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Determination of Dibutylbutylphosphonate in the Presence of Tributylphosphate by Gas Liquid Chromatography

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DETERMINATION OF DIBUTYLBUTYLPHOSPHONATE IN THE PRESENCE OF TRIBUTYLPHOSPHATE BY GAS LIQUID CHROMATOGRAPHY

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ABSTRACT

A gas chromatographic determination of dibutylbutylphosphonate in the presence of tributylphosphate was developed. The separation was done on a 183 cm by 3 mm stainless steel column packed with 10% Carbowax 20M-TPA on 80/100 mesh Chromosorb W AW and detected by flame ionization. A nitrogen carrier gas flow of 40 cm^3*/min and an oven temperature of 180° C produced optimum resolution and column efficiency. The use of temperature programming reduced retention times and thus analysis time. An internal standard of 10% v/v n-tridecane was added to all samples and standards.*

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INTRODUCTION

Solvent Extraction has been widely applied to reprocessing spent fuel elements and resultant waste solutions. In the plutonium recovery process tri-*n*-butylphosphate (TBP) is used to separate plutonium from other fission products. The aqueous waste from this extraction contains significant quantities of americium-241, a beta decay product of plutonium-241, and a small quantity of plutonium-239 not extracted by the TBP. The Am and Pu must be removed from this effluent prior to disposal. Dibutylbutylphosphonate (DBBP) is used for decontamination. This solvent extraction process is shown in Figure 1.

After the acidic feed is contacted with 20% volume per volume (v/v) TBP in carbon tetrachloride (CCl_4) it is acid-adjusted and contacted with 30% DBBP in CCl_4. Americium and remaining Pu are coextracted into the DBBP and partitioned, respectively, into dilute HNO_3 and nitric acid-hydrofluoric acid (HNO_3-HF). The HNO_3-HF containing Pu is then recycled to the feed stream. Due to incomplete phase separation the HNO_3-HF can carry entrained DBBP back to the feed and thus contaminate the TBP extraction column. Dibutylbutylphosphonate has such a high affinity for Pu that its presence in the TBP hinders the ability to strip Pu into an aqueous phase. The maximum level of DBBP tolerable has been estimated at 2.5% v/v. A quick, uncomplicated method of analysis was required to monitor solvent quality on a routine basis.

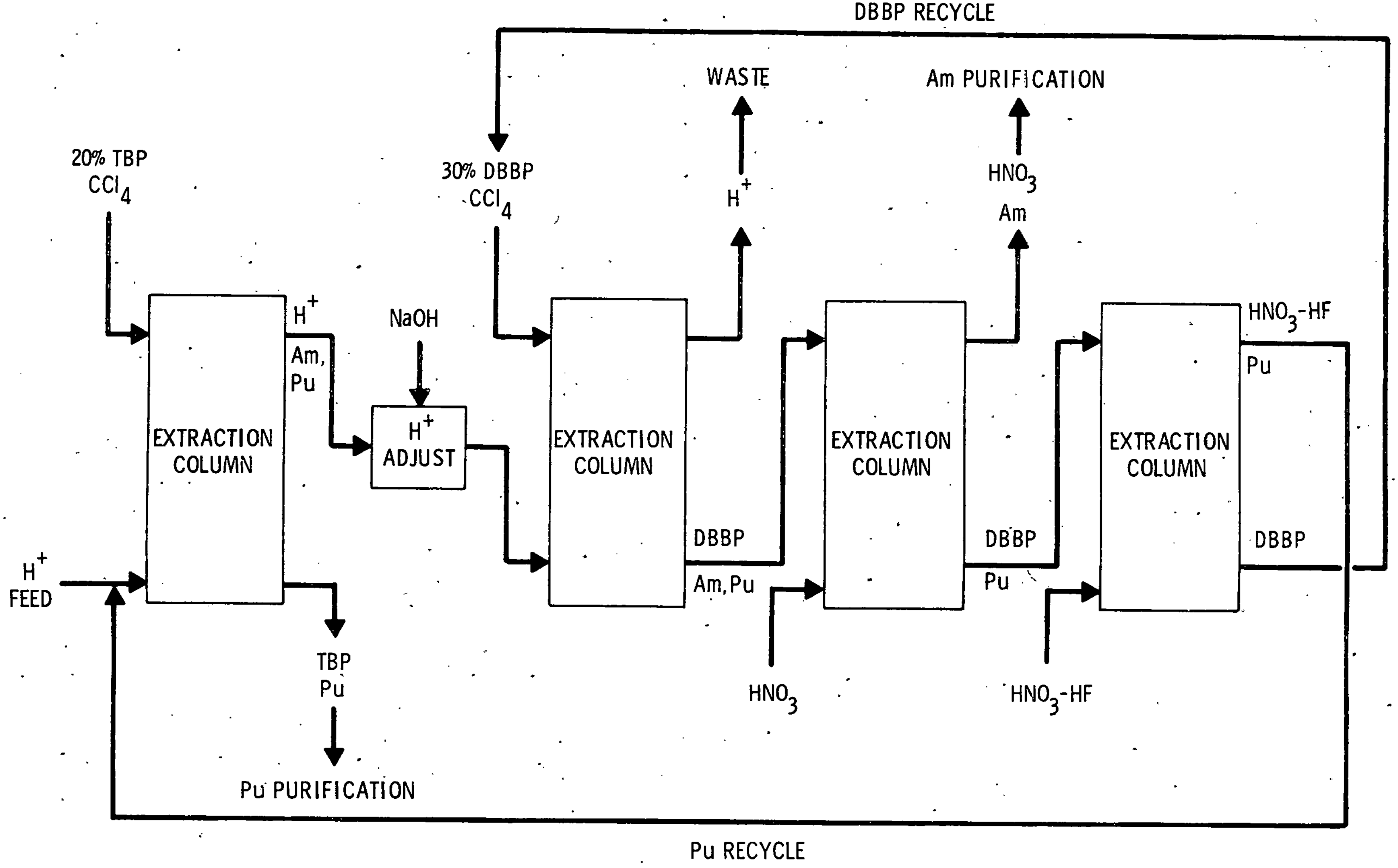

FIGURE 1

TBP AND DBBP SOLVENT EXTRACTION PROCESSES

Gas chromatography has been used for quantitative analysis of TBP and its degradation products, mono- and dibutylphosphate, since the early 1960's.[1] Nonpolar liquid phases, such as SE-30 or Apiezon L® (James G. Biddle Company), have usually been used. Some reports have also employed temperatures programming.[1,2] Mono-, di-, and tributylphosphate have also been determined by gas liquid chromatography (G.L.C.) as their trimethyl sylyl esters[3] or by methylating the sample.[2] The methylated samples were separated on a column packed with Carbowax 20M® (Union Carbide Corporation) on silanized glass beads. Campbell[4] determined TBP in the presence of MBP, DBBP, and DBMP using a flame ionization detector and a 152.5 cm, 7 mm o.d., stainless steel column packed with 20% Apiezon N® (James G. Biddle Company) on 60/80 mesh Chromosorb W® (Johns-Manville Company). The oven temperature was set isothermally at either 175° or 200° C. Resolution of the DBBP and TBP peaks was never achieved. However an indirect method of measuring DBBP was used by determining the concentration of DBMP in the sample. A fairly consistant 5-6% v/v of DBMP is present in process-grade DBBP.

SUMMARY

Gas liquid chromatography was used to develop a direct, reliable method for the determination of DBBP in the TBP process stream. Nonpolar liquid phases which have been used in the past for the determination of DBBP and TBP produce shorter retention times and are highly efficient for single component samples but produce very little peak resolution for mixtures. For this reason a much more polar liquid phase was used. The column used for this analysis was 183 cm x 3 mm o.d. stainless steel packed with 10%

Carbowax 20M on 80/100 mesh Chromosorb W. To prevent sample absorption and prolong the life of the packing, the solid support was acid-washed and the liquid phase treated with terephthalic acid.

Nitrogen was chosen over helium as the carrier gas. Although helium will produce a faster analysis, a higher molecular weight gas will increase column efficiency. This was done to compensate for the efficiency lost with a more polar liquid phase. Nitrogen is also much more economical when routine analyses are made.

Parameters were optimized to produce column efficiencies, $\overline{H}$, of less than 0.5 and resolutions, R, of 1 or greater at reasonable retention times. The following conditions were used to analyze samples isothermally with a flame ionization detector:

Oven temperature	180° C
Injector temperature	200° C
FID temperature	350° C
N_2 flow	40 cm^3/min
H_2 flow	40 cm^3/min
Air flow	350 cm^3/min

Shorter retention times and better resolution of peaks produced by degradation products (butanol, MBP, DBP, and DBMP) was achieved by using temperature programming. The best overall results were produced using a program in which the oven was held at 150° C for 0.5 min after injection. The oven was then heated to 200° C at 10°/min and held there for 5 min.

A calibration for DBBP was made for concentrations ranging from 0.1 to 80% v/v. All standards contained an internal standard of 10% v/v *n*-tridecane. A calibration curve having a slope of 0.0486 ± 0.008 was produced by plotting DBBP concentration against the ratio of peak area of DBBP to peak area of *n*-tridecane.

EXPERIMENTAL

APPARATUS

Gas Liquid Chromatograph: Bendix-2200® (Bendix Corporation) equipped with flame ionization detector (F.I.D.) and temperature programming abilities. A microswitch was installed at the injection port to activate the integrator and temperature programmer at the time of injection. A glass liner was also used in the injection port.

Recorder: Leeds and Northrup Speedomax® having a 0-1 mV range.

Integrator: Vidar 6230 Digital Integrator® (Autolab, Inc.) with output to a Teletype terminal.

Syringe: 1,5, or 10 l Pressure-Lok® (Precision Sampling Company) liquid syringe.

Column: 183 cm x 3 mm o.d. stainless steel packed with 10% Carbowax 20M-TPA® on 80/100 mesh Chromosorb W AW®.

REAGENTS

Tributylphosphate (TBP): Research Organic/Inorganic Chemical Company.

Dibutylbutylphosphonate (DBBP): Research Organic/Inorganic Chemical Company.

50% Monobutylphosphate--50% Dibutylphosphate (MBP-DBP): Research Organic/Inorganic Chemical Company.

n-Tridecane: Aldrich Chemical Company, Inc., 99+%.

Carbon Tetrachloride: Matheson, Coleman, and Bell, purified.

Hydrogen Gas: Liquid Air Inc.

Nitrogen Gas: Union Carbide, purified grade.

Compressed Air: Liquid Air Inc. breathing quality.

PROCEDURE

Instrument Conditions	Comments
1. Oven temperature: 180° C, if operating isothermally; if programming set appropriate program	Condition columns at 200° C whether operating isothermally or programming temperature.
2. Injection port temperature: 200° C	Use glass-lined injection ports.
3. F.I.D. temperature: 350° C	
4. N_2 flow: 40 cm^3/min	Used as carrier gas.
5. H_2 flow: 40 cm^3/min	Used for F.I.D.
6. Air flow: 350 cm^3/min	Used for F.I.D.

Sample Preparation	Comments
1. Pipet 900 μl of sample into a small septum vial	
2. Add 100 μl *n*-tridecane	10% v/v $C_{13}H_{28}$ is used as in internal standards.

Analysis	Comments
1. Inject appropriate sample size into injection port and push microswitch.	1 μl for <30% v/v DBBP or TBP; 0.5 μl for >30% v/v DBBP or TBP.
2. Inject standards containing 10% v/v $C_{13}H_{28}$ which are of similar DBBP or TBP concentrations	These should be alternated with sample injections.
3. Acquire integrated areas and retention times on teletype	Check that areas are not over-running the integrator.

CALIBRATION

Prepare standards of known vol% of DBBP and TBP in carbon tetrachloride. Each standard should contain an internal standard of 10% v/v *n*-tridecane.

Prepare a calibration curve using standards that will include the concentration range of the samples. A calibration curve as in Figure 2 is produced by plotting concentration versus the ratio of peak area of the component to the peak area of the internal standard.

Rather than graph a calibration curve an average response factor ($\overline{\text{R.F.}}$) may be used. The R.F. is determined by dividing the area ratio of the component to the internal standard by the concentration of the component. An average $\overline{\text{R.F.}}$ should be determined from injections of a standard of higher concentration and of lower concentration than the sample. The $\overline{\text{R.F.}}$ is basically the slope of the calibration curve described above.

CALCULATIONS

Sample concentration from a calibration curve is easily done by calculating the area ratios for the sample.

In order to determine sample concentrations using an $\overline{\text{R.F.}}$, an area ratio must also be calculated for the sample. This ratio is then divided by the $\overline{\text{R.F.}}$, giving the answer in % v/v.

RESULTS AND DISCUSSION

RESOLUTION (R)

The determination of DBBP and TBP has been hindered in the past due to poor resolution. Figure 3 shows a chromatogram of 30% v/v DBBP and 30% v/v TBP separated on a

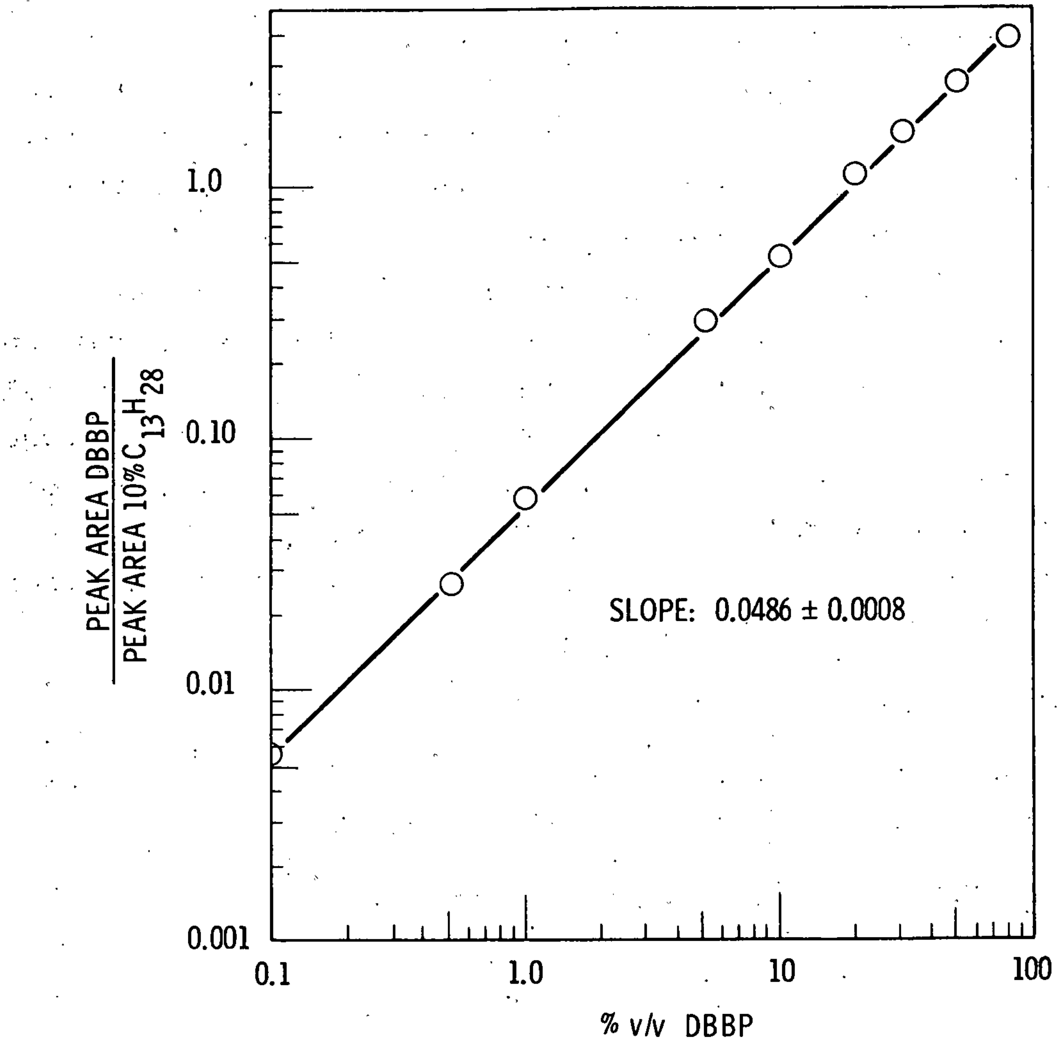

FIGURE 2

DBBP CALIBRATION CURVE

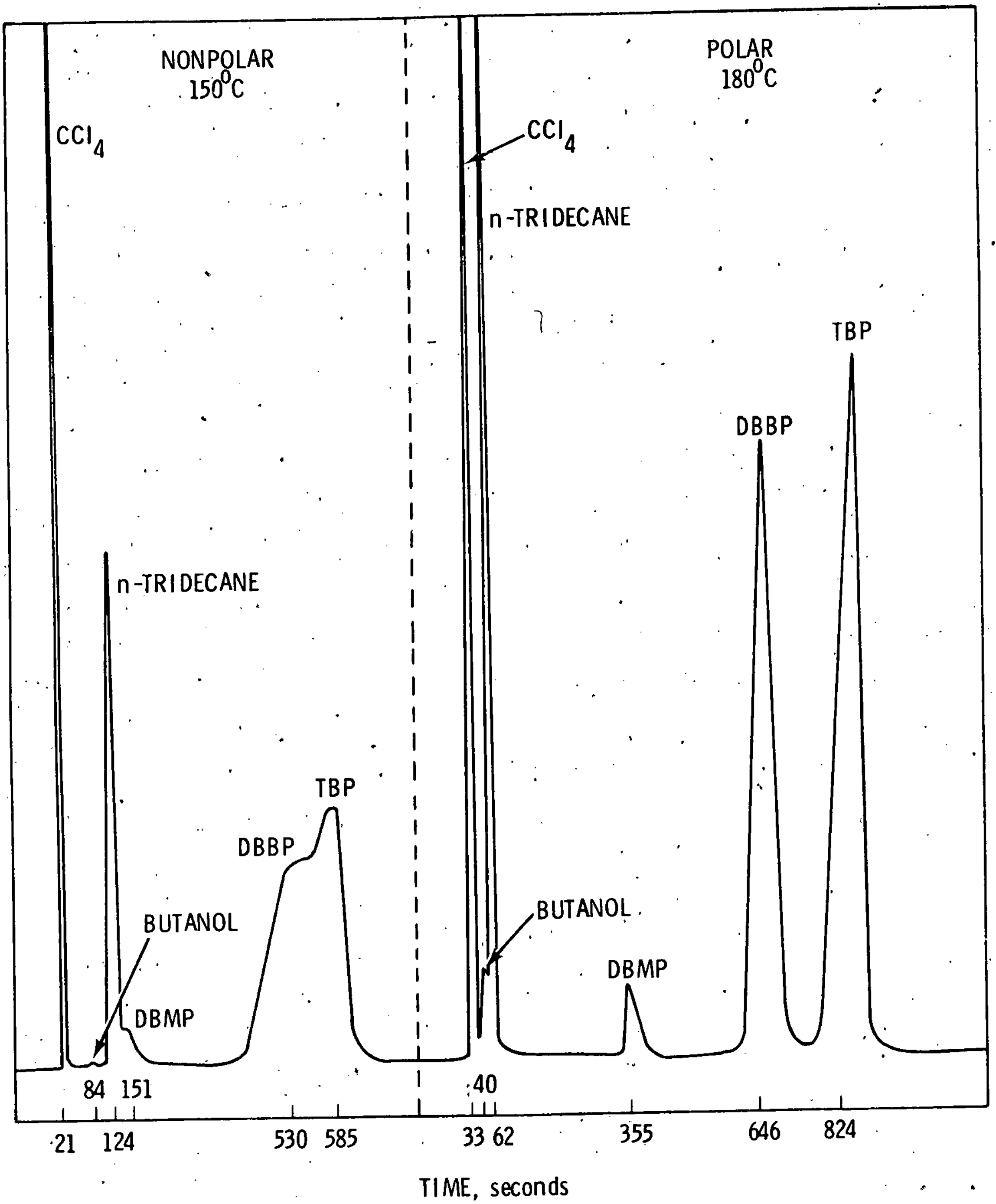

FIGURE 3

EFFECT OF COLUMN POLARITY ON SEPARATION OF DBBP-TBP

183-cm x 3-mm o.d. stainless steel column packed with 7% OV-1® (Ohio Valley Specialty Chemical Company) on 100/110 mesh Anakrom Q® (Analabs, Inc.). This chromatogram was obtained with an isothermal oven temperature of 150° C, an N_2 flow of 40 cm^3/min, and an F.I.D. Similar chromatograms have been obtained in the past on other nonpolar columns.

As also can be seen in Figure 3, high resolution was obtained by using a more polar column packing. A liquid phase of 10% Carbowax 20M was chosen. In order to minimize tailing and liquid phase degredation, the solid support, 80/100 mesh Chromosorb W, was acid-washed (AW) and the liquid phase treated with terephthalic acid (TPA).

Resolution, being the most important factor in this analysis, was optimized with respect to oven temperature and carrier gas velocity. Figure 4 shows resolution versus oven temperatures. The data for this graph were obtained by injecting at each temperature 0.4 μl of a standard containing 30% v/v DBBP, 30% v/v TBP, 10% v/v $C_{13}H_{28}$ in CCl_4. An N_2 flow of 30 cm^3/min was used.

Resolution was calculated using the equation

$$R = \frac{2(x_{TBP} - x_{DBBP})}{y_{DBBP} + y_{TBP}}$$

where x is the retention time in seconds from the point of injection and y is the peak width in seconds at base line. A resolution of 1 indicates approximately 98% separation and would be sufficient for this analysis. This resolution was achieved at about 180° C, with even greater resolution at lower temperatures.

The average linear velocity, $\overline{\mu}$, for the carrier gas, N_2, was determined by injecting methane and determining its

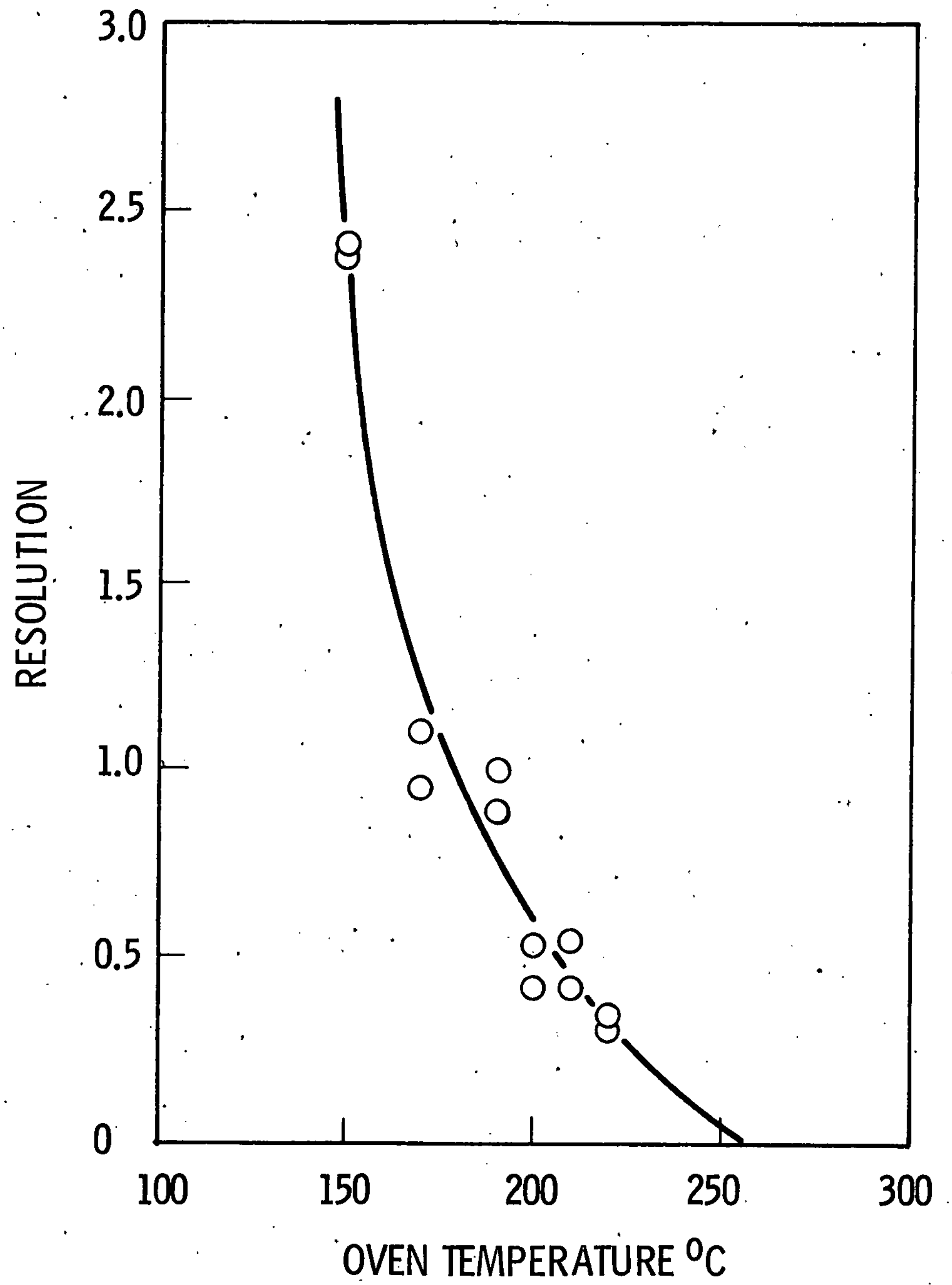

FIGURE 4

EFFECT OF TEMPERATURE ON RESOLUTION

velocity through the column. Resolution was plotted against linear velocity in Figure 5. The same DBBP-TBP standard as before was used in this experiment with an oven temperature of 180° C. As can be seen, greater resolution is attained with lower gas velocities. However the results show all resolutions to be greater than 1, indicating that the higher velocities could be used for this analysis.

COLUMN EFFICIENCY ($\bar{H}$)

For the purpose of this work, efficiency will be measured as the average height equivalent to a theoretical plate, $\bar{H}$. The equation used is

$$\bar{H} = \frac{L}{16\left(\frac{x}{y}\right)^2}$$

where L is the column length in centimeters. It is desirable for this analysis to minimize $\bar{H}$ to less than 0.5 cm when possible, although $\bar{H}$ values of 0.15 cm have been reported using nonpolar columns.[4]

Carrier gas velocity is an important contributor to minimizing $\bar{H}$, particularly when using nitrogen. An optimum average linear velocity, $\bar{\mu}$, can be determined from a Van Deempter curve shown in Figure 6 for both DBBP and TBP. An optimum velocity was not reached in this experiment due to difficulties in sustaining a detector flame and the impracticality of operating at such low gas flows. Although a velocity of 6.3 cm/sec ($\sim$25 cm^3/min) produced an $\bar{H}$ of 0.2 cm, the $\bar{H}$ at higher velocities ($\sim$40 cm^3/min) is sufficient for this analysis particularly when the resolution is also greater than 1.

The concentration of the sample injected also appeared

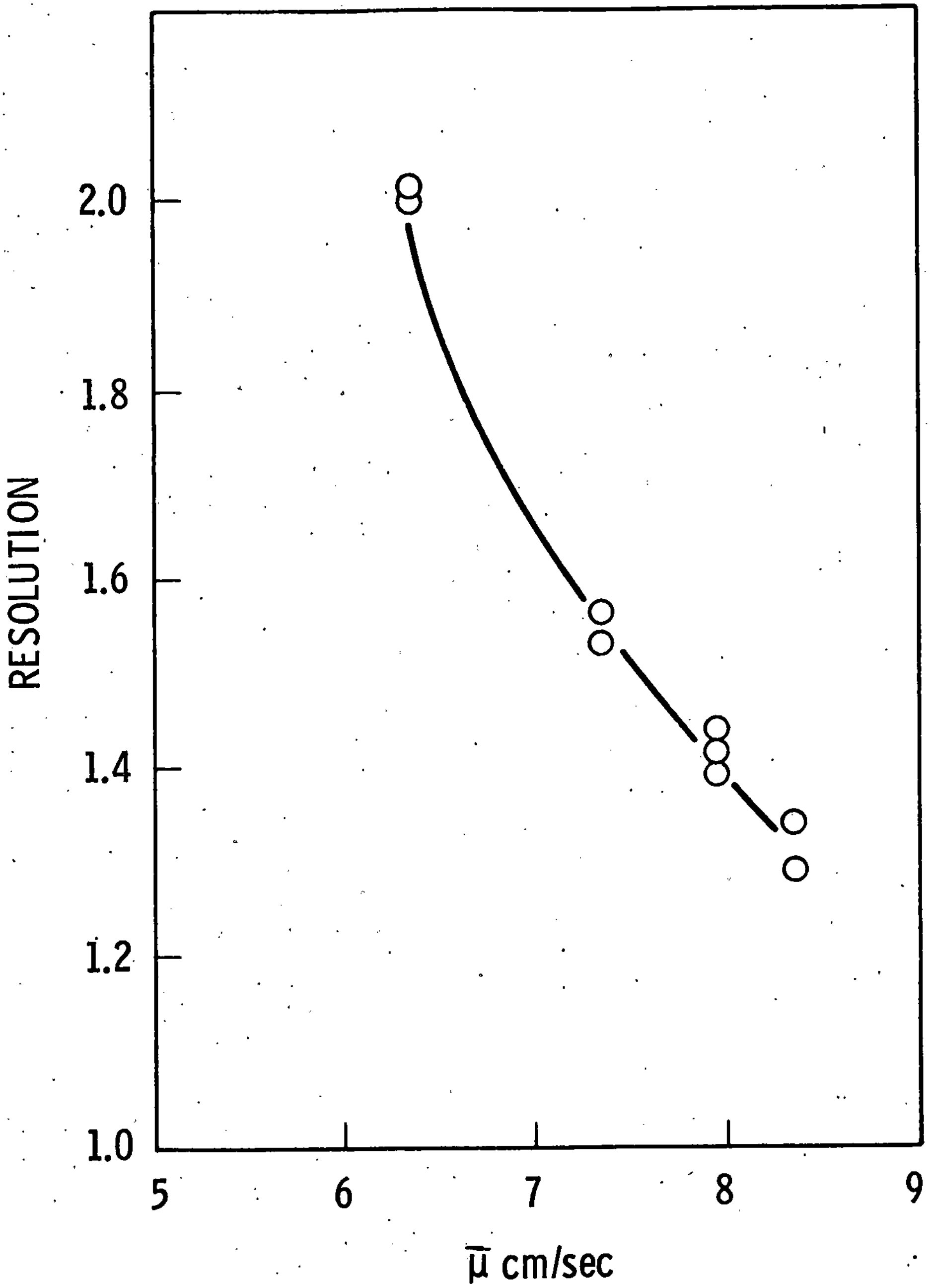

FIGURE 5

EFFECT OF CARRIER GAS VELOCITY ON RESOLUTION

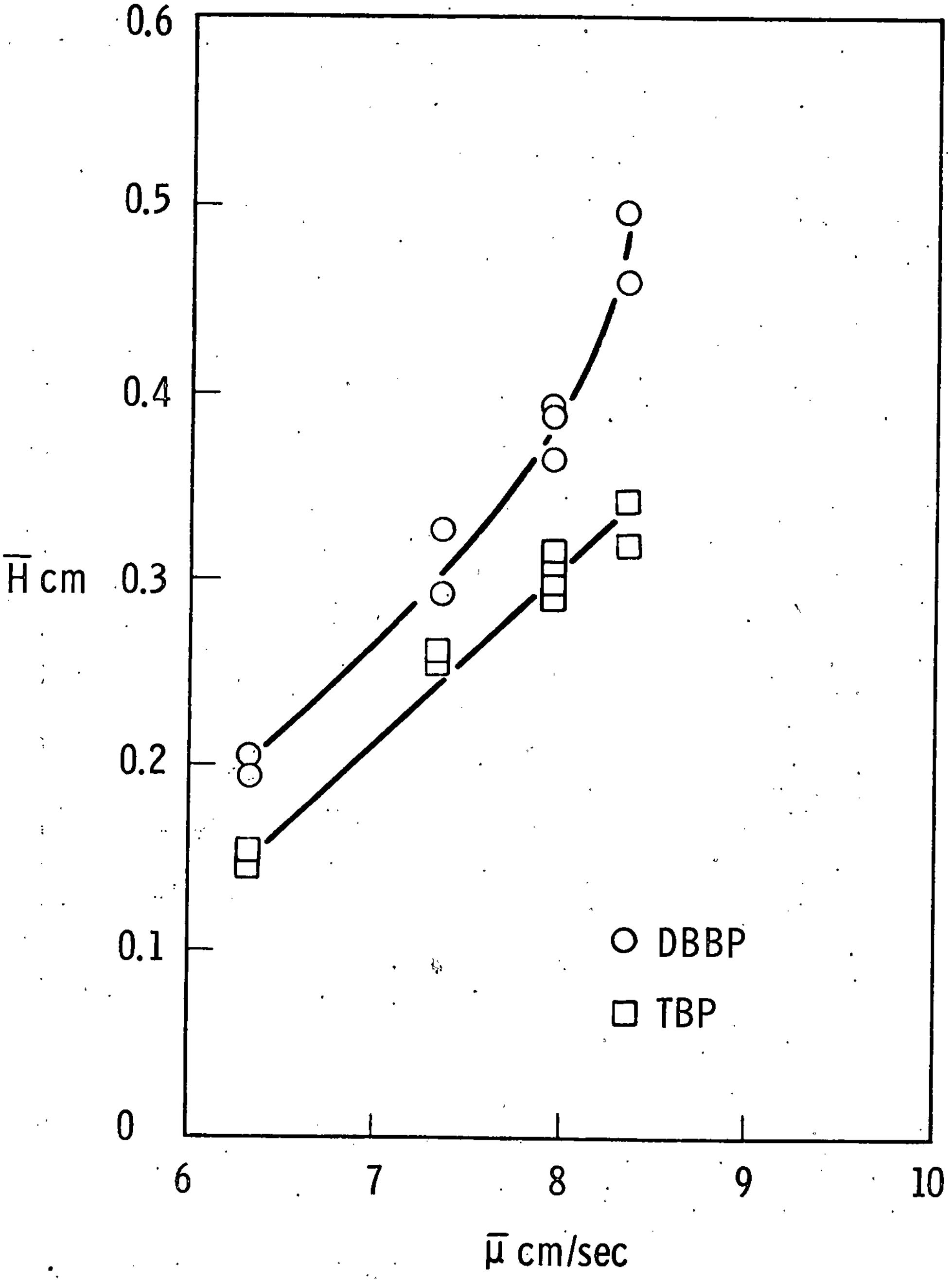

FIGURE 6

EFFECT OF CARRIER GAS VELOCITY ON EFFICIENCY to have an effect on the efficiency of this column. The $\overline{H}$ was plotted against concentration of DBBP in Figure 7. A 1 μl injection was made with an oven temperature of 180° C and an N_2 flow of 40 cm^3/min. Above a concentration of 30% v/v DBBP, the $\overline{H}$ values increased beyond the desired 0.5 cm. This condition could be improved, however, by using smaller sample sizes or a lower flow rate.

DETECTOR RESPONSE

When there is a possibility of working over a wide range of concentrations it is necessary to know if the detector response is linear with respect to concentration. Rather than plot a linearity curve of actual detector response versus concentration, Figure 8 demonstrates the nonlinearity much more readily by plotting response factor, R.F., versus concentration. As described previously, R.F. is the ratio of the component peak area to the internal standard peak area divided by the concentration of the component. Ideally the response factor would be constant at all concentrations.

In this analysis of DBBP the R.F. was determined to be 0.055 ± 0.002 for concentrations less than 30%. At higher concentrations the R.F. began decreasing due to detector over-loading. These determinations were made with an N_2 flow of 40 cm^3/min and 180° C oven.

RETENTION TIME (x_T)

The retention times for DBBP and TBP are significantly shorter using a nonpolar column. However to gain resolution, a polar column was used at the expense of time. The analytical need, though, is still for the most expedient

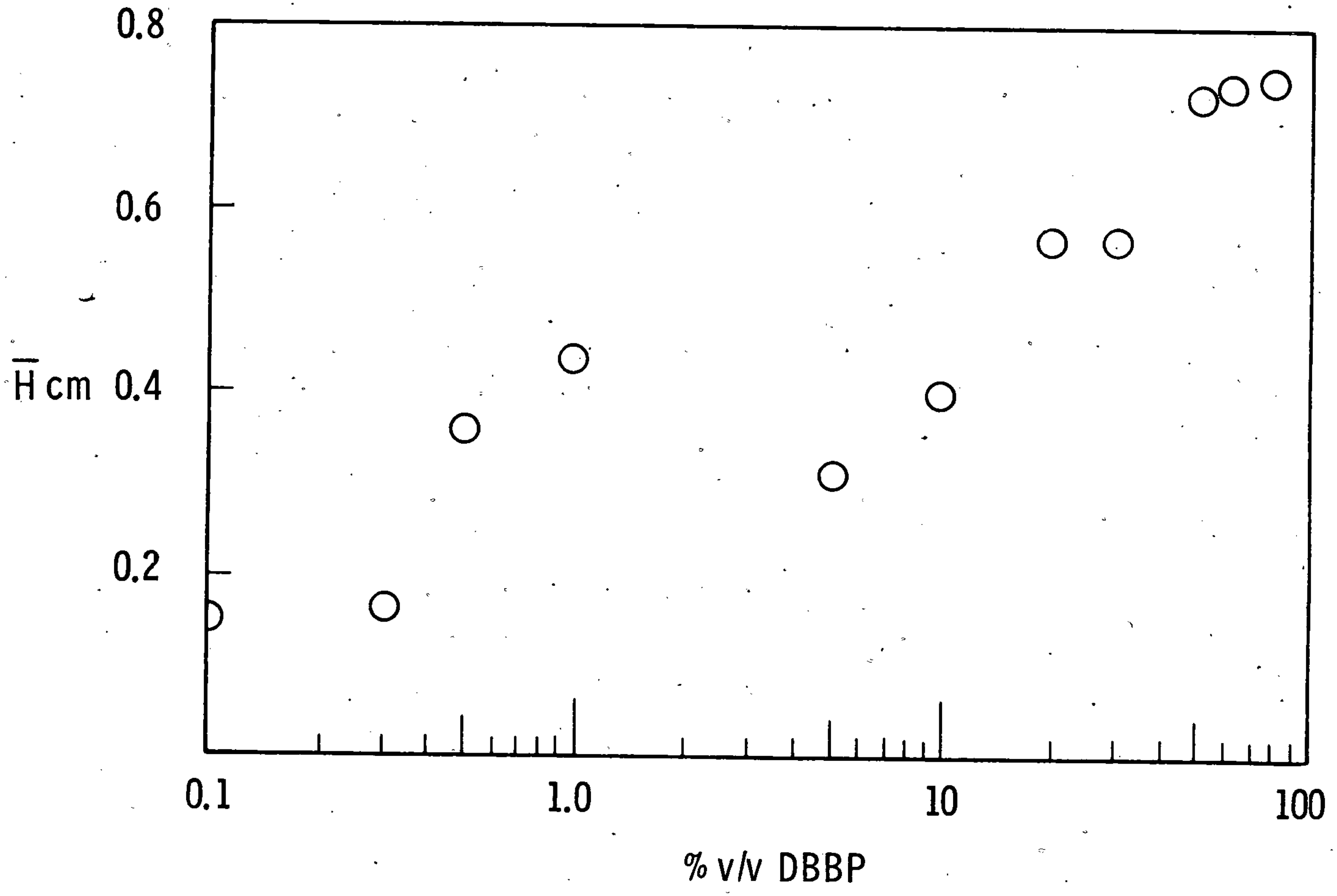

FIGURE 7

EFFECT OF CONCENTRATION ON EFFICIENCY

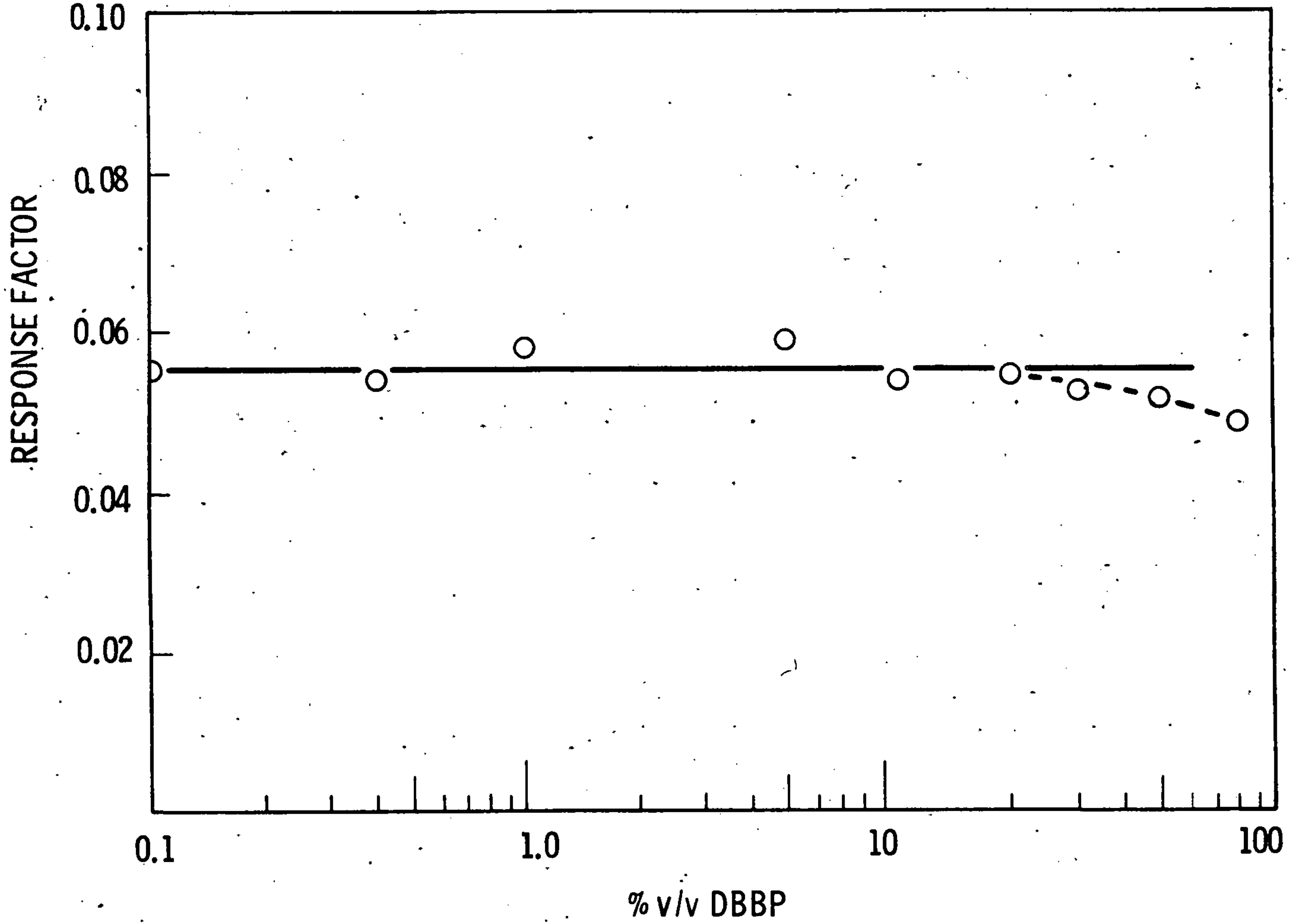

FIGURE 8

LINEARITY OF DETECTOR RESPONSE FOR DBBP

method possible, indicating that some compromises must be made with resolution and efficiency.

The parameters that most drastically affect retention time, other than column polarity, are oven temperature and carrier gas flow. Tables I and II show the effects of these on x_T.

TABLE I

EFFECT OF TEMPERATURE ON RETENTION TIME

Temperature °C	x_{DBBP} seconds	x_{TBP} seconds	R
150	1,970	2,625	2.389
170	940	1,204	1.032
190	483	599	0.952
200	362	438	0.486
210	278	330	0.487
220	220	257	0.328

TABLE II

EFFECT OF N_2 FLOW ON RETENTION TIME

$\bar{\mu}$ cm/sec	x_{DBBP} seconds	x_{TBP} seconds	R
6.31	825	1,053	2.00
7.32	701	593	1.41
7.96	653	833	1.55
8.32	628	802	1.31

Retention times can also be affected by the concentration of the component injected. The graph in Figure 9 indicates how the x_T for DBBP increases with concentration.

These retention times can be shortened and resolution and efficiency retained by employing temperature programming. The optimum program achieved with the system being used was to hold the oven at 150° C for 0.5 min after injection; then raise the temperature at 10°/min to 200° C and

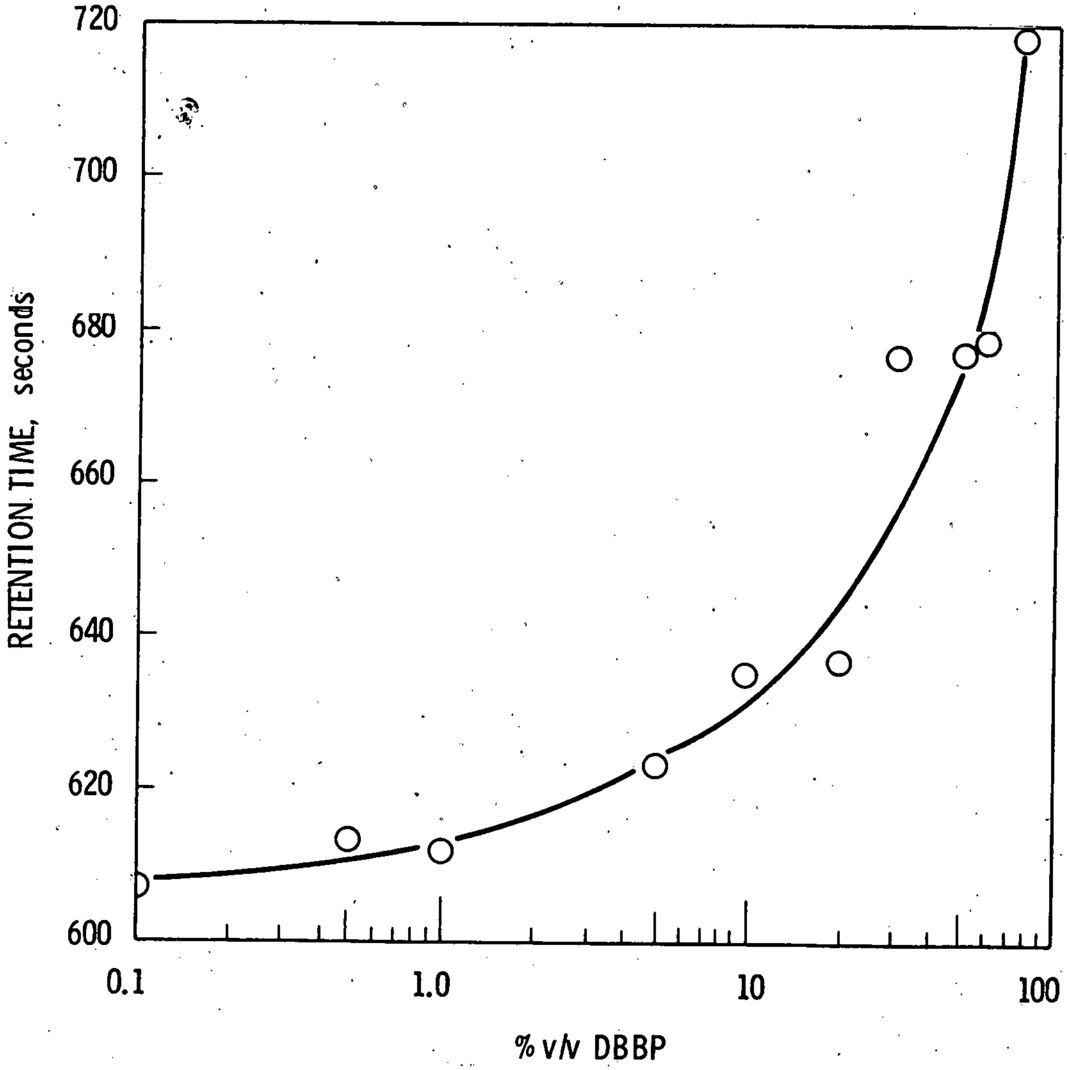

FIGURE 9

EFFECT OF CONCENTRATION ON RETENTION TIME hold for ∿5 min. This program produced the following results when using Process DBBP:

x_{DBMP}	368	sec
x_{DBBP}	540	sec
x_{TBP}	634	sec
$\bar{H}_{DBBP}$	0.332	cm
$\bar{H}_{TBP}$	0.308	cm
R	0.959	

This temperature program also improved the resolution between the CCl , butanol, and *n*-tridecane. A programmed and isothermal chromatogram are shown in Figure 10.

CONCLUSIONS

The optimum instrument conditions for analyzing DBBP in the TBP process stream are as follows:

Oven Temperature	180° C
Injector Temperature	200° C
F.I.D. Temperature	350° C
N_2 Flow	40 cm^3/min
H_2 Flow	40 cm^3/min
Air Flow	∿350 cm^3/min

For shorter retention times temperature programming can be employed. The above conditions will produce efficiencies of <0.5 and resolutions of 1 or greater. Recovery for samples should be 100 ± 5%.

Although these conditions produce the most usable analysis in this G.C. system, they may vary somewhat in other systems.

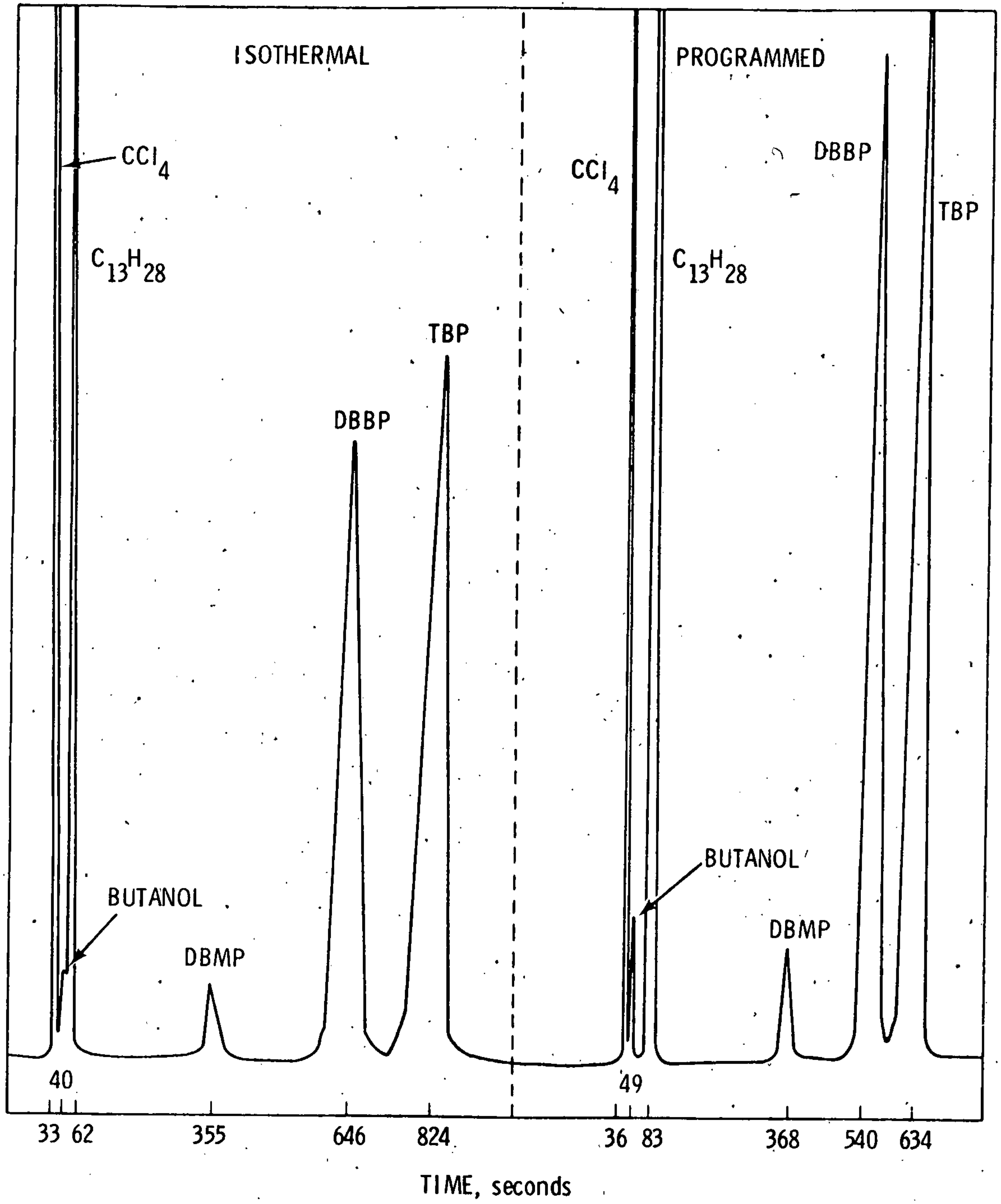

FIGURE 10

CHROMATOGRAMS OF A MIXTURE OF 30% v/v DBBP + 30% v/v TBP + 10% v/v $C_{13}H_{28}$ IN CCl_4

ACKNOWLEDGMENTS

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