

DETERMINATION OF RESIDUAL VINYL CHLORIDE
MONOMER IN VINYL RESINS

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1 PURPOSE

This is a method for determining small amounts of residual vinyl chloride monomer present in vinyl resins. The resin sample is dissolved in a suitable solvent and is analyzed by means of a gas chromatographic technique utilizing a backflush mode. The method is applicable to poly(vinyl chloride), vinyl chloride-vinyl acetate copolymers and other vinyl resins in which there are no volatiles capable of interfering with the determination. It resolves vinyl chloride from the major impurities found in vinyl resins and can be quantitated with proper calibrations.

2 EQUIPMENT AND REAGENTS

- 2a Gas chromatograph, Hewlett-Packard (F and M) Model 5750 or equivalent, equipped with a hydrogen flame ionization detector.
- 2b Backflush valve, Bendix 8-port sliding plate valve or equivalent.
- 2c Tetrahydrofuran, reagent grade
- 2d Balance with accuracy to 0.01 gram
- 2e Fritted glass sparger, fine

3 INSTRUMENT PARAMETERS

Instrument	Hewlett-Packard (F and M) Model 5750 or equivalent, equipped with hydrogen flame ionization detector
Column	20 feet x 1/8-inch stainless steel tubing packed with 20 percent TERGITOL E-35 on Chromosorb W AW, 60/80 mesh
Backflush valve	Bendix, 8 port sliding plate valve or equivalent

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Temperatures	
Column	70°C isothermal
Injection port	100°C (maximum)
Detector	300°C
Carrier gas	helium
Flows	
Helium carrier gas	
a) inject	40 cc/minute
b) backflush	40 cc/minute
Hydrogen	20 psi at cylinder heat
Compressed air	40 psi at cylinder head
Sample size	40 microliters
Electrometer	
Range	1
Attenuation	8
Approximate elution time	
Vinyl Chloride	2.8 minutes

4 SCHEMATIC OF FLOW SYSTEM

A schematic of the flow system utilizing the Bendix 8-port sliding plate valve is shown in Figure 1.

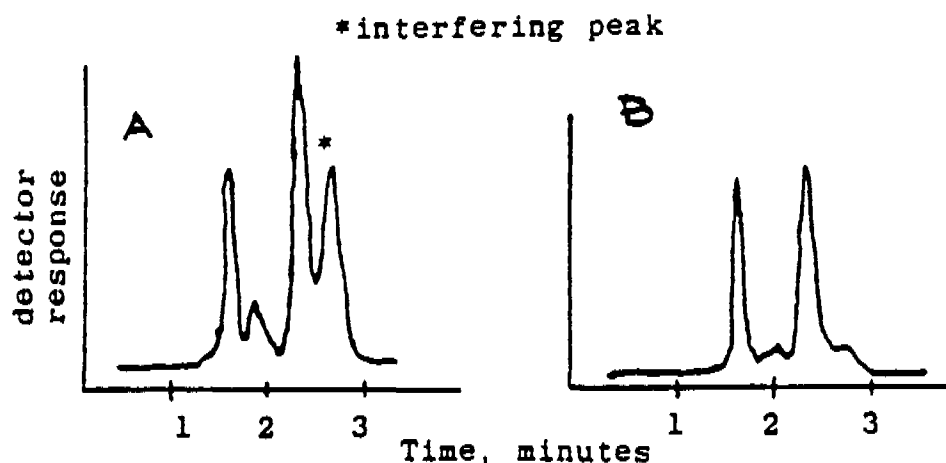
5 PROCEDURE

5a Analyze the tetrahydrofuran (THF) prior to preparing any samples or calibration standards using the parameters listed in Section 3. A backflush valve has been incorporated into the system to facilitate the analysis. Four minutes after the sample injection, the column is backflushed and vented to the atmosphere thus preventing the solvent from reaching the detector. A backflush time of 10-15 minutes should be sufficient to elute the solvent. After the backflush period, return the valve to its original position. The base line should be allowed to equilibrate before injecting another sample.

NOTE 1: An alternative backflush technique can be employed which significantly reduces the analytical time required to elute the solvent from the column and reestablish a stable base line. In this procedure, a four-foot section of the twenty-foot analytical column is employed as a precolumn, with the remaining sixteen-foot section functioning as the analytical column. The columns may be connected to the backflush valve as described in Section 2b of this method or to a 6-port rotary valve. Flow schematic diagrams for both valves are shown in Figures 4 and 5.

The sample of vinyl chloride monomer in THF is carried directly in the 4' precolumn from the heated injection port with the backflush valve in the Inject position. After approximately 1.0 minute, the VCM monomer elutes from the precolumn into the analytical column. The valve is then switched to the Backflush position to flush the THF (which remains in the precolumn) to vent.

- 5b Compare the THF chromatogram with those shown below. If the scan is comparable to A, the THF will have to be sparged with nitrogen at a medium flow rate for approximately 2 hours in an effort to remove the interfering peak. Reanalyze the sparged THF to determine if it is acceptable. If the scan is comparable to B, the THF should be acceptable for use in the analysis.



- 5c Accurately weigh one gram of the resin to be analyzed into a 6-dram vial** containing 9 grams of THF. Cap the vial and shake to effect solution. Analyze the sample using the parameters listed in Section 3 and follow the above instructions for the backflush.

** A glass vial and a phenolic cap equipped with a polyethylene liner are used to insure gas retention.

- 5d Measure the peak height of the vinyl chloride peak in millimeters. The area can also be measured using an acceptable technique (e.g. planimeter, automatic integrator, computer, etc.).

6 CALIBRATION

Prepare solution mixtures of varying amounts of vinyl chloride in THF to cover the expected ppm range of concentration. Obtain the gas chromatogram for each sample using the parameters listed in Section 3. Prepare a chart plotting the peak height (or area) obtained from the chromatogram of each sample versus the known concentration to establish a relative detector response. See Figure 2 for typical calibration curve.

7 CALCULATIONS

- 7a Determine the monomer content in the test solution from the calibration chart. Apply the peak height (or area) of the monomer obtained from the chromatographic scan of the test solution to the calibration curve and read the corresponding concentration in parts per million (ppm).
- 7b The concentration value obtained from the calibration curve is total monomer in the solution. In order to convert the data to monomer concentration based on total resin, the value must be multiplied by a factor of 10.

8 GAS CHROMATOGRAM

A gas chromatogram is attached as Figure 3 showing the response for 1.3 ppm vinyl chloride.

9 LIMIT OF DETECTABILITY

The lower limit of analytical detectability as defined using poly (vinyl chloride) and vinyl chloride-vinyl acetate copolymers has been shown to be < 0.2 ppm.

10 REPORT

Full identification of sample

Identification of the test method

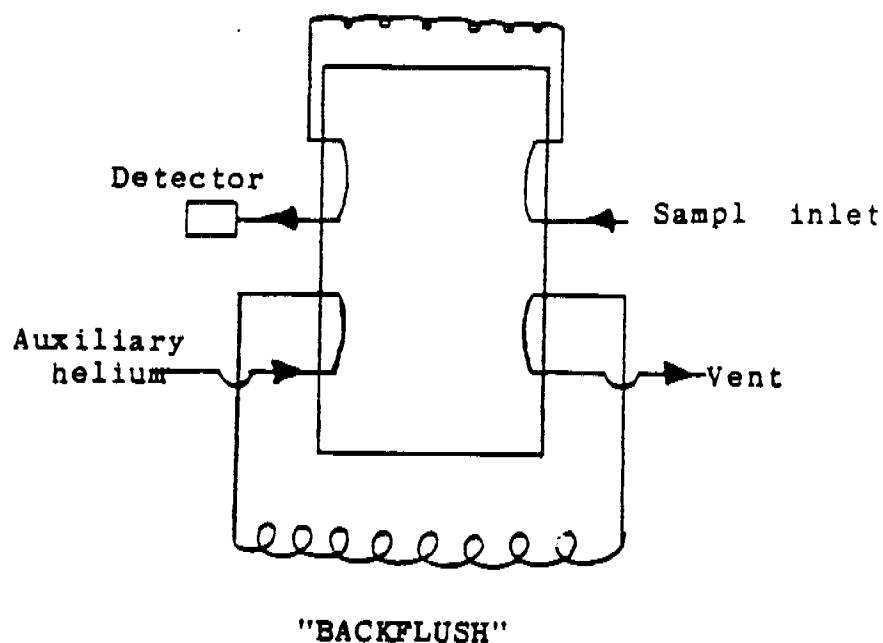
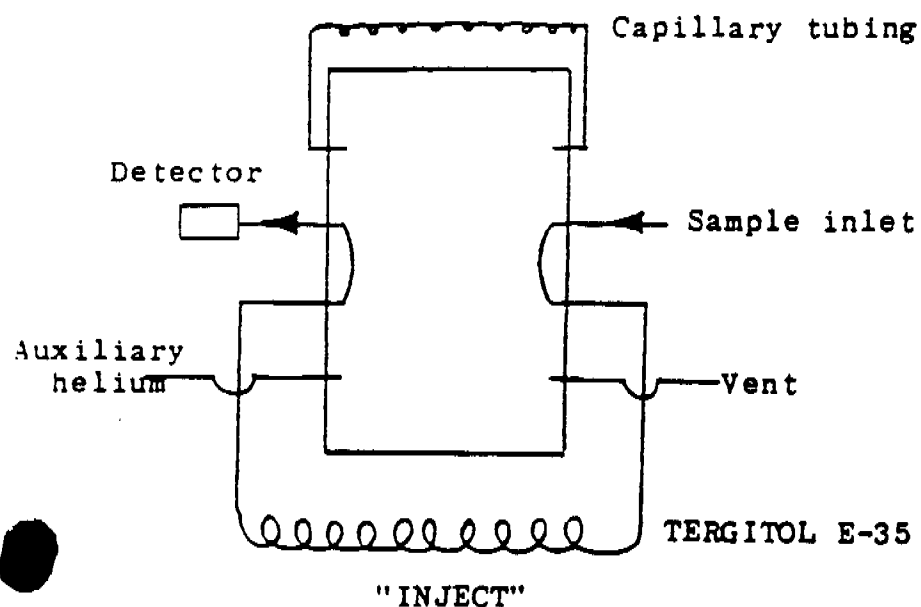
Vinyl Chloride Monomer, ppm.

Analyst and Date

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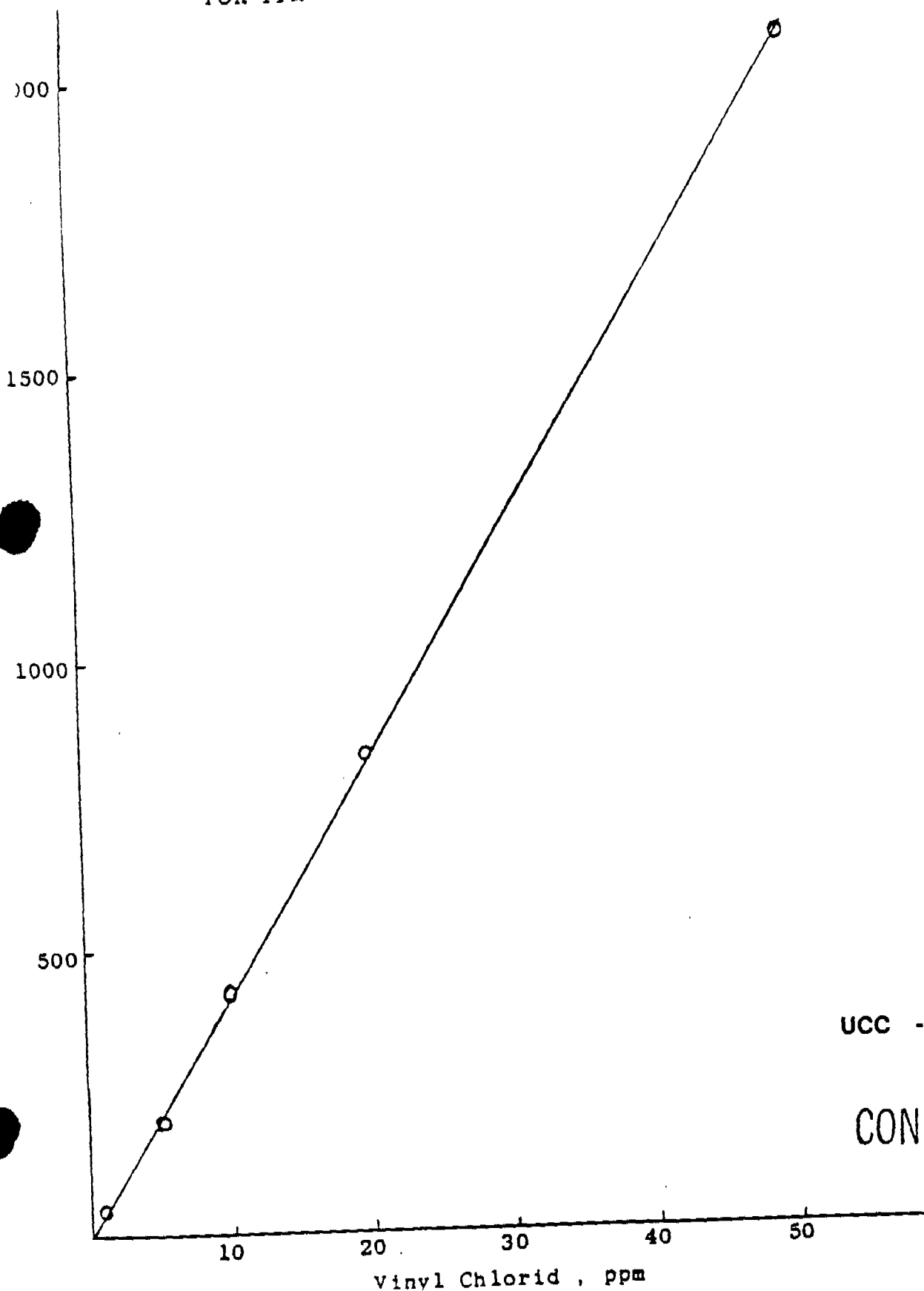
FIGURE 1
SCHEMATIC OF FLOW SYSTEM UTILIZING THE
BENDIX 8-PORT SLIDING PLATE VALVE



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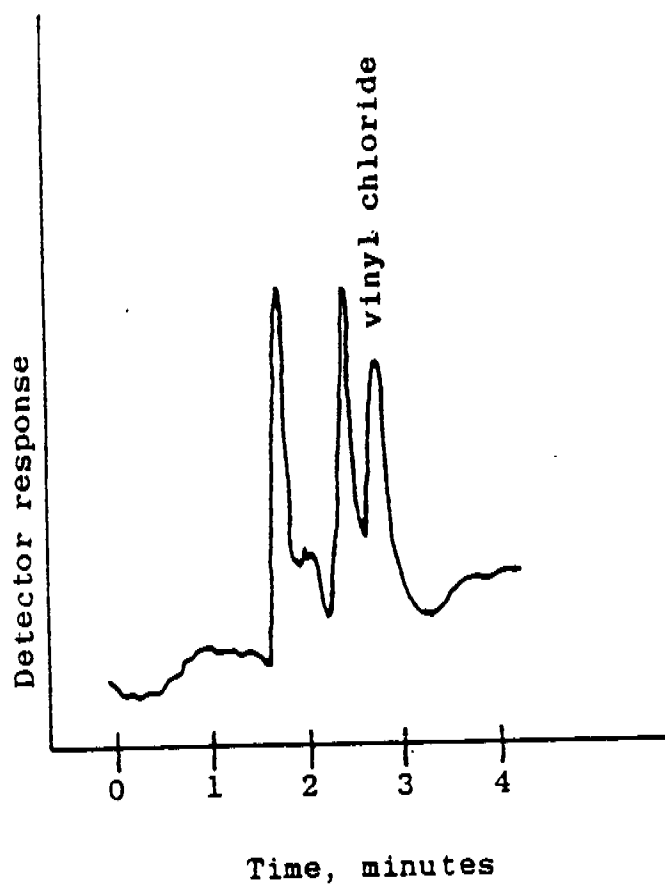
FIGURE 2
TYPICAL GAS CHROMATOGRAPHIC CALIBRATION CURVE
FOR PPM VINYL CHLORIDE VS AREA IN TETRAHYDROFURAN



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FIGURE 3
GAS CHROMATOGRAM OF VINYL RESIN
WITH 1.3 PPM VINYL CHLORIDE MONOMER

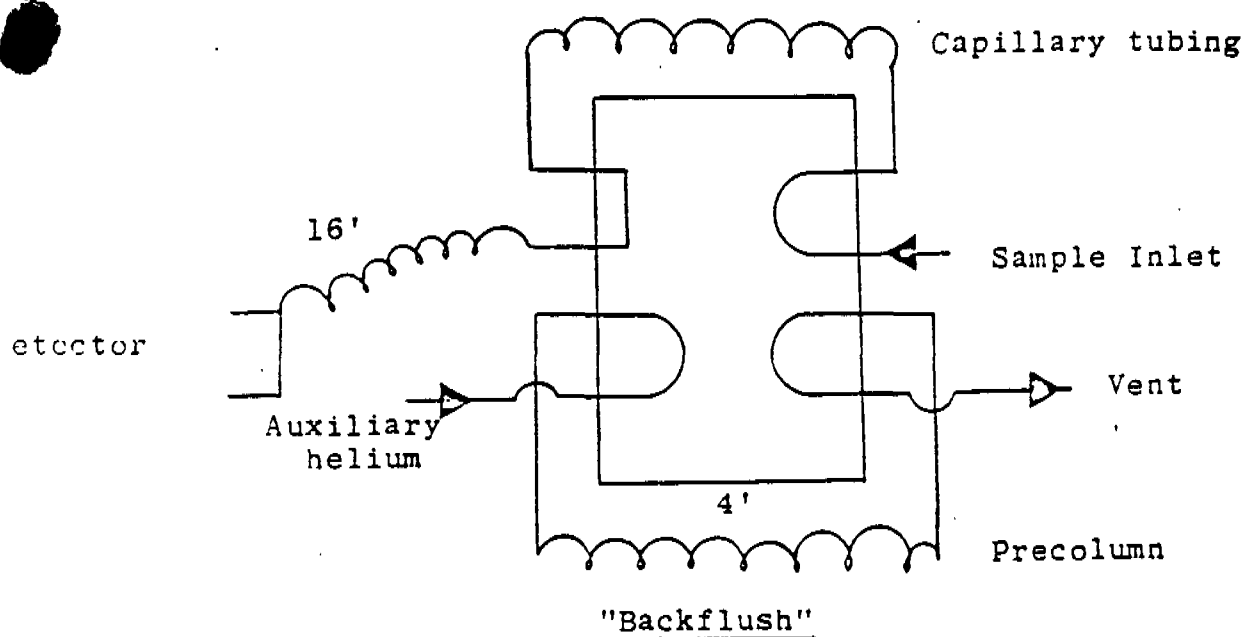
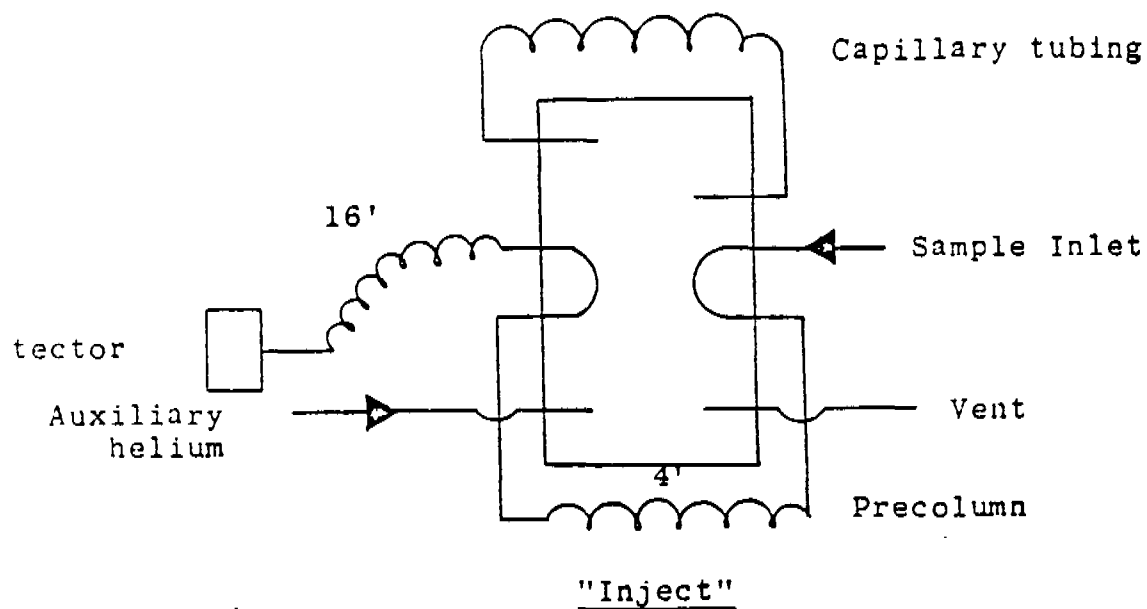


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FIGURE 4

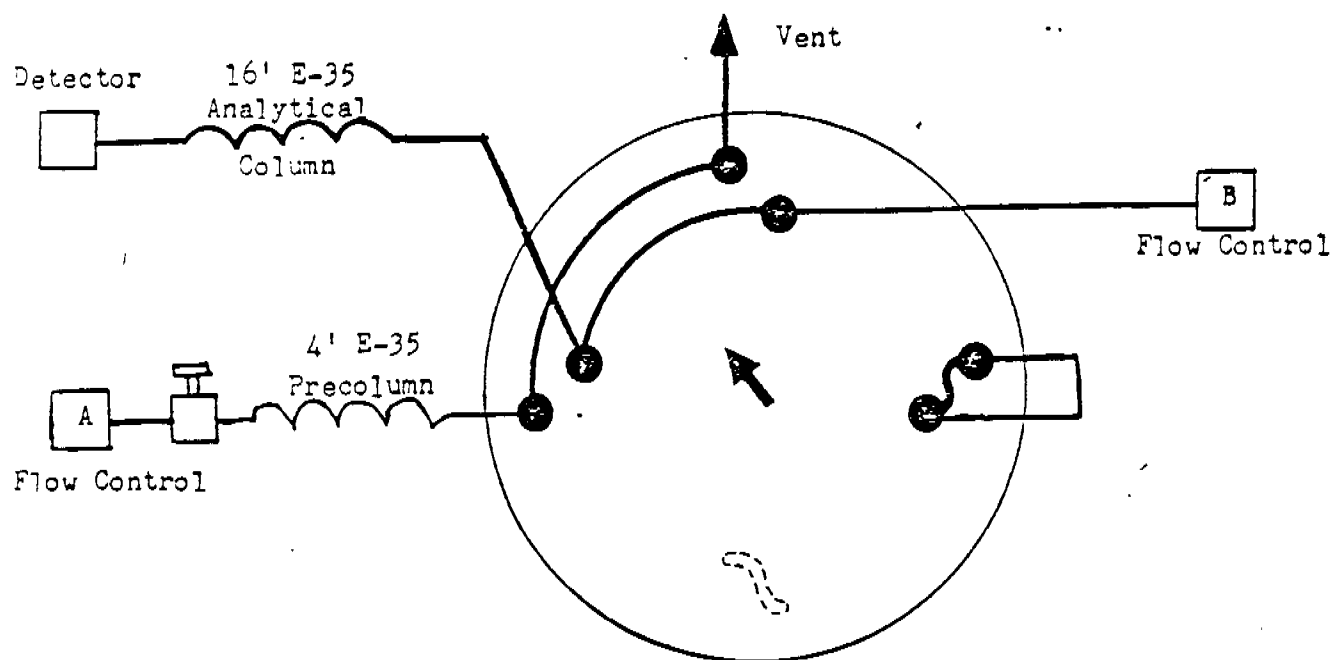
Schematic of Flow System Utilizing
Bendix 8-Port Sliding Plate Valve



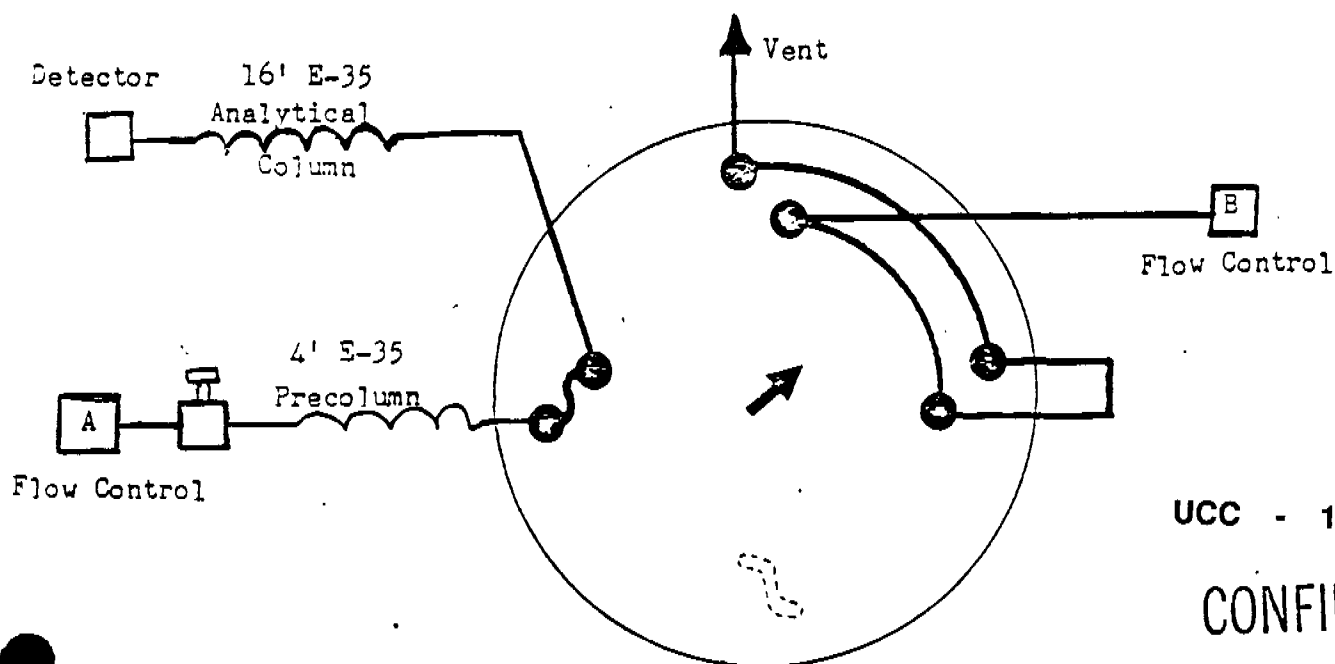
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FIGURE 5
SCHEMATIC OF FLOW SYSTEM UTILIZING THE
VALCO 6-PORT ROTARY VALVE



POSITION A
BACKFLUSH MODE



POSITION B
INJECT MODE

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*Valco Instruments
Houston, Texas