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ANALYSES FOR CHAIN AND STEREO ISOMERS IN DIPROPYLENE GLYCOL BY GAS - LIQUID PARTITION CHROMATOGRAPHY

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CONTENTS

TABLES

FIGURES

FIGURES (Cont'd)

ABSTRACT

35274

A study was made of the separation of dipropylene glycol (DPG) into its chain and stereo isomers by gas - liquid partition chromatography (GLPC) using DPG from seven different commercial sources. These materials were further characterized by adjunct analyses for hydroxyl, unsaturation, water, and propylene glycol contents, and by index of refraction, infrared spectrum, and bulk viscosity. For the qualitative analysis, packed columns, prepared with liquid phases of Carbowax 20M, Polyox WSR 35, or Reoplex 400, and capillary columns, prepared with Carbowax 1540, were used. For quantitative analyses, packed columns prepared with Carbowax 20M were used. The quantities of the three chain isomers of DPG and the two diastereomers of one of the chain isomers present in each of the seven commercial samples were determined by the method of an internal standard. Significant differences in the isomer contents were observed among the commercial DPG's.

I. INTRODUCTION

Dipropylene glycol (DPG) is the first homolog of the polyoxypropylene glycols (POPG) and is prepared from the reaction of one mole of propylene glycol and one mole of propylene oxide. It consists of three positional

isomers, (I) 1, 5-dihydroxy-2, 4-dimethyl-3-oxapentane; (II) 2, 6-dihydroxy-4-oxaheptane; and (III) 1, 5-dihydroxy-2-methyl-3-oxahexane. Also, for each of the positional isomers I and II there are a dl pair and a meso form, while for isomer III there are two dl pairs. A suitable analytical method for I, II, and III and their diastereomers would be of value in a study designed to determine the factors that control the positional and stereo arrangements of oxypropylenes during the formation of DPG. These factors could also be expected to be of importance in determining the positional and stereo arrangements of oxypropylene sequences in the commercially available POPG's.

Analytical methods specific for primary and secondary hydroxyls lead to values for the amounts of I, II, and III in DPG. General methods for the quantitative analysis of primary and secondary hydroxyl groups in substances of both low and high molecular weight have received considerable attention (7, 24, 9, 6, 1, 2, and 21) over the past few years, with a good deal of the attention directed to the POPG's. The quantities of primary and secondary hydroxyl groups in DPG have been estimated by nuclear magnetic resonance spectroscopy (15) and kinetic analysis techniques (14). Methods for the quantitative and qualitative determinations of the stereoisomers of I, II, and III have not been reported. Recently, however, gas - liquid partition chromatography (GLPC) has been used to show the presence of I, II, and III in Udex extraction solvent (11) and has also proved to be useful in the analysis of mixtures of diastereomerically related substances (12, 5, 23).

This communication presents the results of an investigation into the qualitative and quantitative analysis by GLPC of the chemical composition of DPG in terms of I, II, and III and their diastereomers. Adjunct analyses of the DPG's are also reported. These consisted of chemical analyses for hydroxyl, unsaturation, water, and propylene glycol contents, and of other physical characterizations by index of refraction, infrared spectra and bulk viscosity. A study of the syntheses and characterization of the positional isomers and their diastereomers is reported elsewhere (16).

II. EXPERIMENTAL

A. Materials

Samples of commercially available DPG's were obtained from Dow Chemical Company, Eastman Organic Chemicals; Fluka A.G. (Bücks, S. G., Switzerland); Jefferson Chemical Co., Inc., (Sample No. H-5851); Matheson, Coleman & Bell (practical grade); Olin Mathieson Chemical Corporation; and the Union Carbide and Carbon Corporation. Samples of the pure positional isomers and diastereomers were obtained in the course of a separate study (16) and from preparative GLPC experiments as reported herein.

Propylene glycol was obtained from the Wyandotte Chemicals Corporation and was distilled (b.p. 96-98°/21 mm. Hg) before use. Hexyl alcohol (practical grade) (b.p. 153-157/760 mm. Hg) was obtained from Matheson, Coleman & Bell and was used as received.

Liquid phases were obtained from commerical sources: Carbowax 20M and Reoplex 400 from Wilkens Instrument & Research, Inc., and Polyox WSR 35 from the Union Carbide and Carbon Corporation. The solid support used throughout this study was Chromosorb P (non-acid-washed) from Johns-Mansville.

B. Gas - Liquid Partition Chromatography Equipment

1. Apparatus. All the measurements for the qualitative characterizations of the DPG's were carried out on a GLPC apparatus designed and built in the laboratory. (See Fig. A-1 in the Appendix.) The unit consisted of (a) a heated injection port assembly obtained from a Loenco Model 15 gas chromatograph (Loenco, Inc.), (b) columns formed from 6-foot sections of aluminum tubing of 0.25-inch o.d. and 0.035-inch wall thickness, which were wound into helical configurations, and (c) a Gow-Mac (Gow-Mac Instrument Co.) thermal conductivity detector (Model No. 9285D) fitted with four mutually matched tungsten filaments and attached to a Gow-Mac power supply control unit (Model No. 9999C). The helium used as the carrier gas was dried by passing through a Model F Hydro Purge (Coast Engineering Laboratory, Hermosa Beach, Calif.), and the flow at the head of the column was controlled by a sequence of three regulators. A high-pressure SR-200

regulator (Victor Equipment Co.) was attached to the tank of helium and was followed by two Type 20AG-2 regulators (0-50 p.s.i.) (C. A. Norgren Co., Denver, Colo.), one before and the other after the Hydro Purge unit. The second regulator was immersed in a constant-temperature bath which was also used as a source of temperature control for a soap bubble meter used to monitor the rate of flow of the carrier gas. The inlet pressure was monitored with either an aneroid barometer, Model FA 129 (Wallace & Tiernan, Inc., Belleville, N. J.), or a Bourdon tube - type test guage (readable to within 0.05 p.s.i.). To insure identical mass rates of gas flow at the reference and sample sides of the detector, the carrier gas was first passed through the reference side of the detector and through a buffer coil and then to the injection block.

Values for the rate of flow of helium at barometric pressure and ambient temperature were obtained from readings taken with a 50-ml. soap bubble meter (13) (Fig. A-2 in the Appendix). The design of the bubble meter insured that the carrier gas was at ambient temperature as controlled by the constant-temperature bath described earlier. Close control of column temperature was carefully maintained by immersing the entire GLPC apparatus, with the exception of the injection block, which was electrically heated, in a Kinematic Viscosity bath (Hallikainen Instruments). For temperatures from 35 to 200°C, this combination permitted temperature control within ±0.002°C. The output from the thermal conductivity cell of the assembled unit was monitored by a Leeds and Northrup Speedomax recorder with a 5-mv. range and a 2-second response time. Retention times were determined from the recorder chart and were checked by a calibrated stopwatch. The times of injection were recorded directly on the chart by an auxiliary marker pen arrangement (Chronograph event marker pen, Leeds and Northrup part No. 124115).

In the course of this study three other gas chromatographs were used: an F & M 720 (F & M Scientific Corporation); a Model 226 (Perkin-Elmer Corporation), and an Aerograph A-700 Autoprep (Wilkens Instrument & Research, Inc.). No modifications were made to the preparative unit or to the PE 226; however, slight but significant modifications were made to the F & M 720. To improve the flow control on both the reference and sample sides of the apparatus, the extant flow control valves were replaced with micrometer-type valves (Nuclear Products Co., Cleveland, Ohio). Also,

pressure gauges with a range of 0 to 30 p.s.i. (Ashcroft Gauges, Stratford, Conn.) were attached to both the sample and reference sides of the flow system.

To monitor the areas of the chromatographic peaks, either of two commercially available voltage-to-frequency integrators was used. They were the CRS-1 (Infotronics Corporation, Houston, Texas) and the Chromad (Consolidated Electrodynamics Corporation, Pasadena, Calif.). The characteristics and performances of these units were investigated and are the subject of a separate memorandum (18).

2. Columns. A total of 13 columns was used during the course of this investigation. The type, weight, and weight percent of the liquid phase, the length and diameter of the column, the mesh size of the solid support, and the solvent used in the coating of the solid support for each column are given in Table I. Columns 1-11 and 13 were prepared from the appropriate liquid phase and solid support. Column 12, a 200-foot capillary, was obtained from the Perkin-Elmer Corporation and used with the Perkin-Elmer Model 226 Gas Chromatograph. Columns 1-3, 5-11, and 13 were analytical columns; seven of these were used in the F & M 720 Gas Chromatograph, while the others were used in the assembled unit. Column 4 was used for the preparative separations on the Aerograph A-700 Auto-prep unit.

To coat the solid support, a slurry of it suspended in the liquid phase, which had been dissolved in an appropriate solvent (see Table I), was prepared. The solvent was removed until the coated support was free-flowing by (a) evaporation at ambient temperatures under a hood, or (b) evaporation at elevated temperatures in a vented oven maintained between 90 and 110°C.

The coated support was placed into each column by one of several methods. For columns 5 through 11, an identical and predetermined amount of coated support was used for each column. Columns 5 through 11 were filled by the following methods:

1. Column 5 was mounted vertically over a metal plate, the coated support was added one gram at a time, and after each addition the column was raised 6 inches above the plate and dropped a total of six times.

2. Column 6 was filled similarly to column 5 except that the coated support was added 3 grams at a time.

3. Column 7 was filled similarly to column 5 except that all of the coated support was poured in at one time, and the column was then dropped from a height of 6 inches six times.

4. Column 8 was mounted vertically, all of the coated support was added, and then the column was subjected to vibration by a Vibrator (Type SA, Cleveland Vibrator Co., Cleveland, Ohio) operated at 20 p.s.i. until the height of the coated support in the column did not change.

5. Column 9 was mounted vertically, and the Vibrator was attached to the column at a point 18 inches from the bottom and turned on. The coated support was added 1 gram at a time at 1-minute intervals.

6. Column 10 was mounted vertically, the packing was added 3 grams at a time, and after each addition the column was forcibly pounded on the metal base six times. After all the coated support was added, the column was pounded against the metal base an additional 50 times.

7. For column 11, the coated support was added a little at a time, and between additions the column was tapped against the floor. After all the coated support was added to the column, the column was tapped against the floor about 20 times.

8. Columns 1 through 4 and column 13 were of a predetermined length. These columns were filled with the coated support in a manner similar to that used for column 11.

All columns except No. 12 were bent into coils of about 4 inches in diameter. A glass wool plug approximately 1/4 inch long was placed into each end of each column.

C. Gas - Liquid Partition Chromatography Analysis Procedures

For either the qualitative or quantitative analysis by GLPC, a 1- to 10-μl. sample of the material under study was injected into the GLPC apparatus with a No. 701N Hamilton syringe (Hamilton Company, Inc.).

Neat DPG was too viscous for the injection device of the Autoprep unit; therefore, a 70 weight % solution of DPG in benzene was used. For each preparative separation, a 50-μl. sample of the benzene solution was injected into the unit.

The numerous solutions of dry samples of the positional isomers of DPG (I, II, and III) were prepared in the anhydrous environment of a Dri-Lab (D. L. Herring Corporation). These solutions were used in the

preparation of the calibration plots needed for the quantitative analysis work.

1. Chemical Analyses. The analyses for the hydroxyl groups were carried out by an acetylation technique (3). The unsaturation contents were obtained by the mercuric acetate procedure (4); the water content, by the Karl Fischer method; and the propylene glycol contents, by the periodate analysis for vicinal hydroxyls (10).

2. Physical Analyses. The infrared spectra were determined on a Perkin-Elmer Model 421 spectrophotometer. Each spectrum was taken with the slit program at 1,000, the gain at 4, the attenuation speed at 1,100, the suppression at 4, the source current at 0.3 amperes and the scale set at 1X. The spectra were taken on neat samples 0.023 mm. thick.

The indices of refraction were determined on an Abbé-type refractometer (Model 450A, Valentine Instruments, Vista, Calif.) which was previously calibrated against samples obtained from Eastman Organic Chemicals. The results of the calibration work suggest that the values for n_D are accurate to ±0.0002 units. The densities were determined by a micropycnometer method (22).

Kinematic viscosities were determined in Canon-Ubbelohde suspended-level capillary viscometers which had been calibrated with standard oils from the National Bureau of Standards. The efflux times for the various samples of DPG ranged from 230 to 275 seconds.

III. RESULTS AND DISCUSSION

A. Qualitative Characterization

Representative separations of dipropylene glycol on packed analytical columns (columns 1, 2, and 3) are shown in Figure 1 a - c. Three different liquid phases, Carbowax 20M, Polyox WSR 35, and Reoplex 400, are represented. The first two liquid phases are members of the same homologous series, the polyoxyethylenes, and differ only in their molecular weights (17). Reoplex is a high molecular weight polyester prepared from adipic acid and a low molecular weight glycol. The conditions used to obtain these chromatograms are given on the figure. For the

Reoplex column, the conditions are similar to those previously reported (11). Figure 1a - c clearly shows the separation of a commercial sample of DPG into five components.

The separation of DPG was also accomplished on a preparative scale. Figure 2 shows such a separation using column 4 prepared with Carbowax 20M as the liquid phase. The conditions used to obtain the preparative separation are given on the figure. By combining the effluent representative of each peak from a number of separations of this type, a usable sample, representative of each peak, was obtained for characterization and identification.

Samples of the individual positional isomers I, II, and III and the diastereomers of I and II were available from a separate study (16). The specific retention volumes, $\underline{V}_g^{760}$ (20) for each of these substances as well as for propylene glycol were determined and compared with the $\underline{V}_g^{760}$ for each of the five resolvable components of commercial DPG. A similar comparison was made with the fractions collected from the preparative separations. The $\underline{V}_g^{760}$ for each of the components obtained from each experiment is given in Table II. The values of $\underline{V}_g^{760}$ for samples of propylene glycol, II, III, IA, and IB are in excellent agreement with the $\underline{V}_g^{760}$ values for the five peaks of a chromatogram of DPG. The data in Table II also show that the diastereomers of II and III were not resolved on these columns. Qualitative characterizations were also made to establish the order of elution for the other two liquid phases, Polyox WSR 35 and Reoplex 400. For each of the three different liquid phases, the order was propylene glycol, II, III, and the diastereomeric forms of I, with A followed by B. For the Reoplex liquid phase, this sequence is in disagreement with that recently reported (11).

The two GLPC analyses of the commercial DPG (columns 3 and 4 of Table II) were made at different times. The $\underline{V}_g^{760}$ values for the synthetic samples were determined at the time of GLPC analysis 1, and the $\underline{V}_g^{760}$ for the samples isolated from preparative GLPC were determined at the time of GLPC analysis 2. For each analysis the order of elution of the components is the same; however, small but significant differences exist between the $\underline{V}_g^{760}$ values for each component as determined on the two separate occasions. Values for the flow rates and the ratio of the inlet to outlet pressures used to obtain the $\underline{V}_g^{760}$ values, however, remained constant

over this period of time. Also, the number of theoretical plates n (8), which ranged from 1,100 to 1,400 for the components, remained, within experimental error, the same over this period. This behavior of the column with time suggests that the changes in the values for V_g^{760} are due to changes in the nature of the coated support.

In order to improve the separation of commercial DPG into its components, an empirical study was made of the importance of the method of packing a column. For this purpose, seven columns were filled with coated support by seven different methods as described in the Experimental section. Each of these columns contained identical weights of coated support, and all were prepared from the same batch of solid support coated with Carbowax 20M. The length of the column depended upon the tightness of packing, the longer columns being more loosely packed than the shorter ones. The ratio of the inlet (P_i) to outlet (P_o) pressures required to obtain a given flow rate (41.8 ±0.8 ml./min. at STP) in each of the columns was measured. Samples of hexyl alcohol were injected into each column. The values for the P_i/P_o ratios and for n for hexyl alcohol, obtained from six chromatograms on each of the seven columns, are given in Table III. Similar determination of the theoretical plates for each of the components of DPG for each column was not worthwhile because of the unsymmetrical form of the peaks. A typical chromatogram of DPG from the seven columns is shown in Figure 3. The data in the table clearly show that, with the exception of column 10, the P_i/P_o ratios are reasonably constant, the one exception being the most tightly packed column as would have been expected. No significant differences in the values for the theoretical plates for hexyl alcohol were observed among six of the seven columns. One column, the most loosely packed (column 7), exhibited a wide variation in the values for the theoretical plates. However, none of the seven columns separated DPG into five components. One of the seven columns (column 11) was prepared by the same procedure as was used to prepare the Carbowax 20M column (column 1) that gave the separation shown in Figure 1a. The major difference between these two columns (column 1 and 11) is one of age. The older column, after having been heated at various temperatures and exposed to numerous samples, separated DPG into five components, while the new, conditioned column did not. This difference in behavior probably stems from changes in the coated support.

The nature of these changes was not investigated further. However, they may be similar in nature to those reported by Keller and coworkers (19).

In another attempt to improve on the separation of DPG into its components, the use of a capillary column (column 12) coated with Carbowax 1540 was investigated. The results are shown in Figure 4. The conditions used to obtain the separation are given in the figure. These data show that the DPG was separated into six components. If the order of elution of the components from the capillary column is the same as for a packed column, the diastereomers of either positional isomer III or II have been resolved. Unfortunately, because of column deterioration, further study of this improvement in separation was not possible on this column. Other capillary columns containing the same liquid phase and prepared in a similar manner failed to duplicate these results.

Samples of each of the other six commercially available DPG's were analyzed on an aged Carbowax 20M column (column 1). In all cases except one, the qualitative features of the chromatograms were identical with those in Figure 1a. The exception was the sample of DPG obtained from Fluka. A chromatogram for this material is shown in Figure 5. This figure shows that a sixth peak appears at a larger retention time in this material than for any of the other samples of DPG. The material corresponding to this peak was identified on the basis of its $\underline{V}_{\underline{g}}^{760}$ value as diethylene glycol (DEG). Significant quantities of DEG, however, were not found in another sample of DPG from Fluka. Actually, DEG can be detected in all of the seven different DPG's if large enough samples ($\geq$10μl) of DPG are analyzed by GLPC. The source of the DEG as an impurity could arise from trace amounts of ethylene present in the propylene that is used to prepare DPG via epoxidation and hydrolysis. Coproducts from ethylene oxide and propylene oxide, however, were not observed on the chromatograms.

B. Quantitative Characterization

The seven samples of DPG from commercial sources were thoroughly characterized by a number of chemical and physical analyses. The chemical analysis consisted of the determinations of the hydroxyl concentrations and the water, unsaturation, and propylene glycol contents, while the physical characterizations were by index of refraction, bulk viscosity, and infrared spectra. With the exception of the infrared spectra,

the results of the analyses are given in Table IV. These data show that no significant differences exist in the values of the index of refraction and the unsaturation and water contents for the samples of DPG from the seven different commercial sources. The sample of DPG from Fluka shows a value for the density which is about 1% larger than the others. This is the same sample that contained the DEG impurity. The density of the other Fluka sample (sample 2), which contained only trace amounts of DEG, was in good agreement with the density values for the others. The weight % of hydroxyl groups of five of the samples were within ±1% relative to the theoretical values of 25.4 weight % hydroxyl. Two DPG's, Union Carbide and Fluka, however, showed significantly larger weight % hydroxyl group contents, 26.5 and 26.0, respectively, than the theoretical value. These two samples also contained relatively large quantities of propylene glycol, 4 and 2%, respectively, which could account for the high hydroxyl group values. The bulk viscosities of the samples ranged from 67.5 to 81.0 centistokes and undoubtedly reflected the sum total of all the differences in chemical composition among the DPG samples, including the relative amounts of the three positional isomers and their diastereomeric forms.

The infrared spectra for six of the seven samples were very similar to each other, the major peaks occurring at positions that would be expected on the basis of the gross chemical structure of DPG. The sample of DPG from Fluka (sample 1), however, showed a significant increase in absorption at 900 cm^{-1} in comparison with the others. Addition of 10 weight % of DEG to a sample of DPG from one of the other six samples gave an infrared spectrum identical with that of the Fluka sample 1. This furnishes further evidence that DEG was an impurity in this DPG.

The quantities of I, II, and III present in the DPG's were determined by GLPC. Of the three liquid phases, Carbowax 20M, Polyox WSR 35, and Reoplex 400, which were shown capable of separating DPG into five components, Carbowax 20M has advantages over the other two. First, it is easier to prepare coated solid support from Carbowax 20M than from Polyox WSR 35, because of the solubility and viscosity differences of these two phases. Second, while support coated with Reoplex 400 is as easily prepared as that from Carbowax 20M, we found that the performance of our Reoplex columns deteriorated rapidly after about 12 hours at

temperatures (ca. 190°C) needed for the separation of DPG. Therefore, an aged Carbowax 20M column (column 13) was selected for the quantitative analysis work.

To optimize the performance of the 20M column for the separation of the components of DPG, a series of experiments was made with the column and a crystalline diastereomer of DPG, IIA. Ideally, the column should have been optimized for the component most difficult to separate, IA, but not enough of this material was available for this purpose. The dependencies of the values for the theoretical plates for IIA on column 13 as a function of flow rate of carrier gas, size of sample, and temperature were investigated. The conditions that gave the largest value for the theoretical plates for IIA would be considered as being the best for the separation of II, III, IA, and IB and would be used for quantitative analysis. The results of these experiments are shown in Figure 6.

The figure shows that the value for the number of theoretical plates, n, is dependent upon the size of sample and the rate of flow of the carrier gas. The largest values of n, about 1,650, occur for the 0.2-μl. sample at about 41 ml./minute at STP. For the large samples, the optimum values of n are smaller and less sensitive to the rate of flow of the carrier gas than for the 0.2-μl. sample. The data in the figure are for experiments at 191°C only. Additional experiments, not shown on this figure, were made at 161°C. Here, for 1-μl. samples, and at an optimum rate of flow of the carrier gas (38 ml./minute at STP), n was about 1,900. The larger value for n at 161°C than at 191°C suggested this temperature for the quantitative analysis. However, in contrast to the peaks at 191°C, those at 161°C were wider, with the leading and trailing regions contributing significantly to the total area. The integrators used in this study for the measurement of peak area operated more reproducibly (20) on tall, narrow peaks than on low, wide peaks. At temperatures higher than 200°C, the resolution of DPG on Carbowax 20M deteriorates badly. It has also been our experience that at these higher temperatures, the useful life of Carbowax 20M as a liquid phase is severely limited for the analysis of DPG. Therefore, 191°C was chosen as the temperature for the quantitative analysis.

The analysis by GLPC for the amounts of I, II, and III present in the seven samples of DPG was carried out by the internal standard method

(8). Initially, propylene glycol was tried as the internal standard. This choice was not suitable because of tailing by the propylene glycol peak and the attendant problems with the integrators. The isomer II, however, proved to be a satisfactory internal standard. Areas of peaks were obtained for a series of samples containing different quantities of III and II, or of I and II. Plots of the ratio of the areas of the positional isomers to the ratio of the weights are shown in Figure 7a-b. The plots cover the ranges of concentrations of I, II, and III found in the seven samples of DPG from commercial sources. For these ranges, Figure 7 shows that the weight ratios are proportional to the area ratios. The slopes of the lines shown in Figure 7a and 7b are 1.48 and 1.08, respectively.

The results of the quantitative analysis for I, II, and III present in the seven samples of DPG are given in Table V. Correction for the quantity of propylene glycol present in the DPG's was made on the basis of the results previously given in Table IV. From the earlier experiments with propylene glycol as the internal standard, an estimate of the amount of propylene glycol present in the Union Carbide DPG was obtained from GLPC and found to be 5.0 ±0.2 weight %, which is in reasonable agreement with 4.5 weight % as reported in Table IV. For the calculation of the values shown in Table V, the sensitivity of the thermal conductivity detector for the diastereomers of I was considered to be the same. The separation of II and III by column 13 was complete, but IA was not separated completely from III. For the purpose of the calculations, the peak areas of IA and III were obtained by using the areas to the right and the left, respectively, of the minimum between IA and III. While this is somewhat arbitrary, especially for peak areas of different magnitude, the values so obtained were in good agreement (within about 1%) with those obtained by considering IA and IB to be present in equal amounts and subtracting the area for IB from the area for III plus IA.

As shown by the results given in Table V, significantly different quantities of I, II, and III are present in samples of DPG from commercial sources. The DPG's from Olin Mathieson and Fluka contain the smallest, 8.8 weight %, and largest, 27 weight %, quantities, respectively, of the diprimary isomer, I. The samples from Dow; Eastman; Jefferson; Matheson, Coleman & Bell; and Union Carbide contain intermediate amounts, 14 to 17 weight %. The smallest, 21 weight %, and largest, 43 weight %,

quantities of the disecondary isomer, II, are present in the Fluka and Olin Mathieson samples, respectively. Samples from the other five sources contain intermediate amounts, 33 to 38 weight %, of II. The amount of III present in the seven samples ranges from 46 to 51 weight %.

The results of this study clearly demonstrate that the quantities of primary and secondary hydroxyl groups present in commercially available DPG are different for different sources. Further improvements in the resolution capabilities and the performance stability of gas chromatography columns should lead to separations which would give values for the quantities of the diastereomers of I, II, and III, respectively. The present results suggest that equal concentrations of the diastereomers, IA and IB, are present in each of the seven samples of DPG.

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Table I. Characteristics of Gas Chromatography Columns

Column number	Liquid phase			Columns		
	Type	Weight[a] grams	Solvent	Length[b] inches	Conditioning treatment[c] hours/°C	Mesh size solid support
1	Carbowax 20M	4.40	Benzene-Methanol, 50-50	72.0	12.0/100	30-60
2	Polyox WSR 35	3.16	Water	72.0	12.0/170	30-60
3	Reoplex 400	3.79	Chloroform	60.0	0.5/191	100-120
4	Carbowax 20M	13.0	Chloroform	72.0	12.0/200	45-60
5	↓	4.25	Chloroform	54.1	16.5/120	30-60
6		4.25	↓	53.9	↓	30-60
7		4.25		56.6		30-60
8		4.25		54.6		30-60
9		4.25		55.1		30-60
10		4.25		51.4		30-60
11	↓	4.25	↓	54.0	↓	30-60
12	Carbowax 1540	–	–	2400.	0.5/150	–
13	Carbowax 20M	3.42	Benzene	72.0	12.0/100	30-60

[a] The weight % liquid phase: columns 1 and 3-11, 25%; 2 and 13, 20%.
[b] Diameter (inches) of column 4, 0.38; column 12, 0.02; all others, 0.25.
[c] Helium gas was passed through the columns during conditioning.

Table II. Specific Retention Volumes (V_g^{760}) for the Isomers of Dipropylene Glycol on a Carbowax 20M Column at 195°C[a]

Substance	V_g^{760}, ml./gram			
	Synthetic samples	Commercial DPG		Samples isolated by preparative GLPC
		Analysis 1[b]	Analysis 2	
1, 2-dihydroxypropane	41.7	43.3	41.0	40.7
2, 6-dihydroxy-4-oxaheptane (II)				
Liquid diastereomer (IIA)	101.3			
Crystalline diastereomer (IIB)	101.3			
Mixed diastereomer (IIA-B)	100.4	101.7	94.0	94.1
1, 5-dihydroxy-2-methyl-3-oxahexane (III)	121.6	123.6	113.6	114.0
1, 5-dihydroxy-2, 4-dimethyl-3-oxapentane (I)				
Diastereomer IA	139.7	137.6	127.3	128.4
Diastereomer IB	158.1	158.0	146.4	145.5

[a]Values for V_g^{760} at 161°C were: 1, 2-dihydroxypropane, 106.4; IIAB, 279.9; III, 349.2; IA, 466.6; IB, 554.1. These values were determined at the time of Analysis 2.

[b]Analysis 1 was made five months prior to Analysis 2.

Table III $\underline{P}_i/\underline{P}_o$ Ratios and Theoretical Plates for Hexyl Alcohol on Seven Different Carbowax 20M Columns

Column number	$\underline{P}_i/\underline{P}_o$ [a]	Theoretical plates
5	1.19	988-1,083
6	1.19	955-1,034
7	1.16	301- 884
8	1.18	887- 993
9	1.18	965- 989
10	1.23	889- 975
11	1.16	947-1,060

[a]These are average values with range limits of less than ±0.01.

Table IV. Some Chemical and Physical Analyses of Dipropylene Glycols From Seven Commercial Sources

Source	%OH[a]	Unsaturation >C = C< x 10^5 moles/gram	$\%H_2O$	Weight % propylene glycol	Index of refraction at 25.0° C	Density at 25.0° C grams/ml.	Viscosity centistokes
Dow	25.68 25.85	<0.1	0.1	0.26 0.26	1.4391	1.019 1.019	75.3
Eastman	25.16	<0.1	0.1	0.057 0.067	1.4390	1.018 1.019	77.6
Fluka (sample 1)	25.85 26.19	<0.1	0.1	2.13 2.21	1.4389	1.028 1.028	67.5
(sample 2)	25.75 25.92	<0.1	0.1	1.29	1.4392	1.021	69.5
Jefferson	25.68 25.68	<0.1	0.1	0.70 0.71	1.4391	1.018 1.019	76.6
Matheson, Coleman & Bell	25.17 25.17	<0.1	0.1	0.07 0.11	1.4384	1.018 1.019	77.1
Olin Mathieson	25.82	<0.1	0.1	0.01 0.02	1.4390	1.018 1.018	81.0
Union Carbide	26.53 26.53	<0.1	0.1	4.3 4.6	1.4386	1.018 1.019	72.3

[a]Theoretical value, 25.36%.

Table V. Percentages of Positional Isomers and Propylene Glycol Present in Dipropylene Glycol From Seven Commercial Sources

Source	Weight %[a]			
	I A and B	II	III	Propylene glycol
Dow	16.2	36.3	47.2	0.26
	15.9	36.4	47.4	
Eastman	14.0	38.2	47.8	0.06
	14.2	36.8	48.9	
Fluka	28.1	20.5	49.1	2.20
(sample 2)	25.9	21.8	50.1	
Jefferson	14.4	37.1	47.8	0.70
	14.5	37.0	47.8	
Matheson,	14.9	34.3	50.7	0.10
Coleman & Bell	16.0	34.0	49.9	
Olin Mathieson	8.8	42.6	48.6	0.02
	8.8	42.6	48.6	
Union Carbide	14.9	34.0	46.6	4.45
	16.7	32.7	46.1	

[a]The figures for the positional isomers represent two separate analyses.

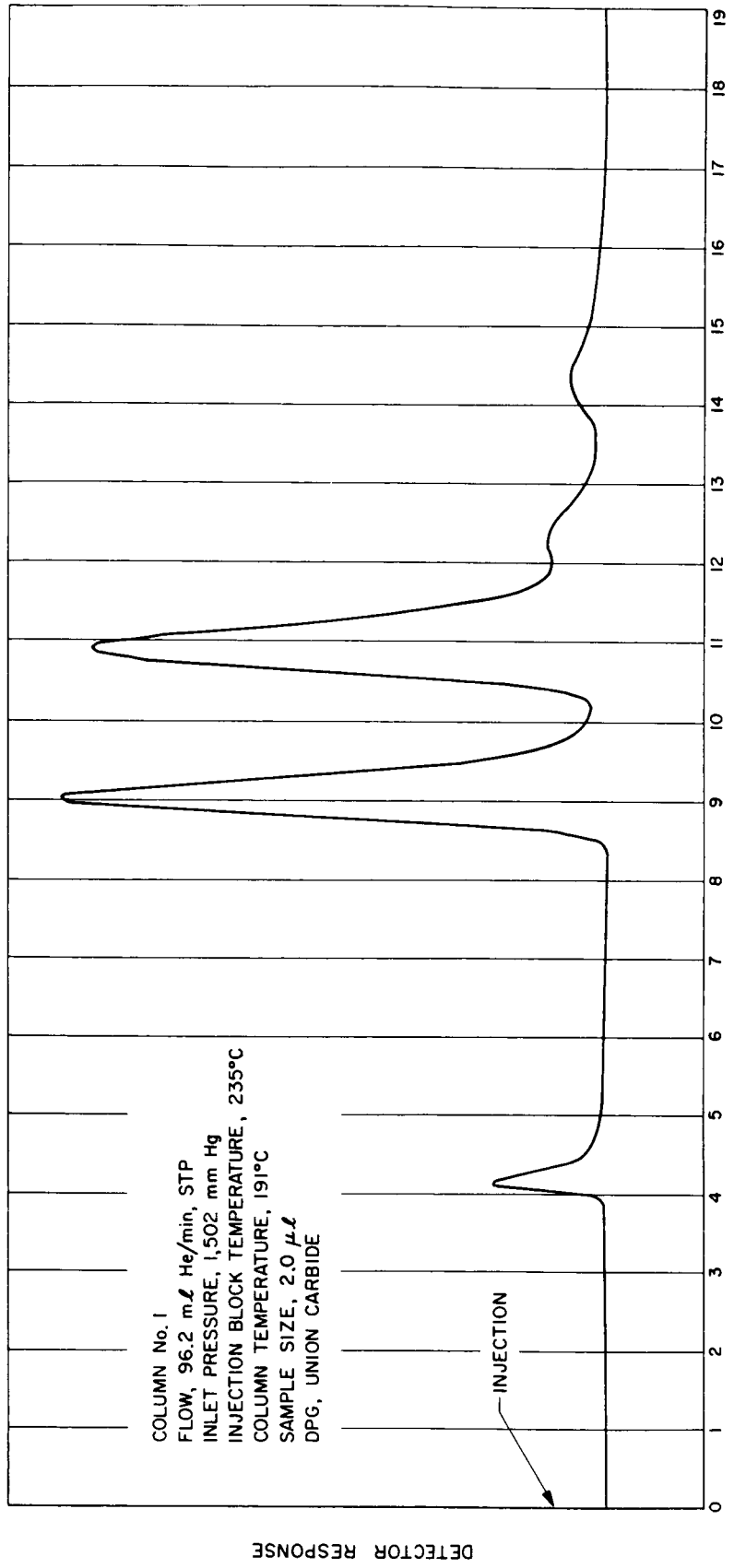


Fig. 1a. Representative separation of dipropylene glycol on a packed analytical column prepared with Carbowax 20M

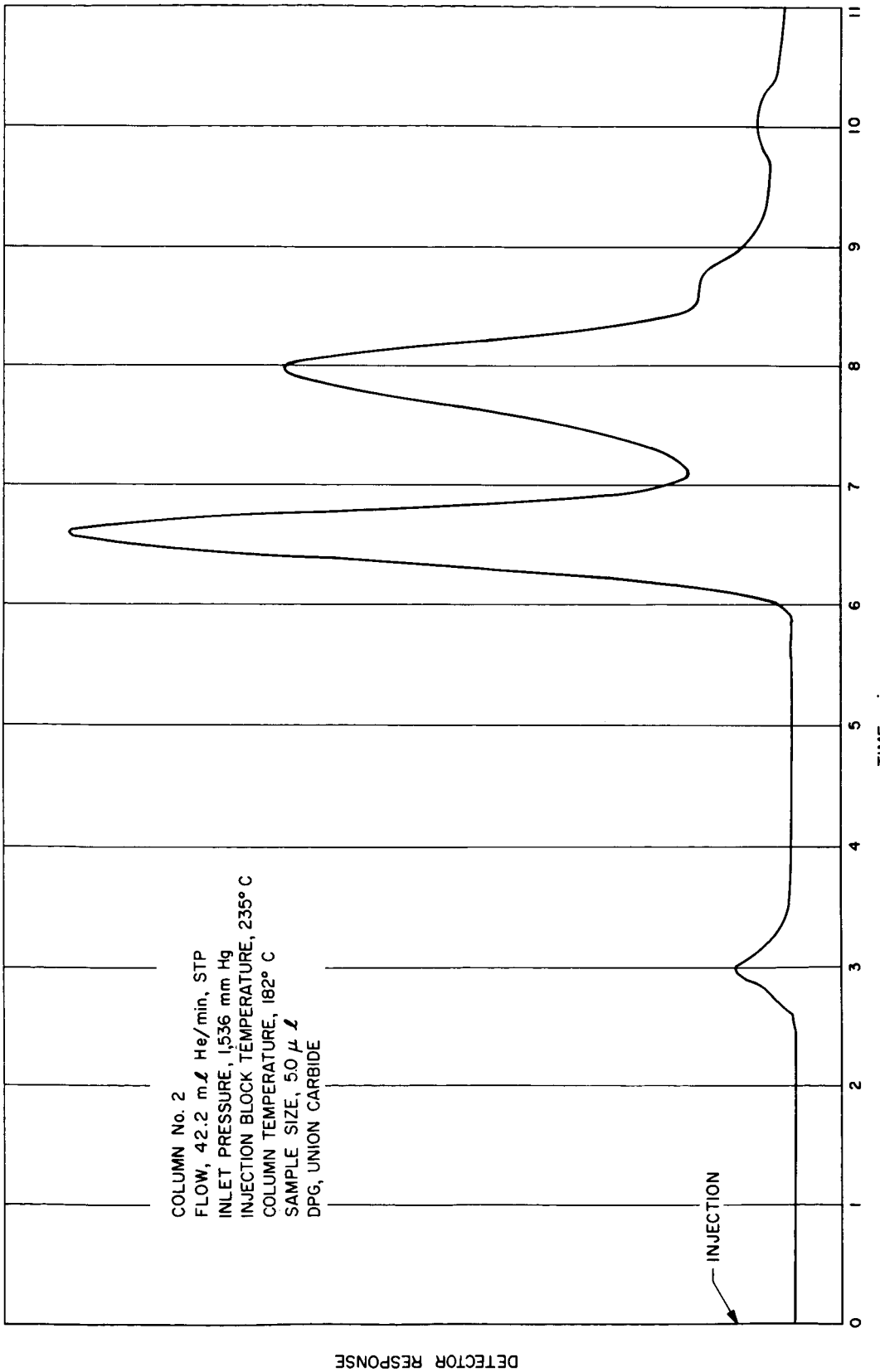


Fig. 1b. Representative separation of dipropylene glycol on a packed analytical column prepared with Polyox WSR 35

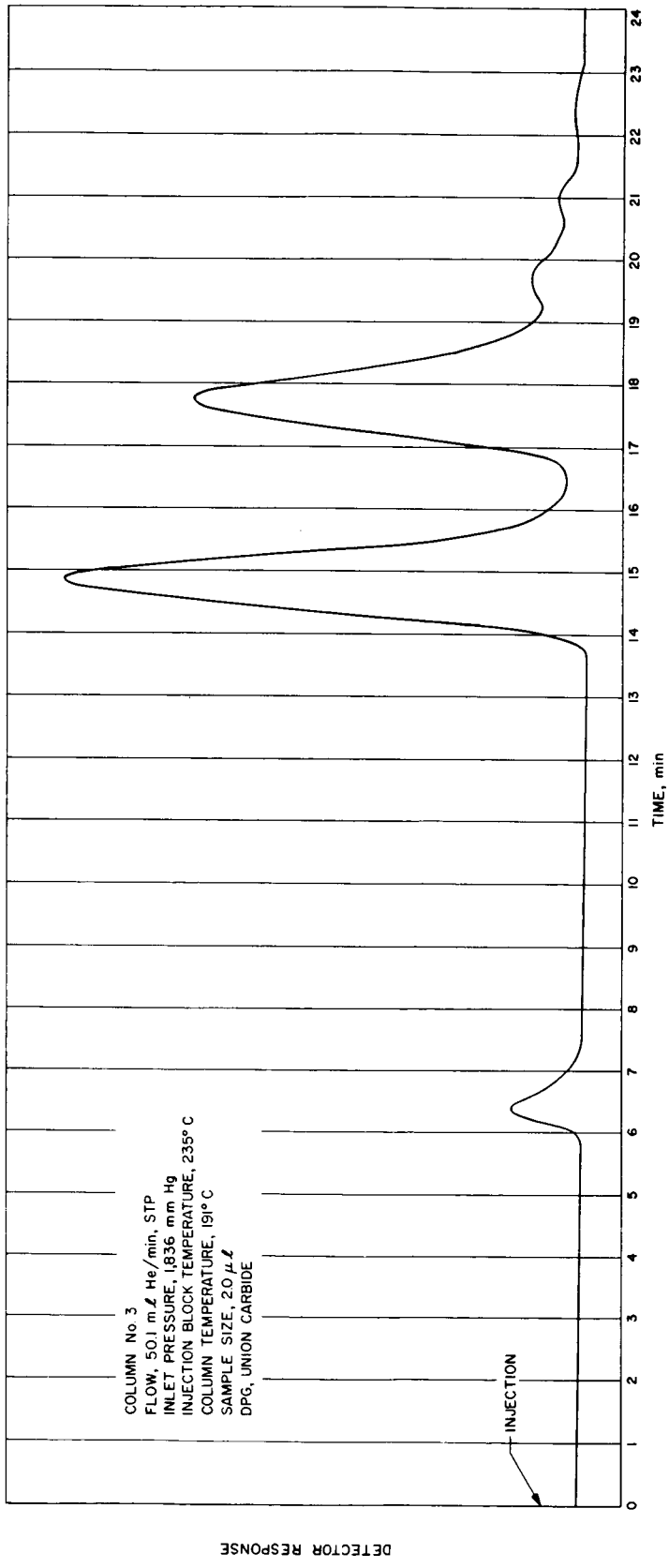


Fig. 1c. Representative separation of dipropylene glycol on a packed analytical column prepared with Reoplex 400

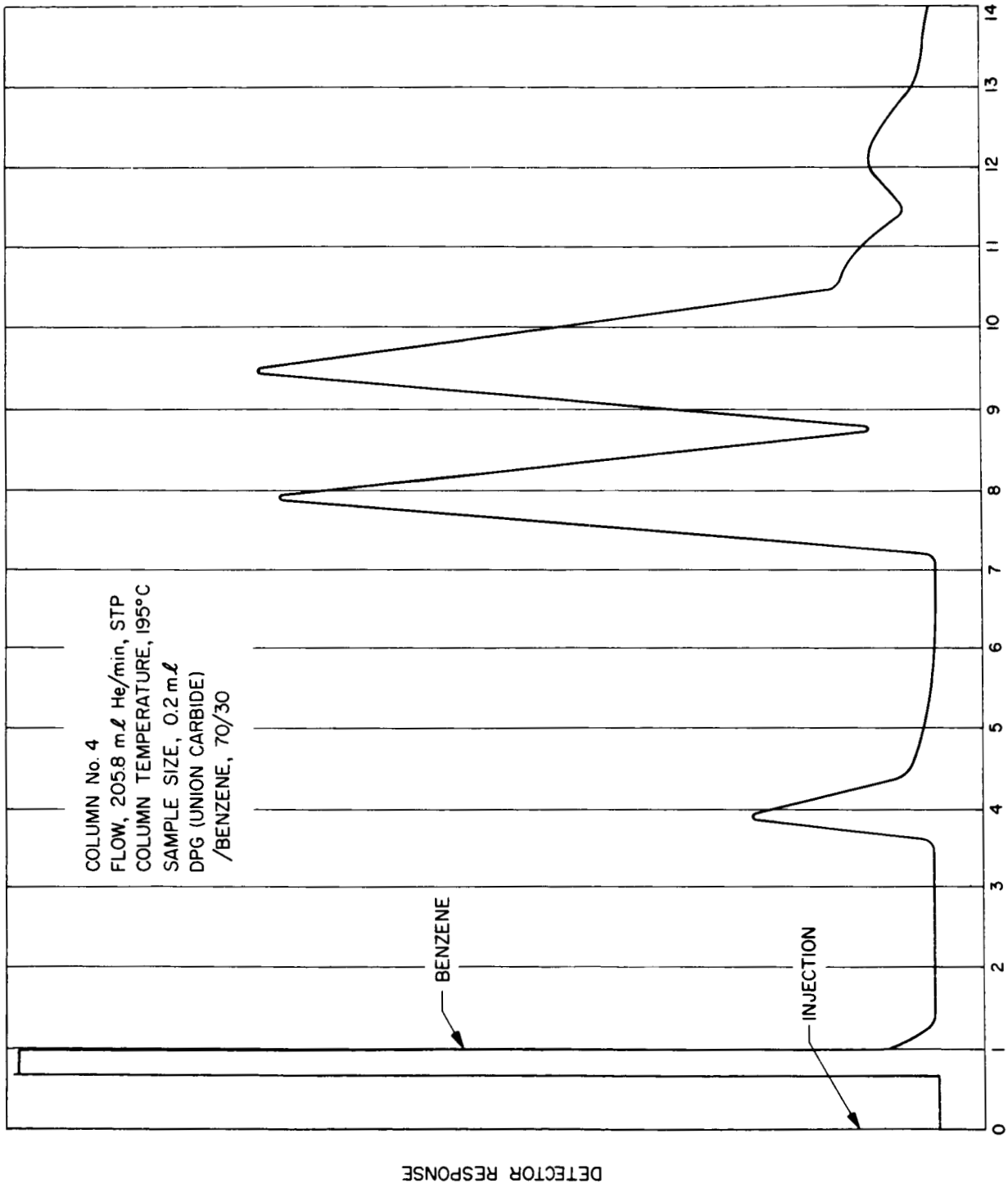


Figure 2. Separation of dipropylene glycol on a Carbowax 20M preparative column

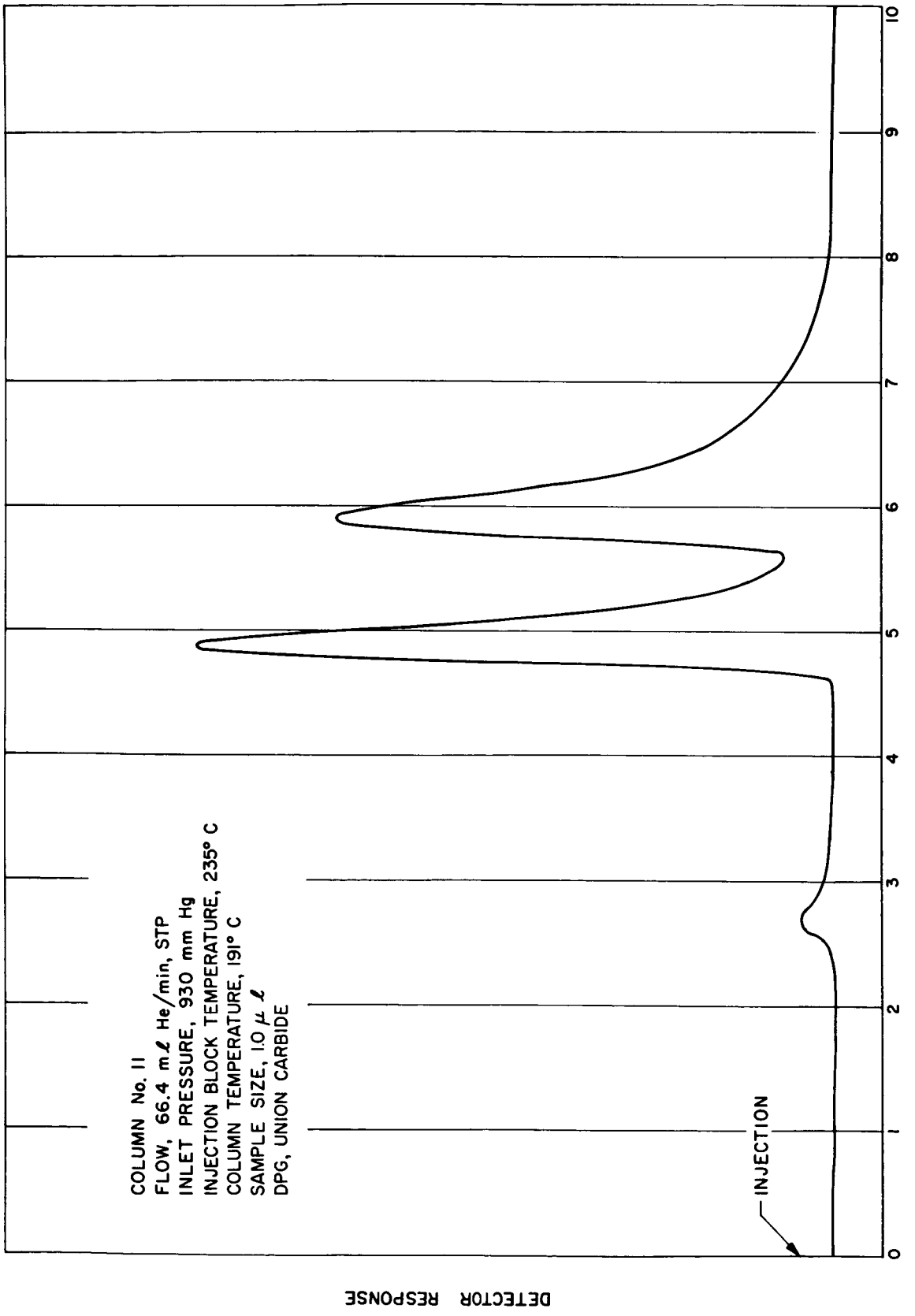


Figure 3. Typical separation of dipropylene glycol on a new Carbowax 20M column

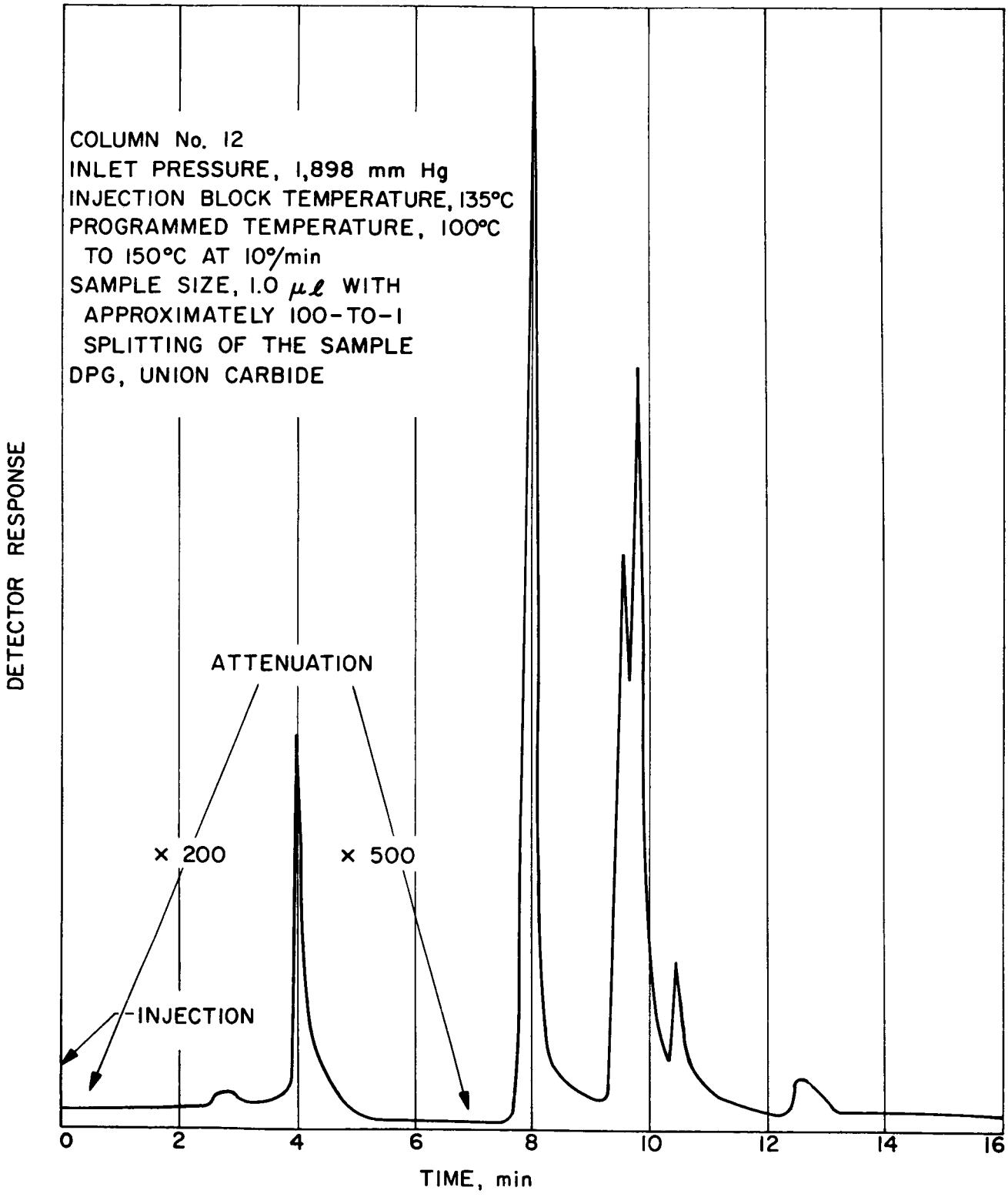


Figure 4. Separation of dipropylene glycol on a Carbowax 1540 capillary column

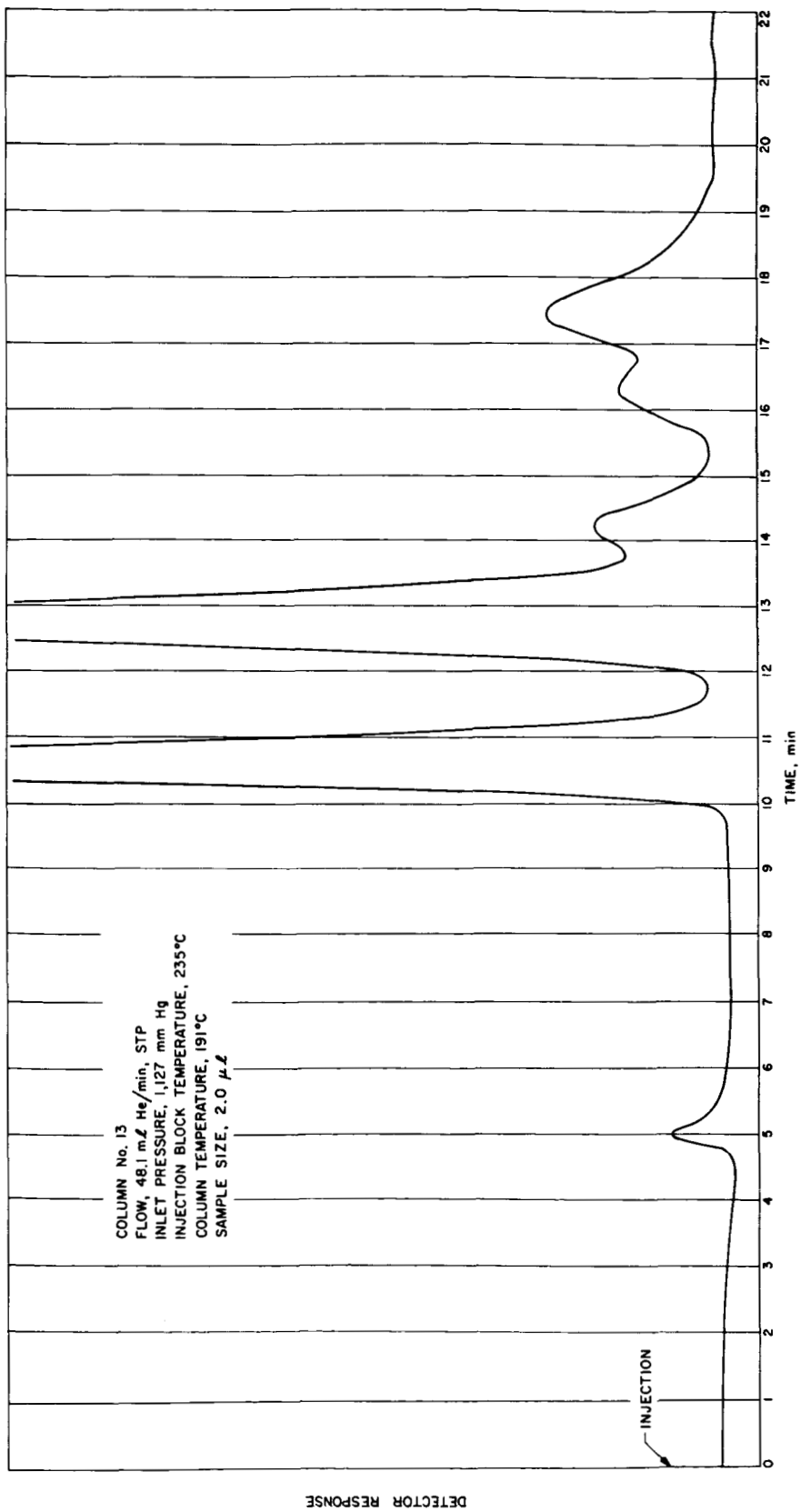


Figure 5. Chromatogram of Fluka dipropylene glycol on a Carbowax 20M column

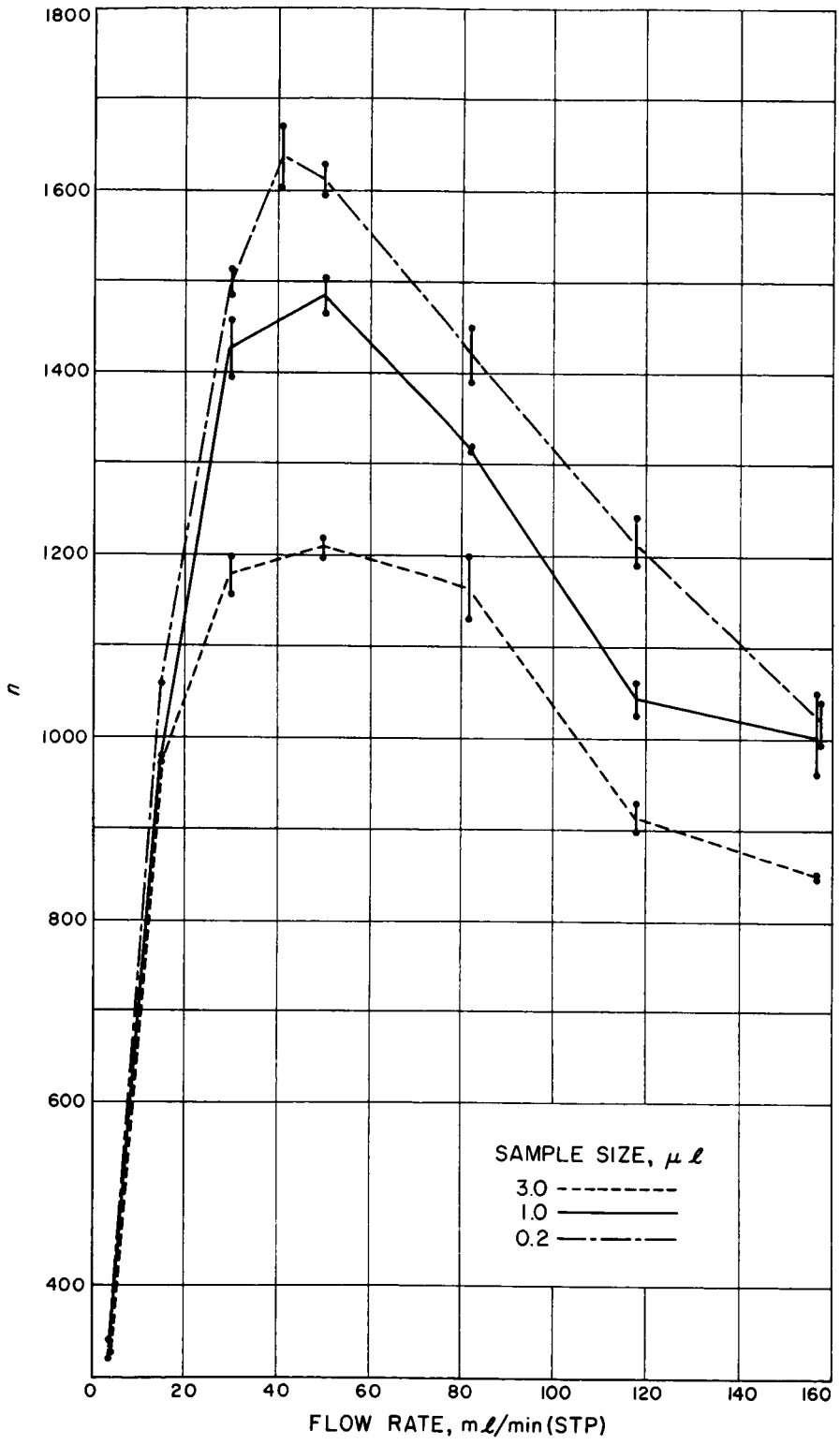


Figure 6. Dependencies of theoretical plates on sample size and flow rate of carrier gas for the crystalline diastereomer, II A, on a Carbowax 20M column at 191° C

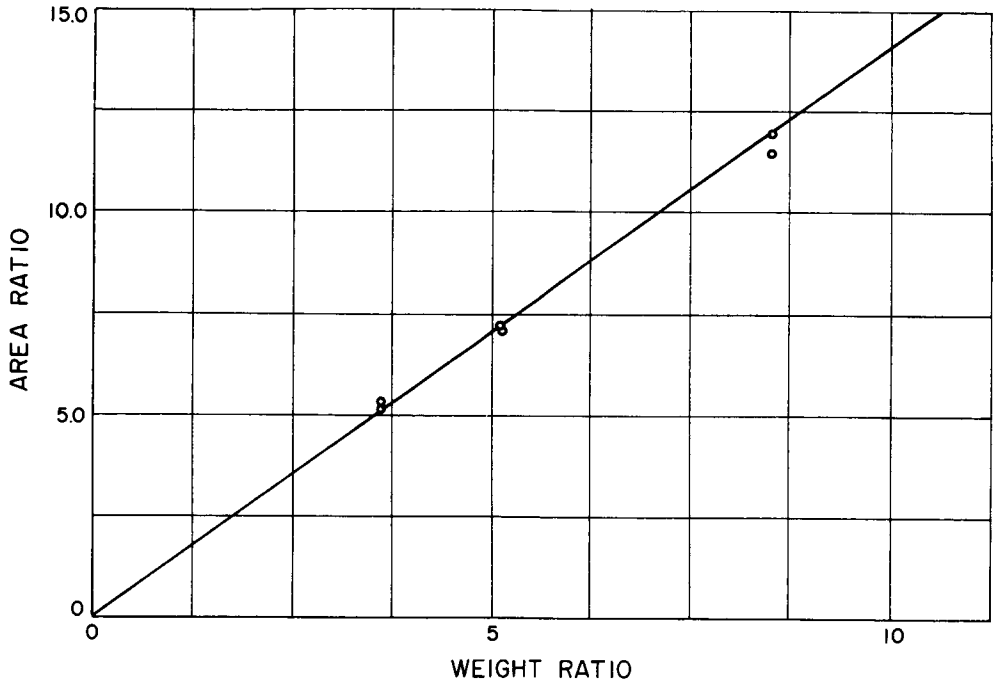


Fig. 7a. Weight ratio vs. area ratio for isomers of dipropylene glycol, IIA/IA

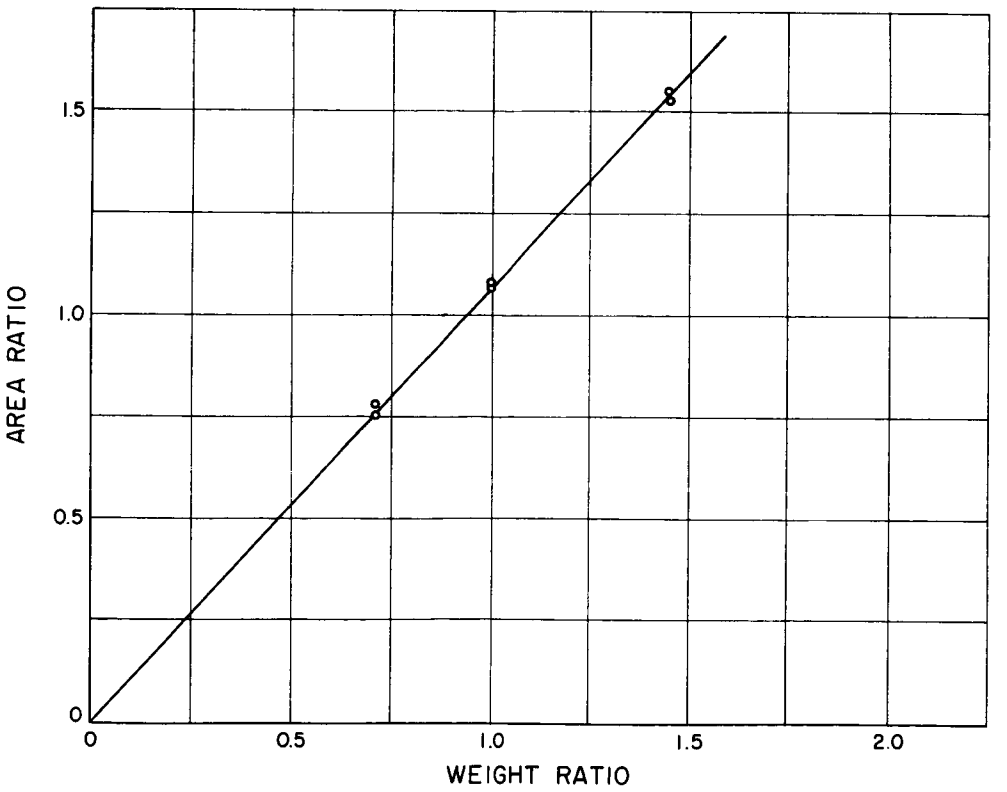
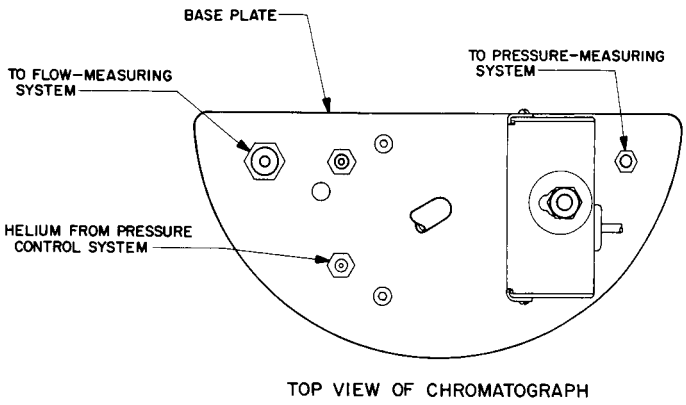
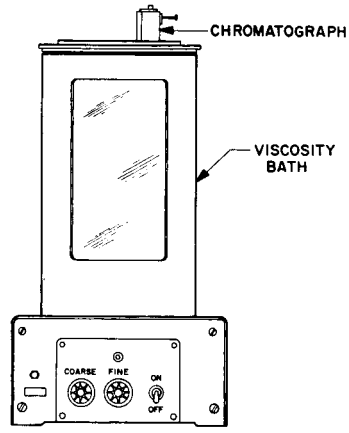


Fig. 7b. Weight ratio vs. area ratio for isomers of dipropylene glycol, IIA/III

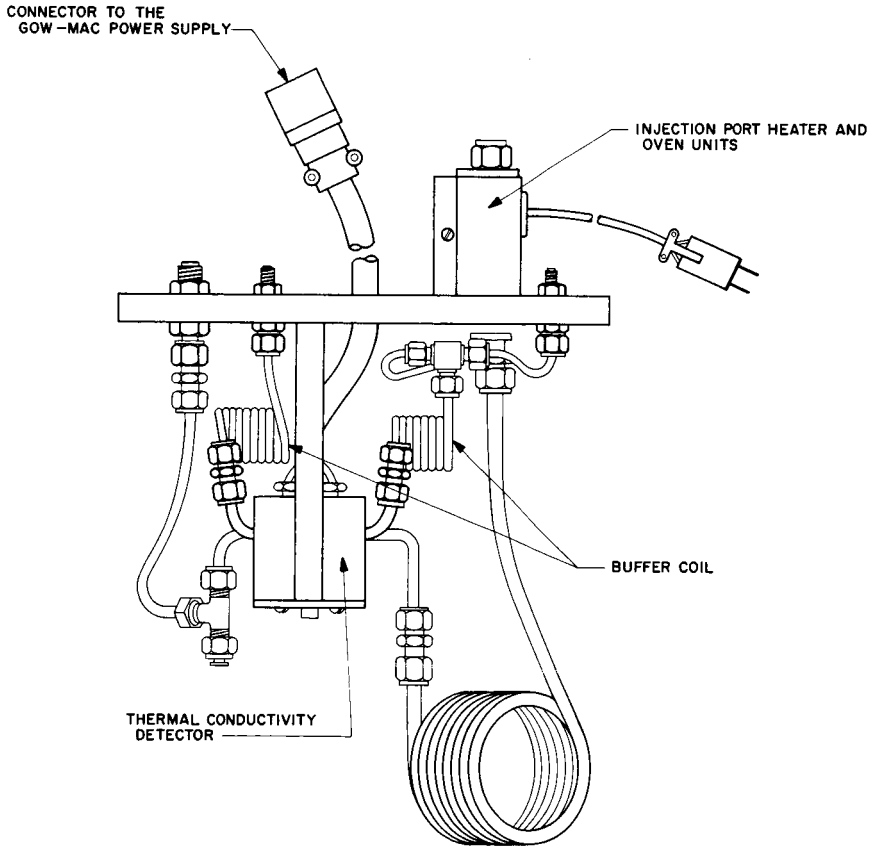
APPENDIX



TOP VIEW OF CHROMATOGRAPH



GAS CHROMATOGRAPH SHOWN IMMERSED IN HALLIKAINEN KINEMATIC VISCOSITY BATH



SIDE VIEW OF CHROMATOGRAPH

Fig. A-1. Detailed drawing of the gas chromatograph unit. For further details, see "Gas Chromatograph Assembly," JPL Drawing No. J 125408

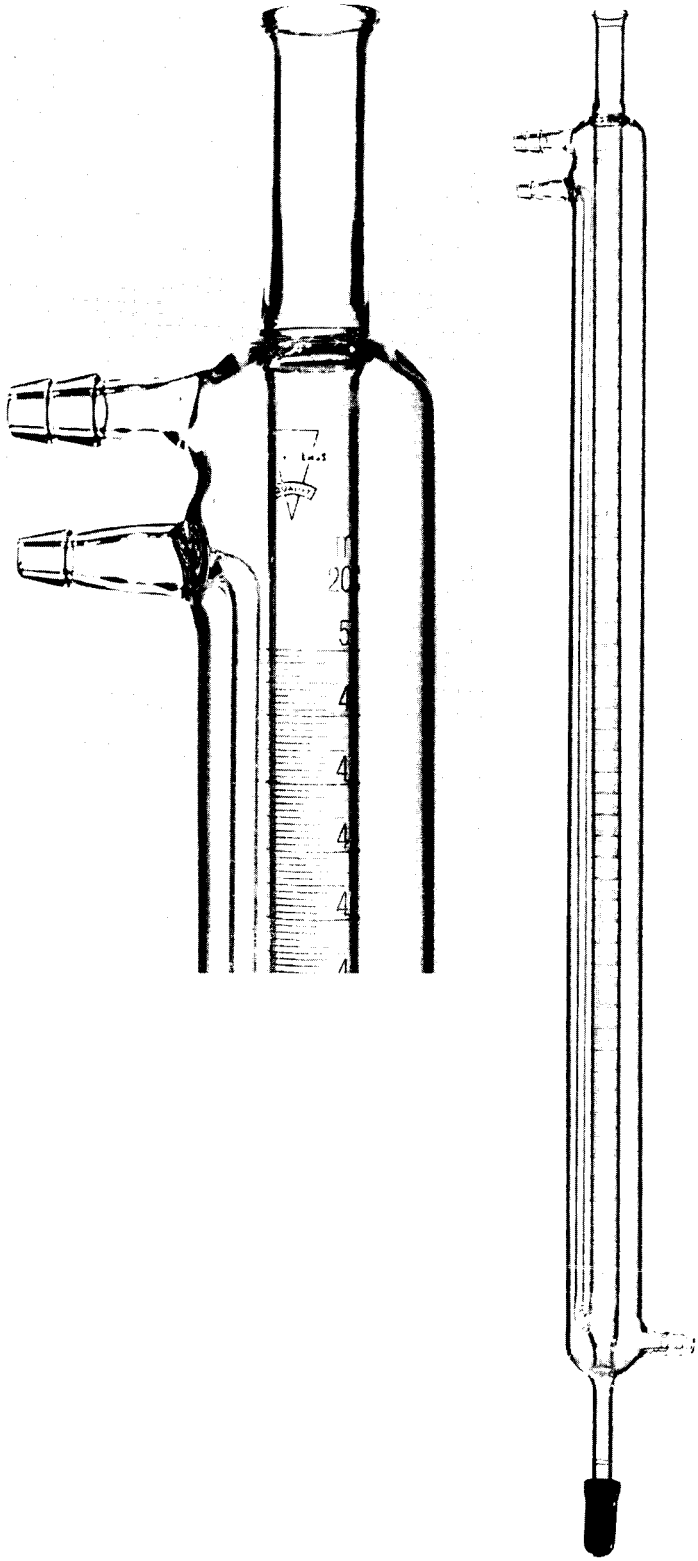


Fig. A-2. Thermostatically controlled flow-meter