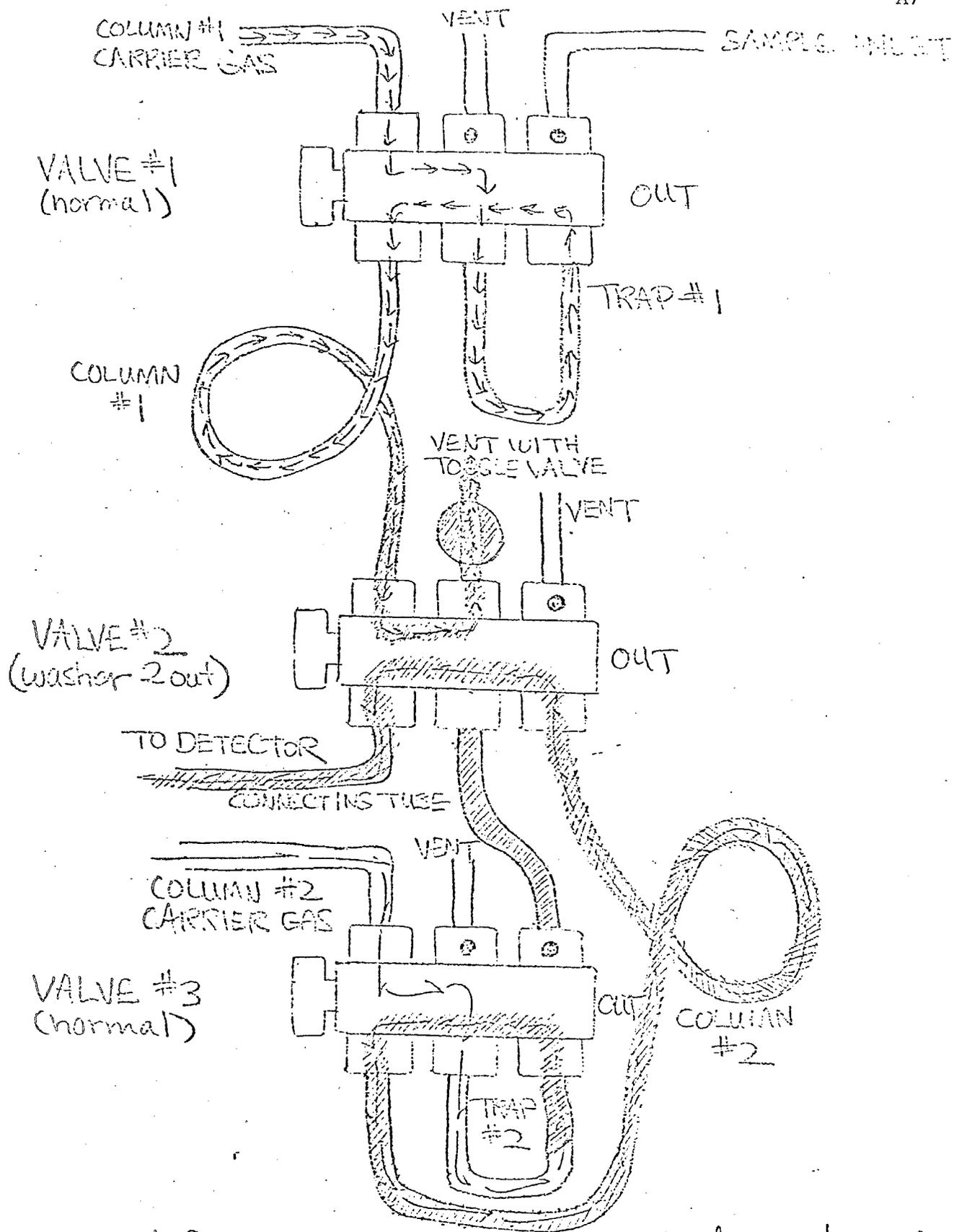
QUICKLY PUSH VALVE #1 FROM IN TO OUT

IMMEDIATELY THAW TRAP #1

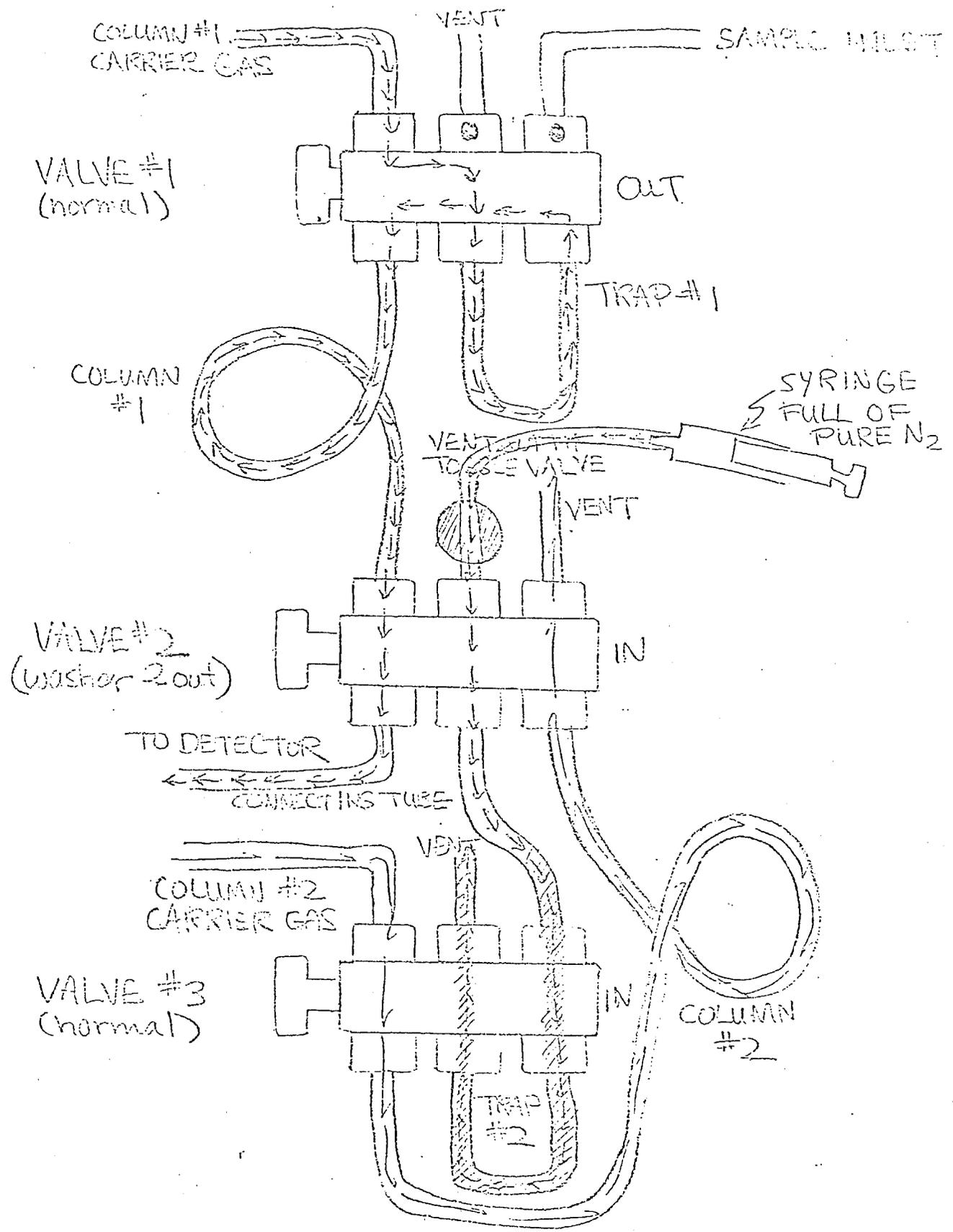
stop here if column #2 is not to be used



4. peak of interest frozen out in trap #2
 STEPS: PUT LOX ON TRAP #2
 WHEN PEAK STARTS TO ELUTE
 SIMULTANEOUSLY PUSH
 VALVE #2 FROM IN TO OUT AND
 VALVE #3 FROM OUT TO IN



5. modified sample thawed and analyzed
 STEPS: OPEN VENT WITH TOGGLE VALVE WHEN
 PEAK IS FINISHED ELUTING
 REMOVE LOX FROM TRAP #2
 QUICKLY PUSH VALVE #3 FROM IN TO OUT
 IMMEDIATELY THAW TRAP #2

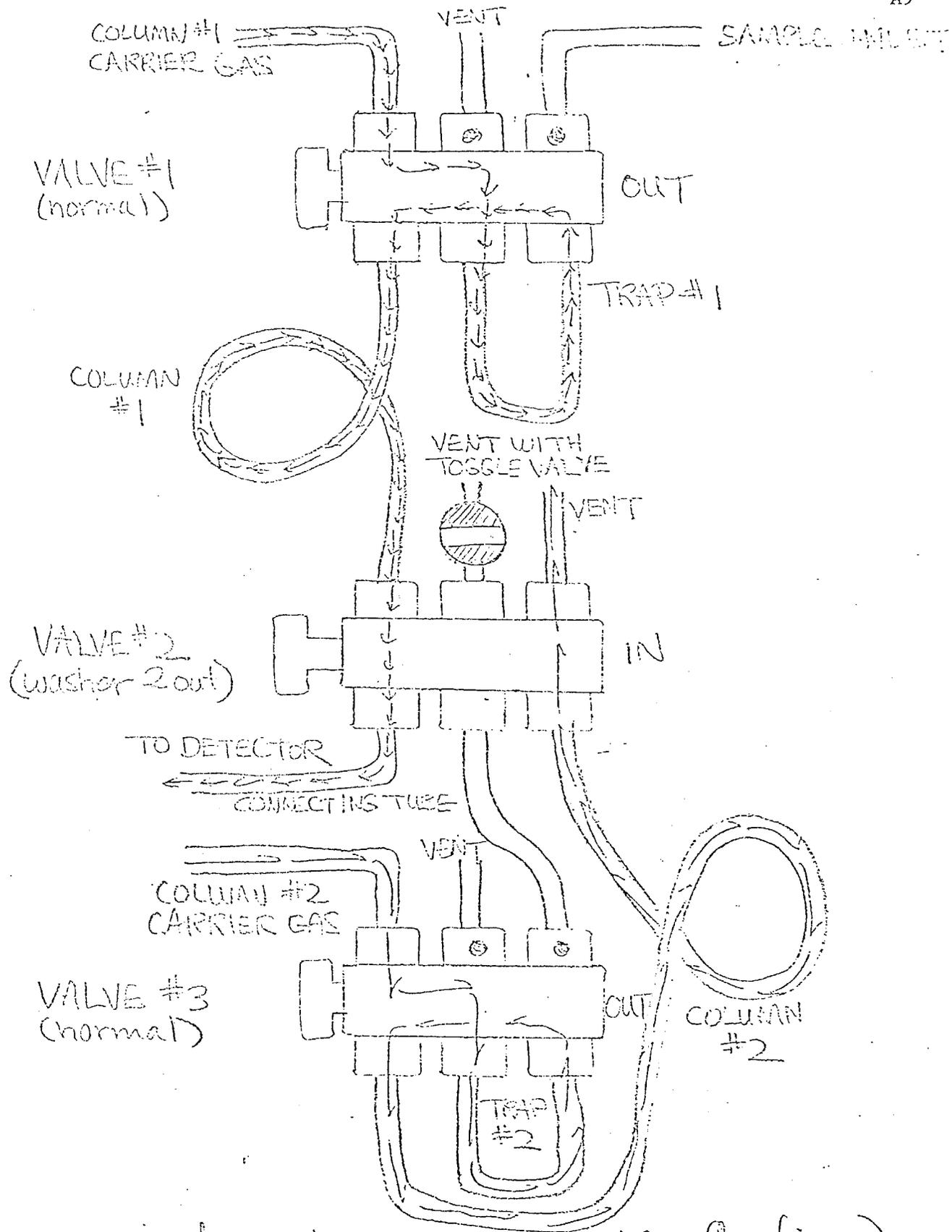


6. contamination in connecting tube may be flushed out with pure N₂ if desired

STEPS: SIMULTANEOUSLY PUSH

VALVE #2 FROM OUT TO IN AND
VALVE #3 FROM OUT TO IN

... THROUGH VENT WITH TRUCK VALVE



7. Return to normal (idle flushing)
STEPS: PUSH VALVE #3 FROM IN TO OUT

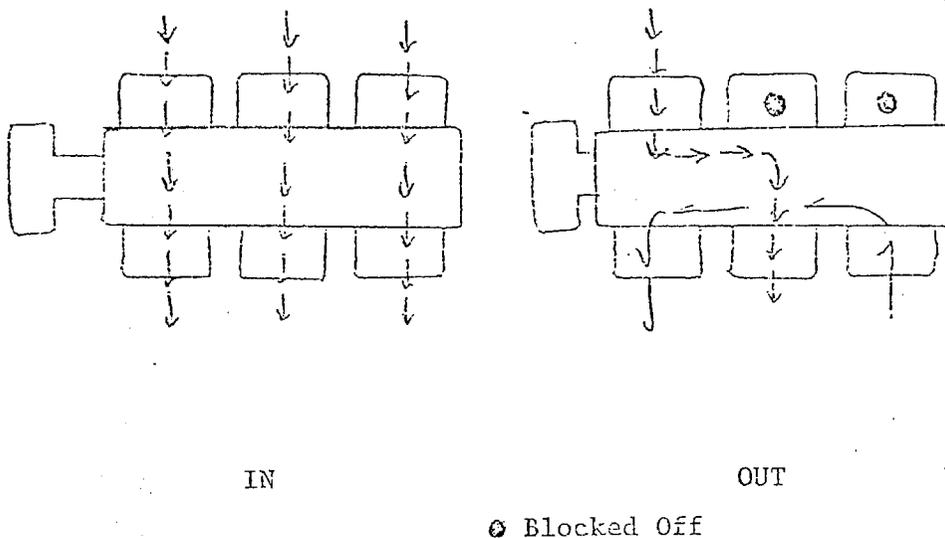
APPENDIX

Dual Column - Dual Trapping System

This system uses two traps, two columns and three slide valves to provide the option of using trap #1 and column #1 only, or using column #1 until the compound of interest starts to elute, then use trap #2 and column #2 to analyze this portion of the original sample.

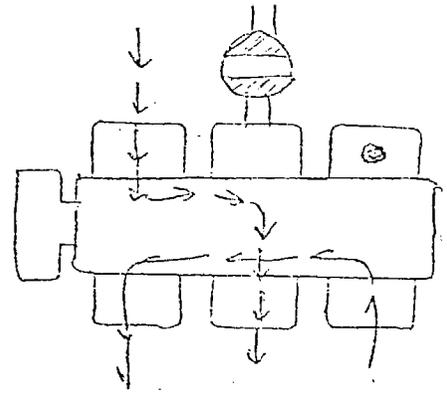
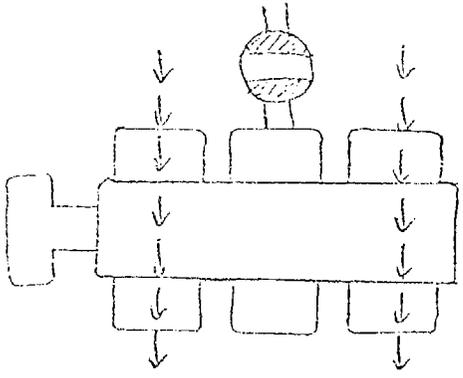
Each slide valve has six ports and four internal O-ring seals. In normal operation the slide valve has two different positions illustrated here. The arrows represent gas flow.

#1 OR #3 SLIDE VALVE



In order to make this system work as described, it was necessary to remove the O-ring second from the knob end of the plunger on #2 slide valve and add on an external toggle valve. It now works as shown here:

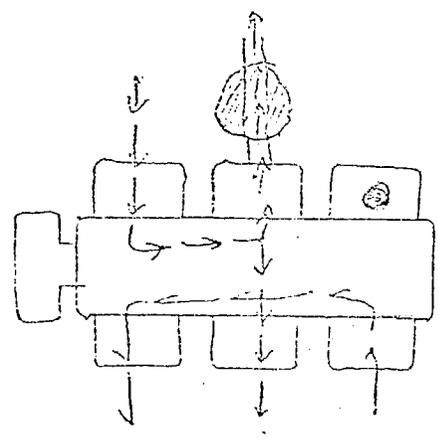
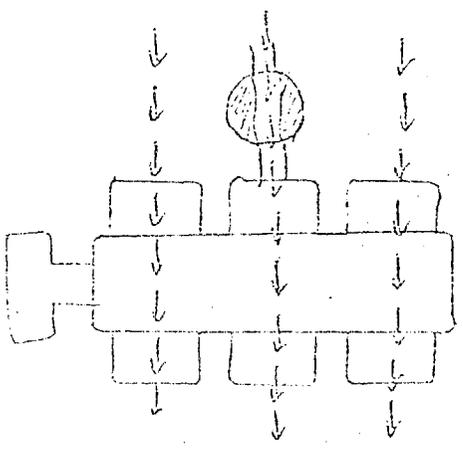
#2 SLIDE VALVE



TOGGLE VALVE CLOSED

or

or



TOGGLE VALVE OPEN

IN

OUT

The construction and operation of the system is illustrated on the following pages. Each diagram shows the system after the steps have been followed.