Column fractionation of polymers

XI. Constant volume pulseless pump for gel permeation chromatography

The technique of gel permeation chromatography (GPC) requires a constant volume flow of solvent to prevent loss in resolution from fluctuating flow and to facilitate the rapid comparison of chromatograms[1-4].

A common solution to this problem has been the use of a variable stroke piston-type pump[5]. Because of the pressure fluctuations, a buffering system is required—otherwise, the pressure fluctuations cause a high noise level in the very sensitive differential refractometer detector frequently employed.

A pulseless constant volume pump has been in use for some time in this laboratory with a gel permeation chromatograph. Fig. 1 is a schematic representation of the pump. The instrument achieves constant volume flow by the use of commercially available constant volume pumps (Zenith Products Company, West Newton, Mass.

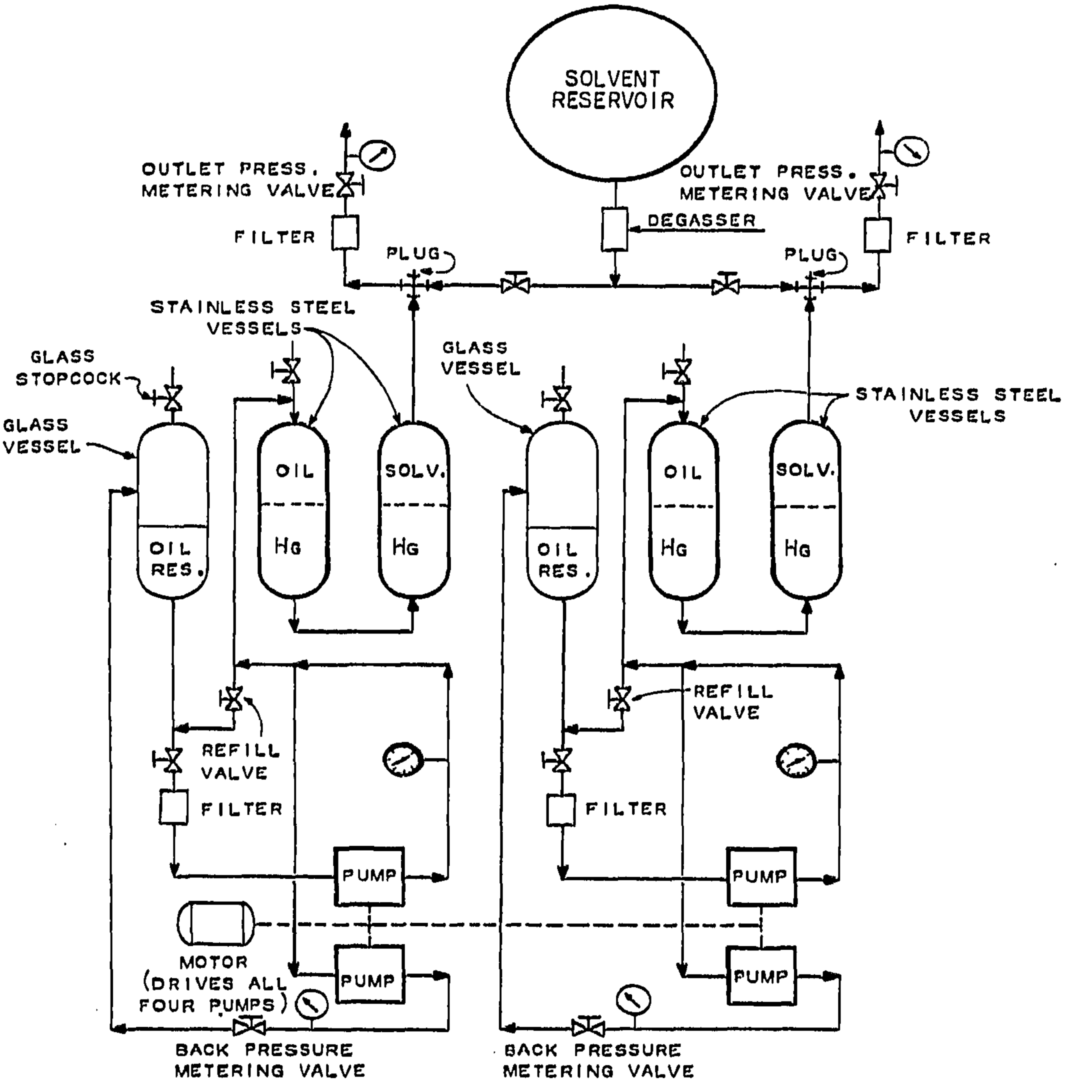

Fig. 1. Dual constant volume pumping unit, schematic.

No. 1/2 B-4391 with Teflon U-seals). To obtain the necessary low flow rates, two pumps are operated differentially. In differential operation one constant volume pump delivers a volume, V-1, as the source for the second pump which delivers a slightly smaller volume, V-2. The excess V-1 minus V-2 from a T-connection between the two pumps is the flow delivered to the chromatograph. To achieve constant volume flow, these gear-type pumps must operate on a fluid with considerable viscosity. This precludes their delivering directly the low viscosity solvents employed in GPC. Therefore, the pumps are operated on a mineral oil with an approximate viscosity at room temperature of about 200 centistokes. The reservoir containing the oil is made of glass. The mineral oil enters a stainless steel chamber (high pressure cylinder 1800 p.s.i. No. 8HD1000, Hoke, Inc., One Tenakill Park, Creskill, N.J.) where it displaces mercury into another stainless steel chamber. There the mercury displaces the solvent to the chromatograph. The output of the second pump, V-2, returns to the mineral oil reservoir. The pump is, therefore, not a continuous one but a batch type. The solvent capacity, however, is over 500 ml, which is more than sufficient for a fractionation on the usual GPC analytical scale.

The pump is driven by a synchronous motor operating at 16 2/3 r.p.m. (Superior Electric Slo-Syn SS 250 PI 115V, 1 phase, Superior Electric Co., Bristol, Conn.). A common gear drives the two metering pumps. The gears from the pumps that engage the common gear vary in the number of teeth to provide for the differential flow rate. By changing the pump gears, which is a simple operation, various flow rates can be attained. Use of different constant speed motors, other sizes of pumps, and so on, could provide many other flow rates. The pump and pressure vessels are operable to 1000 p.s.i. —pressures far in excess of those required by the conventional GPC, which are usually under 200 p.s.i.

It is highly undesirable to get mercury into the system. Two safety features have been provided. First, the oil in the reservoir is put in volumetrically so that there is insufficient oil to displace mercury into the system. Additionally, the pump is controlled by a timer which can be preset to shut it off after a selected time interval.

Conventionally, gel permeation chromatographs use differential detectors. Solvent flows through a reference column and through the fractionating column. Therefore, the pump is a dual-type pump with identical arrangements for the reference and fractionating side. The two pairs of metering pumps are driven from the same motor.

Although the viscosity of the oil being pumped is relatively high, there is some backward flow through the pump. The amount of this flow depends on the backpressure. Therefore, a backpressure metering valve is installed between the pump furnishing volume, V-2, and the oil reservoir. This permits adjusting the backpressure to any desired value. If the pressure drop across each pump is the same, the leakage rate across the pumps should be the same. This occurs when the backpressure on pump V-2 is twice that of the outlet pressure as the pressure drop across pump V-1 is the outlet pressure and that on V-2 is the pressure at the metering valve minus that of the outlet pressure. Fig. 2 illustrates the performance of the pump under these conditions. The flow rate is constant within experimental error regardless of outlet pressure.

The pressure drop across pump V-2 may be varied to attain a variety of flow rates without changing gears. When the pressure drop is less than that of the outlet

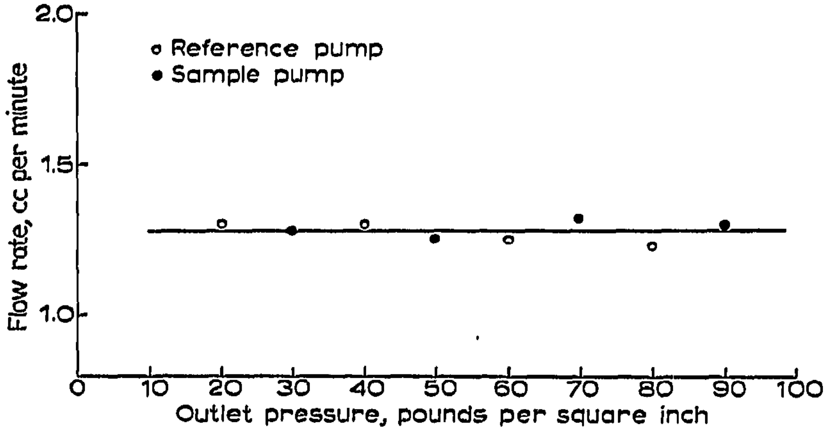

Fig. 2. Flow rate when back pressure is twice outlet pressure.

pressure, the leakage through pump V-2 is less than through pump V-1, and the differential flow rate decreases. Increased flow rate is achieved by use of a higher pressure drop across pump V-2 than across pump V-1.

Chevron Research Company, Richmond, Calif. 94802 (U.S.A.)

JULIAN F. JOHNSON
MANFRED J. R. CANTOW

1 P. I. BREWER, *J. Inst. Petrol.*, 48 (1962) 277.
2 H. E. ADAMS, K. FARHAT AND B. L. JOHNSON, *Ind. Eng. Chem., Prod. Res. Develop.*, 5 (1966) 126.
3 G. MEYERHOFF, *Ber. Bunsenges. Physik. Chem.*, 69 (1965) 866.
4 W. B. SMITH AND A. KOLLMANSBERGER, *J. Phys. Chem.*, 69 (1965) 4157.
5 L. E. MALEY, *J. Polymer Sci.*, C8 (1965) 253.

Received November 28th, 1966