



Standard Test Method for Residual Vinyl Chloride Monomer Content of Poly(Vinyl Chloride) Resins, Compounds, and Copolymers by Solution Injection Technique¹

This standard is issued under the fixed designation D 3680; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

^{ε1} NOTE—Editorial changes were made throughout in November 1996.

1. Scope

1.1 This test method can be used to determine small amounts of residual vinyl chloride monomer (VCM) in poly(vinyl chloride) (PVC) resins. It may be possible to use it for other resins or compounds containing vinyl chloride provided there are no other volatile components present with the same retention time as vinyl chloride monomer.

1.2 The values stated in inch-pound units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For a specific hazard statement, see Section 9.

2. Referenced Documents

2.1 ASTM Standards:

E 260 Practice for Packed Column Gas Chromatography²

E 355 Practice for Gas Chromatography Terms and Relationships²

3. Terminology

3.1 Abbreviations:

3.1.1 *VCM*—vinyl chloride monomer.

3.1.2 *PVC*—poly(vinyl chloride) resin.

3.1.3 *RVCM*—residual vinyl chloride monomer.

3.1.4 *DMAC*—dimethyl acetamide.

3.1.5 *THF*—tetrahydrofuran.

4. Summary of Test Method

4.1 The resin, compound, or copolymer specimen is dissolved in a suitable solvent and is then analyzed by conven-

tional gas chromatographic (GC) techniques. Analysis time can be decreased by utilizing a backflush mode to eliminate the solvent.

5. Significance and Use

5.1 Poly(vinyl chloride) (PVC) resins must contain a minimum possible amount of unreacted, or free vinyl chloride monomer.

5.2 Under optimum conditions approximately 1 ppm VCM can be detected in PVC resins.

6. Interferences

6.1 Any material that elutes at approximately the same retention time as VCM will cause erroneously high RVCM results.

6.2 Special care must be exercised in interpreting the RVCM results obtained from the analyses of PVC copolymers or compounds. Many ingredients are added to PVC resins to obtain compounds with desired properties for each particular end use. These additives, or components in them, could possibly have the same retention time as VCM. In general, if a PVC compound apparently has a much larger VCM content than the starting resin, then the presence of some interfering component can be suspected as the probable cause of the larger than expected amount in the compound.

7. Apparatus

7.1 *Gas Chromatograph*, with dual flame ionization detector, and heated injection port with removable glass inserts. For further information see Practice E 355.

7.2 *Recorder*, 0 to 1-mV full scale.

NOTE 1—Electronic integrators, or computer systems can be used to obtain peak areas and make the required calculations.

7.3 *Analytical Balance*, capable of weighing to ± 0.0001 g.

7.4 *Soap Film Flowmeter*.

7.5 *Stopwatch*.

7.6 *Pressure Regulators*, for all the required gas cylinders.

7.7 *Filter Dryer Assemblies*, for each of the GC gas cylinders.

7.8 *Vials*, 6-dram, with polyethylene-lined screw caps.

¹ This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.33 on Polymers and Resins.

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² *Annual Book of ASTM Standards*, Vol 14.02.

NOTE 2—Caps with wax liners should not be used for sample dissolution.

NOTE 3—Vials and caps should be used only once and discarded.

7.9 *Serum Bottles, 60-mL, and Stoppers.*

7.10 *Liquid Sampling Syringes, 10 and 50- μ L. GC Liquid Sampling Syringes, 10 and 50- μ L.*

7.11 *Gas Syringes, 0.1 and 1-mL, equipped with valve locks.*

7.12 *Ball Valve, two-way, stainless steel.*³

7.13 *Flow Controller.*⁴

7.14 *Screw Cap, 6-dram, with Needle Seal Septa.*

7.15 *Reciprocating or Wrist-Action-Type Shaker.*

7.16 *Column and Packings*—Any of the following may be used: For further information see Practice E 260.

7.16.1 $\frac{1}{8}$ in. outside diameter by 1 ft plus $\frac{1}{8}$ in. outside diameter by 6 ft stainless steel packed with 80/100 mesh copolymerized divinyl benzene/4 vinyl pyridine porous polymer beads (UPS code S8); or silanized divinyl benzene porous polymer beads.⁵

7.16.2 $\frac{1}{8}$ in. outside diameter by 20 ft stainless steel packed with 20 % nonyl phenyl poly(ethylene glycol) on 60/80-mesh acid washed, white flux-calcined diatomite (USP code S1A).⁶

7.16.3 $\frac{1}{8}$ in. outside diameter by 3 ft plus $\frac{1}{8}$ in. outside diameter by 6 ft with 0.2 % polyethylene glycol 1500⁷ on graphitized carbon black (surface area or 10 m²/g).⁸

7.16.4 $\frac{1}{8}$ in. outside diameter by 20 ft packed with 20 % polymeric hydrocarbon (fraction L, 300°C maximum tempera-

ture,⁹ on 60/80-mesh acid and based washed, neutralized, silanized, white flux-calcined diatomite.¹⁰

NOTE 4—The above-mentioned column lengths and packing have been used successfully for this analysis. However, any column that will elute VCM in reasonable lengths of time (1 to 4 min) can be used provided any interfering components are not eluted at the same time as VCM.

7.17 *Jars, 2-oz (60-mL), with aluminum or polyethylene-lined screw caps.*

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,¹¹ where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Air, breathing or water-pumped.*

8.3 *N,N-Dimethyl Acetamide (DMAC)* (Note 5).

NOTE 5—Either solvent (DMAC or THF) may be used. However, they must be free of any contaminants that have the same retention time as VCM or any internal standard that may be used. To determine this, inject 10 μ L of solvent and obtain a chromatogram under the conditions of Section 11.

8.4 *Hydrogen, prepurified or zero gas.*

8.5 *Nitrogen, oxygen-free.*

NOTE 6—Helium may also be used as the carrier gas.

8.6 *Pentane, at least 99 %.*

8.7 *Tetrahydrofuran (THF)* (Note 5).

8.8 *Vinyl Chloride Monomer, polymerization grade.*

9. Hazards

9.1 In addition to other precautions, conduct all operations including the preparation of standards, transfer of solvents, and column backflushing (if the technique described in 11.1 is used) in a properly functioning fume hood.

10. Sampling and Storage

10.1 Keep all resin samples in tightly sealed jars. Samples should be analyzed within 24 h. If 24 h are exceeded, report the age of the sample. Use 2-oz (60-mL) bottles with aluminum or polyethylene-lined screw caps, completely filled, and seal with electrical tape.

⁹ The sole source of supply of the material, Apiezon L, known to the committee at this time is James F. Biddle Co., 510 Township Line Rd., Blue Bell, PA 19422. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

¹⁰ The sole source of supply of the material, Gas-Chrom Q, known to the committee at this time is Applied Science Laboratories, 111 Ballard, Parkway Suite 208, P.O. Box 16118, Tampa, FL 33687. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

¹¹ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

³ The sole source of supply of the ball valve, Catalog Number 4152-A-316, known to the committee at this time is Whitey Co., 318 Bishop Rd., Highland Heights, OH 44143. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

⁴ The sole source of supply of the flow controller, Model 8744A, known to the committee at this time is Brooks Instrument Co., Div. Emerson Electric Co., 407 W. Vine St., Hatfield, PA 19440. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

⁵ The sole source of supply of the porous polymer beads, Poropak S or Poropak Q-S, known to the committee at this time is Dow Chemical Co., 2020 Dow Ctr., Midland, MI 48674 and marketed for gas chromatograph use by Waters Associates, Inc. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

⁶ The sole source of supply of the flux-calcined diatomaceous earth, Chromosorb W-AW, known to the committee at this time is Celite Corp., 717 17th St., P.O. Box 5108, Denver, CO 80217-5108. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

⁷ The sole source of supply of the polyethylene glycol, Carbowax 1500, known to the committee at this time is Union Carbide Corp., 39 Ridgebury Rd., Danbury, CT 06817. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

⁸ The sole source of supply of the material, Carbpak C, known to the committee at this time is Supelco Inc., Supelco Park, Bellefonte, PA 16823. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

10.2 Compound samples can be kept in the same type jars. The remaining precautions are not required as long as the jar is tightly sealed.

11. Preparation of Chromatograph

11.1 Install the chromatographic column and condition at least overnight at the temperature limit for the packing being used. Do not connect the exit end of the column to the detector while conditioning. Turn off hydrogen and air to the detector while the column is disconnected. One method of achieving the backflushing of the solvent is shown schematically in Fig. 1. The two columns are separated by a "Tee" fitting. Connect the short column between the injection port and one end of the "Tee." Connect the longer column between the other end of the "Tee" and the detector. Connect a line from the outlet of the ball valve to the center inlet of the "Tee." This auxiliary line may be filled with a suitable column packing if desired to act as a pressure buffer when switching to the backflush mode. Insert "Tee" into the carrier gas supply line to supply the auxiliary flow controller.

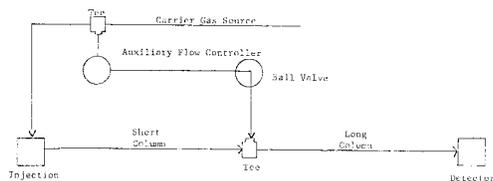


FIG. 1 Schematic of Backflushing Method

11.2 Adjust the carrier gas flow as follows (Note 7):

- 11.2.1 Close off the auxiliary flow with the ball valve.
- 11.2.2 Set flow at 30 mL/min with the chromatograph flow control valve.
- 11.2.3 Remove the septum from the injection port.
- 11.2.4 Open the ball valve.
- 11.2.5 Again adjust the flow to 30 mL/min with the auxiliary flow control valve.
- 11.2.6 Close the auxiliary flow with the ball valve.
- 11.2.7 Replace the septum on the injection port.
- 11.2.8 The system is now ready for an analysis.

NOTE 7—If possible with the chromatograph being used, adjust the carrier flow at the analysis temperature.

11.3 Set detector air and hydrogen flows and pressures at the optimum conditions for the make and model of chromatograph being used.

11.4 Set temperatures as follows:

- 11.4.1 Optimize oven (chromatograph column) temperature to elute VCM between 1 and 4 min after injection.
- 11.4.2 *Injection Port*—200°C.
- 11.4.3 *Detector*—At least 20°C above maximum column temperature.

NOTE 8—Other systems of backflushing have been evaluated. However, none of them have been very successful. This is probably due to the fact

that a small amount of solvent seems to remain in the column and injection port. This small amount of solvent is always detected at the extreme detector sensitivity required for this analysis. It may then take as long as 30 to 40 min to return to a stable baseline. Two alternative methods of flushing solvent from the column are described in Annex A1.

NOTE 9—A trial-and-error method is used to determine the optimum time to remove and replace the septum holder for backflushing the solvent. The objective is to wait as long as possible to be sure that the VCM has passed through the short column but still to retain all, or most, of the solvent in the short column before removing the septum to backflush it, then to replace the septum after the solvent has backflushed out through the injection port.

12. Calibration by External Standard

12.1 Prepare solution mixtures of varying amounts of VCM in solvent to cover the expected parts per million range of concentration. These can be prepared as described for the internal standard method in 13.2 and 13.3 without adding the internal standards. Obtain a gas chromatogram for each calibration standard using the parameters listed in Section 11. Prepare a chart plotting the peak height (or area) from the chromatograms versus the known concentration of VCM in each calibration standard to establish a detector response curve.

13. Calibration with an Internal Standard

13.1 Prepare a polymer solvent solution containing a known amount of internal standard as follows:

- 13.1.1 Partially fill a 1-L volumetric flask with solvent.
- 13.1.2 Into a separate beaker or flask containing a tared weight of solvent, add, by means of a syringe, approximately 0.0150 g of pentane. Reweigh the container immediately and determine the exact amount of pentane added to the nearest 0.1 mg.
- 13.1.3 Immediately upon reweighing, quantitatively add the contents of the container to the 1-L volumetric flask. Do so by rinsing the container with aliquot portions of the solvent. Bring to the mark with fresh solvent. Mix thoroughly and calculate the grams of pentane per 20 mL of solution as follows:

$$\text{Grams pentane/20 mL} = \text{weight of pentane}/50$$

13.1.4 Store the internal standard solution, thus prepared, in an amberized bottle. Label the bottle Solution A.

13.2 Weigh 50.00 ± 0.01 g of the solvent into a tared, serum bottle to the nearest 0.1 mg. Immediately seal the vial. Record the weight of the solvent.

13.3 Using a 0.1-mL syringe¹², add about 0.025 mL of liquid vinyl chloride monomer to the sealed bottle. Reweigh to the nearest 0.1 mg. Determine the weight of vinyl chloride added and the total weight of the solution. Calculate the grams of vinyl chloride per gram of solution. Identify this as Solution B.

¹² Use syringes made specifically to maintain liquids and gases under pressure within the syringe. Syringes must be gas-tight with a valve between the syringe barrel and needle.

$$\text{Grams VCM/gram Solution B} = \frac{\text{grams VCM}}{\text{grams VCM} + \text{grams solvent}}$$

13.4 Pipet 20.0 mL of Solution A into a vial equipped with a screw cap and a TFE-fluorocarbon valve.¹³ Immediately cap, weigh, and record the weight of the solution and the sealed container.

13.5 Using the 1-mL syringe, inject approximately 1 mL of Solution B into the contents of the vial. Reweigh and determine the weight of Solution B that was added to Solution A. Once prepared, this standard solution is not to be opened. Prepare a new standard solution each time a fresh Solution A is prepared.

13.5.1 Calculate the amount of vinyl chloride in the prepared standard as follows:

$$\begin{aligned} \text{weight of VCM} &= \text{weight of Solution B} \\ &\times \text{grams VCM/grams of Solution B (from 13.3)} \end{aligned}$$

13.6 Using the operating conditions described in Section 11 and the procedure described in Section 14, inject 10 μL of this standard solution containing known amounts of pentane and VCM into the chromatographic system. Determine a Response Factor (RF) from the ratio of peak areas of the vinyl chloride and pentane and their known weights as follows:

$$\text{RF} = \frac{\text{weight of pentane} \times \text{peak area VCM}}{\text{weight of VCM} \times \text{peak area pentane}}$$

13.6.1 Example:

	Weight	Area
Pentane	0.0002940	6471
VCM	0.0005190	8921

$$\text{RF} = \frac{0.0002940 \times 8921}{0.0005190 \times 6471} = 0.781$$

NOTE 10—For highly accurate determinations of the response factor, it is advisable to run the calibration standards a minimum of five times. The average of these runs is then used. The stability of the response factor must be verified at least once per week.

14. Sample Analysis Procedure

14.1 Sample Preparation:

14.1.1 Mix the sample to be analyzed completely so that the portion selected will be as representative as possible. Weigh 1 g of the sample to be analyzed into a tared 6-dram vial and recap the vial and contents and determine the specimen weight to the nearest 0.1 mg.

14.1.2 By means of a pipet, add 20.0 mL of solvent or Solution A (see Section 13) containing the solvent and internal standard solution to the specimen vial.

NOTE 11—Twenty millilitres of solvent yields a 5 weight % solution. Ten millilitres of solvent will yield a 10 weight % solution.

14.1.3 Place the vial on a shaker until the specimen is completely dissolved. Once it is visually in solution, the specimen must be shaken for at least one additional hour. Leave all specimens on the shaker until they are analyzed.

¹³ The sole source of supply of the valve, Mininert, and caps, known to the committee at this time is Dynatech Precision Sampling Corp., P.O. Box 15886, Baton Rouge, LA 70895. The caps are designed so that the contents of the vial can be removed with a syringe without removing the cap. The valves attach to the lever fitting of a syringe to permit sampling or storage under pressure. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

14.2 Inject 10 μL of the prepared specimen.

NOTE 12—A larger volume of prepared specimen (greater than 10 μL) may be utilized when analyzing for very low levels of vinyl chloride. Care must be taken, however, to backflush the extra solvent from the system before injecting subsequent specimens. Also with larger injection volumes (20 to 40 μL) there is sometimes a possibility that some of the solvent does not volatilize. For cases in which backflush capability does not exist, the use of a smaller specimen size and another solvent, for example, acetone, has been found to be acceptable.

NOTE 13—The syringe used to inject specimens into the chromatographic system must be rinsed with solvent between each specimen injection.

NOTE 14—The glass insert in the injection port will catch and retain the solid particles from the specimen that would gradually foul the column. Loosely pack the $\frac{1}{4}$ in. at the outlet end of the glass tube with glass wool. Change this trap after every specimen. Change the septum at the beginning of each shift. Do not force the septum tightly against the glass tubing as this will restrict flow to the column.

14.3 At the predetermined time (see Note 9) remove the septum and actuate the ball valve to backflush the solvent.

14.4 At the end of the predetermined time (see Note 9) first actuate the ball valve to stop the backflush flow, then replace the septum on the injection port.

14.5 Allow at least 2 min for the baseline to equilibrate. Allow the equipment to sit longer if necessary until there is minimal baseline drift at the attenuation to be used for the analysis.

NOTE 15—After running the last specimen prior to a break in the analysis routine (of a limited time span) leave the system in the backflushing mode. An example of this would be a lunch break. When the down time will be of a longer nature, such as an entire shift, perform the normal backflushing operation after the last specimen and then leave the equipment with carrier flow in the forward position.

15. Calculation—External Standard Method

15.1 Determine the monomer content of the specimen from the calibration chart (see Section 12). Compare the peak height (or area) of the VCM peak of the chromatogram to the calibration curve and read the corresponding concentration in parts per million (ppm).

NOTE 16—The use of the external standard technique is extremely dependent on specimen size. The amount of specimen injected must be as much the same as it is possible to obtain for each injection.

NOTE 17—The concentration value obtained from the calibration curve is the total VCM in solution. In order to convert the VCM concentration to a specimen weight basis, if a 10 weight % specimen solution was prepared, the chart value must be multiplied by a factor of 10. If a 5 weight % specimen solution was made, then the multiplying factor is 20.

16. Calculation—Internal Standard Method

16.1 Calculate weight percent VCM as follows:

$$\text{Weight \% VCM} = \frac{\text{area VCM} \times \text{weight pentane in sample} \times 100}{\text{area pentane} \times \text{sample weight} \times \text{RF}}$$

16.2 Calculate parts per million VCM as follows:

$$\text{ppm VCM} = \frac{\text{area VCM} \times \text{weight pentane in sample} \times 10^6}{\text{area pentane} \times \text{sample weight} \times \text{RF}}$$

NOTE 18—See 13.6 for calibration instructions for determining the Response Factor (RF).

16.3 Example:

Weight pentane in specimen
 = 20 mL × 0.0000147 g/mL = 0.0002940 g
 RF = 0.781
 Specimen weight = 0.9385 g
 Area VCM = 1 211
 Area pentane = 11 868
 Weight % VCM = $\frac{1211 \times 0.0002940 \times 100}{11\ 868 \times 0.9385 \times 0.781}$
 = 0.0041 % VCM, and
 ppm VCM = 0.004 (× 10 000) = 4 ppm VCM

17. Precision and Bias

17.1 *Precision*—The following values were determined for the coefficients of variation of this test method, using an internal standard, on the basis of an interlaboratory test program (1976) involving twelve laboratories reporting averages of duplicate analyses.

17.1.1 *Precision for Resin Samples:*

Intralaboratory 8.3 %
 Interlaboratory 24.8 %

17.1.2 *Precision for Compounds:*

	At 2 ppm	At 30 ppm
Intralaboratory	5.8 %	5.8 %
Interlaboratory	28.8 %	10.3 %

17.2 *Bias*—Since no absolute method is available for comparison, no statement of accuracy can be presented for this test method.

18. Keywords

18.1 gas chromatographic; poly(vinyl chloride) (PVC) resins; residual vinyl chloride monomer (VCM); solution injection technique

ANNEX

(Mandatory Information)

A1. POLYMER SOLVENT REMOVAL BY ALTERNATIVE CARRIER GAS FLOW SYSTEMS

A1.1 Alternative carrier gas flow systems for removing the polymer solvent from the column system are shown schematically in Figs. A1.1-A1.4. Valve actuating times, both to eliminate the solvent and to return to baseline equilibrium conditions, must be determined experimentally for each individual column system being used.

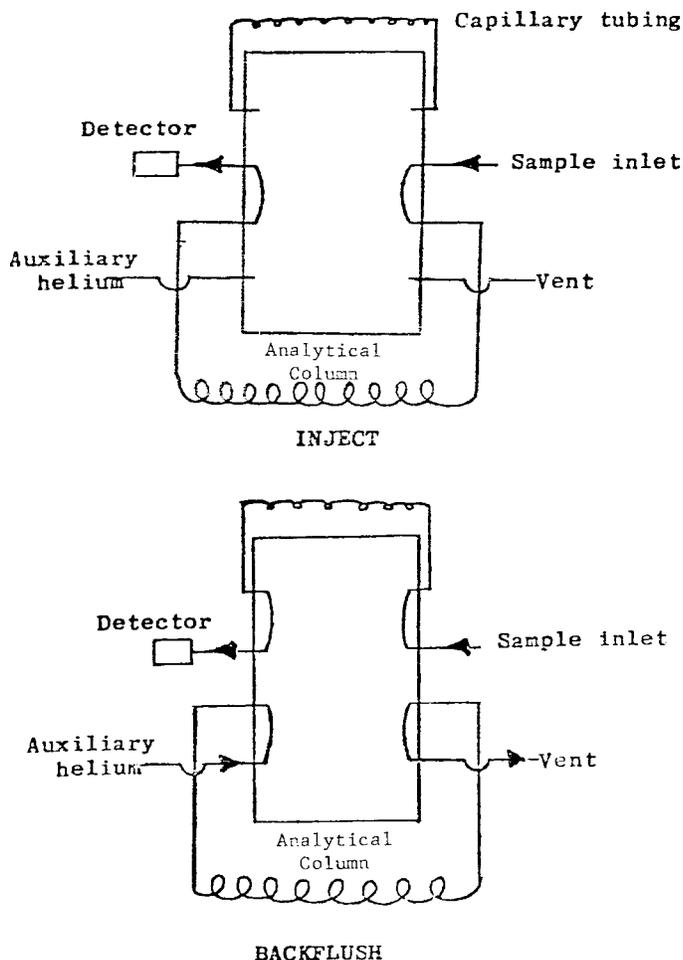


FIG. A1.1 Schematic of Flow System Utilizing an 8-Port Sliding Plate Valve with a Single Column

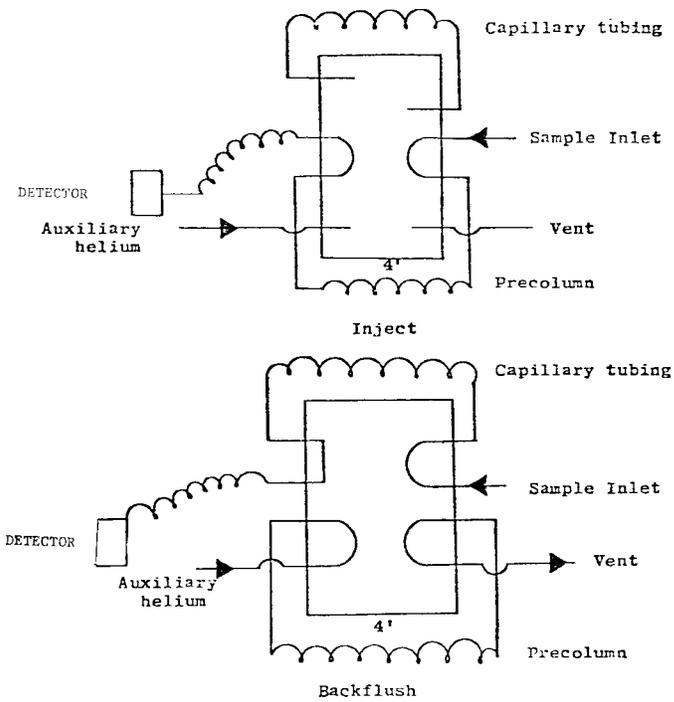


FIG. A1.2 Schematic of Flow System Utilizing an 8-Port Sliding Plate Valve with Two Columns

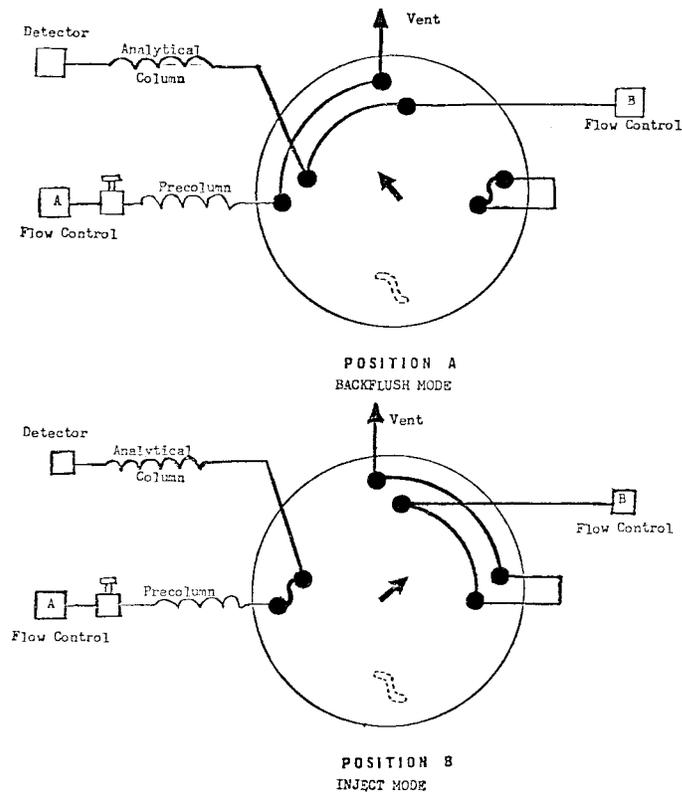
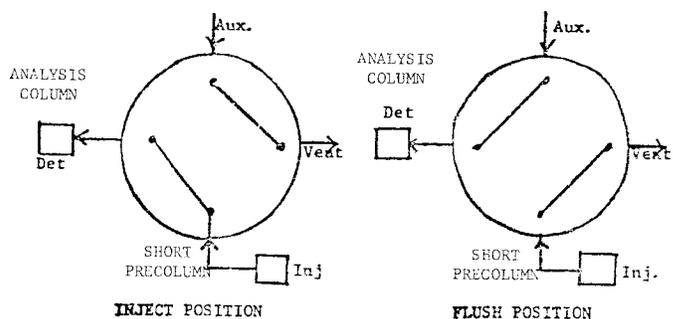


FIG. A1.3 Schematic of Flow System Utilizing a 6-Port Rotary Valve with Two Columns



NOTE 1—At a predetermined time, after the monomer peak has passed through the precolumn, the valve is activated to flush the solvent out the injection port and short precolumn.

FIG. A1.4 Schematic of Flow System Utilizing a 4-Port Rotary Valve with Two Columns

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