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Analytical gas chromatography on catalytically generated synthetic fuels

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Analytical Gas Chromatography on Catalytically
Generated Synthetic Fuels

by

Victor Kuzmicz

A research report presented in partial fulfillment of the
requirements for the Degree of Master of Science in
Chemical Engineering

Lehigh University

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Analytical Gas Chromatography on Catalytically
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ABSTRACT

The application of capillary gas chromatography for the analysis of the C₁ through C₆ higher alcohol synthesis products and related oxygenates is the topic of this research. Three columns were tested on a Hewlett-Packard Model 5880A gas chromatograph (GC) with a flame ionization detector (FID) coupled to a 5880A series GC terminal integrator. The three columns tested were (A) 30m long by 0.32 mm I.D. 50% phenyl methyl silicone capillary column, (B) 26m long by 0.33 mm I.D. Carbowax capillary column, and (C) a 60m long by 0.75 mm I.D. wide bore bonded methyl silicone capillary column. Column C was selected as the best overall column for the total analysis of the C₁ through C₆ products of higher alcohol synthesis. Response factors were determined for all the alcohols, aldehydes, esters, ketones, and ethers present in the reactor product mixture. The response factors were used to perform a total analysis of the products generated over a Cu/Zn/Al/Cs (36.8/36.8/23.3/3.1) catalyst. The results were compared with those obtained when the same mixture was analyzed on a Hewlett-Packard Model 5730A gas chromatograph with a Porapak Q column and a thermal conductivity detector. It was found that the wide bore bonded methyl silicone capillary column separated more components than the Porapak Q column.

I. Introduction

1.1 Purpose of Investigation

The application of capillary gas chromatography as an analytical method for the characterization of products generated from higher alcohol synthesis reactions is the subject of this research. Until now, packed columns and a number of columns in series have been used to separate higher alcohol synthesis products (12) but no single column has achieved the separation of C₁ through C₆ products. This research was conducted to find one suitable column for the separation of all the C₁ through C₆ products which would greatly simplify the present analysis methods. Separation of C₁ through C₄ products has been achieved primarily by using a 6' x $\frac{1}{8}$ " diameter column packed with Porapak Q. The instrument used was a Hewlett-Packard Model 5730A gas chromatograph equipped with an automatic sampling valve and a thermal conductivity detector. Identification of the compounds was based on the retention time of the unknown compounds, and quantitative information was obtained with a Hewlett-Packard Model 3388A integrator coupled to the GC. Complications arose when attempts were made at separating the higher alcohol synthesis products, e.g. the C₅, C₆, and C₇ products with the Porapak Q column. Peaks were observed to broaden and overlap in this region for all conditions. Therefore, to achieve separation of the C₅ and C₆ products appearing in small amounts, possibly trace quantities, three different capillary columns varying in degree of polarity were tested to see which would give optimum separation and resolution of the products. Columns were separately tested and used in a Hewlett-Packard Model 5880A gas chromatograph with a flame ionization detector. Also coupled to the GC was a

Hewlett-Packard Model 5880A series GC terminal integrator providing quantitative information by determining the areas under the peaks in the chromatogram.

To optimize peak resolution the following parameters were studied: column flow rate, oven temperature programming, and sample dilution in various solvents. Response factors were determined to give sensitivity values for the flame ionization detector. The values were later used in quantitative determination of mol percentages of all higher alcohol synthesis products identified by the gas chromatograph.

2. Experimental

2.1 Higher Alcohol Synthesis Reactor Flow System

Schematic diagrams of the experimental arrangement used for the synthesis of higher alcohols have previously been presented with the reactor design included (1). The reactor effluent was either passed through a Hewlett-Packard 5730A gas chromatograph by an automatic sampling valve, or gas and liquid samples were collected by placing the tubing containing the effluent into a liquid nitrogen bath. The samples were kept in liquid nitrogen until they were warmed up to room temperature and manually injected into the 5880 GC. Gas samples were also drawn directly from the exit stream tubing with a 0.25 ml gas syringe and then manually injected into the gas chromatograph.

2.2 The 5880A Gas Chromatograph

2.2.1 Column and Detector Gas Control Module Parameters

A standard start up procedure was always followed before any sample injections into the Hewlett-Packard 5880A gas chromatograph. This procedure insured reproducible results for all sample injections. Helium was used as

the carrier gas and its head pressure was maintained at 2.1 atm. For the FID operation, the air pressure was held at 2.1 atm, and hydrogen pressure was also kept at 2.1 atm. These pressures were routinely checked on the front column and detector gas control module. The carrier gas was maintained at a flow of 7.32 ml/min which corresponded to a head pressure of 0.6 atm on the front module. The carrier flow was checked each day by injecting 0.25 ml of methane in the 5880A GC with a 0.25 ml Pressure-Lok syringe. The retention time of methane was 3.62 minutes for the flow rate of 7.32 ml/min. In case there was any deviation in methane retention time the carrier gas pressure was adjusted to reestablish the original flow. Finally, the septum purging vent was kept at a flow rate of 6.0 ml/min. This was routinely checked by placing a bubble flow meter over the purging vent. The split vent was kept at a flow rate of 15 ml/min and a bubble flow meter was used to measure this flow. Detailed instructions and maintenance of the control module are given in Volume 3 of the 5880A gas chromatograph instrument manual accompanying the instrument. A sample calculation of the carrier flow is given in Appendix A.1.1 of this text.

2.2.2 Parameter Settings for the Oven and Integrator of the H.P. 5880A Gas Chromatograph

The injection port, oven, detector, and the GC terminal integrator were programmed and operated by the keyboard of the 5880A terminal integrator. The following is a listing of all the commands used in programming the injection port, oven, detector, and integrator for the separation of higher alcohol products. These parameters and the corresponding values were used for all analyses conducted by the author. A thorough description and procedure is

given in Volume 2 of the 5880A instrument manual, accompanying the instrument, for entering the values.

1. Month, Day, Year
2. Time
3. Injection Port 1 Temperature = 220°C
4. Detector 1 Temperature = 250°C
5. Oven Temperature Initial Value = 30°C
6. Oven Temperature Initial Time = 4.0 (min)
7. Oven Temperature Program Rate = 3.0°C/min
8. Oven Temperature Final Value = 80°C/min
9. Oven Temperature Final Time = 15.0 (min)
10. Chart Speed = 0.50 (cm/min)
11. Runtime 3.0 (min), chart speed = 2.5 (cm/min)
12. Runtime 4.40 (min), chart speed = 1.5 (cm/min)
13. Runtime 3.85 (min) Tangent Skim

The last parameter, tangent skim, allows peaks appearing on the tail end of the methanol peak in the chromatogram to be integrated properly without being integrated as part of the component methanol. This is further explained in Volume 2 of the instrument manual. After parameters were entered and the instrument was given time to equilibrate, the samples were injected.

2.2.3 Sample Collection and Injection Technique

Samples were injected into both the H-P 5730A GC and the 5880A GC as liquids and gases. As stated earlier, liquid samples were collected by placing the effluent line into a U-shaped glass tube and immersing the collection vessel

into a liquid nitrogen bath. After approximately 5 ml of liquid were collected, the sample, while remaining in the nitrogen, was taken to the chromatograph to be manually injected with a 1.0 microliter (μl) Hamilton syringe Model # 7001. The injection technique for liquid samples was a modified technique used by many chromatographers (2,3,4). The syringe filling sequence was: an air space (ca. 0.05 μl), then 0.01 μl of sample solution, and then another air space of approximately 0.02 μl . The syringe was placed into the injection port and the syringe bar pushed all the way in while starting the integrator. This method insured that all of the sample entered the injection port.

The injection method for gas samples was slightly easier. A 0.25 μl Pressure-Lok syringe made by the Precision Sampling Corporation was used for injecting gas samples. The syringe needle was pierced through the effluent line, then the valve on the syringe was opened and the piston drawn upward until 0.25 ml were collected. The syringe valve was closed, the needle withdrawn and the sample immediately taken to the gas chromatograph. The syringe needle was pushed into the injection port, its valve once again opened and the syringe was pushed all the way down while the integrator was started.

2.3 Chemicals and Purity Testing

All chemicals used in response factor determination and peak identification were purchased from the Aldrich Chemical Company, Milwaukee, Wisconsin. Before any quantitative analysis was carried out, each chemical was separately injected into the H-P 5880A gas chromatograph to insure sample purity. All chemicals were found to be at least 99% pure. Any trace of impurities were noted and true weight percents were taken into account when determining response factors.

2.4 Column Selection

2.4.1 Types of Columns Tested

The columns which were tested for their ability to separate all products produced in the higher alcohol synthesis are listed below and the reasons for selecting each column are given subsequently.

A.) Bonded Methyl Silicone Wide Bore Capillary Column.

60 m x 0.75 mm ID; 1.00 μ m film thickness.

B.) 50% Phenyl Methyl Silicone Capillary Column.

30 m x 0.32 mm ID; 1.00 μ m film thickness.

C.) Carbowax Capillary Column

26 m x 0.33 mm ID; 1.4 μ m film thickness.

Column A was selected because it is nonpolar and permits elution of most samples in order of their boiling points and carbon numbers. The stationary phase is often used for the separation of solvents, petroleum products, and other industrial chemicals. The inertness of this column allows acidic, basic, and other active compounds to be separated. The operating temperature range of this column is 0°C to 360°C (5) which was the temperature range of the boiling points of all the higher alcohol synthesis products. Also, the column could accept 15,000 ng per component, thus allowing injection of relatively large samples.

Column B was selected because the phenyl methyl silicone stationary phase is very polar. This allows separation of alcohols, solvents, oils, and aromatic isomers. However, the sample size is limited to 100 ng per component because of the column narrow diameter (4).

Column C was chosen for testing because Carbowax (Dimethyl Silicone) is said to separate alcohols, solvents, and halogenated compounds (4).

All columns were tested under various flow rates, oven conditions, and with different solvents to find the optimum column for the desired product analysis.

2.4.2 Solvent Testing

The C₁ through C₃ products required oven temperatures between 30°C - 35°C for the separation of components. For good separation initial oven temperature should always be 10-30 degrees Celcius below the boiling point of the solvent. With initial conditions already specified by the requirement of the C₁ through C₃ product separation, the following solvents were tested:

<u>Solvent</u>	<u>Boiling Point (°C)</u>	<u>Initial Oven Temp. (°C)</u>
n-Pentane	36	10-25
n-Hexane	69	40-60
n-Heptane	98	70-90

Aside from diluting the higher alcohol synthesis products in these solvents, the products were injected without being diluted in a solvent and the resolution and separation of peaks in the solvent-free sample was compared with the separation achieved when samples were diluted with each solvent. Sample solutions were always diluted to 2%-5% by weight to insure that the quantity of any component would not exceed the column's capacity.

2.5 Qualitative Analysis

2.5.1 Peak Identification

In order to identify all the components of the higher alcohol synthesis products, pure chemicals which were suspected to be components in the product mixture were mixed together, with no more than 3 chemicals added each time and then injected after each mixing until all the C₁ through C₆ alcohols, esters, aldehydes, ketones, hydrocarbons, and ethers suspected to be possible products were mixed into one sample, injected, and identified on one chromatogram. Each peak was identified, after being separated with the wide bore methyl silicone capillary column, by comparing its retention time in the complete mixture with the same peak's retention time in the simpler mixture with only a few components positively identified. The retention time of each peak was recorded and a master chromatogram shown in Figure XII was used to compare the retention times of the components of the reactor effluent for new samples with the retention times of the master chromatogram. To insure a correct identification of the reactor products, the samples were spiked with pure components, injected, and if the suspected peaks increased in size from the spiking of the presumed component then identification was completed.

2.5.2 Identification Technique for all Product Mixtures

To make the identification process as simple as possible and to eliminate the need for repeated spiking of samples, the conditions were always kept the same as those explained in the experimental sections 2.2 through 2.3 such that retention times were reproducible to within 0.02 minutes. All that need be done was to overlay the sample chromatogram on the master chromatogram shown in Figure XII and peaks were easily identified.

2.6 Quantitative Analysis

2.6.1 Determination of the FID Response Factors

Different materials have different responses to detectors. Previously, a few investigators determined the correction factors, or the response of a given component to the detecting devices (6,7,8,9). However, most of the work was done in the mid 1960's when the flame ionization detectors were first being used and improvements on the detectors were not wide spread. Therefore, the most important part of this research was to establish new response factors for the FID detector of the H-P Model 5880A GC. These response factors are not supplied by the manufacturer. The liquid samples obtained from Aldrich Chemical Company were each mixed with the internal standard cyclohexane which was arbitrarily assigned a value of 1.00. Each sample was diluted from 10% by weight to 1% by weight and the samples were each injected 3 times to determine the relative response factor for each particular C₁ through C₆ component. The average relative response factors for the hydrogen flame ionization detector are summarized in Table II. A sample calculation for obtaining these response factors from raw data is given in Appendix A.1.2.

2.6.2 Application of Response Factors to Product Analysis

After each sample was chromatographed and all peaks identified, the report given by the H-P 5880A GC terminal integrator was used along with the response factors of Table II to calculate the true weight and mol percents of all the higher alcohol synthesis products. Each peak area was divided by the relative sensitivity to get the true area. Normalizing the results gave the

weight percent of each component. Dividing each weight percent by the molecular weight of the component and once again renormalizing the results gave the true mol percent of each reactor product. Results for the recently tested Cu/Zn/Al/Cs catalyst are shown in Tables III, IV, VII, VIII, and sample calculations are given in Appendix A.1.3.

2.7 Cool On-Column Injection vs. Standard Injection at 220°C

A modification of cool-on-column injection was attempted by the author. Previous investigators (10) found that by installing an on-column sampling device, which extends into the first 2 mm to 3 mm of the capillary and forces the complete sample into the column at low temperatures (<70°C), that discrimination by volatility of sample constituents is minimal and only slightly dependent on the type of carrier gas. The H-P 5880A gas chromatograph used throughout the analysis was not equipped with this modified on-column injection port so to try and compensate for this the end of the wide bore bonded methyl-silicone capillary column was pushed approximately $1 \frac{1}{2}$ " into the splitless injection liner which was simply a 3" narrow bore glass tube. Injections were made into this system at 70°C and compared to injections made at the standard injection port temperature of 220°C. The results are shown later in the Results and Discussion section.

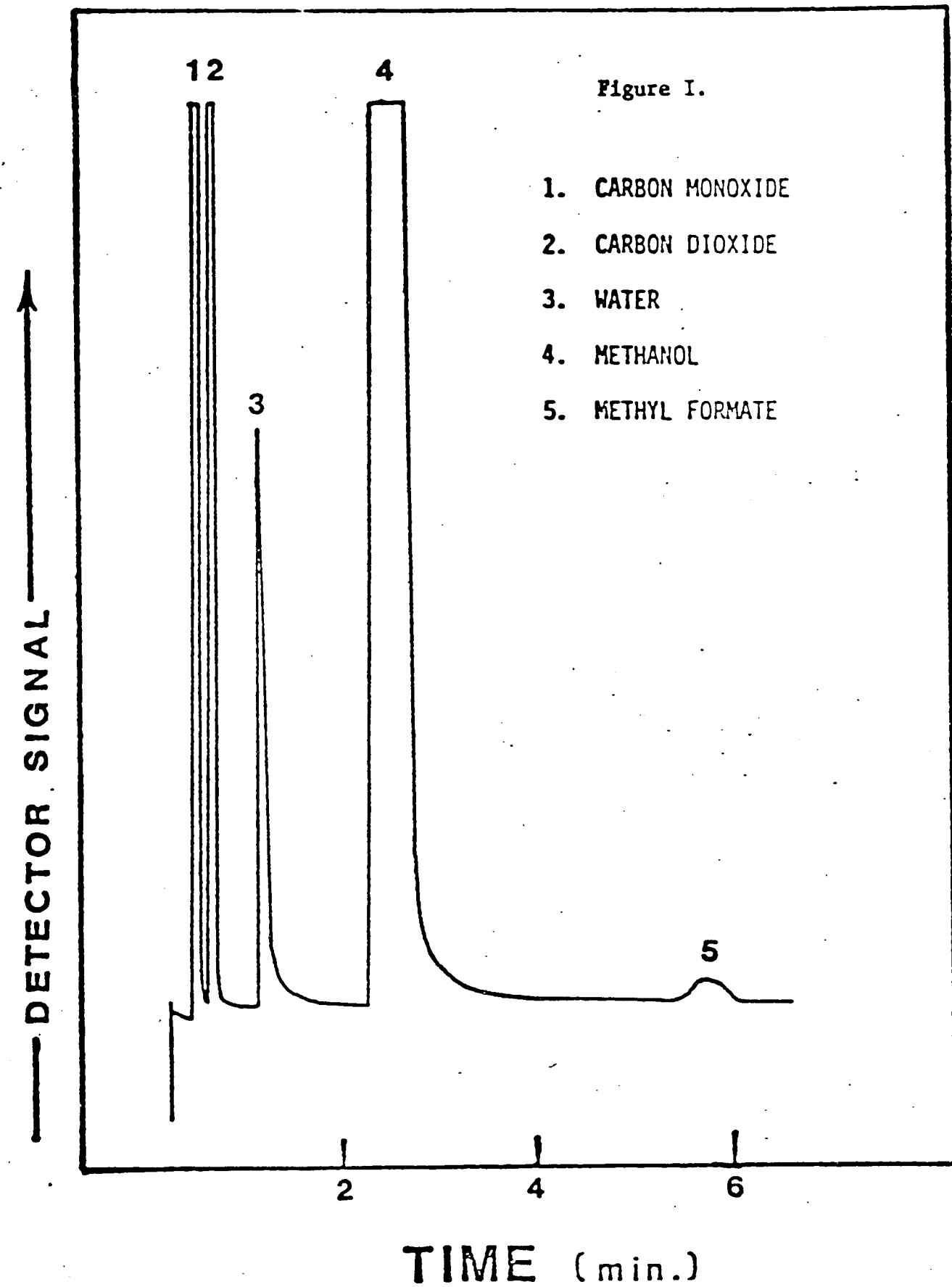
3.1 Results and Discussion

3.1.1 Qualitative Analysis

The selection of the appropriate capillary column for the total analysis of the C₁ through C₆ higher alcohol synthesis products by the Hewlett-Packard 5880A gas chromatograph equipped with a flame ionization detector is assisted

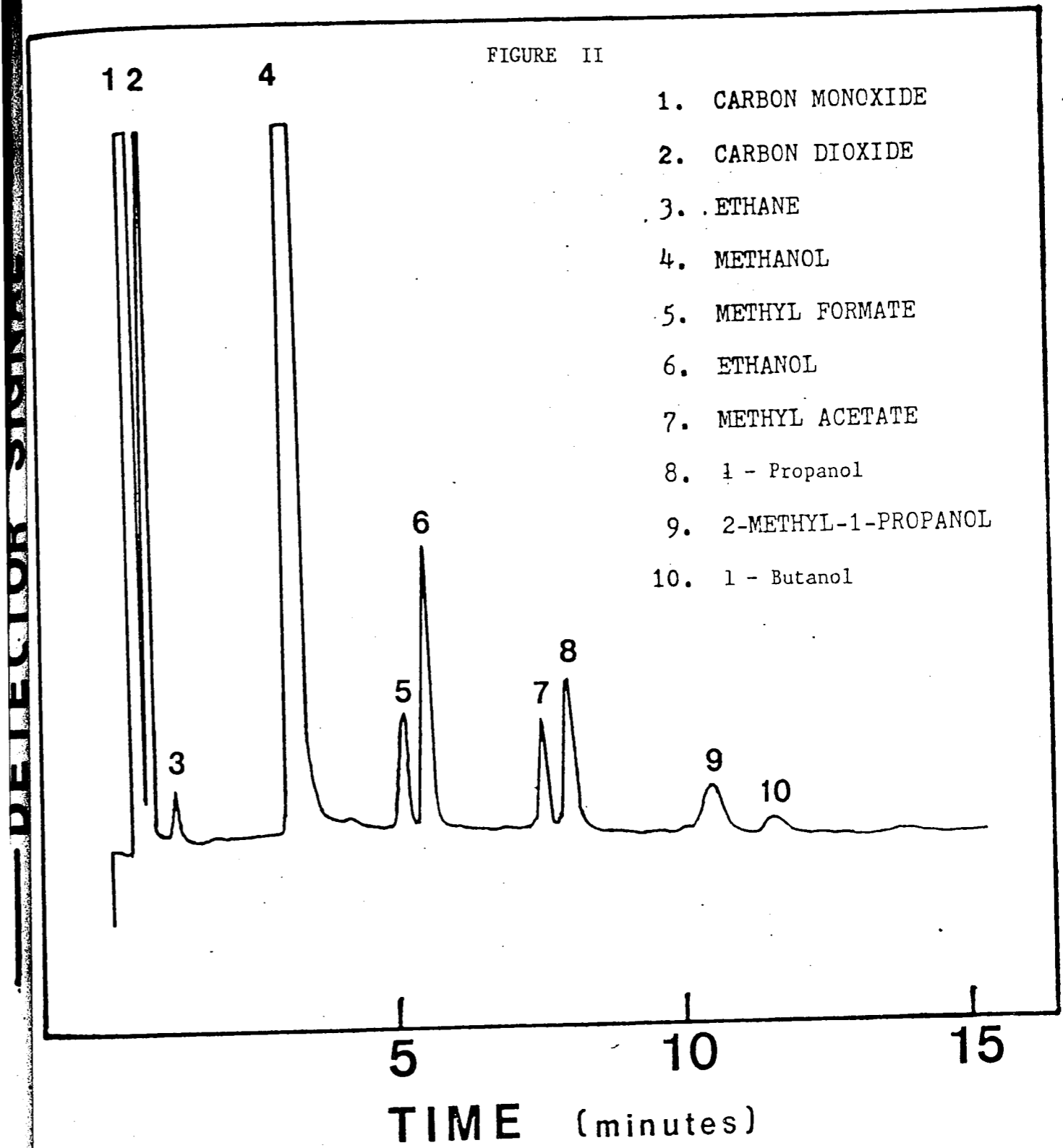
by an initial inspection of chromatograms obtained with the use of the Porapak Q packed column 6' by $\frac{1}{8}$ " diameter used in the Hewlett-Packard Model 5730A gas chromatograph equipped with a thermal conductivity (TC) detector. Figure I shows the separation of the reactor products of methanol synthesis achieved by the Porapak Q column. It must be remembered that catalysts in the previous research were studied with the primary emphasis on the methanol regime, at which the main product methanol is accompanied by a few C_1 and C_2 side products, and water. The Porapak Q column separated the few C_1 and C_2 products without any peak overlap or other analytical problems.

The analysis became more complex when studying the products obtained over the alkali-doped catalysts as seen in Figure II. Here products now ranged from C_1 through C_4 but could still be resolved on the Porapak Q column without much broadening or peak-overlap allowing quantitative work to be done accurately. The separation problem arose when products with a higher carbon number (C_5^+) were added to the feed gas. Figure III shows the gas chromatogram of higher alcohol synthesis products from the synthesis gases H_2 and CO with 2-methyl-1-propanol also being injected into the feed. The peaks overlapped to a large extent, particularly in the C_5 region where retention times were longer than those for the C_4 products. Peak number 6 in Figure III which was the overlap of 3-methyl-1-butanol and 2-methyl-1-butanol was later separated by the use of a bonded methylsilicone capillary column. This separation is seen in Figure IV-B where the bonded methyl silicone capillary column was used on the H-P 5880A GC with an FID detector. Here it was clearly seen how poorly the Porapak Q (Figure IV-A) actually resolved the product components. Spiking the Porapak Q column had led to erroneous identification



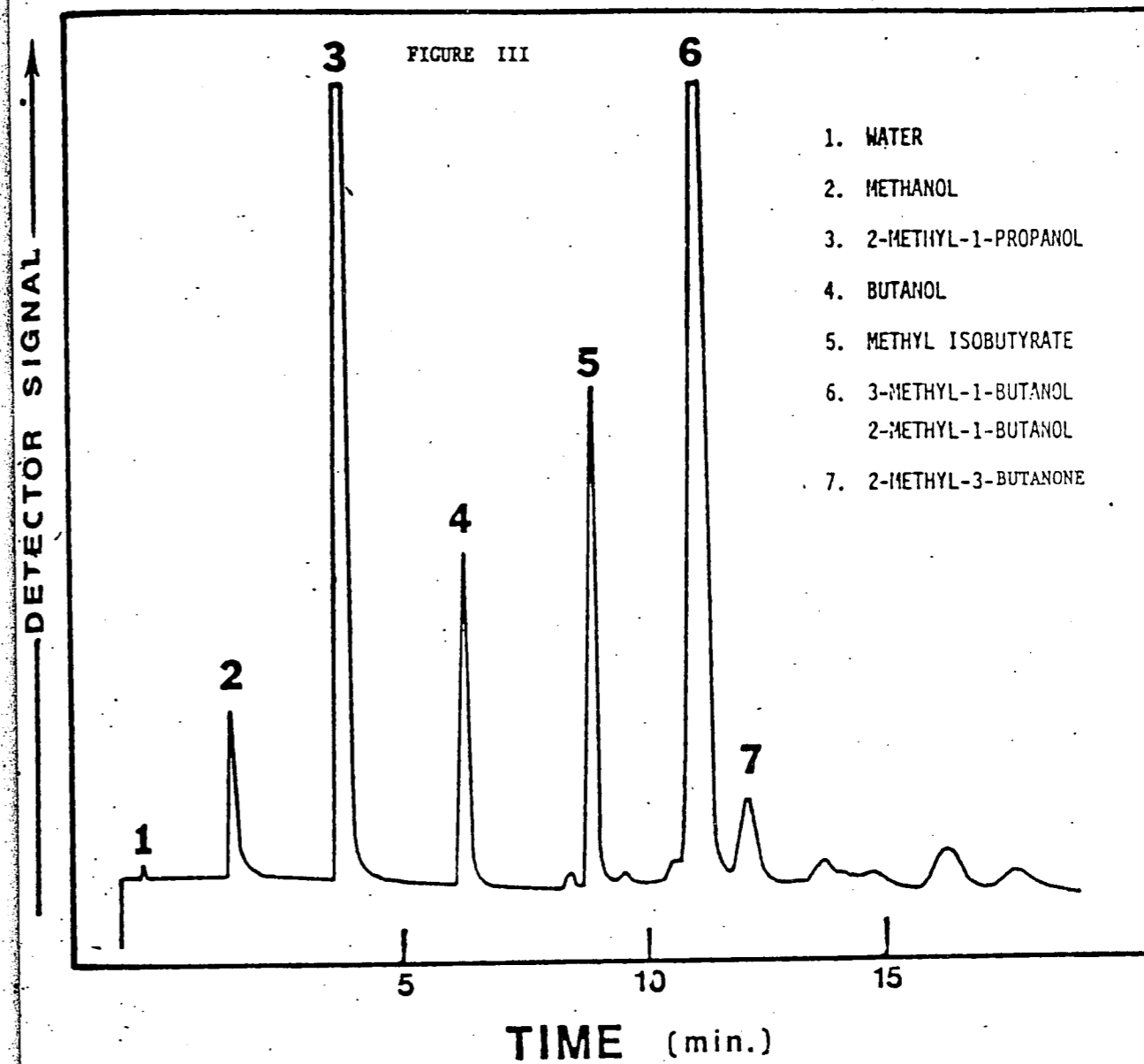
Gas Chromatogram of the Reactor Products for Methanol Synthesis from Synthesis Gas ($H_2/CO = 2.33$) at 15 l/hr, $288^\circ C$, 75 atm., over 2.45 gm. of a Cu/ZnO 30/70 Catalyst.

Column: Porapak Q. Isothermal Run at $90^\circ C$.



Gas Chromatogram of the Reactor Synthesis Products for Higher Alcohol Synthesis from Synthesis Gas ($H_2/CO = 0.45$) at 8 l/hr, $288^\circ C$, 75 atm., over 2.45 gm of a Cu/ZnO/KOH 30/70/0.4 Catalyst.

Column: Porapak Q.
 Temperature Program: Hold 2 min. at $90^\circ C$,
 then to $200^\circ C$ at $16^\circ C/min$.



Gas Chromatogram of the Reactor Products of Higher Alcohol Synthesis from Synthesis Gas ($H_2/CO = 0.45$) at 8 l/hr, $309^\circ C$, 75 atm., and Pumping 2-Methyl-1-Propanol at $5.0 \mu l/min.$ over 2.45 gm of a Cu/Zn/Cs 30/70/0.4 Atomic Percent Catalyst Doped with CsOOC after Calcination.

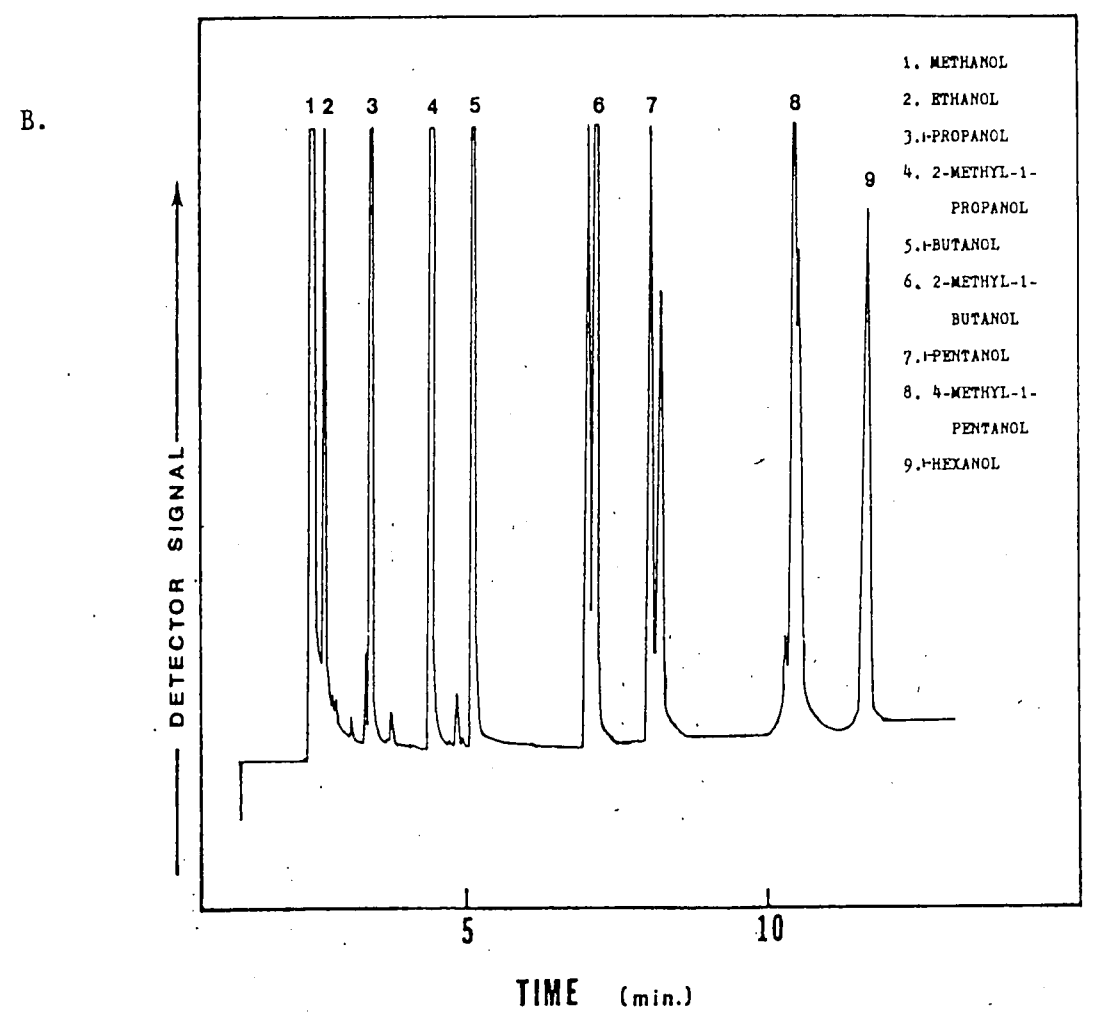
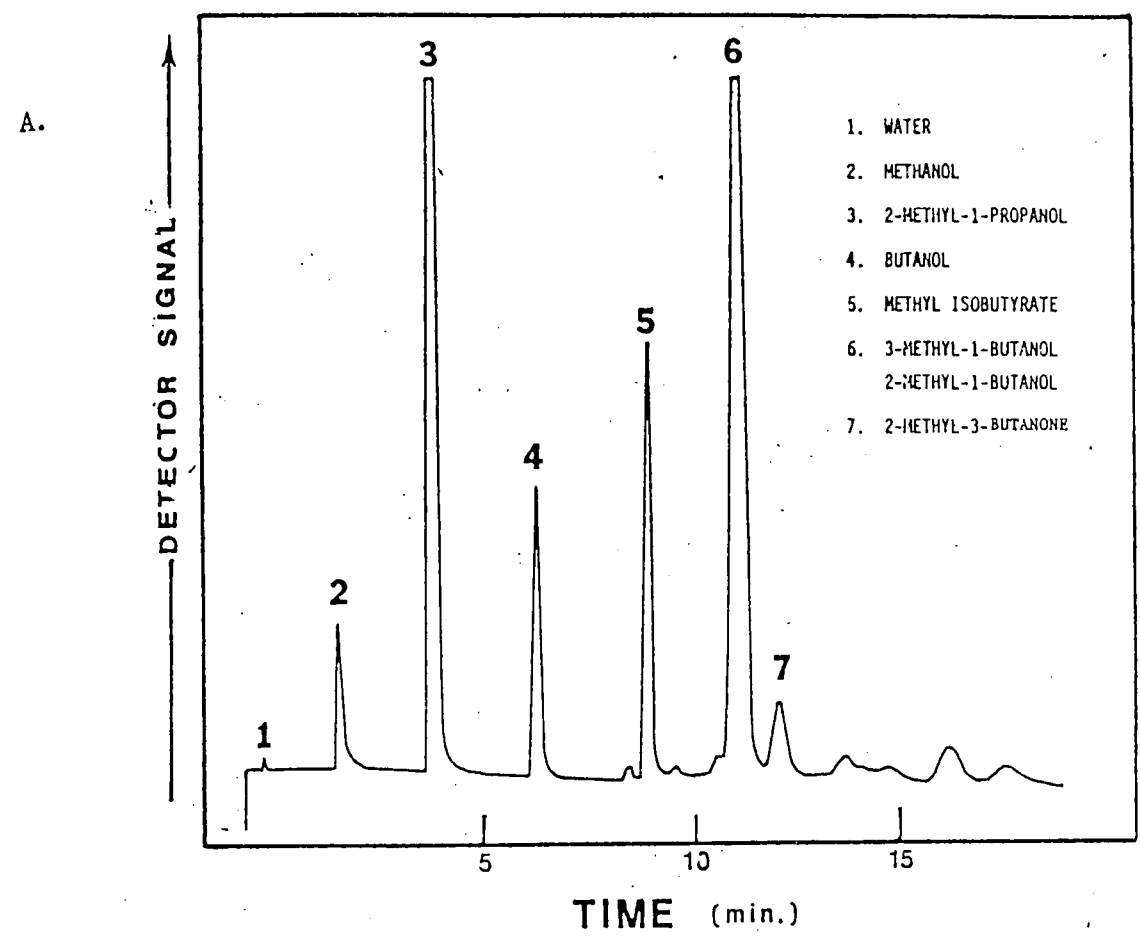
Column: Porapak Q.

Temperature Program: Hold 2 min. at $90^\circ C$, then to $200^\circ C$ at $16^\circ C/min.$

of higher alcohol synthesis products, because as Figure IV-B shows, one broad peak in Figure IV-A was actually a combination of a few minor, but vital, products needed for accurate mechanistic and modelling studies to be conducted. Unless products were completely separated, even the use of a GC/mass spectrometer would give ambiguous identifications.

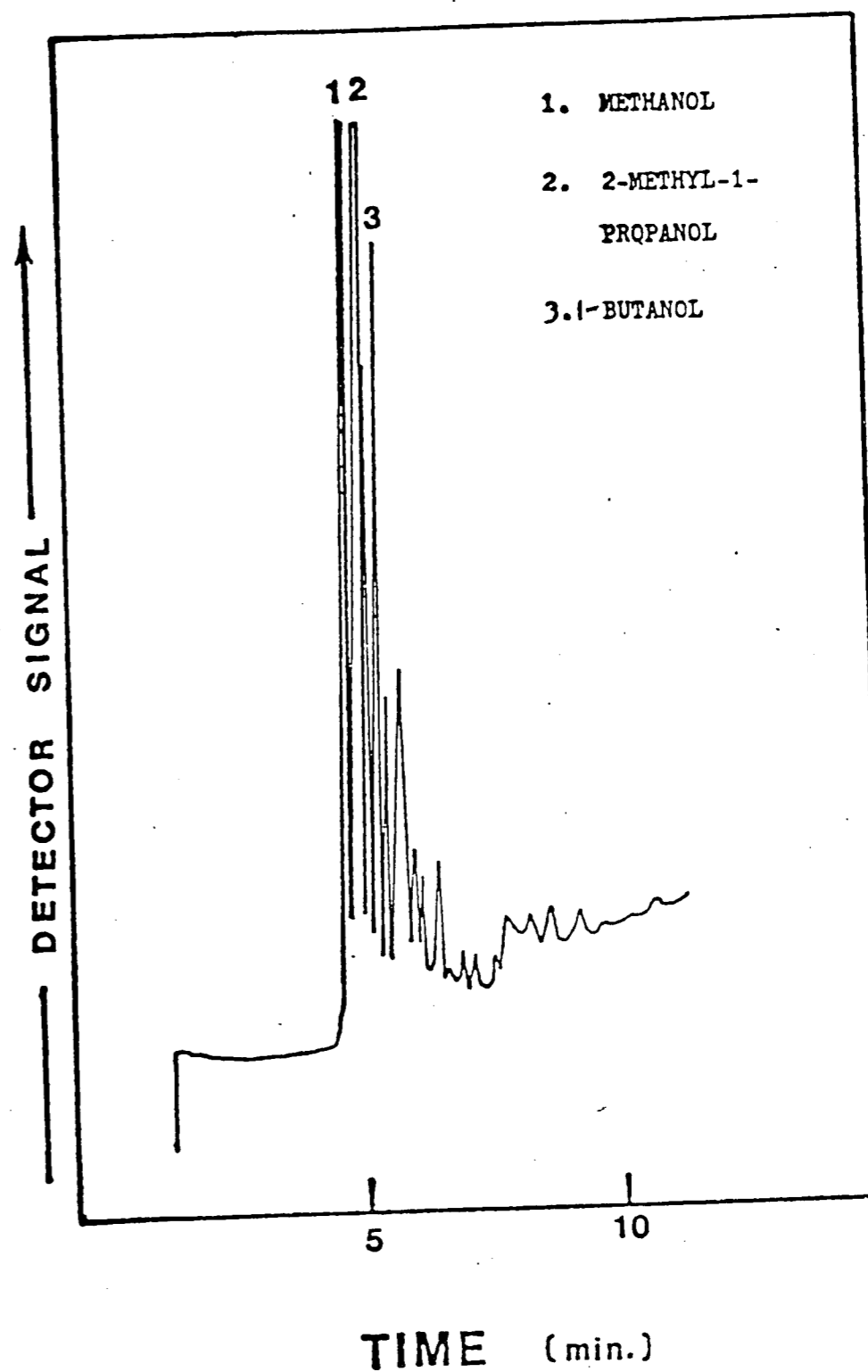
The chromatogram in Figure IV-B showed that the use of a smaller diameter and longer column length of a capillary column would give the more efficient separation of the complex higher alcohol synthesis product mixtures. Three columns having different types of stationary phase coating the capillary column were investigated with a view of providing an optimum separation of all isomers present and to also permit analyses of samples with wide concentration ranges. Previously, Carbowax columns have been used for the separation of C_1 through C_5 alcohols or mixtures of alcohols with other low molecular weight compounds (11,12,13,14). The Carbowax, because of its high polarity, seemed to be a reasonable choice for separation of alcohols, esters, aldehydes, and ketones, so a 26m x 0.33mm ID Carbowax column with a 1.4 μ m film thickness was tested at various flow rates and different oven temperature programs. The best separation obtained with this column was not good enough to resolve the higher alcohol synthesis products as Figure V demonstrated for the C_5 and C_6 regions. The column examined next was a 50% phenyl methyl silicone capillary column 30m x 0.32mm ID with a 1.00 μ m film thickness. Various flow rates and a large temperature range were studied, and one of the better separations of the complex higher alcohol mixture is shown in Figure VI. Separation is very poor with peaks eluting from the column too close together. The high degree of overlap indicated complete identification and quantification were once again

FIGURE IV



Comparison of the Porapak Q packed column (A) to the Bonded Methyl Silicone capillary Column (B).

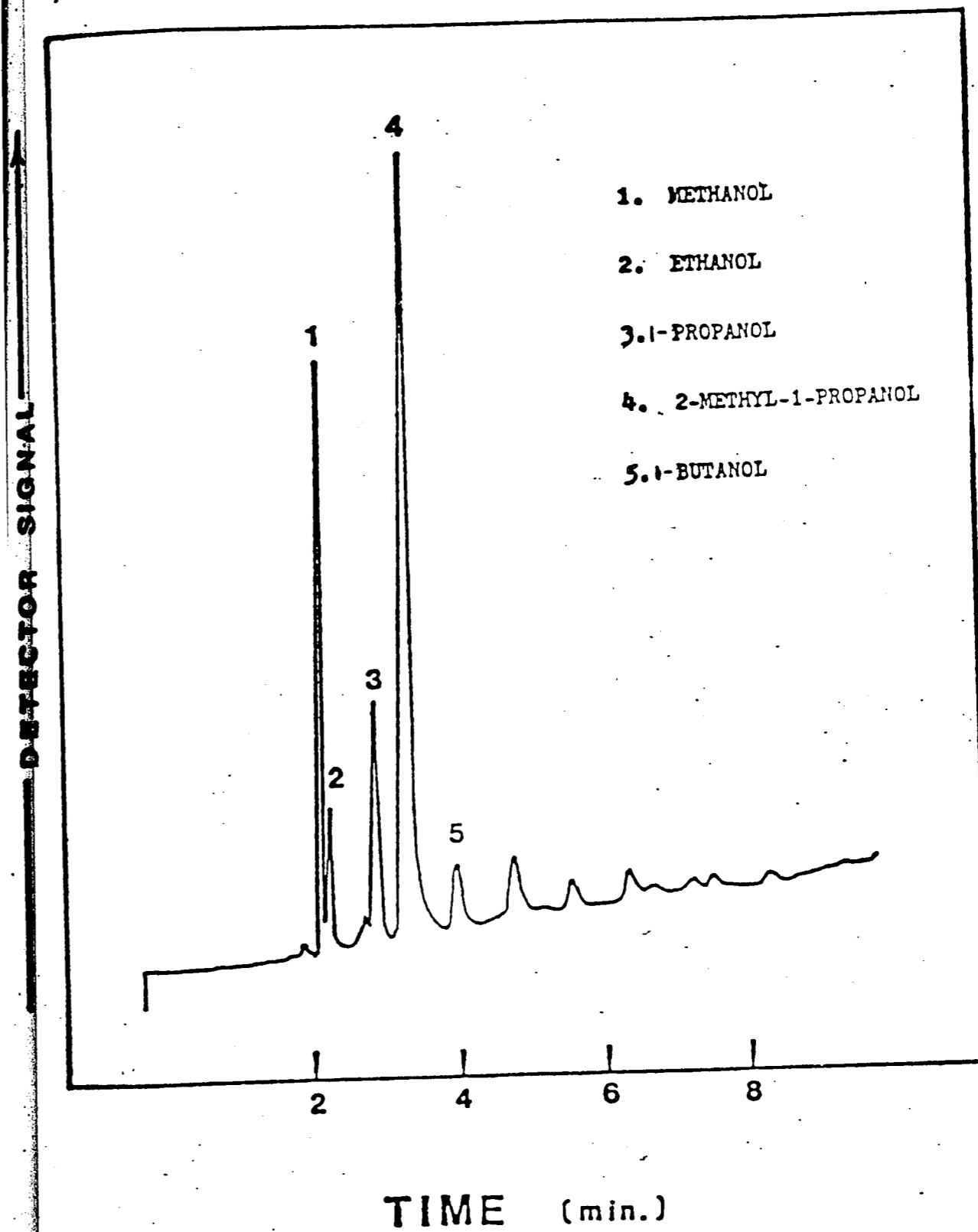
Figure V



Gas Chromatogram of the Higher Alcohol Synthesis Products over a Cu/ZnO/Cs 30/70/0.4 Catalyst.

Column: 50% Phenyl Methyl Silicone Capillary Column.
- Very Polar Phase -

Figure VI



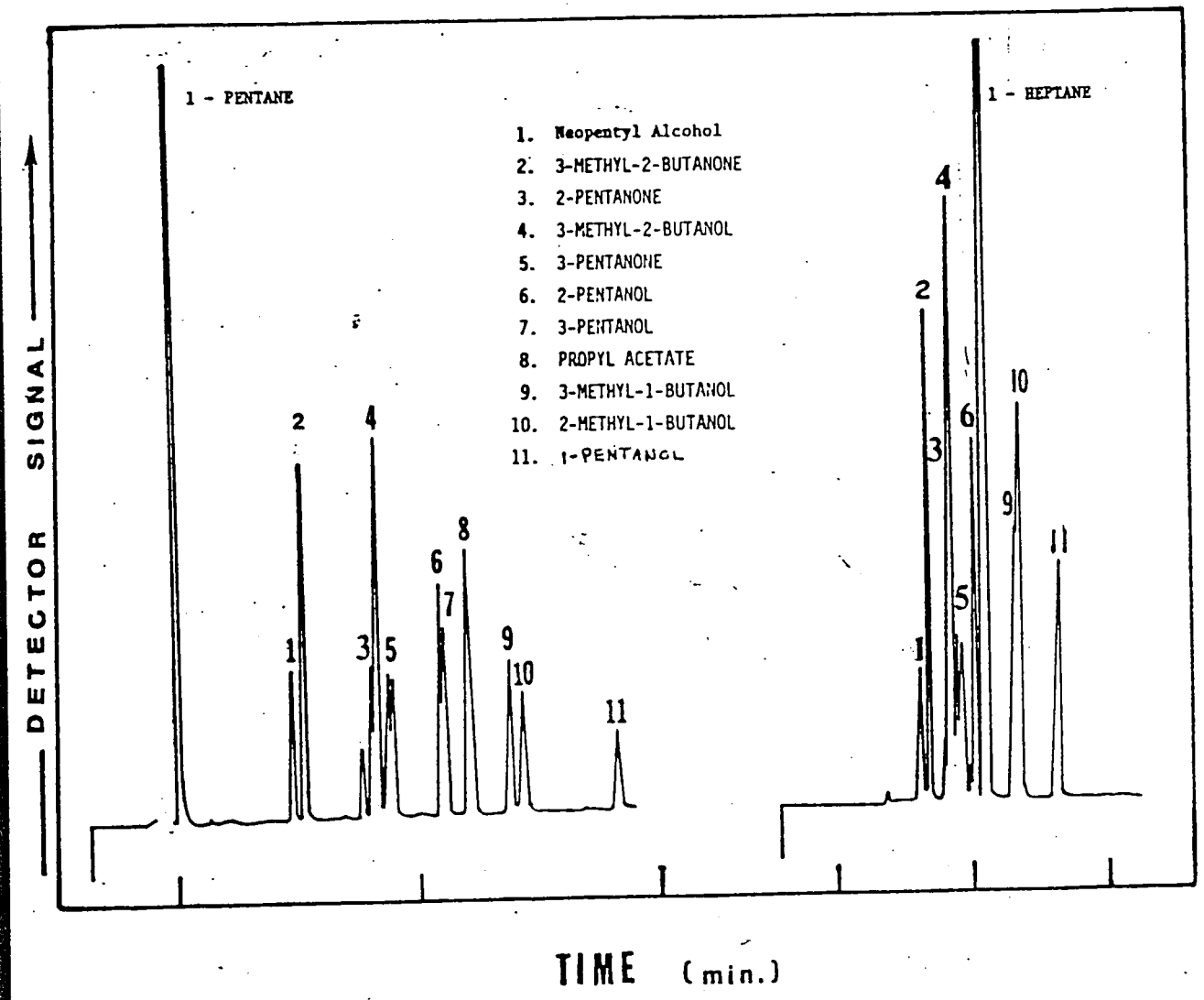
Gas Chromatogram of the Higher Alcohol Synthesis Products over a Cu/ZnO/Cs 30/70/0.4 Catalyst.

Column: Carbowax Capillary Column.
- Polar Phase -

not possible. The last column chosen was the bonded methyl silicone wide bore capillary column 60m x 0.75mm ID. This column is non-polar and generally permits elution of most samples in the order of boiling points and carbon numbers (11). The column, when tested under varying flow rates and different oven temperature programs, provided the desired separation and resolution of the higher alcohol products as seen in Figure IV-B. The C_1 through C_6 regions have been separated as indicated by the labelled peaks in the chromatogram. A complete identification of all the components in the C_1 through C_6 range is shown in Figure XII. The larger diameter of this wide bore bonded methyl silicone column also enabled relatively large sample volumes (15,000 ng per component) to be injected.

After selection of the bonded methyl silicone column and an optimum temperature program for the analysis (Experimental Section 2.2.1 - 2.2.2), experiments were carried out to determine whether further resolution of the components could be obtained by utilizing different solvents. 1-Pentane and 1-heptane solutions were compared to the original undiluted higher alcohol sample, and Figure VII shows the sample in both solvents. 1-Pentane appeared to be the better of the two solvents because the C_5 components were more completely separated and the solvent did not overlap with any of the components as is the case with 1-heptane which obscures 2-pentanol and 3-pentanol. 1-Pentane also enabled the separation of 2-methyl-1-butanol and 3-methyl-1-butanol, where as 1-heptane did not separate these two components making quantification difficult. The same degree of resolution as obtained with the 1-pentane solvent system was obtained from the pure sample with no solvent added. This is probably due to the fact that methanol and a few of the other

FIGURE VII



Gas Chromatogram of the C₅ Alcohols in the Solvents Pentane and Heptane.

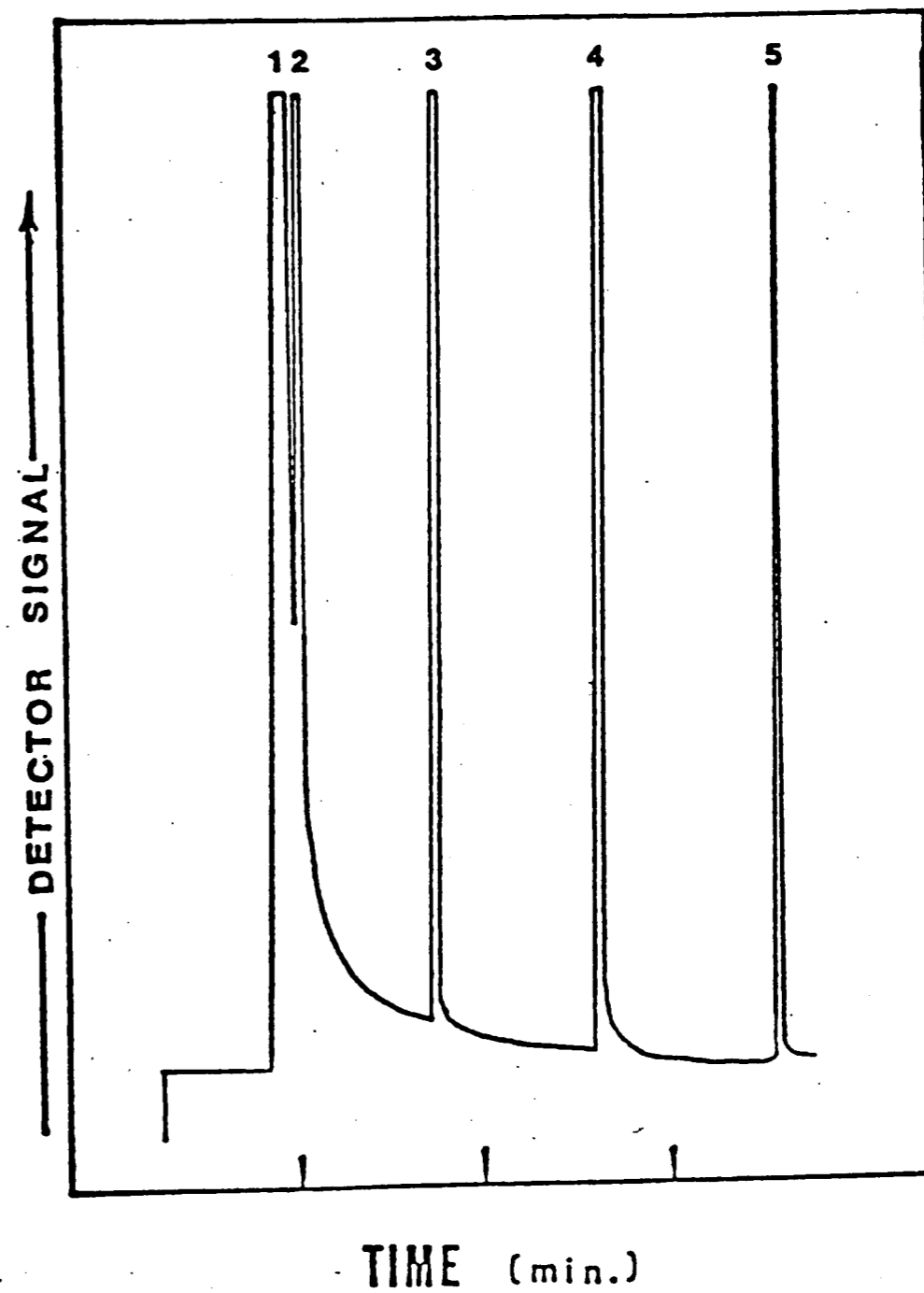
Column: Wide Bore Bonded Methyl Sil-cone Capillary Column.
- Nonpolar Phase -

lower alcohols were present in such large amounts that they acted as a solvent for the product mixture of the type investigated here.

The last phase of the qualitative analysis involved the comparison of two different injection techniques to see if this aided the separation of components. The technique of cool "on-column" injection involved having a modified injection port (10) where the end of a glass injection port liner was tapered to fit into the end of the capillary column. This technique could not be used because the bonded methyl silicone capillary column inside diameter of 0.75mm was too narrow for any existing glass liners.

Therefore, a modified technique of pushing the end of the capillary column into a spitless injection port liner $1\frac{1}{2}$ " was tested. The injection port temperature was kept at 70°C and a standard mixture of C₁ through C₆ compounds was injected. The resulting chromatogram is shown in Figure VIII. This same mixture was injected at the normal operating temperature of 220°C as shown in Figure IX. At 220°C the injected sample showed the presence of a few small peaks, which were not present when the modified cool injection technique was used. These small peaks may have been the result of one or more of the higher molecular weight components in the mixture decomposing under the high temperature condition. These peaks were not present for the cool "on-column" injection at 70°C. However, when quantitative results were compared for the two different injection techniques, the injection temperature of 220°C provided the most accurate analysis with only a 0.1% deviation from the actual weight percent of the standard mixture. Therefore, the cool "on-column" injection technique was discarded and all further injections were done at 220°C.

Figure VIII

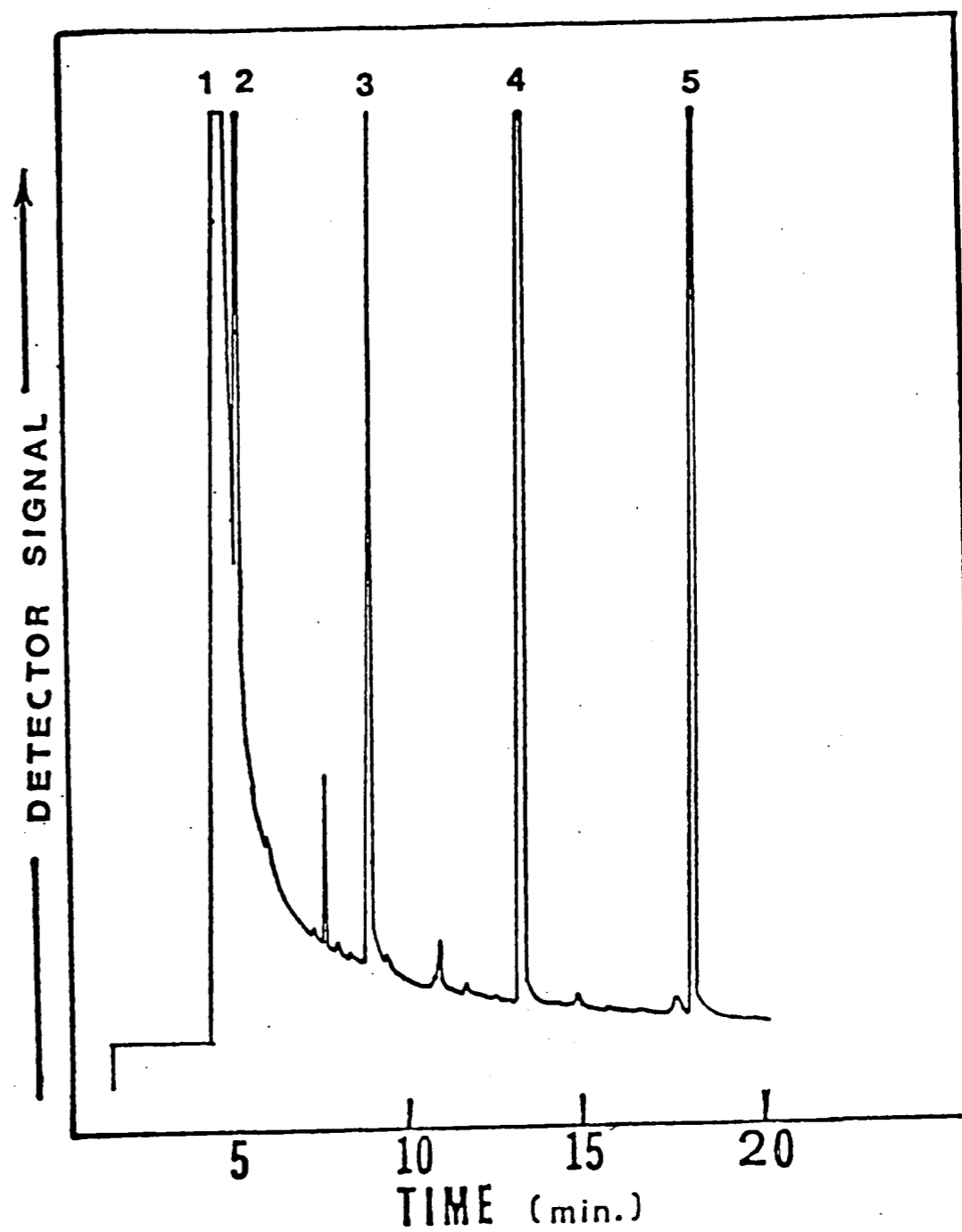


Wide Bore Methyl Silicone Capillary Column with the Injection Temperature being 70°C.

Components:

1. Methanol
2. 2-Propanol
3. 3-Methyl-2-Butanol
4. 2-Hexanol
5. Methyl Caproate

Figure IX



INJECTION AT 220°C.

WIDE BORE BONDED METHYL SILICONE CAPILLARY COLUMN

COMPONENT

1. METHANOL
2. 2-PROPANOL
3. 3-METHYL-2-BUTANOL
4. 2-HEXANOL
5. METHYL CAPROATE

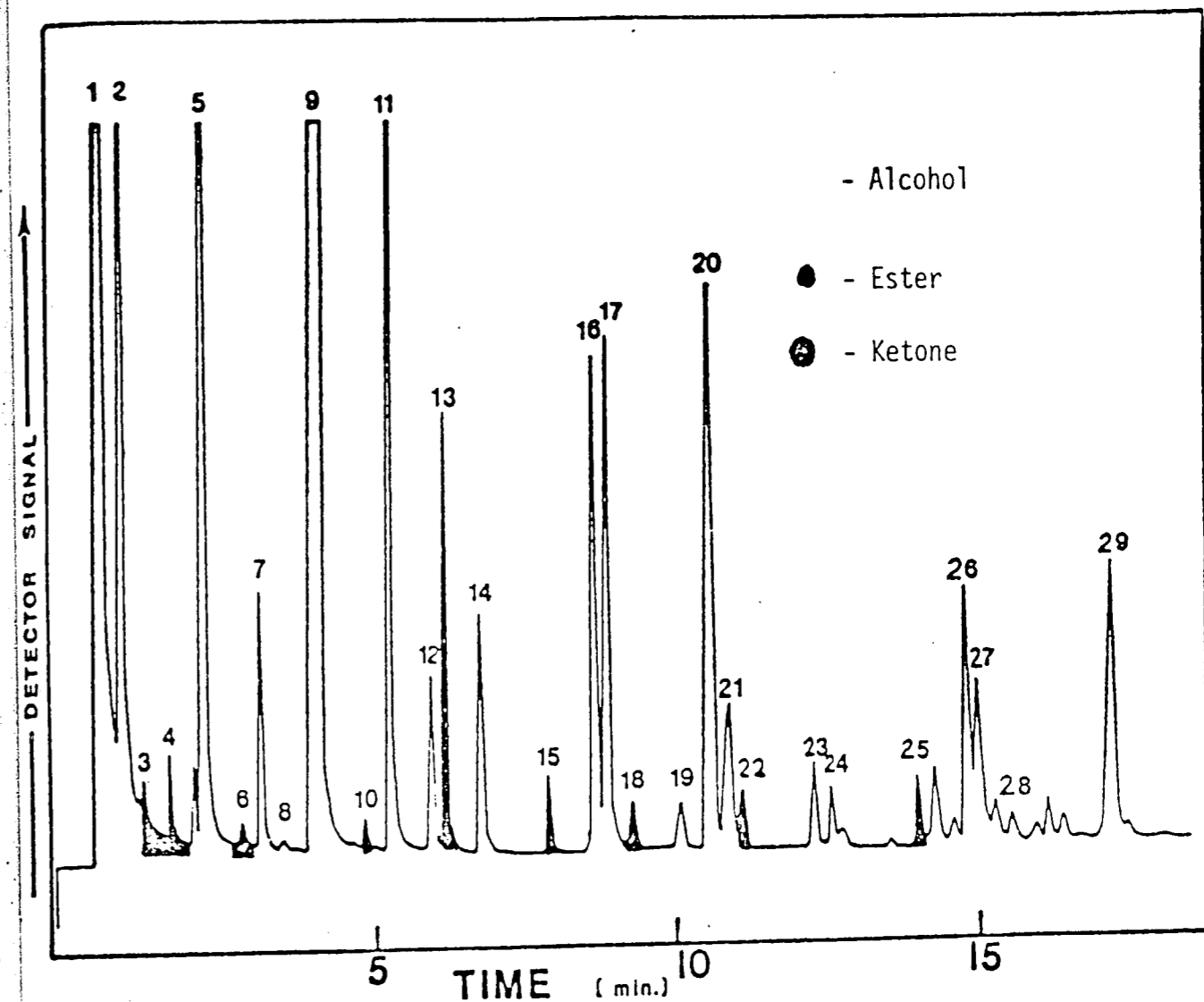
Samples of products of CO hydrogenation were collected over a range of conditions on a standard Cu/Zn/Cs catalyst doped with CsOOCH after calcination with a metal atomic ratio of 30/70/0.4. The chromatographic result is shown in Figure X. The reactor conditions during the collection are spelled out in the figure legend. Another sample was collected at a more severe condition of 309PC and it is seen in Figure XI that the wide bore bonded methyl silicone capillary column was still able to separate the higher alcohol products in the C₅ and C₆ region, making this column very suitable for total analysis of higher alcohol synthesis products. Figure XII shows a manually injected mixture of all the C₁ through C₆ possible components contained in one standard and under the same conditions as all previous injections. When the helium carrier gas flow was kept at 7.32 ml/min as described in the experimental section, Figure XII could be used as a master chromatogram to identify all the C₁ through C₆ components for the products of any catalyst testing generating oxygenates of the investigated type. Table I lists the identity of each peak with its corresponding retention time. The retention times are reproducible to within ± 0.01 minutes and allow components to be easily identified. A copy of the master chromatogram (Figure XII) was left on file in the Mudd Building, room 182 for future use.

3.2 Quantitative Results and Discussion

3.2.1 Response Factors

One of the major tasks of this research was to prepare a table of the relative sensitivity values for all the possible C₁ through C₆ components using the flame ionization detector of the Hewlett-Packard 5880A gas chromatograph. This was needed because every compound responds differently to the detector and

Figure X



GAS CHROMATOGRAM OF THE REACTOR PRODUCTS FOR HIGHER ALCOHOL SYNTHESIS FROM SYNTHESIS GAS ($H_2/CO = 0.45$) AT 8 l/hr, 290 °C, 75 ATM, AND PUMPING 2-METHYL-1-PROPANOL AT 5.0 ml/min. OVER THE CATALYST:

Cu/Zn/Cs THEORETICAL METAL MOLAR RATIO = 30/70/0.4
DOPED WITH CsOOC AFTER CALCINATION.

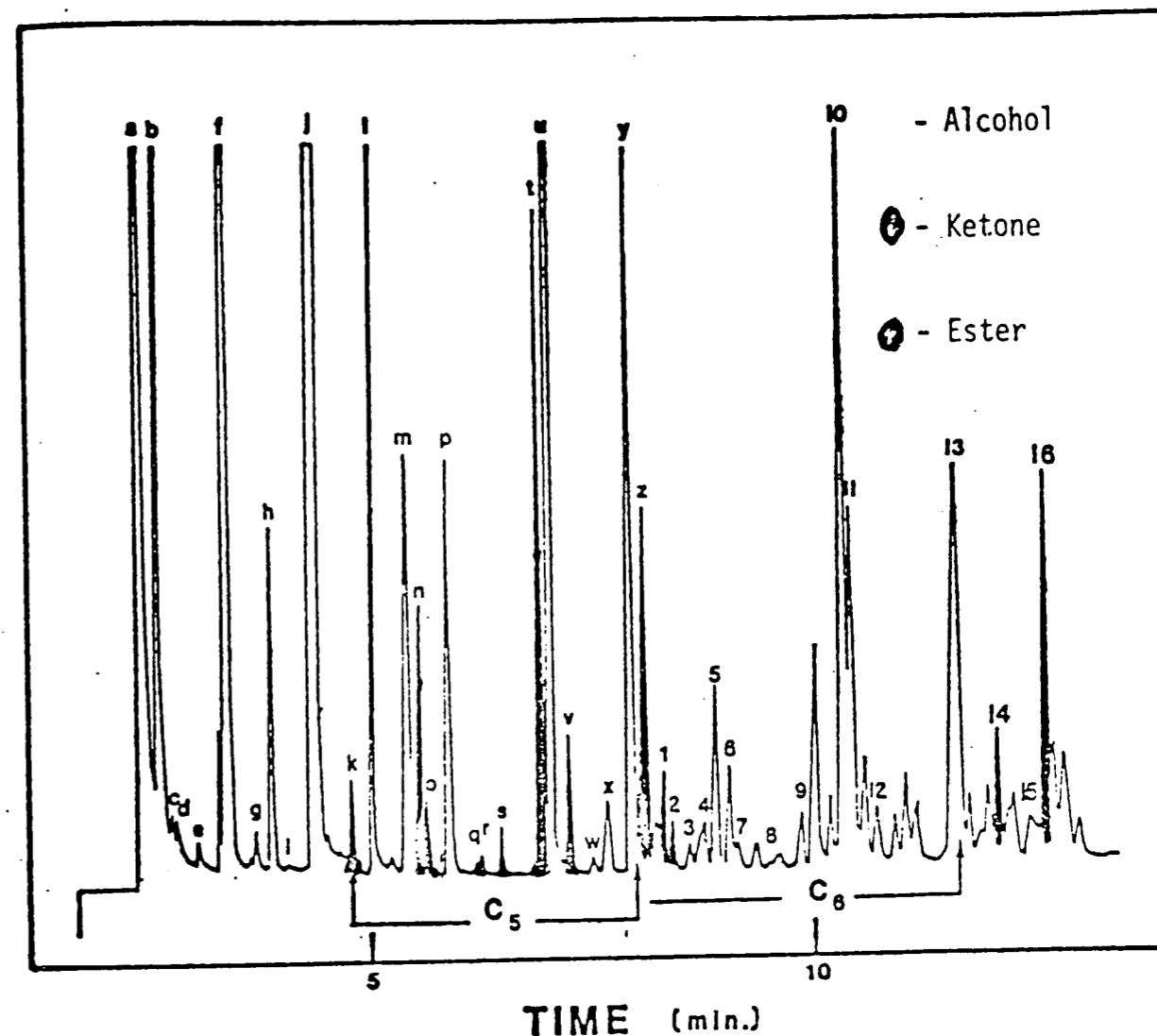
COLUMN: BONDED METHYL SILICONE WIDE BORE CAPILLARY COLUMN.

TEMPERATURE PROGRAM: HOLD 25 SEC. AT 25 °C, THEN TO 100 °C AT 3.0 °C/min.

COMPONENTS:

1. METHANOL	11. 1-BUTANOL	21. 2-METHYL-3-PENTANOL
2. ETHANOL	12. 3-METHYL-2-BUTANOL	22. 3-HEXANONE
3. ETHYL FORMATE	13. METHYL ISOBUTYRATE	23. 3-HEXANOL
4. METHYL ACETATE	14. 2-PENTANOL, 3-PENTANOL	24. 2-HEXANOL
5. 1-PROPANOL	15. METHYL BUTYRATE	25. METHYL PENTANOATE
6. BUTYRALDEHYDE	16. 3-METHYL-1-BUTANOL	26. 4-METHYL-1-PENTANOL
7. 2-BUTANOL	17. 2-METHYL-1-BUTANOL	27. 2-ETHYL-1-BUTANOL
8. ETHYL ACETATE	18. 2-METHYL-3-PENTANONE	28. 3-METHYL-1-PENTANOL
9. 2-METHYL-1-PROPANOL	19. 4-METHYL-2-PENTANOL	29. 1-HEXANOL
10. 3-METHYL-2-BUTANONE	20. 1-PENTANOL	

Figure XI

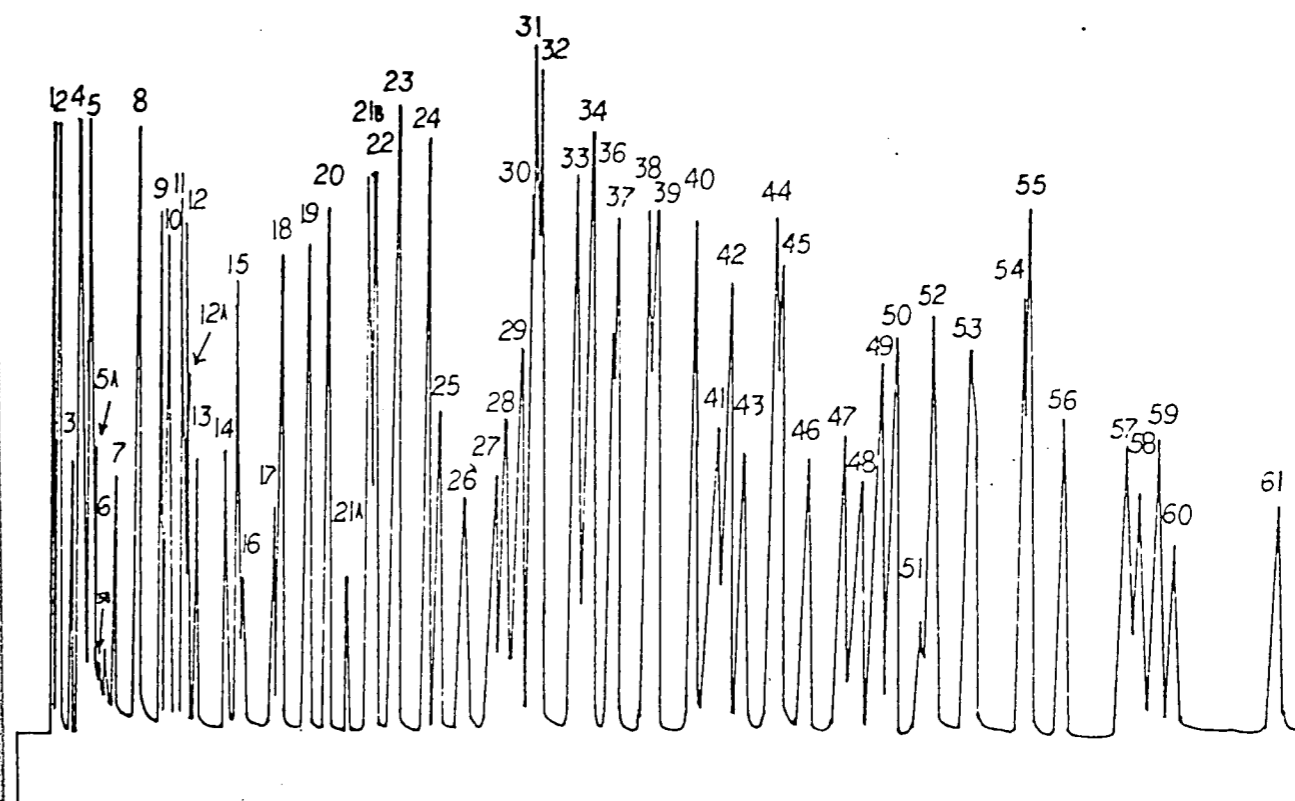


REACTOR PRODUCTS FOR HIGHER ALCOHOL SYNTHESIS FROM SYNTHESIS GAS ($H_2/CO = 0.45$) AT 309 °C, 75 ATM, AND PUMPING 2-METHYL-1-PROPANOL AT 5.0 μ l/min. OVER Cu/Zn/Cs WITH A THEORETICAL MOLAR RATIO OF 30/70/0.4.
 COLUMN: WIDE BORE BONDED METHYL SILICONE CAPILLARY COLUMN.

COMPONENTS:

- | | | |
|------------------------|---|-------------------------|
| A. METHANOL | P. 2-PENTANOL, 3-PENTANOL | 5. 3-HEXANOL |
| B. ETHANOL | Q. ETHYL PROPIONATE | 6. 2-HEXANOL |
| C. PROPIONALDEHYDE | R. PROPYL ACETATE | 7. ETHYL BUTANOATE |
| D. ETHYL FORMATE | S. METHYL BUTYRATE | 8. BUTYL ACETATE |
| E. METHYL ACETATE | T. 4-METHYL-2-PENTANONE | 9. METHYL PENTANOATE |
| F. 1-PROPANOL | U. 3-METHYL-1-BUTANOL
2-METHYL-1-BUTANOL | 10. 4-METHYL-1-PENTANOL |
| G. BUTYRALDEHYDE | V. 2-METHYL-3-PENTANONE | 11. 2-ETHYL-1-BUTANOL |
| H. 2-BUTANOL | W. 2-METHYL VALERALDEHYDE | 12. 3-METHYL-1-PENTANOL |
| I. ETHYL ACETATE | X. 4-METHYL-2-PENTANOL | 13. 1-HEXANOL |
| J. 2-METHYL-1-PROPANOL | Y. 1-PENTANOL | 14. 2-HEPTANONE |
| K. 3-METHYL-2-BUTANONE | Z. 2-METHYL-3-PENTANONE | 15. 4-HEPTANOL |
| L. 1-BUTANOL | 1. 3-HEXANONE | 16. PROPYL BUTANOATE |
| M. 3-METHYL-2-BUTANOL | 2. 2-HEXANONE | |
| N. METHYL ISOBUTYRATE | 3. 3-METHYL-2-PENTANOL | |
| O. 3-PENTANONE | 4. 1-HEXANAL | |

Figure XII



Gas Chromatogram of all the Possible C_1 through C_6 Components for higher alcohol synthesis.

Column: Bonded Methyl Silicone Capillary Column
Numbers correspond to Peak Identification which are given in Table I.

TABLE I

Retention times for all the C₁ through C₆ components shown in Figure XII, and done on the bonded methyl silicone wide bore capillary column with helium carrier flow of 7.32 ml/min at the start of injection

<u>Peak Number</u>	<u>Component</u>	<u>Relative Retention Time (min)</u>
1	Methane	3.62
2	Ethane	3.66
3	Propane	3.76
4	Dimethyl Ether	3.82
5	Methanol	3.93
5A	Acetaldehyde	3.95
6	Butane	4.05
7	Methyl Formate	4.11
8	Ethanol	4.29
9	Propionaldehyde/Acetone	4.54
10	2-Propanol	4.66
11	1-Pentane	4.82
12	Ethyl Formate	4.87
12A	Diethyl Ether	4.90
13	Methyl Acetate	5.03
14	Isobutyraldehyde	5.42
15	1-Propanol	5.57
16	Formaldehyde	5.60
17	Butyraldehyde	6.04
18	2-Butanone	6.14
19	2-Butanol	6.50
20	Ethyl Acetate	6.75
21A	Propyl Formate	7.12
21B	2-Methyl-1-Propanol/Methyl Propionate	7.29
22	Tertiary Butyl Formate	7.34
23	Tertiary Pentyl Alcohol	7.67
24	3-Methyl-2-Butanone	8.07
25	2-Methyl-1-Butyraldehyde	8.23
26	1-Butanol	8.58

TABLE I (continued)

<u>Peak Number</u>	<u>Component</u>	<u>Relative Retention Time (min)</u>
27	Neopentyl Alcohol	8.96
28	2-Pentanone	9.09
29	3-Methyl-2-Butanol	9.28
30	Methyl Isobutyrate	9.40
31	1-Valeraldehyde	9.48
32	3-Pentanone	9.56
33	2-Pentanol	10.06
	3-Pentanol	10.08
33A	IsoOctane	10.09
34	Pinacolone	10.24
36	Ethyl-Propionate	10.50
37	Propyl Acetate	10.59
38	Methyl Butyrate	11.04
39	Isobutyl Formate	11.11
40	2-Methyl-2-Pentanol	11.68
40A	4-Methyl-2-Pentanone	11.69
41	3-Methyl-1-Butanol	11.92
42	2-Methyl-1-Butanol	12.11
43	2-Methyl-3-Pentanone	12.29
44	3-Methyl-3-Pentanol	12.68
45	2-Methyl-Valeraldehyde	12.76
46	4-Methyl-2-Pentanol	13.12
47	1-Pentanol	13.61
48	2-Methyl-3-Pentanol	13.81
49	3-Hexanone	14.07
50	2-Hexanone	14.25
51	3-Methyl-2-Pentanol	14.61
52	1-Hexanol	14.76
53	2-Hexanol	15.30
53A	Ethyl-Butyrate	15.31

TABLE I (continued)

<u>Peak Number</u>	<u>Component</u>	<u>Relative Retention Time</u>
54	Butyl-Acetate	16.02
55	1-Octane	16.10
56	Ethyl-Butyrate	16.56
57	2-Methyl-1-Pentanol	17.37
58	4-Methyl-1-Pentanol	17.56
59	2-Ethyl-1-Butanol	17.79
60	3-Methyl-1-Pentanol	18.01
61	1-Hexanol	19.41
62	Methyl-Pentanoate	20.22

to produce accurate quantitative results the response factors must be used to account for the varying FID sensitivities of all the compounds. Previously, Dietz (6) and Messner (7) produced relative response factors for a number of compounds, but the list had to be expanded for our use, and rechecked for possible errors in the old values. Table II lists the response factors which were determined for the FID detector and also shows the old values determined by Dietz and Messner. The experimental procedure for these factors was discussed in section 2.6.1 and a sample calculation is given in Appendix 2.6.2 showing how to apply the response factors to obtain from peak areas the weight percents and mol percents of all the products.

3.3 Total Analysis of the Products Generated over a Cu/Zn/Al/Cs Catalyst

The complete analysis of higher alcohol synthesis products by capillary column gas chromatography was done for a Cu/Zn/Al/Cs catalyst with a metal molar ratio of 36.8/36.8/23.3/3.1. Liquid and gas samples were collected at 310°C, 75 atm, with the synthesis gas $H_2/CO = 0.48$. The feed rate was 8 l/hr at STP over 2.45 gm of the catalyst. Liquid samples were collected under liquid nitrogen as explained in section 2.2.3. Gas sample collection method was the same as that discussed in 2.2.3. The gas and liquid samples were first injected into the H-P 5730A GC with the Porapak Q column and TC detector. Automatic injections were also made into the H-P 5730A GC. Figure XIII and Table III show the chromatogram of the gas sample and the corresponding mol percent of each component analyzed by the H-P 5730A GC. The major products were methane (36.45%), water (0.21%), methanol (5.85%), and 2-methyl-1-propanol (0.24%). 54.67% of the mixture was unreacted CO. A complete mass balance was

TABLE II

Relative Sensitivity Data for Hydrogen Flame Ionization Detector

HYDROCARBONS	Molecular Weight	Response Factor	Dietz & Messner Response Factors (6)
Methane	16	0.97	0.97
Ethane	30	0.97	0.97
n-Propane	44	0.98	0.98
n-Butane	58	1.09	1.09
n-Pentane	72	0.93	1.04
n-Hexane	86	0.96	1.03
n-Heptane	100	1.01	1.00
n-Octane	114	0.97	0.97
IsoOctane	114	0.97	-
ESTERS			
Methyl formate	60	0.18	-
Ethyl formate	74	0.31	-
Propyl formate	88	0.44	-
Butyl formate	102	0.52	-
Secondary butyl formate	102	0.53	-
Tertiary butyl formate	102	0.53	-
Methyl Acetate	74	0.30	0.20
Ethyl Acetate	88	0.41	0.38
Methyl Propionate	88	0.42	-
Ethyl Propionate	102	0.42	-
Methyl Butyrate	102	0.57	-
Methyl Isobutyrate	102	0.53	-
Methyl Valerate	116	0.61	-
Ethyl butyrate	116	0.64	-
ETHERS			
Dimethyl Ether	46	0.97	-
Diethyl Ether	74	0.91	-
ALCOHOLS			
Methanol	32	0.29	0.23
Ethanol	46	0.41	0.46
n-Propanol	60	0.57	0.60
n-Butanol	74	0.71	0.66
2-Butanol	74	0.63	0.63
2-methyl-1-propanol	74	0.72	0.68
3-methyl-1-butanol	88	0.73	-
2-methyl-1-butanol	88	0.73	-

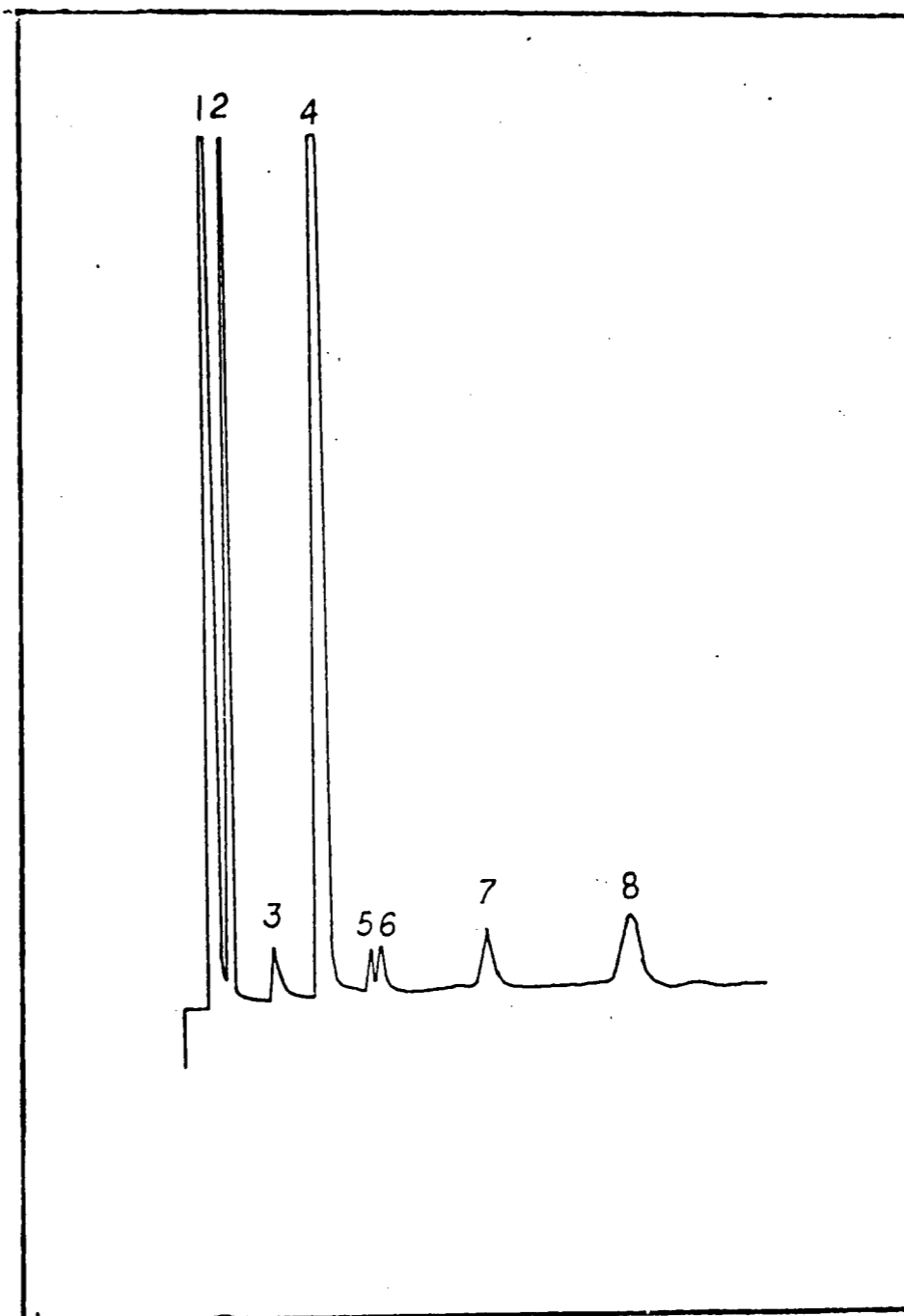
TABLE II (continued)

ALCOHOLS (continued)		Molecular Weight	Response Factor	Dietz & Messner Response Factors (6)
2-methyl-1-pentanol	102	0.73	-	
3-methyl-1-pentanol	102	0.72	-	
4-methyl-1-pentanol	102	0.71	-	
1-pentanol	88	0.81	0.71	
2-pentanol	88	0.77	-	
3-pentanol	88	0.72	-	
3-methyl-2-butanol	88	0.71	-	
2-methyl-3-pentanol	102	0.72	-	
2-hexanol	102	0.71	-	
3-hexanol	102	0.70	-	
1-hexanol	102	0.75	0.74	
4-methyl-2-pentanol	102	0.71	-	
3-methyl-2-pentanol	102	0.70	-	
2-methyl-2-pentanol	102	0.71	-	
2-ethyl-1-butanol	102	0.69	-	
KETONES				
Acetone	58	0.48	0.49	
2-butanone	72	0.60	0.61	
2-pentanone	86	0.66	-	
3-pentanone	86	0.67	-	
3-methyl-2-butanone	86	0.70	-	
Pinacolone	100	0.78	-	
2-methyl-3-pentanone	100	0.72	-	
3-hexanone	100	0.75	-	
2-hexanone	100	0.75	-	
4-methyl-2-pentanone	100	0.73	0.71	
ALDEHYDES				
Acetaldehyde	44	0.25	-	
Formaldehyde	30	0.28	-	
Propionaldehyde	58	0.31	-	
Isobutyraldehyde	72	0.51	-	
Butyraldehyde	72	0.59	0.62	
2-methyl-1-butyraldehyde	86	0.57	-	
Valeraldehyde	86	0.57	-	
2-methyl-1-valeraldehyde	100	0.53	-	
Hexaldehyde	100	0.69	-	

Average coefficient of variation for these compounds was 0.02.

Cyclohexane was the internal standard and assigned a value of 1.00.

Figure XIII



Gas Chromatogram of the higher alcohol synthesis products from synthesis gas ($H_2/CO = 0.48$) at 8 l/hr, $310^\circ C$, 75 atm, over 2.45 gm of the catalyst $Cu/Zn/Al/Cs = 36.8/36.8/23.3/3.1$ atomic percent

Column: Porapak Q

Temperature Program: Hold 2 min. at $90^\circ C$, then to $200^\circ C$ at $16^\circ C/min$.

TABLE III

Composition of product of higher alcohol synthesis from synthesis gas ($H_2/CO = 0.48$) at 8 /hr, 310°C, 75 atm. over 2.45 gm of catalyst Cu/Zn/Al/Cs = 36.8/36.8/23.3/3.1 atomic percent.

Column: Porapak Q, Thermal Conductivity Detector
Temperature Program: Hold 2 min at 90°C, then to 200°C at 16° C/min.

Gas Sample

Component	Response Factor (R.F.)	Peak Area/R.F.	Mol% after normalization
1 Carbon Monoxide	42	207.57	54.67
1 Methane	35.7	172.11	36.45
2 Carbon Dioxide	48	9.46	2.27
3 Water	33	9.46	0.21
4 Methanol	45	24.39	5.85
5 Methyl Formate	72	0.22	0.05
6 Ethanol	72	0.33	0.07
7 1-Propanol	83	0.51	0.12
8 2-Methyl-1-Propanol	96	1.03	0.24
	Total	416.50	100%

Peak # 1 was composed of CO and CH_4 . After a methane check CH_4 was found to make up 0.40% of the peak area.

not done for this gas sample and the one injected into the H-P 5880A GC with the FID detector and bonded methyl silicone capillary column because before each injection the gas sample syringe had time to cool allowing condensation of a portion of the products and therefore accurate mol percents were not obtained upon injection.

The same gas sample was then injected onto the H-P 5880A GC. Figure XIV and Table IV show the components resolved by the bonded methyl silicone capillary column and FID detector. One condition must be remembered about the FID, this detector responds only to compounds producing CHO^+ ions (3) when burned in a hydrogen flame. Table V shows a list of compounds which produce little or no response to the FID. CO is not seen because it gives virtually no ionization. The carbon burns to CO_2 without going through a CH intermediate. Methanol seemed to be the major product comprising 77.41% of the products. 2-Methyl-1-Propanol was next making up 2.75% of the mixture.

Table VI shows the results of an automatic injection of the products for the Cu/Zn/Al/Cs (36.8/36.8/23.3/3.1) catalyst on to the HP 5730A gas chromatograph. Here methanol once again is the major product (9.69%) with 2-methyl-1-propanol (0.16%). Figure XV and Table VII show this same liquid sample chromatographed on the H-P 5880A GC. The results show methanol being 9.67% of the product with 2-methyl-1-propanol being 0.16%. The C_5 and C_6 components were also resolved. Because the ratio of methanol to 2-methyl-1-propanol agree for the automatic injection onto the H-P 5730A GC with Porapak Q column, and the liquid injection onto the H-P 5880A GC with the bonded methyl silicone capillary column a mass balance was done for the more complete analysis obtained from the liquid injection onto the H-P 5880A GC. Appendix A.1.4 shows both a carbon

TABLE IV

Composition of Products for Higher Alcohol Synthesis Products
from Synthesis Gas $H_2/CO = 0.48$, at 8 l/hr, 310°C, 75 atm, over
2.45 gm of Catalyst Cu/Zn/Al/Cs = 36.8/36.8/23.3/3.1 Atomic %.

Column: Bonded Methyl Silicone Capillary Column.
Flame Ionization Detector

<u>Gas Sample</u>				
<u>Peak Number</u>	<u>Component</u>	<u>Wt.%</u>	<u>Wt.%</u> <u>M.W.</u>	<u>Mo1%</u>
1	Methane	2.90	0.181	6.64
2	Ethane	0.53	0.018	0.66
3	Propane	0.32	0.007	0.26
4	Dimethyl-Ether	3.13	0.068	2.49
5	Methanol	67.55	2.111	77.41
6	Acetaldehyde	0.40	0.009	0.33
7	n-Butane	0.04	0.001	0.04
8	Methyl Formate	1.01	0.017	0.62
9	Ethanol	1.43	0.031	1.14
10	Propionaldehyde Acetone	0.35	0.006	0.22
11	1-Pentane	0.11	0.002	0.07
12	Ethyl Formate	0.33	0.004	0.15
13	Diethyl Ether	0.09	0.001	0.04
14	Methyl Acetate	1.27	0.017	0.62
15	Isobutyraldehyde	0.18	0.003	0.11
16	1-Propanol	2.40	0.040	1.47
17	1-Butyraldehyde	0.00	0.001	0.04
18	2-Butanone	0.26	0.004	0.15
19	2-Butanol	0.17	0.002	0.07
20	Ethyl Acetate	0.13	0.001	0.04
21	2-Methyl-1-Propanol Methyl Propionate	5.58	0.075	2.75
22	3-Methyl-2-Butanone	0.15	0.002	0.07
23	1-Butanol	0.45	0.006	0.22
24	2-Pentanone	0.28	0.029	0.10
24A	3-Methyl-2-Butanol	0.02	0.001	0.01
25	Methyl Isobutyrate	0.03	0.001	0.001
25A	Valeraldehyde	0.62	0.007	0.29

TABLE V
Materials Producing Little or No Response to the
Flame Ionization Detector

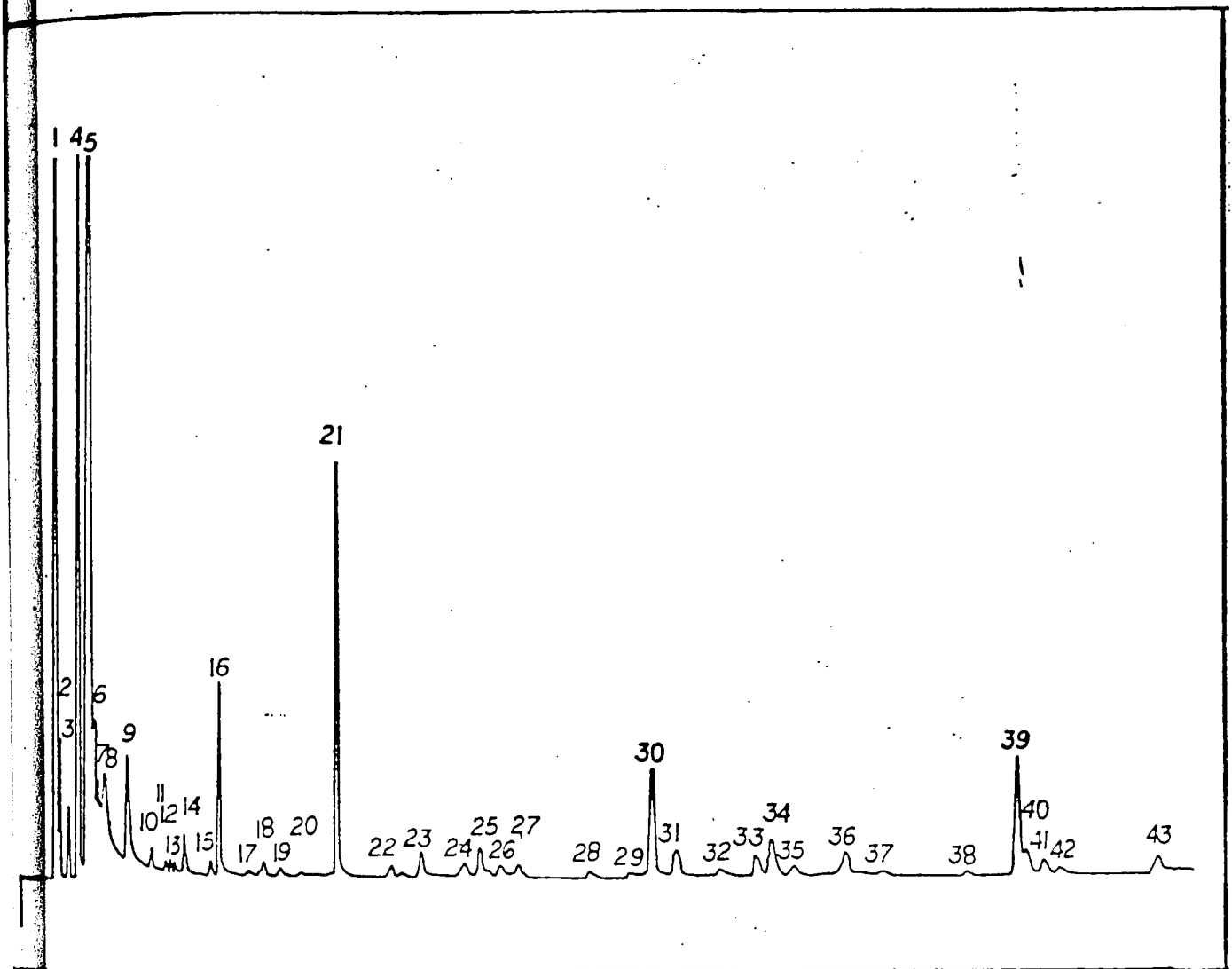
Inert Gases	Hydrogen	Nitrogen
Nitrogen Oxides	Carbon Monoxide	Hydrogen Sulfide
Silicon Halides	Carbon Dioxide	Sulfur Dioxide
Water	Carbonyl Sulfide	Carbon Disulfide
Ammonia	Oxygen	Formic Acid

TABLE VI
Composition of Products for Higher Alcohol Synthesis
Products from Synthesis Gas $H_2/CO = 0.48$ at 8 l/hr, 310°C,
75 atm over 2.45 gm of Catalyst Cu/Zn/Al/Cs = 36.8/36.8/
23.3/3.1 Atomic %.
Column: Porapak Q
Temperature Program: Hold 2 min at 90°C, then to 200°C at 16°C/min.

Automatic Injection Sample

<u>Component</u>	<u>Peak Area/R.F.</u>	<u>Mol%</u>
1. Carbon Monoxide	704.44	49.89
2. Methane	529.86	37.53
3. Carbon Dioxide	32.66	2.31
4. Ethane	0.40	0.03
5. Water	0.97	0.07
6. Dimethyl Ether	0.10	0.01
7. Methanol	136.82	9.69
8. Methyl Formate	0.99	0.07
9. Ethanol	1.57	0.11
10. Methyl Acetate	0.34	0.02
11. 1-Propanol	0.48	0.10
12. 2-Methyl-1-Propanol	2.25	0.16

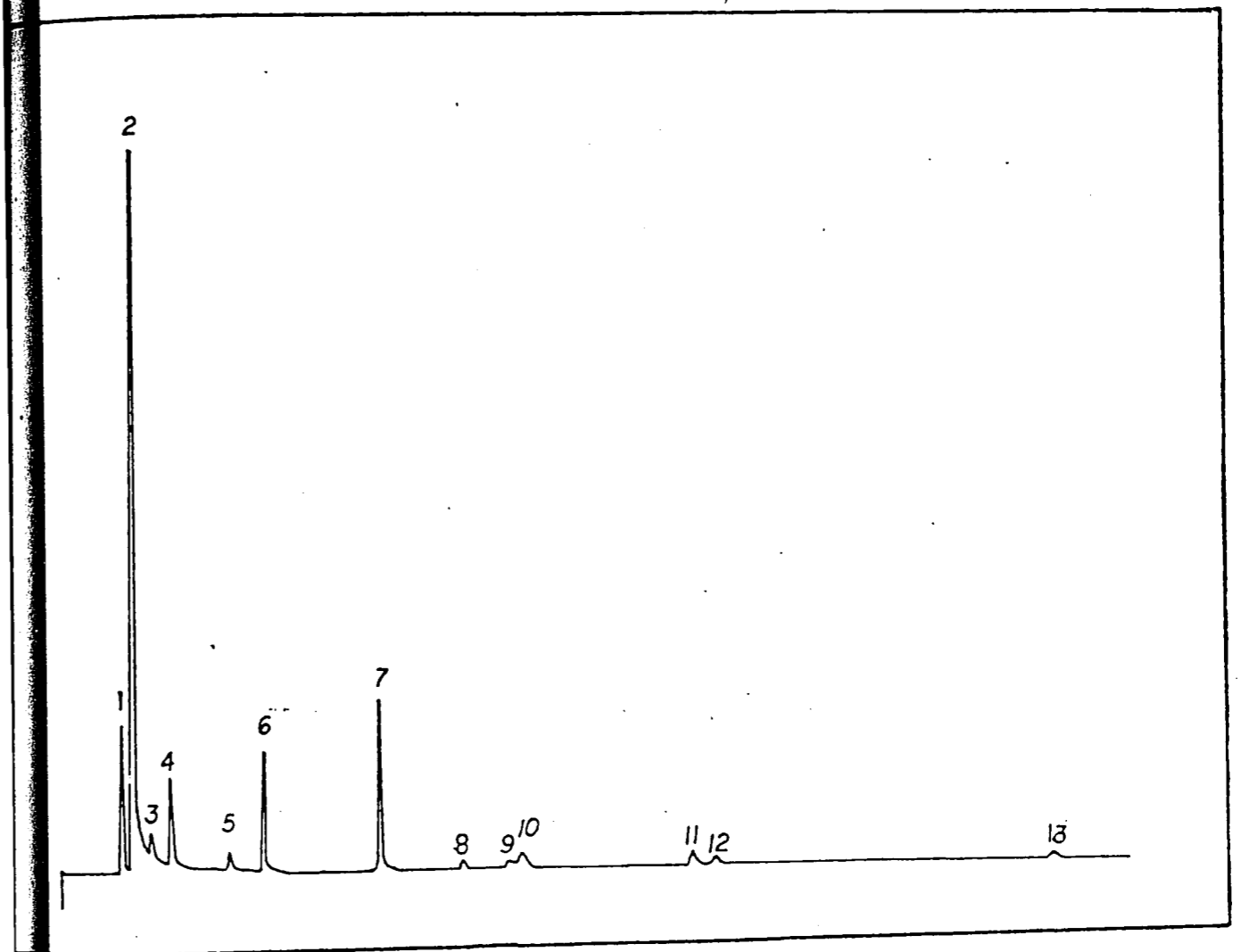
Figure XIV



Gas Chromatogram of the Higher Alcohol Synthesis Products from Synthesis Gas ($H_2/CO = .48$), at 8 l/hr, $310^{\circ}C$, over 2.45 gm of a Cu/Zn/Al/Cs 36.8/36.8/23.3/3.1 Atomic Percent Catalyst.

Column: Bonded Methyl Silicone Capillary Column.

Figure XV



Gas Chromatogram of the higher alcohol synthesis products from synthesis gas ($H_2/CO = 0.48$), at 8 l/hr, $310^{\circ}C$, 75 atm, over 2.45 gm of the catalyst $Cu/Zn/Al/Cs = 36.8/36.8/23.3/3.1$ atomic percent

Column: Bonded Methyl Silicone Capillary Column.

TABLE VII

Composition of Products of Higher Alcohol Synthesis
 Products from Synthesis Gas ($H_2/CO = 0.48$) at 8 l/hr, 310°C,
 75 atm over 2.45 gm of the Catalyst Cu/Zn/Al/Cs = 36.8/36.8/
 23.3/3.1 Atomic %.

Column: Bonded Methyl Silicone Capillary Column
 Flame Ionization Detector

Liquid Sample

<u>Peak #</u>	<u>Component</u>	<u>Mol% After Normalization</u>
A	Carbon Monoxide	49.82
B	Methane	37.44
C	Carbon Dioxide	2.31
D	Ethane	0.03
E	Water	0.07
1	Dimethyl Ether	0.07
2	Methanol	9.67
3	Methyl Formate	0.05
4	Ethanol	0.13
5	Methyl Acetate	0.04
6	1-Propanol	0.14
7	2-Methyl-1-Propanol	0.17
7B	Methyl Propionate	0.17
8	Butanol	0.07
9	2-Pentanone	0.01
9B	3-Methyl-2-Butanol	0.01
10	1-Valeraldehyde	0.02
10B	Methyl Isobutyrate	0.02
11	3-Methyl-1-Butanol	0.02
12	2-Methyl-3-Pentanone	0.01
13	2-Methyl-1-Pentanol	0.01
		<hr/> 100 %

balance and oxygen balance calculated from the analysis of the liquid sample injected into the Hewlett Packard 5880A gas chromatograph.

4.1 Summary

4.1.1 Capillary Column Gas Chromatography

The author has found a suitable capillary column, namely a bonded methyl silicone 60m x 0.75mm ID column which separated the higher alcohol synthesis products on a Hewlett-Packard 5880A gas chromatograph equipped with a flame ionization detector. A detailed description of all parameter settings for this gas chromatograph was given in the experimental section to allow future users to analyze the alcohol synthesis products. The response factors calculated in Table II enabled quantitative analysis to be done easily and should be used for all quantitative future work with the flame ionization detector. Possible remaining uncertainties and errors are discussed in Section 5.1.

4.1.2 Quantitative Analysis of the Products Over the Cu/Zn/Al/Cs Catalyst

The total analysis of a Cu/Zn/Al/Cs 36.8/36.8/23.3/3.1 atomic percent catalyst collected from the synthesis gas $H_2/CO = 0.48$ at 8 l/hr, 310°C, 75 atm, over 2.45 gm of the catalyst was conducted on both the H-P 5730A GC equipped with a thermal conductivity detector, and a Porapak Q packed column and the H-P 5880A GC with a flame ionization detector, and a wide bore bonded methyl silicone capillary column. The most complete analysis was obtained by injecting a liquid sample onto the HP 5880A GC. The results showed that methanol under these conditions yielded 9.67% of the product while 2-methyl-1-propanol yielded 0.17% of the product. CO made up 49.82%, CH_4 37.44%, CO_2 2.31% and H_2O 0.07% of the product mixture. The presence of hydrocarbons and ethers in the product mixture indicated acidic sites still present on the catalyst (16).

5.1 Uncertainties and Errors

Throughout the analysis it was found that a few components such as 2-methyl-1-propanol and methyl propionate (Tables IV, VII) acetone and propionaldehyde have not been completely separated under the conditions used for the H-P 5880 GC and with the bonded methyl silicone capillary column. To improve the separations the oven temperature at the start could be lowered from 30°C to 0°C by placing dry ice into the oven prior to injection. In some instances, the peaks have been partially separated but not enough for the peaks to be integrated separately. The use of the GC/mass spectrometer could help in resolving the problem. By scanning the front, middle, and back of the peak a fragment spectrum will change as different components are encountered. Areas can be added and subtracted by the computer which should allow an almost complete separation to be achieved.

Also, the possibility of using multiple columns for peak separation exists. Previous investigators have placed a number of columns in series (12) splitting the sample at different times and passing solutions through a number of different columns until desired separation was achieved. The Carbowax column would be a good column to place in series with the bonded methyl silicone capillary column and the H-P 5880A GC has the capability of using 4 columns in series.

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APPENDIX

A.1 Analytical Calculations

A.1.1 Calculating Column Flow for the 5880A GC

$$\text{Column flow, ml/min} = \frac{\pi r^2 L}{t}$$

where r is the internal radius of the column in centimeters

L is the column length in centimeters

t appearance time of a non retained peak in minutes

for the Bonded methyl silicone capillary column

$$r = 0.038 \text{ cm}$$

$$L = 6000 \text{ cm}$$

$$t = 3.62 \text{ min for methane}$$

$$\begin{aligned} \text{Column flow} &= \frac{\pi(0.038)^2(6000)}{3.62} \\ &= 7.32 \text{ ml/min} \end{aligned}$$

A.1.2 Sample Calculation for the Flame Ionization Detector Response Factors

<u>Component</u>	<u>Actual Weight Percent Injected</u>			
Ethyl formate	20.96			
Cyclohexane	62.29			
3-Pentanol	16.74			
<u>Component</u>	<u>Peak Area</u>	<u>Wt %</u>	<u>Area/Wt %</u>	<u>Area/Cyclohexane Area =</u>
Ethyl formate	23049.30	20.96	1099.68	0.31
Cyclohexane	220341.00	62.29	3537.34	1.00
3-Pentanol	42031.70	16.74	2510.86	0.71

Response Factors

All components were analyzed relative to cyclohexane which was arbitrarily given a value of 1.00

A.1.3 Sample Calculation for Determining Actual Mol% of Each Component Using

Response Factors

<u>Component</u>	<u>Response Factor</u>	<u>Peak Area</u>	<u>Area R.F.</u>	<u>Wt% after Normalization</u>	<u>M.W.</u>	<u>Wt% M.W.</u>	<u>Mol% after Normalizing</u>
Dimethyl Ether	0.97	2139.60	2205.77	0.95	46	0.021	0.71
Methanol	0.29	58987.80	203406.21	1088.02	32	2.750	93.51
Methyl formate	0.18	330.58	1836.56	0.79	60	0.013	0.44
Ethanol	0.41	1643.99	4009.73	1.74	46	0.038	1.29
Methyl Acetate	0.30	577.02	1923.40	0.83	74	0.011	0.37
Propanol	0.57	3030.02	5333.86	2.31	60	0.039	1.33
2-methyl-1-propanol	0.72	5804.64	8062.00	3.49	74	0.047	1.60
methyl propionate	0.71	330.34	465.27	0.20	74	0.002	0.07
Butanol	0.71	151.59	213.51	0.09	86	0.001	0.03
2-Pentanone	0.71	151.59	213.51	0.09	86	0.001	0.03
3-methyl-2-butanol	0.57	519.51	911.42	0.39	86	0.005	0.17
Valeraldehyde	0.57	519.51	911.42	0.39	86	0.005	0.17
Methyl Isobutyrate	0.73	802.99	1099.99	0.48	88	0.005	0.17
3-methyl-1-butanol	0.73	802.99	1099.99	0.48	88	0.005	0.17
2-methyl-3-pentanone	0.72	481.78	699.14	0.29	100	0.003	0.10
2-methyl-1-pentanol	0.73	679.91	956.04	0.41	102	0.004	0.14
Total = 231092.90						2.939	100%

Taken from Table VIII.

A.1.4 Carbon and Oxygen Balance for Products Collected over 2.45 gm of the Catalyst Cu/Zn/Al/Cs 36.8/36.8/23.3/3.1 atomic percent. Collected at 310°C, 75 atm from Synthesis Gas H₂/CO = 0.48 at 8 l/hr

$$H_2/CO = \frac{32.5}{67.5}$$

$$\text{Flow rate} = (8 \text{ l/hr}) \left(\frac{1 \text{ mol}}{24.45 \text{ l}} \right) (0.675) = .2209 \frac{\text{mol}}{\text{hr}} \text{ of CO}$$

$$CO \text{ in} = CO \text{ out} \quad C \text{ in} = C \text{ out} = .2209 \frac{\text{mol}}{\text{hr}} \quad O \text{ in} = O \text{ out} = .2209 \frac{\text{mol}}{\text{hr}}$$

Component	Mol%	Carbon in Effluent ($\frac{\text{mol}}{\text{hr}}$)	Mol% of C	Oxygen in Effluent ($\frac{\text{mol}}{\text{hr}}$)	Mol% of O
Carbon Monoxide	49.82	0.11005	48.99	0.11005	72.30
Methane	37.44	0.08270	36.82	0.0	0.0
Carbon Dioxide	2.31	0.00510	2.27	0.01021	6.71
Ethane	0.03	0.00013	0.06	0.0	0.0
Water	0.07	0.0	0.0	0.00016	0.11
Dimethyl Ether	0.07	0.00031	0.14	0.00016	0.11
Methanol	9.67	0.02136	9.51	0.03136	20.60
Methyl Formate	0.05	0.00022	0.10	0.00022	0.14
Ethanol	0.13	0.00057	0.25	0.00030	0.20
Methyl Acetate	0.04	0.00027	0.12	0.00019	0.12
1-Propanol	0.14	0.00093	0.41	0.00031	0.20
2-methyl-1-propanol	0.17	0.00150	0.67	0.00075	0.49
1-butanol	0.07	0.00062	0.28	0.00016	0.11
2-Pentanone	0.01	0.00011	0.05	0.00005	0.03
Valeraldehyde	0.02	0.00022	0.10	0.00009	0.06
3-methyl-1-butanol	0.02	0.00022	0.10	0.00005	0.03
2-methyl-3-pentanone	0.01	0.00013	0.06	0.00002	0.01
2-methyl-1-pentanol	0.01	0.00013	0.06	0.00002	0.01
Total =		0.2246		.1541	

$$\text{Error in C balance} = \frac{C_{in} - C_{out}}{C_{in}} = \frac{0.2209 - 0.2246}{0.2209} \times 100 = 1.67\%$$

$$\text{Error in O balance} = \frac{O_{in} - O_{out}}{O_{in}} = \frac{0.2209 - 0.1541}{0.2209} = 30.23\%$$