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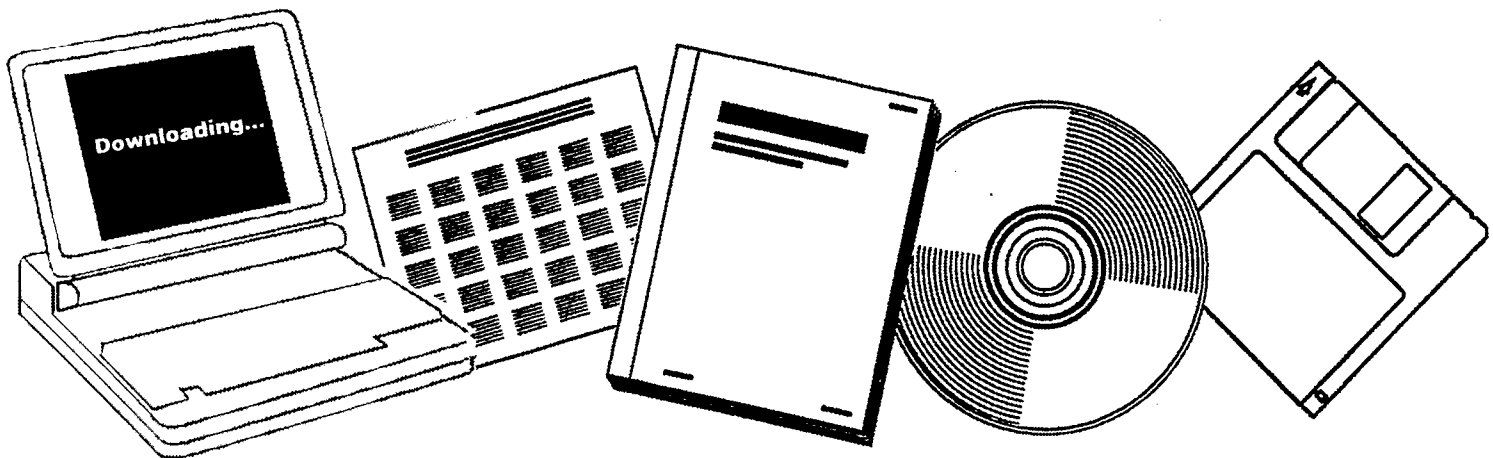
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DETERMINATION OF ALCOHOLS IN ENGINE LUBRICANTS

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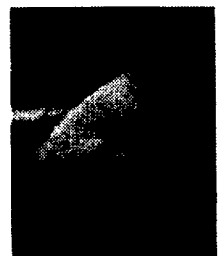
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The recent interest in alcohol and alcohol-containing fuels in spark ignition engines requires new information and analytical methods concerning the presence of alcohols in used lubricants. U.S. Army Fuels and Lubricants Research Laboratory (AFLRL) has developed a straightforward, rapid, and accurate method to determine and measure the alcohols. The oil and alcohols are separated using an adsorber or stripper column, and then the alcohols are resolved on the second column in series and determined with a flame ionization		

20. ABSTRACT (Cont'd)

detector.

Quantitative standards were prepared to include the normally expected range of alcohol content of 0-10 percent. The use of a second alcohol as an internal standard helps offset the reproducibility error involved in the syringe technique. The standard is completed by adding approximately 50 vol% of CS₂. It is suggested that the alcohol chosen as the internal standard be at least 2 carbon numbers higher or lower than the analyte to help enhance the peak resolution and integration.

The samples are prepared in much the same manner as the calibration standards, with 1 to 5 percent of the alcohol chosen to be the internal standard added. Because of the small amounts of samples frequently encountered, it is not always reasonable to maintain the ideal 1:1 internal standard/analyte ratio. With small samples, the 1:1 ratio produces problems, such as the dispensing of micro quantities of isopropanol and the tedious mixing for homogeneous samples. To minimize these complications, a ratio as high as 5:1 of internal standard to analyte has been used satisfactorily to increase precision. A 0.5-microliter sample injection prolongs the stripper column's life.

Employing this method, AFLRL has been able to satisfactorily provide analytical support for several engine/oil tests. The methanol content of these samples has ranged from 10 percent to less than our detection limit of 0.03 percent. Although most of the work has been the determination of methanol in lubricants, it is believed that the method is applicable to other alcohols, up to C₆.

FOREWORD

The work reported herein was conducted at the U.S. Army Fuels and Lubricants Research Laboratory (USAFLRL) located at Southwest Research Institute, San Antonio, Texas, under Contract DAAK70-79-C-0175 for the U.S. Army Mobility Equipment Research and Development Command (USAMERADCOM), Fort Belvoir, Virginia, and under Department of Energy and Department of Defense Interagency Agreement E(49-28)-1021, originated by the Department of Energy. The USAMERADCOM contracting officer's representative was Dr. J.V. Mengershauser, Energy and Water Resources Laboratory, DRDME-GL, while the DOE technical project manager was Mr. E.E. Ecklund, Alternative Fuels Utilization Branch.

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I. INTRODUCTION

In fuels and lubricants research, the analysis of lubricants for additives, wear metals, fuel contamination, and degradation is routinely performed using well established procedures. With new applications or test conditions, new information and analytical methods are required. One such application is the recent interest in alcohol and alcohol-containing fuels in spark ignition engines where the presence of alcohols in used lubricants requires different measurement techniques.

The U.S. Army Fuels and Lubricants Research Laboratory (AFLRL) is evaluating several engine lubricating oils in selected spark ignition engines with a variety of alcohol and alcohol-blended fuels to determine the important parameters affecting engine and lubricant performance.

It is interesting to note that methanol-fueled engines in cold cycle operation have shown excessive wear.^{(1)*} Because of this excessive wear phenomenon, an extensive research program was initiated to learn more about the factors affecting the wear mechanism.

One set of data needed in this research program is the qualitative and quantitative analyses of alcohols in the lubricating oil. AFLRL has developed a straightforward, rapid, and accurate analytical method to determine and measure the alcohols.

II. APPROACH

Various methods of determining the qualitative and quantitative analyses of alcohols were considered. It became evident that the alcohol had to be separated from the lubricant. A water extraction of the alcohol, as in the analysis of gasohol, would only complicate the typically existing alcohol/oil emulsion. Another possible approach is to directly inject the sample into a

*Superscript numbers in parentheses refer to the list of references at the end of this report.

gas chromatograph (GC) boiling point separation column, with the use of a flow reversing or back-flush valve.

The AFLRL approach is to analyze the alcohol/oil mixture by direct injection into the gas chromatograph. The oil and alcohol were separated using an adsorber or stripper column, then the alcohol content was resolved and determined on a second column in series with the first, using a hydrogen flame ionization detector. An internal standard and viscosity-reducing solvent is used to minimize sample injection problems.

III. EXPERIMENTAL

A. Instrumentation

The gas chromatographic columns were prepared and installed in series in the gas chromatograph oven (Figure 1). The stripper/adsorber column packed with

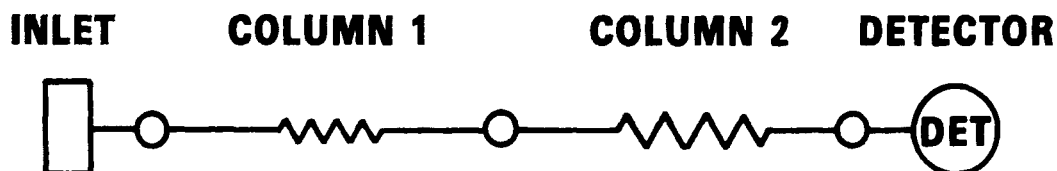


FIGURE 1. G.C. COLUMN CONFIGURATION

Tenax-GC⁽²⁾ precedes the analytical column packed with Chromosorb 101⁽³⁾. The column connections are made with 1/8-inch stainless steel Swagelok⁽⁴⁾ tubing fittings. The flame ionization detector was optimized at a helium flow rate of 60 ml/min. Since the column flow rates were set at 25 ml/min helium, an additional make-up flow of 35 ml/min helium was introduced just prior to the detector. The operating parameters are summarized in Table 1. The columns were initially conditioned by first displacing all oxygen from them, and then temperature programming the oven at 10°C/min to 250°C. The final temperature was held at 250°C for 30 minutes. The oven was then cooled and the con-

TABLE I. OPERATING PARAMETERS

Gas Chromatograph

Injector Temperature: on-column
Sample Injection: 5 microliter syringe
Sample Size: 0.5 microliter - on column
Column Flow: 25 ml/min Helium

Detector

Flame Ionization Detector Temperature: 250°C
Hydrogen: 35 ml/min
Air: 360 ml/min
Helium (makeup): 35 ml/min

Oven Temperature

125°C Isothermal

Data Processing

H.P. 3354 Lab Data System
● Internal Standard Calculation Method

Column

- (1) 13 in. x 1/8 in. Tenax-G.C. (60/80 Mesh)
- (2) 6 ft x 1/8 in. Chromosorb 101 (80/100 Mesh)

nection of the analytical column to the hydrogen flame ionization detector was made. While heating the column oven to the isothermal 125°C analysis temperature, the proper electrometer, recorder, and computer parameters were established. The system is now ready for the analysis of standards and samples. The Tenax-GC-adsorber column should be able to retain the hydrocarbons long enough to elute the alcoholic analyte (Figure 2). At the same time, resolution of the alcohols must be determined (Figure 3).

The columns must not be heated above 125°C while attached in series once an oil sample has been injected. The reason for this precaution is that the light ends of the oil will be carried onto the analytical column, causing an undetermined amount of delay in the analysis of future samples. The usefulness of the Tenax-GC stripper/adsorber column lasts for at least 35 0.5-microliter injections. After these injections, an alternate stripper column was installed and the exhausted column was emptied, cleaned, and refilled with

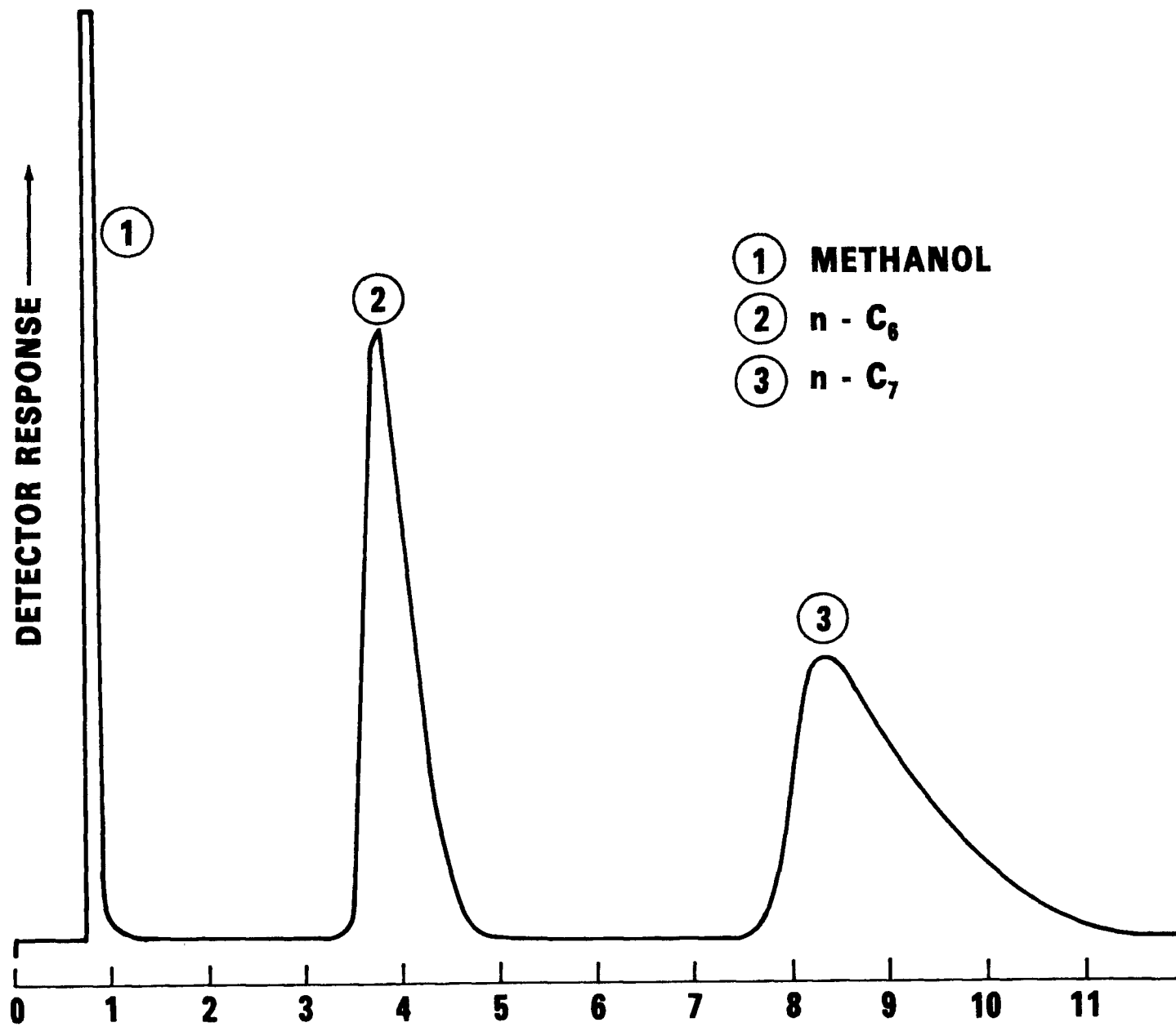


FIGURE 2. STRIPPER COLUMN RETENTION OF NORMAL HYDROCARBONS

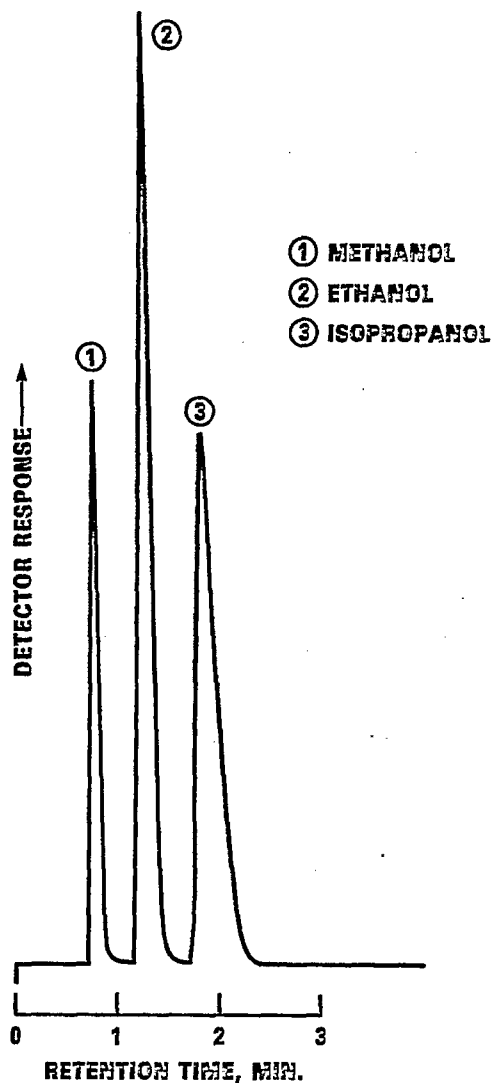


FIGURE 3. CHROMATOGRAM SHOWING RETENTION TIMES OF ALCOHOLS

new Tenax-GC adsorbent. This performance is enhanced by turning off the carrier flow during nonuse periods.

B. Calibration

Quantitative standards were prepared to include the normally expected range of alcohol content of 0 to 10 percent (Figures 4 and 5). The new oil (which is to be tested) was used as the matrix for the calibration standards. To aliquots of this oil, appropriate amounts of two different alcohols were added.

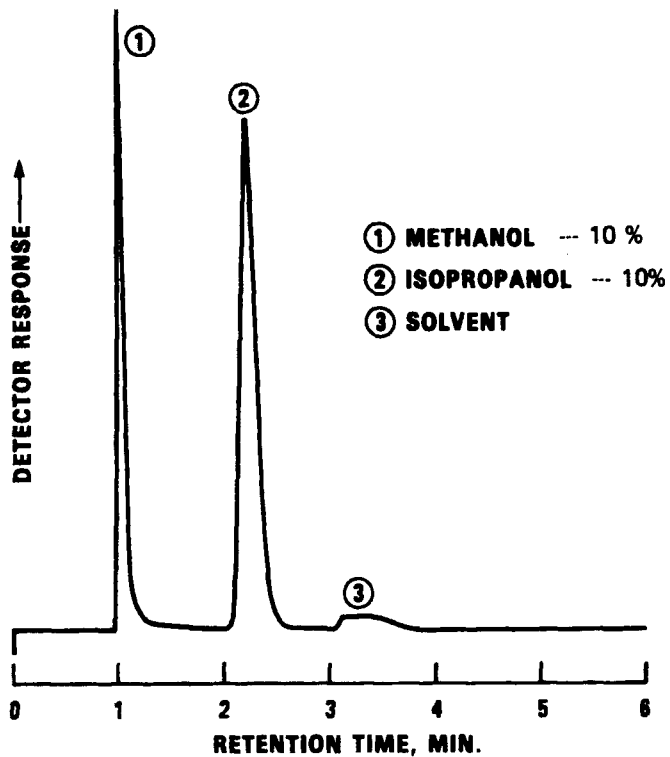


FIGURE 4. TYPICAL CHROMATOGRAM OF CALIBRATION STANDARD

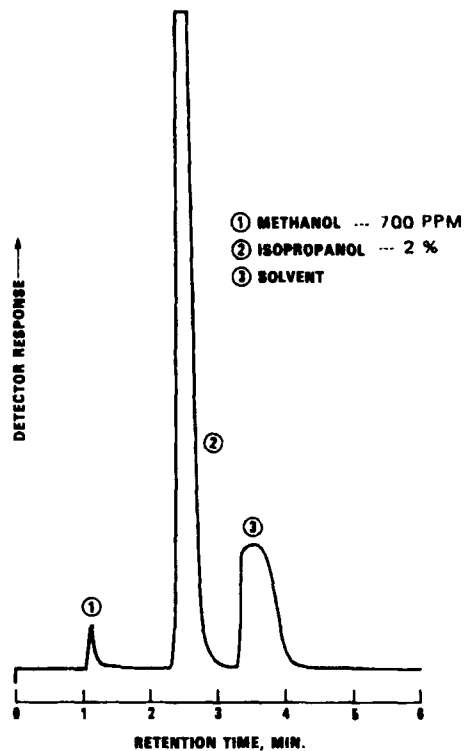


FIGURE 5. CHROMATOGRAM OF 700 PPM METHANOL STANDARD

One of the alcohols serves as the internal standard and the other as the analyte. The use of the internal standard helps to minimize the reproducibility error involved in the syringe technique.

The standard is completed by adding approximately 50 vol% of carbon disulfide. It is recommended that the alcohol chosen as the internal standard be at least two carbon numbers higher or lower than the analyte to help enhance the peak resolution and integration. For this work, isopropanol was chosen because it is not used as an engine fuel and is less volatile. From these standards, a relative detector response is calculated for quantitation of the unknown samples. Table 2 shows the calculation method.

TABLE 2. CALCULATION METHOD

Data Calculations

Response factor:

$$\frac{\% \text{ Internal Standard}}{\text{Internal Standard Area}} = \frac{\% \text{ Analyte Standard}}{\text{Analyte Standard Area (theoretical)}}$$

$$\text{Theoretical Analyte Std Area (x)} = \frac{(\text{Int Std Area}) \times (\% \text{ Analyte Std})}{(\% \text{ Int Std})}$$

$$\text{Analyte Std Response Factor} = \frac{\text{Theoretical Analyte Std Area}}{\text{Actual Analyte Std Area}}$$

$$\text{Sample: } \frac{\% \text{ Int Std}}{\text{Int Std Area}} = \frac{\text{Analyte \%}}{(\text{Analyte Area}) \times (\text{R.F.})}$$

$$\text{Analyte \%} = \frac{(\% \text{ Int Std}) \times (\text{Analyte Area}) \times (\text{R.F.})}{\text{Int Std Area}}$$

C. Sample Preparation

The samples are prepared in much the same manner as the calibration standards except that the analyte is already present in the used oil, and 1 to 5 percent of the alcohol chosen to be the internal standard must be added. Before mixing, approximately 50 vol% carbon disulfide is added. The sample is mixed or shaken thoroughly, and then injected. This injection should be performed with a minimum delay after mixing to prevent phase separation which can occur with 2 percent or greater concentration of alcohol.

IV. APPLICATION

This method has been applied to a variety of mineral oil samples taken from several engine tests. Because of the small amounts of sample frequently encountered, it was not possible to maintain the ideal 1:1 internal standard/analyte ratio. For example, when monitoring the alcohol content of the engine oil sump during a 100-hour test, the analyte received only 1 to 3 grams of used oil sample. The 1:1 ratio could require dispensing micro quantities of isopropanol and laborious mixing to produce a reliable homogeneous sample. In view of these complications, a ratio as high as 5:1 of internal standard to analyte has been satisfactorily used to help increase precision.

In some instances, a 0.5-microliter sample was injected in order to reduce the quantity of oil placed onto the stripper column, thus increasing the column's life.

V. DISCUSSION

The calibration standards prepared in the oil matrix remain stable over a period of several weeks. The relative detector response factors have shown a 2.7 percent mean deviation over a 19-nonconsecutive day interval as shown in Figure 6. The points which showed extreme deviation from the mean were those in which the 5:1 internal standard/analyte ratio criterion was violated (Table 3). Employing this method, satisfactory analytical support has been provided to several engine/oil tests. To date, these tests have generated approximately 100 samples. The methanol contents of these samples have ranged from 10 percent to less than the detection limit of 0.03 percent (Figures 7 through 9). Although the bulk of work has been the determination of methanol in lubricants, the method is believed to be applicable to other alcohols up to C_6 . Figure 10 shows the analysis of C_1 to C_4 alcohols and ethylene glycol.

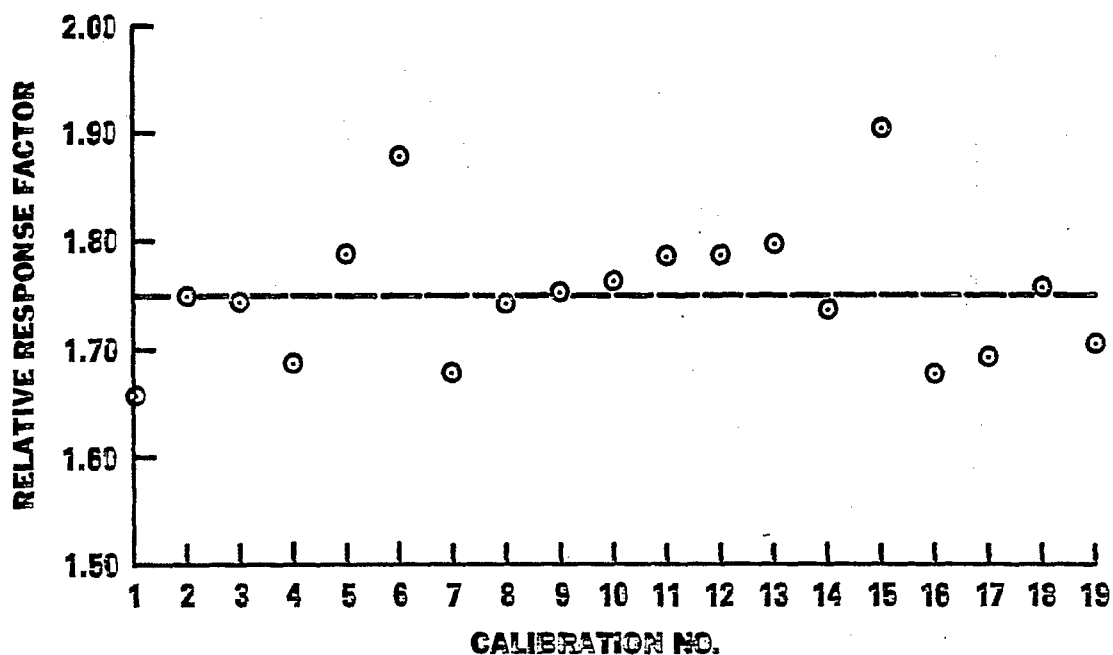


FIGURE 6. RESPONSE FACTOR REPEATABILITY

TABLE 3. INTERNAL STANDARD/ANALYTE RATIO

Standard	Internal Std./Analyte	Methanol Response Factor
10%		
9.168% MeOH	0.984/9.168	3.386
0.984% IPA	1/10	
5%		
4.889% MeOH	1.082/4.889	1.727
1.082% IPA	1/5	
1.0%		
1.019% MeOH	1.050/1.019	1.814
1.050% IPA	1/1	
0.1%		
0.143% MeOH	1.043/0.143	2.233
1.043% IPA	10/1	
0.112% MeOH	1.155/0.112	2.954
1.155% IPA	10/1	
6%		
6.038% MeOH	5.446/6.038	1.855
5.446% IPA	1/1	

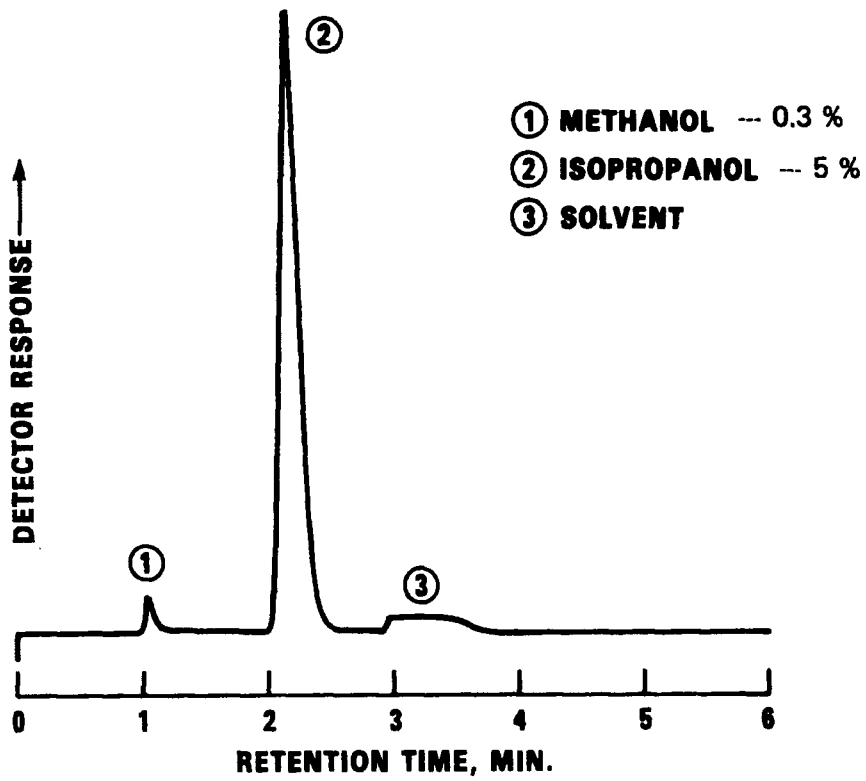


FIGURE 7. CHROMATOGRAM OF ENGINE OIL

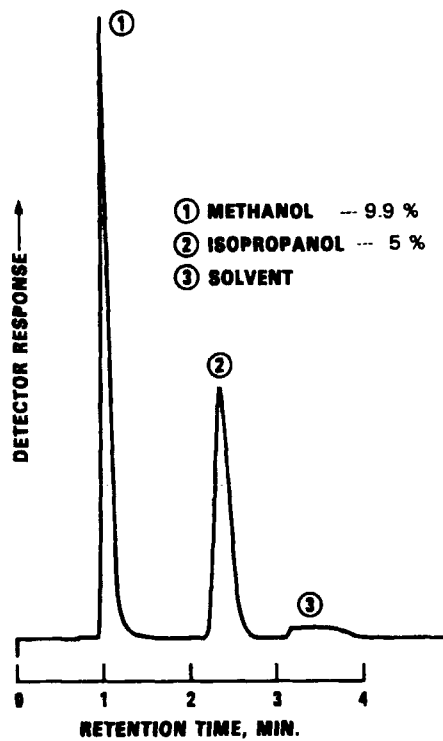


FIGURE 8. CHROMATOGRAM OF ENGINE OIL SAMPLE

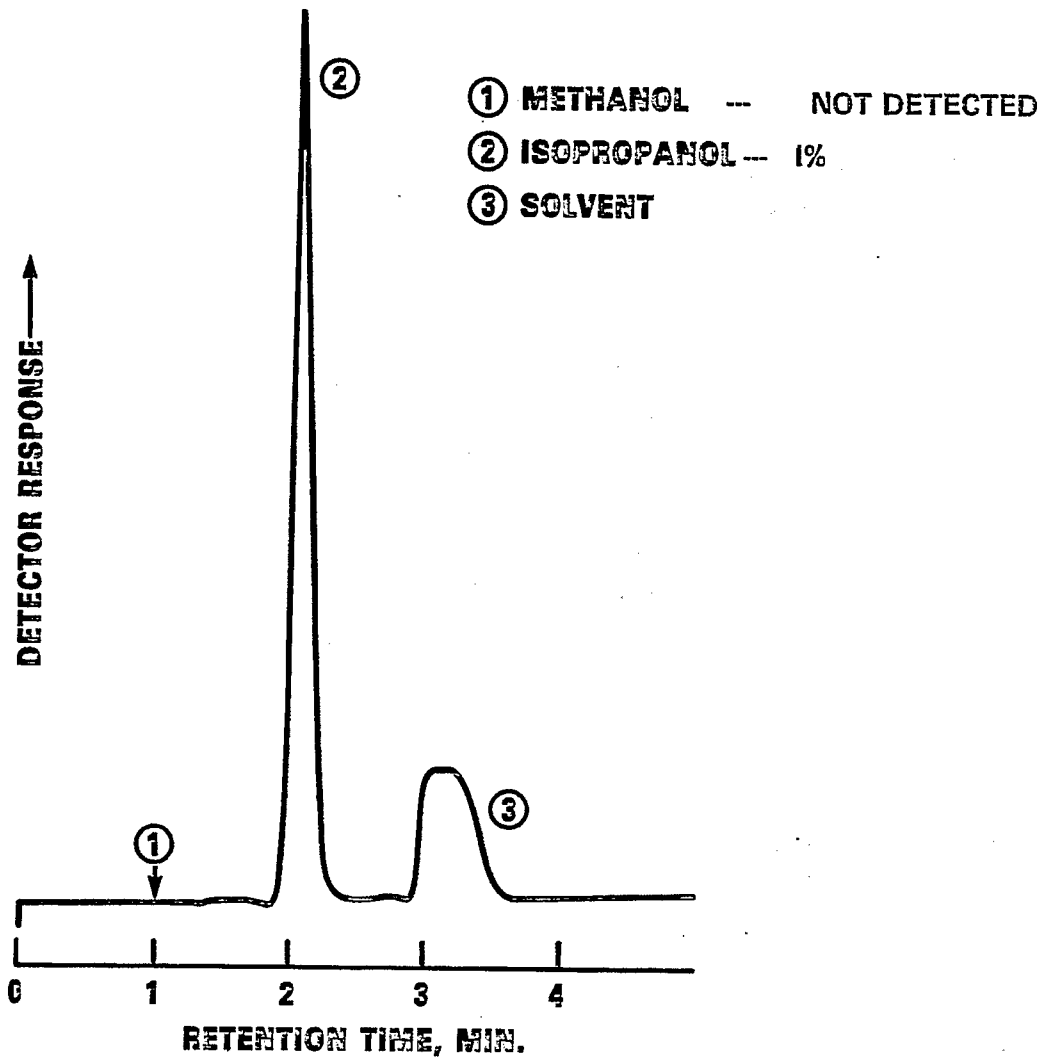


FIGURE 9. CHROMATOGRAM OF ENGINE OIL SAMPLE - METHANOL UNDETECTED

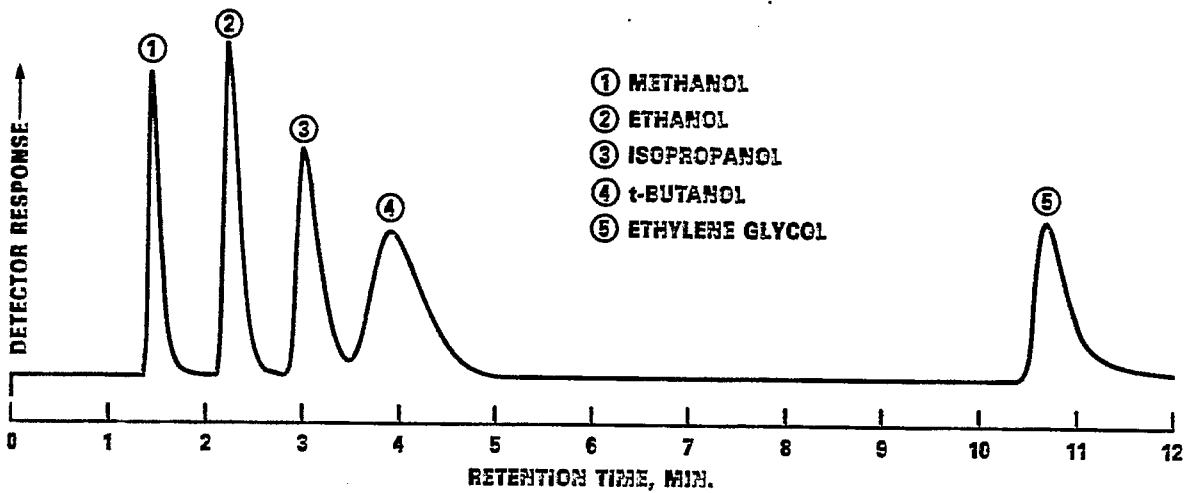


FIGURE 10. TEMPERATURE-PROGRAMMED CHROMATOGRAM OF ALCOHOL COMPOSITES

VI. CONCLUSIONS

This rapid and straightforward method, the analysis of alcohols in engine lubricants, has met the needs of AFLRL by supplying valuable data that have furthered the knowledge in alcohol fuel technology.

Thus, it provides one more criterion for evaluating alcohols as a modern day alternate energy source.

VII. LIST OF REFERENCES

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