

## A Modified Apparatus for the Fractionation of Polymers by Precipitation Chromatography

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### Synopsis

A modified precipitation chromatography apparatus, designed to operate with periodic temperature changes of the entire column, permitted fractionation of larger amounts of polymer. To verify the efficiency, 5 g. of a poly(methyl methacrylate) specimen were fractionated.

### Introduction

The original method of precipitation chromatography, published in 1956 by Baker and Williams,<sup>1</sup> represented a considerable improvement in the technique of fractionation of polymers and soon became one of the most widely employed procedures. Nevertheless, doubts were expressed by some authors as to the favorable influence of the longitudinal temperature gradient.<sup>2-4</sup> Moreover, difficulties in its maintaining are also known. For this reason, we modified the method by using periodical temperature changes of the entire column instead of the longitudinal temperature gradient.<sup>5</sup> Thereupon we carried out a number of fractionations of poly(methyl methacrylate),<sup>5</sup> polychloroprene, polyisoprene, and polybutadiene,<sup>6</sup> and in all cases we obtained very good results, better than those afforded by the methods of successive precipitation, column extraction, and thermal diffusion.<sup>5</sup> Making simplifying assumptions, we also derived a relation approximately describing the motion of the polymer fraction through the column during fractionation.<sup>7</sup> Our first apparatus, however, was of small capacity (ca. 0.5 g. of fractionated polymer). Therefore, we designed a larger apparatus, of about tenfold capacity, which in principle operates in the same way as the small equipment, but differs in construction. The fractionation efficiency was again verified on a specimen of poly(methyl methacrylate).

### Experimental Studies

**Apparatus.** The diagram of the fractionation apparatus is shown in Figure 1. It differs from the equipment already described, not only in size, but also in design of mixer, in a somewhat different method of solvent degassing, and in the mode of realization of the temperature cycles in the column.

**Column and Packing.** The column itself consists of two parts, each of which is fitted with a jacket for heating; the lower part is also heated from the inside, so that the column has an annular cross-section. The upper part, holding 2 kg. of glass beads approximately 0.1 mm. in diameter, is filled with these beads coated with the polymer, whereas the lower part is permanently filled with 3.5 kg. of glass beads of the same diameter and is permanently wetted. In preparation for the fractionation, the upper part is removed from the column, and the glass beads are dried and coated with the polymer. Then the upper part is again placed on the lower part, and the polymer-coated beads are washed into it by means of a precipitant.

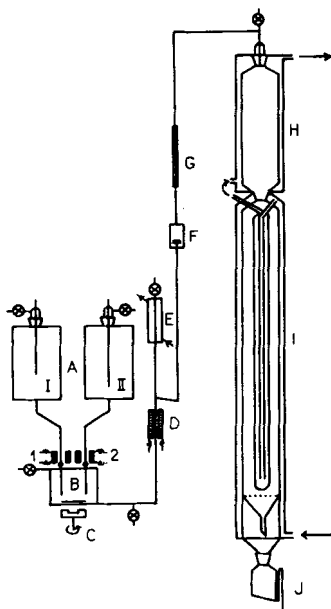


Fig. 1. Precipitation chromatograph apparatus: (A) solvent reservoirs, (B) mixing vessel with 2 solenoid valves, (C) magnetic stirrer, (D) degasser, (E) reflux condenser, (F) back valve, (G) capillary, (H) upper part of the column, (I) lower part of the column, (J) siphon.

After completed fractionation, the entire column is first thoroughly flushed at the upper working temperature with a pure solvent and then with a pure precipitant, whereupon it is ready for the next fractionation.

In distinction to the preceding equipment, the course of the temperature cycles is controlled by a temperature bridge, with a platinum thermometer immersed into a thermostat in one of its branches, while the other branch contains a variable resistor, the value of which changes with time according to a preselected program. The thermostat has an input of 3000 w., and within 4 min. heats the column from the lower working temperature 26 to the upper working temperature 38°C. Thereupon, the temperature drops linearly with time, attaining 26°C. again after 26 min., to complete the 30-

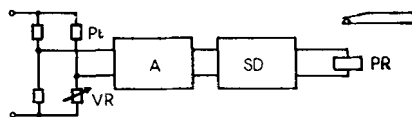


Fig. 2. The temperature bridge for controlling the periodic temperature changes of the column: (*Pt*) Pt thermometer, (*VR*) variable resistor, (*A*) amplifier, (*SD*) synchronous detector, (*PR*) polarized relay.

min. temperature cycle. A schematic diagram of the temperature bridge is presented in Figure 2.

**Solvent Mixer.** In the previously described apparatus,<sup>5</sup> as in most similar equipments, a constant-volume mixer was employed. The volume chosen depends on the amount of the elution mixture passing through the column during fractionation, since the change in the composition of the mixture for this type of mixer is given by the equation<sup>5,8</sup>

$$\ln (C_k - C_i/C_k - C_x) = v/V$$

where  $C_k$  is the concentration of precipitant in the mixture in the reservoir;  $C_i$ , the initial concentration of precipitant in the mixing vessel;  $C_x$ , the concentration of the precipitant in the mixture being delivered to the column;  $v$ , the volume of the mixture delivered from the mixing vessel to the column; and  $V$ , the constant volume of the mixture in the mixing vessel.

It is clear that an increase in the volume of the mixture delivered from the solvent mixer during fractionation requires a proportional increase in the volume of the mixing vessel, if a desirable change in the composition of the mixture is to be maintained. In our case we would have to use a mixer of a constant volume of about 5 liters. Besides the technical difficulties in ensuring the proper functioning of such a mixer (e.g., with respect to agitation), its volume would represent a "dead" volume, and the already large solvent consumption would be further increased.

For this reason, we employed a mixer of new design (Fig. 1). The mixing vessel *B* itself has a volume of approximately 300 ml. and is connected with two reservoirs. At the beginning of the experiment it is filled, as are reservoir I and all tubes of the solvent-mixture delivery system, with the elution mixture of initial composition, while reservoir II contains a mixture of the final composition. The connecting tubes between reservoirs and mixing vessel are fitted with solenoid valves. From the start of the fractionation to the time of the first overflow of the siphon, valve 1 is permanently open. The mixer operates as a constant-volume mixer so that the volume delivered to the column is replaced in this period by an equal volume of the initial mixture. As soon as overflow of the siphon sets in, valve 2 begins to open periodically for short intervals, passing the mixture of final composition into the mixing vessel, valve 1 being closed during these intervals. With increasing number of siphons, the time that valve 2 is open is extended at the cost of the time for valve 1, the sum of both times remaining constant. Moreover, the ratio  $t_2/(t_1 + t_2)$  increases at the beginning of the fractionation faster than at the end.

It is obvious that, in contrast with the previously employed equipment, the composition of the mixture in the mixer does not change continuously. Small discontinuous changes, however, are equalized during the passage of the mixture through the column. The new mixer, on the other hand, has the advantage that its "dead" volume is very small and, the course of the change in the composition of the elution mixture can be easily changed from case to case.

The degassing of the mixture delivered from the mixer to the column was designed so as to let the liberated gases escape from the equipment into the surrounding atmosphere (see Fig. 1).

A satisfactory function of the mixer requires exact equality of the hydrostatic pressure in both reservoirs. This condition is fulfilled by setting the capillaries in the reservoirs to the correct height. For each change of the solvent-precipitant system, these heights must be specially adjusted.

The fractions were collected by a collector of our own design. A description has already been published.<sup>9</sup>

**Fractionation of PMMA.** The fractionation efficiency of the apparatus was verified by fractionating 5 g. of a PMMA specimen whose molecular weight distribution curve was known from previous studies.<sup>5</sup> The polymer film was prepared by dissolving the polymer in 250 ml. of chloroform. Then 2 kg. of glass beads were stirred into solution. The solvent was evaporated at slightly elevated temperature and with continuous agitation, and the agglomerated clumps formed from time to time were disintegrated under light pressure. The fractionation itself was carried out using an acetone-methanol mixture. The initial mixture contained 70 vol.-% of methanol, the final mixture only 40 vol.-% of methanol. The periodic half-hour temperature cycles of the entire column proceeded in the temperature range from 26 to 38°C.

**Viscosity Measurement and Determination of the Amount and Concentration of Polymer in the Fractions.** Individual fractions were dried *in vacuo*, dissolved in benzene, dried again, and after redissolving in benzene the quantity and concentration of polymer in the fractions were determined by the evaporation residue method. Aliquots were first evaporated at slightly elevated temperature and drying was completed at 120°C. at least for 2 hr.

The viscosity of benzene solutions of the fractions was measured at 25°C. in a Ubbelohde-type viscometer. Limiting viscosity numbers of the fractions were calculated from a single-point measurement according to the equation of Schulz and Blaschke<sup>10</sup> with  $N = 1/k' = 5.34^5$ .

## Results

Figure 3 presents the molecular weight distribution obtained by the fractionation of 5 g. PMMA sample. For comparison, the distribution curve of the same sample as obtained by precipitation chromatography in the small apparatus<sup>5</sup> is also shown.

It is obvious that the new apparatus ensures a good fractionation of the PMMA sample. The distribution curve obtained is up to  $W_j = 75\%$  practically the same as the curve obtained with the small apparatus. In the high molecular weight region, the separation in the small apparatus was more selective. It is, however, necessary to bear in mind that while the fractionation of 0.5 g. in the small column was carried out with 1 liter of an elution mixture of variable composition, only somewhat more than 4 liters of this elution mixture (exactly 36 siphons of 114 ml. each) were intentionally employed in the apparatus described here. Consequently, concentration conditions in the column were in this case far less favorable.

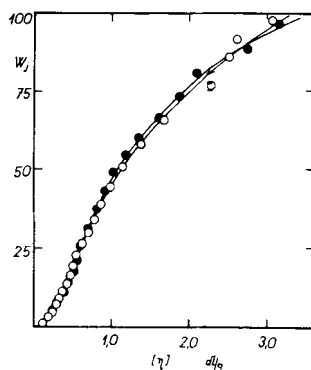


Fig. 3. A comparison of two molecular weight distribution curves of a PMMA specimen, obtained by the precipitation chromatography of 0.5 g. (●) and 5 g. (○).

The results show that the apparatus will be suitable as a preparative fractionation column. An increase in the volume of the elution mixture passing through the column during fractionation will probably lead to a still higher capacity of the equipment.

### References

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### Résumé

Un appareil modifié de chromatographie par précipitation a été mis au point pour travailler avec des variations périodiques de température dans une colonne entière.

Cet appareil permet le fractionnement de grandes quantités de polymère. En vue de vérifier son efficacité 5 g. de polyméthacrylate de méthyle ont été fractionnés.

### **Zusammenfassung**

Ein modifizierter Apparat zur Fällungschromatographie mit periodischen Temperaturänderungen in der ganzen Säule erlaubte die Fraktionierung grösserer Polymermengen. Zum Nachweis der Wirksamkeit wurden 5 g einer Polymethylmethacrylatprobe fraktioniert.