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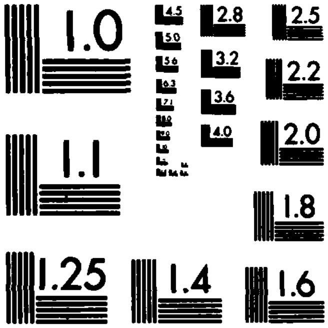

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EVALUATION OF GAS CHROMATOGRAPHIC METHODS FOR ANALYSIS OF GASOLINE/OXYGENATE BLENDS

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AFLRL No. 143

By

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The selection/development of a standard gas chromatographic method for the determination of oxygenates in gasoline-oxygenate blends is in keeping with laboratory characterization and specification testing phase of the U.S. Army's alternate fuels program. This report evaluates six different gas chromatographic methods of analysis. These methods involve water extraction of the oxygenated compounds as well as direct injection techniques. Gaso-

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20. ABSTRACT (Cont'd)

line samples containing varying amounts of methanol, ethanol, t-butanol, and methyl t-butyl ether (MTBE) were analyzed using each of the analytical methods, when possible.

The six methods were employed and evaluated for accuracy and efficiency. In each case, comments have been made pertaining to the application of each method. The analytical results of the methods are graphically compared. This study resulted in a recommendation to use water extraction with an internal standard to quantitate the C_4 and lighter alcohols, while the other oxygenated fuel extenders, such as MTBE, should be determined using a direct-injection method which selectively separates the oxygenates from the hydrocarbons. This work indicates that more work is warranted to develop methodology which is universally applicable to all of the commonly used oxygenated fuel extenders.

FOREWORD

This work was conducted at the U.S. Army Fuels and Lubricants Research Laboratory (USAFLRL) located at Southwest Research Institute, San Antonio, TX, under Contract Nos. DAAK70-80-C-0001 and DAAK70-82-C-0001 during the period March 1980 through August 1981. Work was funded by the U.S. Army Mobility Equipment Research and Development Command (MERADCOM), Fort Belvoir, VA, with Mr. F.W. Schaekel (DRDME-GL) serving as contract monitor. Project technical monitor was Mr. M.E. LePera, MERADCOM, DRDME-GL.

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I. INTRODUCTION

A. Background

As part of the major thrust within the Alternative and Synthetic Fuels Program, the Department of Defense (DOD) specified in late 1979 a task to "develop more efficient military fuel qualification procedures to effect capacity to react quickly to changes encountered in the petroleum refining industry." The normal time required for qualification of a new fuel for the engine and powerplant accessory systems is approximately 5 to 8 years. As an example, the transition to unleaded gasoline within the Department of the Army took 4 to 5 years.(1)* As shown in Figure 1, the first step in this transition is the development of a quality laboratory characterization and specification testing program.

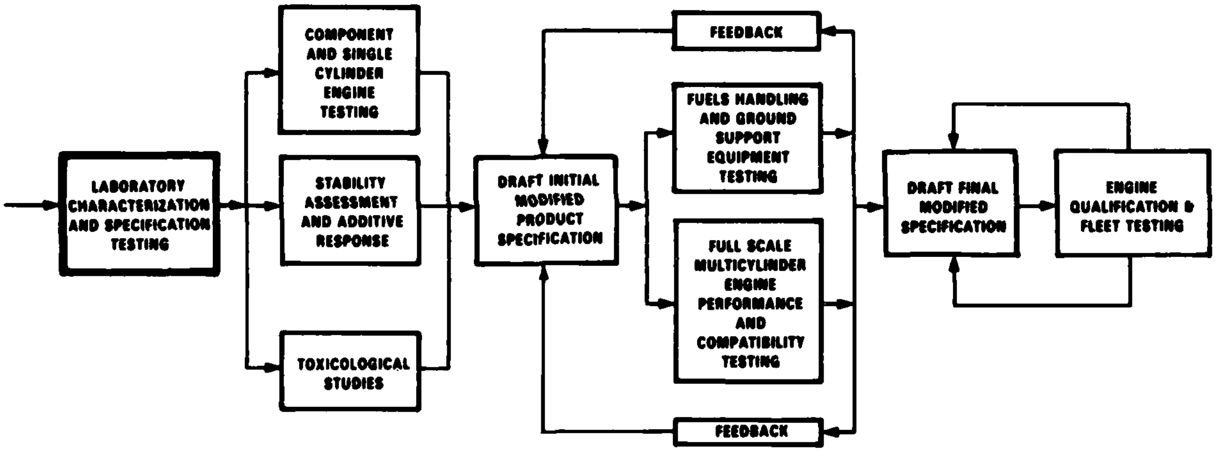

FIGURE 1. PROCESS FOR EVALUATING NEW/SYNTHETIC FUELS

In response to this directive, the use of various oxygenates as fuel additives has been intensively researched for possible environmental and economic advantages over neat gasolines. Gasoline suppliers have been mandated to lower the lead content, still maintaining sufficient octane ratings in their fuels in order to meet air pollution standards established by the Environmental Protection Agency. In addition, the use of alcohols as fuel

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* Underscored number in parentheses refer to the list of references at the end of this report.

extenders is being investigated to reduce U.S. dependence on imported oil and to extend the use of existing fuel supplies. It has been found that a blend of 10 vol% ethanol in gasoline will reduce hydrocarbon and carbon monoxide emissions and increase the antiknock index by 2 to 5 octane numbers over that of base gasolines. Other oxygenates such as methanol, iso-propanol, t-butanol, and methyl-t-butyl ether (MTBE) are also being studied as to their effectiveness as gasoline extenders.

Several analytical methods for the determination of oxygenates in gasoline/oxygenate blends have been developed. Infrared spectrophotometry is one useful method for the quantitative determination of the volume percent of alcohol in an alcohol/gasoline blend.(2) Several qualitative and quantitative methods for the determination of various oxygenated compounds in gasoline by gas chromotography have been developed.(3-6) These include gas chromatographic (GC) analysis of the aqueous-extracted alcohols or direct analysis of the gasohol for alcohols and other oxygenates. A pressing need exists for a standard GC method which can be used to quickly identify oxygenated compounds in a given gasoline and provide an accurate measure of their concentrations.

II. APPROACH

Several gas chromatographic methods for oxygenates have been developed employing water extraction techniques and analysis by direct injection. There is a need, however, for a standardized method of analysis which has high potential for speed, low cost, and specificity. In order to review available methods, a literature search was conducted, and several gas chromatographic methods of both types were selected for evaluation.

The operating conditions for each method were implemented, and standards and samples were run for evaluation. Each method was initially evaluated based on three criteria: 1) ease of set-up; 2) the extraction efficiency of the different alcohols recovered by the water extraction methods; and 3) the effects of different gasolines' hydrocarbon composition. The methods were also evaluated for sample preparation time, analysis time, analyte resolution, and interferences. Finally, suggestions were made to modify and improve the existing method as necessary.

III. EXPERIMENTAL

Each analysis was performed using a Hewlett-Packard 7620A Research Chromatograph equipped with a flame ionization detector. A Hewlett-Packard 3354 Laboratory Data System was used to accumulate and store the raw digitized data, to integrate the peak areas, and to generate the data reports. An internal standard calculation method was used to produce the presented data.

A. Standard Preparation And Calibration

All standards were prepared to cover the concentration range expected in samples of typical oxygenate/gasoline blends.

1. Standards For Water Extraction Methods

Standards of 0.5, 1.0, 5.0, and 10.0 vol% each of methanol, ethanol, and t-butyl alcohol (TBA) in water were prepared. An internal standard was added as directed by each method. Unless otherwise specified, 1 vol% isopropyl alcohol (IPA) was used as the internal standard.

Calibration curves were prepared by plotting the ratio of alcohol peak area to internal standard peak area as a function of concentration for each alcohol standard. The curves were linearized by a least-squares program and forced through zero to obtain a response factor for each alcohol.

2. Standards For Direct Injection Method

Standards for analysis by direct injection were prepared in gasoline as directed in the method. The standards contained 0.5, 1.0, 5.0, and 10.0 vol% methanol, ethanol, TBA, and MTBE. Peak areas or peak area ratios were obtained for each oxygenate. Calibration curves were prepared and linearized using a least-squares program, and a response factor calculated for each oxygenate relative to the internal standard.

B. Sample Handling and Preparation

To represent gasolines having different compositions, each of the alcohols was blended with different base fuels and analyzed to study the gasoline matrix effect (see Table 1). AFLRL studies have shown that the differences in aromatics content affect the solubility of alcohols in the water extraction methods, and the varying components of the base stock can also interfere with the oxygenate analysis in the direct injection methods.

TABLE 1. GASOLINE COMPOSITION BY HYDROCARBON TYPES
ASTM D 1319

	Vol%		
	Saturates	Olefins	Aromatics
AL-10155-G	56.2	11.6	32.2
AL-9253-G	65.4	4.3	30.3

1. Water Extraction Methods

Samples containing 0.5, 1.0, 5.0, and 10.0 vol% each of methanol, ethanol, and TBA were prepared with two different gasolines. This range represents actual alcohol/gasoline blends. MTBE was not used since it cannot be successfully recovered by water extraction because of its low solubility in water.

Each alcohol/gasoline sample was prepared and water extracted as directed in each method. The water extracts were injected into the gas chromatograph. Peak area ratios were obtained for each extracted alcohol, and the appropriate predetermined calibration factor was used to calculate the volume percent of each alcohol present. If a different method of calculation was specified in a particular method, it was evaluated and compared to the results obtained by using the factors from the linear fit program.

2. Direct Injection Method

Samples containing 0.5, 1.0, 5.0, and 10.0 vol% each of methanol, ethanol, TBA, and MTBE were prepared with two different gasolines for analysis by direct injection. Each sample was injected and analyzed as directed by each method. An internal standard was added if specified by a particular method. Peak areas or peak area ratios were obtained, and the volume percent of each oxygenate present was calculated using the appropriate predetermined calibration factors. The calculation procedures outlined in each method were evaluated and compared to the results obtained by using the factors derived from the linear fit standard calculation program.

IV. EVALUATION OF SELECTED METHODS

In the search for a standard gas chromatographic method to analyze for the commonly used oxygenated gasoline extenders, six analytical techniques were evaluated at the U.S. Army Fuels and Lubricants Research Laboratory (Appendices A-F). This section evaluates those methods.

A. Standard Oil Of Indiana Method

The Research Department of Standard Oil Company of Indiana in Naperville, Illinois, has developed an internal standard method for the determination of t-butanol (TBA) in gasoline(6) (see Appendix A). The analysis for methanol and ethanol was also performed by using this method. In this method, alcohols are extracted with water, and the aqueous layer is analyzed by gas chromatography.

The retention time for each alcohol and its respective response factor is listed in Table 2. Sample preparation requires approximately 10 minutes, and maximum analysis time was 6 minutes.

TABLE 2. RETENTION TIMES AND RESPONSE FACTORS, (RELATIVE TO IPA) STANDARD OIL OF INDIANA METHOD

Component	RT, min	Factor
MeOH	0.76	2.063
EtOH	1.45	1.259
IPA	2.49	1.000
TBA	3.86	0.7905

This method prescribes the preparation of a single calibration standard composed of 5 wt% each of TBA and isopropyl alcohol (IPA). Using the IPA as an internal standard, a response factor is obtained, and the wt% TBA in a gasoline sample is calculated using the weight of the actual sample. This technique may not be adequate for higher or lower concentrations of alcohols, but if a range of standards is prepared (e.g., 0.5 through 10 percent), and if a linear calibration curve is prepared for each alcohol, the response factors obtained from these curves could be used for a given range of alcohol concentrations. Both techniques were used to calculate the percent of methanol present in four samples covering the range 0.5 through 10 vol%. Table 3 lists the values determined using both methods of calibration.

TABLE 3. METHANOL CONCENTRATIONS DETERMINED COMPARING STANDARD OIL OF INDIANA SINGLE STANDARD METHOD AND THE MULTIPLE STANDARD MODIFICATION

	Concentration, Vol %	
Known	Found, Single Std*	Found, Mulitple Stds
0.5	0.11	0.21
1.0	1.38	1.57
5.0	4.95	5.66
10.0	8.87	10.15

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* These values have been converted from wt% to vol% for comparison

The chromatograms displayed sharp, well-resolved peaks for methanol, ethanol and <u>iso</u>-propanol. The <u>t</u>-butanol peaks were well resolved but slightly broadened due to the 160°C isothermal column-oven temperature.

Good technique must be maintained to prevent the top layer of gasoline from entering the syringe while removing the bottom aqueous layer. When the sample is injected, the soluble hydrocarbons elute simultaneously with the alcohols and can possibly cause errors in alcohol quantitation.

Single-component standards in water and alcohol/gasoline samples of known concentrations were run in tests of reproducibility. Standard and average deviations for all standards and samples can be found in Table 4. The higher standard deviations found in the water extractions of the gasolines can be attributed to interference by hydrocarbons lighter than C_6 in the gasoline. This interference is due to lack of chromatographic resolution which adversely affects peak area quantitation. That is, the integrated peak area is not exclusively alcohol but a mixture of eight hydrocarbons and alcohol.

B. U. S. Army Energy and Water Resources Laboratory Method

The Fuels and Lubricants Division of the Energy and Water Resources Laboratory, U. S. Army Mobility Equipment Research and Development Command (MERADCOM) at Fort Belvoir, Virginia has developed a gas chromatographic procedure for analyzing the amounts of ethanol in gasohol samples(7) (See Appendix B). Evaluation of the method included extended application for the analysis for methanol and *t*-butanol. This method involves a one-to-one water extraction procedure with analysis of the water/alcohol solution.

The retention times (RT) used in this evaluation are listed in Table 5. The chromatograms show good resolution, peak symmetry for the methanol and ethanol peaks, but the *t*-butanol peak is broad and difficult to detect at low concentrations. Therefore, it is necessary to increase the electrometer sensitivity for the low-level detection of TBA. Due to the temperature programming and a high carrier flow rate of 60 ml/min., column bleed affects the elution of TBA.

This method routinely uses methanol as the internal standard, but for the analysis of methanol, ethanol was used as the internal standard. For vari-

TABLE 4. GC ANALYSIS OF ALCOHOL/GASOLINE BLENDS BY THE STANDARD OIL OF INDIANA METHOD

		Aqueous Standard			AL-10155-G, extracted			AL-9253-G, extracted		
Alcohol	Known	Found, %	Std Dev	Avg Dev	Found, %	Std Dev	Avg Dev	Found, %	Std Dev	Avg Dev
MeOH	0.5	1.81	0.01	0.003	0.21	0.08	0.06	0.69	0.13	0.10
	1.0	2.30	0.01	0.01	1.57	0.11	0.09	1.38	0.11	0.08
	5.0	5.72	0.02	0.01	5.66	0.32	0.25	6.28	0.22	0.17
	10.0	9.44	0.03	0.02	10.15	1.28	0.99	10.80	0.90	0.69
EtOH	0.5	1.57	0.08	0.06	0.63	0.01	0.01	0.68	0.03	0.02
	1.0	1.98	0.01	0.003	1.38	0.19	0.14	1.09	0.12	0.09
	5.0	5.33	0.02	0.01	5.72	0.10	0.06	5.42	0.10	0.06
	10.0	9.68	0.03	0.02	10.86	0.50	0.38	10.57	0.11	0.08
TBA	0.5	1.51	0.01	0.003	0.69	0.02	0.01	0.68	0.02	0.01
	1.0	1.91	0.01	0.003	1.09	0.04	0.03	1.19	0.03	0.02
	5.0	5.27	0.02	0.02	6.09	0.15	0.12	5.85	0.11	0.08
	10.0	9.73	0.03	0.02	9.94	0.59	0.42	10.33	0.03	0.02

TABLE 5. RETENTION TIMES RECORDED AT THE U.S. ARMY ENERGY AND WATER RESOURCES LABORATORY

Component	RT, min
MeOH	2.41
EtOH	4.65
TBA	8.17

ous combinations of alcohols, another alcohol, such as iso-propanol, may be used as the internal standard.

Maximum elution time using this method was 11 minutes. An additional time of 10 to 15 minutes is necessary for sample preparation, which requires the use of separatory funnels and weighing of the samples. This time was reduced by using a single 118-ml (4-oz) sample bottle for the extraction.

A 25-ml sample and 0.25 ml (1 vol%) of the internal standard are pipetted into the bottle, and 25 ml of distilled water are added. The bottle is stoppered and shaken for 1 minute, with the pressure being released every 15 seconds. After allowing the layers to separate, the extracted alcohol-in-water sample (bottom layer) is taken directly from the bottle with a microsyringe and injected into the gas chromatograph. This technique eliminates transferring the sample, which can result in evaporation. Although this technique uses volume percent for preparation, the method does contain a conversion factor for converting weight percent to volume percent.

The calibration procedure in this method calls for the preparation of a blend of alcohol and gasoline by weight. For evaluation of the method, a set of standards, 0.5 through 10 vol% alcohol in water, was prepared. Calibration curves were prepared and response factors obtained for each alcohol. Both techniques were used to calculate the percentage of methanol present in four samples, covering the range 0.5 through 10 vol%. The results shown in Table 6 indicate that there is little difference between the values obtained for each technique.

TABLE 6. METHANOL CONCENTRATIONS DETERMINED COMPARING U.S. ARMY ENERGY AND WATER RESOURCES LABORATORY METHOD AND THE MULTIPLE AQUEOUS STANDARDS LINEAR CALIBRATION METHOD

Concentration, Vol%		
	Found	
Known	U.S. Army*, Extraction	Aqueous Std
0.5	0.16	0.17
1.0	1.54	1.16
5.0	5.00	5.25
10.0	9.37	9.83

---

* These values have been converted to vol% for comparison.

Ideally the standards should be prepared in an aliquot of the neat gasoline if available; otherwise, water can be used as the standard matrix. Table 7 shows the different response factors derived from water standards as well as two different gasoline samples. Table 7 also shows the large variation in the response factors obtained for the different alcohols. As a result, a standard should be prepared for each gasoline undergoing analysis. The data in Table 8 shows in detail the effect of the gasoline aromatic composition.

TABLE 7. RESPONSE FACTORS (RELATIVE TO INTERNAL STANDARD) FOR U.S. ARMY ENERGY AND WATER RESOURCES LABORATORY METHOD

	Factors		
Component	Water Standard	AL-10155-G	AL-9253-G
MeOH	0.5236	1.1090	1.5460
EtOH	0.2990	0.9452	0.9107
TBA	0.3180	1.1490	1.0456

C. Standard Oil Company (Ohio) Method

The Standard Oil Company (Ohio) (SOHIO) Standard Test Method No. R-6-77, as presented in Appendix C, determines methanol in gasoline by gas chromatog-

TABLE 8. GC ANALYSIS OF ALCOHOL/GASOLINE BLENDS BY U.S. ARMY ENERGY AND WATER RESOURCES LABORATORY METHOD

	Concentration, Vol%			
		Found		
Alcohol	Known	Aqueous Standard	AL-10155-G	AL-9253-G
MeOH	0.5	0.40	0.17	0.13
	1.0	2.06	1.61	2.16
	5.0	5.54	5.25	6.19
	10.0	9.84	9.83	9.31
EtOH	0.5	0.39	0.27	0.29
	1.0	2.01	1.65	2.87
	5.0	5.48	5.14	5.36
	10.0	9.66	9.88	9.64
TBA	0.5	0.05	0.07	0.03
	1.0	1.31	1.36	2.12
	5.0	5.14	5.04	5.58
	10.0	9.93	9.96	9.62

raphy.(8) It may also be suitable for the determination of any alcohol lower than *n*-hexanol. During this evaluation, this method was used for the determination of methanol, ethanol, and *t*-butanol using *iso*-propanol as an internal standard. All alcohols present in a fuel were extracted with distilled water, and the water extract was analyzed by gas chromatography.

The retention times and response factors for each alcohol relative to internal standard obtained with this method are listed in Table 9. Typical GC analysis time was 4 minutes, with an additional 5 to 10 minutes required to prepare the water extractions using separatory funnels. This technique can be simplified by using a 118-ml (4-oz) sample bottle. After the layers have separated, the extracted alcohol-in-water sample (bottom layer) can be taken directly from the bottle with a microsyringe.

TABLE 9. RETENTION TIMES WITH RELATIVE RESPONSE FACTORS FOR SOHIO METHOD

Component	RT, min	Factor
EtOH	2.12	1.2230
IPA	1.53	1.0000
TBA	1.13	0.7339

In this method, standards are prepared in a gasoline matrix covering the concentration range of 0.01 to 1.0 vol% methanol. To avoid any interference from the gasoline matrix effect, the standards were prepared in water, and covered the concentration range of 0.5 to 10.0 vol% to represent actual alcohol/gasoline blends.

Calibration curves were prepared, and response factors were calculated using the computerized linear least-squares program. Peak areas were integrated by a computer, which also calculated the concentration of each component present relative to an internal standard.

The alcohol peaks obtained with this method were sharp, symmetrical, and well resolved. There was some lack of resolution between the TBA and IPA peaks. The loss of resolution became more pronounced at higher concentrations and caused problems with the integration of the peak areas. This effect may account for the low values found for the 10 vol% TBA samples. The results obtained for the GC analysis of methanol, ethanol, and TBA using the linear response factors are listed in Table 10.

Values were also calculated using the procedure outlined in the method. The results for methanol calculated with both techniques are shown in Table 11. The values found using the SOHIO method are lower in all cases except at 10 vol%. Both techniques appear to work equally well.

1. U.S. Army Fuels and Lubricants Research Laboratory Method

The U.S. Army Fuels and Lubricants Research Laboratory (USAFLRL) of the Energy Systems Research Division at Southwest Research Institute (SwRI) has modified the SOHIO method (Appendix D)(9). This version, still in the developmental stage, is intended for the gas chromatographic determination of methanol or ethanol in gasoline. The modified method also provides for the analysis of t-butanol and was included in the evaluation.

The retention times and response factors used in this method are listed in Table 12. Maximum instrument analysis time was 4 minutes, preceded by 5 to 10 minutes to prepare a sample for injection. The water extraction of the alcohols was performed in a 118-ml (4-oz) sample bottle as prescribed.

TABLE 10. GC ANALYSIS OF ALCOHOL/GASOLINE BLENDS BY THE SOHIO METHOD

Alcohol	Known	Aqueous Standard			AL-10155-G, extracted			AL-9253-G, extracted		
		Found, %	Std Dev	Avg Dev	Found, %	Std Dev	Avg Dev	Found, %	Std Dev	Avg Dev
MeOH	0.5	----	----	----	0.66	0.01	0.01	0.62	0.02	0.02
	1.0	1.09	0.01	0.01	1.22	0.02	0.01	1.12	0.01	0.003
	5.0	5.14	0.12	0.09	5.24	0.01	0.01	5.24	0.07	0.05
	10.0	9.92	0.09	0.06	10.46	0.09	0.06	10.79	0.03	0.02
EtOH	0.5	----	----	----	0.53	0.01	0.003	0.71	0.01	0.01
	1.0	1.07	0.01	0.01	1.09	0.01	0.003	1.24	0.01	0.003
	5.0	5.12	0.02	0.01	5.19	0.02	0.01	5.22	0.11	0.08
	10.0	9.96	0.03	0.02	10.61	0.13	0.10	10.39	0.01	0.003
TBA	0.5	----	----	----	0.66	0.01	0.003	0.64	0.01	0.01
	1.0	1.03	0.01	0.003	1.13	0.01	0.003	1.14	0.02	0.02
	5.0	5.04	0.06	0.04	5.51	0.10	0.08	5.17	0.15	0.11
	10.0	9.97	0.11	0.05	7.62	0.15	0.12	8.67	0.25	0.15

TABLE 11. METHANOL CONCENTRATIONS DETERMINED COMPARING SOHIO METHOD VALUES AND MULTIPLE AQUEOUS STANDARDS LINEAR CALIBRATION

	Concentration Vol%			
	AL-10155-G		AL-9253-G	
Known	SOHIO	Aqueous Std	SOHIO	Aqueous Std
0.5	0.48	0.62	0.52	0.66
1.0	0.98	1.12	1.08	1.22
5.0	5.18	5.24	5.19	5.24
10.0	10.86	10.79	10.51	10.46

TABLE 12. RETENTION TIMES AND RELATIVE RESPONSE FACTORS OBTAINED IN AFLRL METHOD

Component	RT, min	Factor
MeOH	0.69	0.5904
EtOH	1.17	0.8218
IPA	1.66	1.0000
TBA	2.26	0.7964

In this version, two sets of standards are prepared. One set is in a gasoline base covering the concentration range of 0.01 to 1.0 vol% methanol, and one set is in water covering the concentration range from 0.5 to 10.0 vol%.

The methanol, ethanol, and IPA chromatographic peaks are sharp, symmetrical, and well resolved. As in the SOHIO method, the TBA peaks are broader with less resolution between TBA and IPA. Here, the lack of resolution does not appear to cause as much interference as in the original SOHIO method. The results for the gas chromatographic analysis of methanol, ethanol, and TBA are shown in Table 13. Since this method is still in the developmental stage, more tests of reproducibility are warranted.

2. Recovery Efficiency

The AFLRL version of the SOHIO method was used to evaluate the recovery efficiency of various alcohols in different gasolines and to determine the necessity of an internal standard. To determine the ideal extraction ratio, each blend studied was extracted in the water to sample ratios 0.5:1, 1:1,

TABLE 13. GC ANALYSIS OF ALCOHOL/GASOLINE BLENDS BY THE AFLRL METHOD

		Aqueous Standard			AL-10155-G, extracted			AL-9253-G, extracted		
Alcohol	Known	Found, %	Std Dev	Avg Dev	Found, %	Std Dev	Avg Dev	Found, %	Std Dev	Avg Dev
MeOH	0.5	----	----	----	0.73	0.05	0.04	0.77	0.04	0.03
	1.0	1.09	0.01	0.01	1.16	0.08	0.05	1.18	0.03	0.02
	5.0	5.17	0.01	0.01	5.83	0.30	0.22	5.02	0.14	0.10
	10.0	9.91	0.02	0.02	9.53	0.04	0.03	10.38	0.40	0.29
EtOH	0.5	----	----	----	0.53	0.001	0.0003	0.73	0.02	0.02
	1.0	1.08	0.01	0.004	1.10	0.03	0.01	1.31	0.02	0.02
	5.0	5.22	0.02	0.01	5.42	0.29	0.22	5.31	0.02	0.02
	10.0	10.12	0.02	0.02	10.12	0.20	0.15	10.31	0.04	0.03
TBA	0.5	----	----	----	0.56	0.05	0.03	0.66	0.02	0.01
	1.0	1.08	0.01	0.01	1.12	0.04	0.02	1.15	0.04	0.03
	5.0	5.22	0.03	0.02	5.51	0.10	0.07	5.77	0.28	0.19
	10.0	9.88	0.03	0.02	9.42	0.10	0.06	9.37	0.08	0.07

2:1, and 3:1. Four subsequent separations were performed for each extraction ratio. The percent alcohol recovered was calculated using the following equation:

$$\%A = \frac{a}{f} \cdot \frac{V_w}{V_g}$$

$\%A$ = concentration of alcohol extracted from the gasoline, vol%

a = alcohol peak area, counts

f = detector response factor, counts/% alcohol in standard

V_w = total volume of water used to extract the alcohol, mL

V_g = volume of gasoline sample being extracted, mL

Blends of 10 vol% ethanol in two different gasolines were extracted with distilled water to determine if differences in gasoline composition had any effect on the recovery efficiency of ethanol. Blends of 10 vol% ethanol and 10 percent methanol in the same gasoline were extracted to compare the extraction efficiency of each alcohol. Table 14 lists the percent recovery for each water/gasoline ratio in four successive extractions for each blend. The percent recovery for each set of ratios was plotted as a function of the number of extractions.

TABLE 14. EFFICIENCY OF RECOVERY OF ALCOHOLS FROM GASOLINE BY WATER EXTRACTION

Sample	Water/Gasoline Ratio	Percent Recovery in Successive Extractions			
		1	2	3	4
10% EtOH/AL-10155-G	0.5:1	69.3	93.3	92.1	90.7
	1:1	84.2	93.2	90.5	93.0
	2:1	84.5	92.2	96.1	86.7
	3:1	83.8	93.8	99.8	92.4
10% EtOH/AL-9253-G	0.5:1	35.6	39.6	43.6	45.2
	1:1	41.5	49.8	54.1	49.0
	2:1	60.3	55.9	61.5	52.0
	3:1	59.7	57.7	65.1	61.6
10% MeOH/AL-9253-G	0.5:1	25.5	31.7	31.4	28.6
	1:1	30.6	39.1	37.9	41.9
	2:1	41.8	41.9	47.8	40.3
	3:1	39.0	42.8	38.3	37.9

As partition coefficients would predict, the recovery increased as the water-to-sample ratio was increased from 1:1 to 3:1. Beyond this ratio, the amount of water-extracted alcohol did not increase. As shown in Table 14, the amount of alcohol extracted appears to decrease with the 0.5 to 1 water/sample ratio as well as with the third and fourth successive extractions. This is probably caused by the detector's inability to respond accurately to low concentrations of the analyte in aqueous solutions.

Samples 1 and 2 of Table 14 show that the water extraction of the alcohol is affected by variations in the composition of the gasoline. Samples 2 and 3 illustrate the recovery of two different alcohols from the same gasoline. Because the composition of the gasoline (aromatic content) and the type of alcohol being extracted affect the efficiency of alcohol recovery, it is highly recommended that water extraction methods employ an internal standard to enhance alcohol quantitation.

D. ASTM Technical Division A-1 Method

Technical Division A-1 of ASTM has developed a method for the direct analysis of gasohol for ethanol using an internal standard (methanol) technique. This method was prepared as an appendix to the Informational Document on Gasohols from the ASTM Committee D-2 on Petroleum and Petroleum Products and is presented in this report as Appendix E. The procedure can be used for the determination of ethanol in gasohol using either a flame ionization or thermal conductivity gas chromatographic detector. For AFLRL evaluation of this method, a flame detector was used for the analysis of methanol, ethanol, t-butanol, and methyl-t-butyl ether in gasoline.

The retention times found with this method are listed in Table 15. MTBE has a retention time of 3.75 minutes, but could not be accurately determined due to interference from other hydrocarbons. There is little hydrocarbon interference with the methanol and ethanol peaks, but there were significant interferences with t-butyl alcohol when its concentration was low.

While only 3 to 4 minutes were needed for the determination of the alcohols, 35 minutes were required for the complete elution of the gasoline sample.

TABLE 15. COMPONENT RETENTION TIMES FOR ASTM TECHNICAL DIVISION A-1 METHOD

Component	RT, min
MeOH	0.52
EtOH	0.77
TBA	2.21

This procedure as developed is considered too time consuming. To reduce the total analysis time, some modifications were made to the temperature programing conditions: 85°C for 2 minutes after injection to 105°C at 10°C/min (this allows the alcohols to completely elute), 105° to 190°C at 30°C/min, hold at 190°C for 20 minutes. With these changes, total analysis time has been reduced to 27 minutes.

Since no standard is prepared in this method, a calibration curve must be prepared for each gasoline. The factors obtained for the four blends analyzed are listed in Table 16. Of particular interest is the difference between the factors for the two different methanol/gasoline blends. The values obtained for various blends of methanol in the two fuels are shown in Table 17. The gas chromatographic analysis for methanol, ethanol, and TBA in the same fuel is shown in Table 18. The differences between the known value of the alcohol and the analyzed value is attributed to simultaneous elution of the light hydrocarbons in the gasoline not resolved from alcohols.

TABLE 16. RELATIVE RESPONSE FACTORS USED IN ASTM TECHNICAL DIVISION A-1 METHOD

Sample	Factor
MeOH/AL-9253-G	11.24
MeOH/AL-10155-G	26.18
EtOH/AL-10155-G	5.07
TBA/AL-10155-G	3.01

TABLE 17. GC ANALYSIS OF METHANOL/GASOLINE BLENDS BY ASTM TECHNICAL DIVISION A-1 METHOD

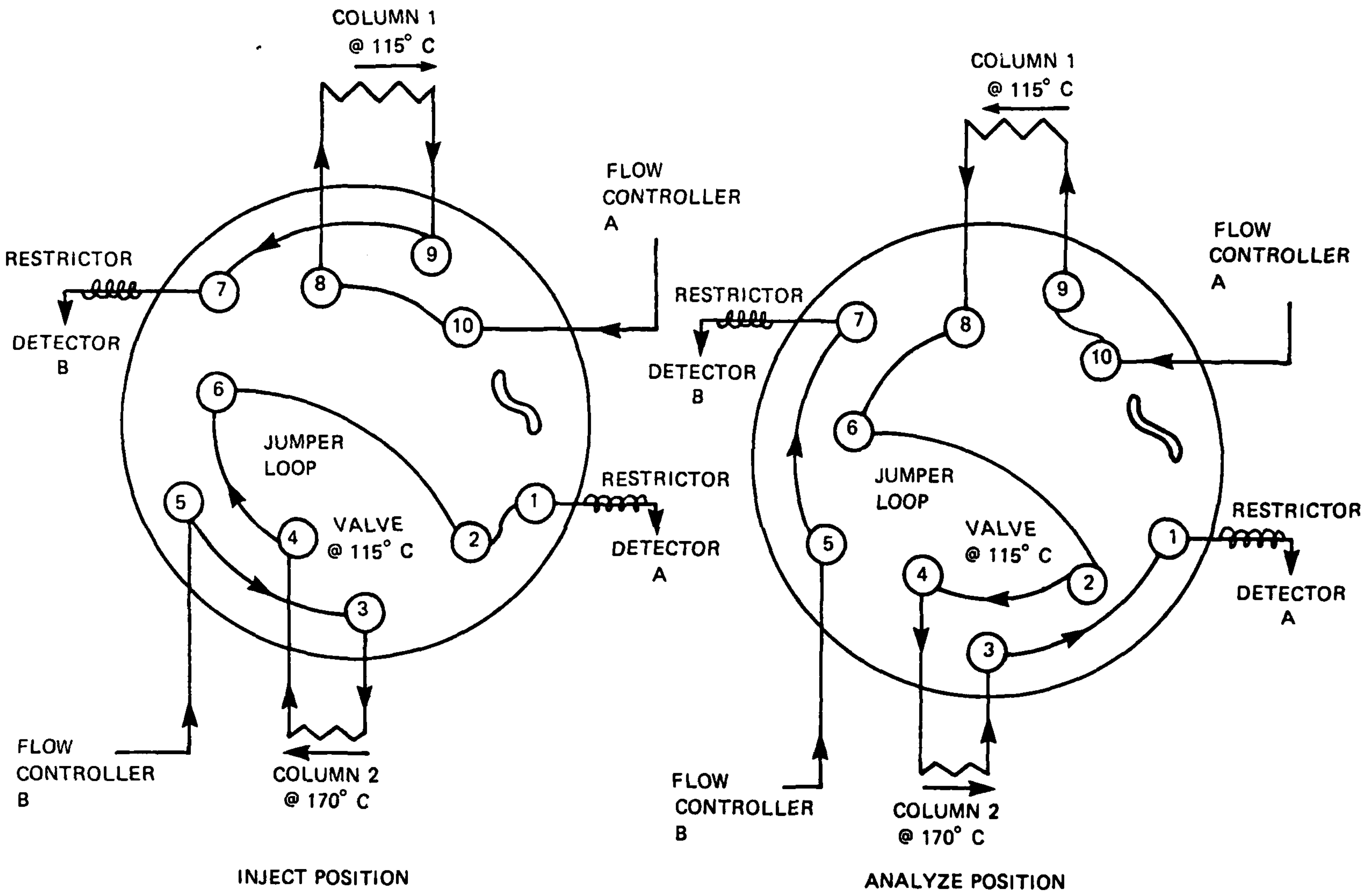
Methanol Concentration, Vol%		
	Found	
Known	AL-9253-G	AL-10155-G
0.5	0.19	0.31
1.0	1.80	1.59
5.0	5.05	1.26
10.0	9.91	9.96

TABLE 18. GC ANALYSIS OF ALCOHOL/ AL-10155-G BLENDS BY ASTM TECHNICAL DIVISION A-1 METHOD

	Concentration, Vol%	
Alcohol	Known	Found
MeOH	0.5	0.31
	1.0	1.59
	5.0	1.26
	10.0	9.96
EtOH	0.5	0.24
	1.0	1.52
	5.0	5.43
	10.0	9.74
TBA	0.5	0.78
	1.0	2.26
	5.0	5.78
	10.0	9.50

E. UOP Inc. Method

UOP Inc. has developed a method for the determination of "Oxygenates in Gasohols by Gas Chromatography" (see Appendix F).(10) This method is used for the determination of specific alcohols and ethers in hydrocarbon mixtures. Blends of methanol, ethanol, t-butanol, and methyl-t-butyl ether in gasolines were analyzed using this direct injection method. The following modifications were made to evaluate this method: 1) Because of availability, 1/8-in. stainless steel tubing (10 and 15 feet lengths, respectively) was substituted for the recommended 3/16-in. column material. 2) The method specified the use of a thermal conductivity detector, but this laboratory chose to employ a flame ionization detector also because of availability. 3) A readily available 10-port valve was substituted for the specified 8-port valve. The valve modification is shown in Figure 2.



INJECT POSITION

ANALYZE POSITION

FIGURE 2. COLUMN SWITCHING VALVE SCHEMATIC FOR UOP METHOD

A Bendix Valve Oven was used to heat the first column and valve, while column 2 was located in the gas chromatograph oven. The valve and columns were installed as shown in Figure 3. Because of the gas chromatograph/auxiliary oven configuration, this setup required long connecting lines between the detectors, the valve, and the columns. Small bore tubing with 0.76-mm ID and 2-mm (1/16-in.) OD was used to reduce the integrated volumes.

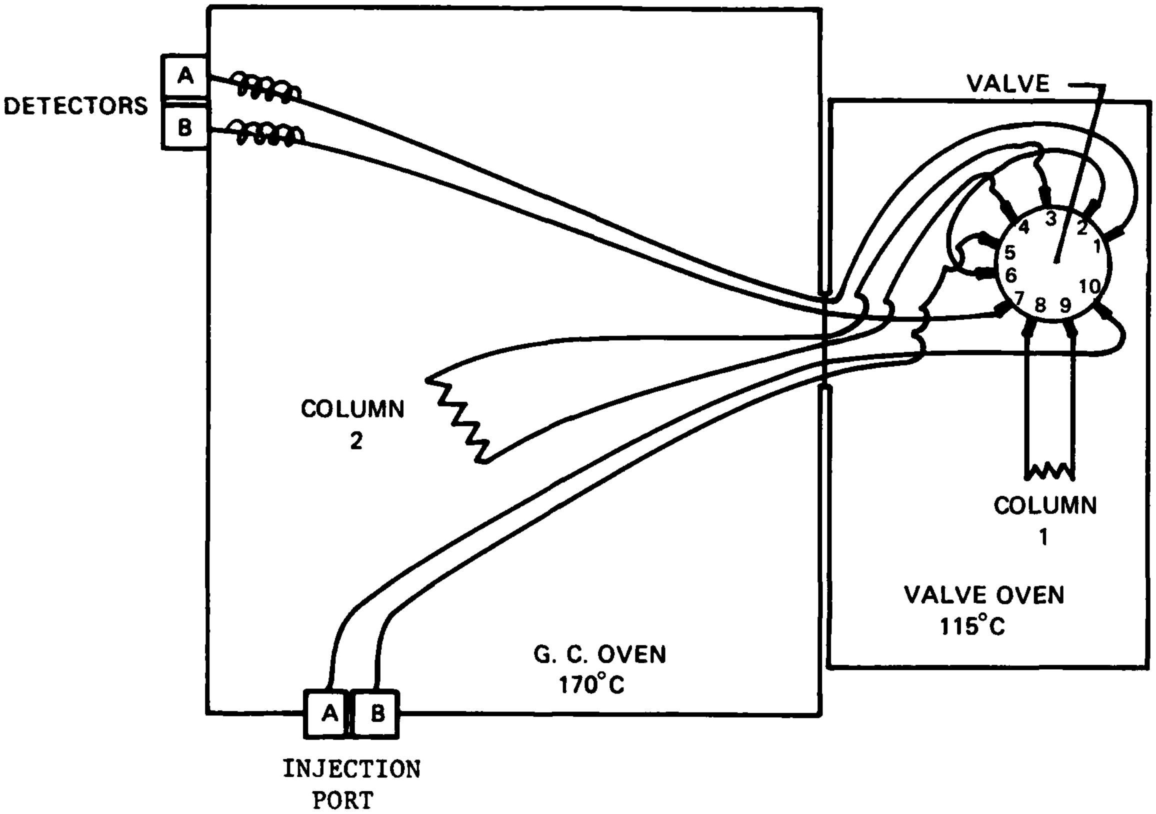


FIGURE 3. AFLRL COLUMN/OVEN/VALVE SCHEMATIC

A second restrictor was required prior to detector A to prevent extinguishing the detector flame when the valve was switched. This restrictor would not be necessary using a TC detector. After the second restrictor was installed, the flow rate and back pressure of the columns were equalized. The final flow rate was established at 25 ml/min with a back pressure of 56 psig.

Both columns were packed as directed in the method. It should be noted that the Chromosorb P coated with tetracyanoethylated pentaerythritol (TCEPE) had a distinct odor similar to burned plastic after drying on the rotary evaporator.

Standards of 0.5, 1.0, 5.0, and 10 vol% each of methanol, ethanol, TBA, and MTBE in toluene with 10 vol% methylcyclopentane to establish the first switching time, T_1, were prepared and analyzed. Valve switching times, T_1 and T_2, were established at 3.6 minutes and 17.2 minutes, respectively. The resulting retention times for the analytes are shown in Table 19. The total elution time is approximately 25 minutes per sample. Calibration curves were prepared from the peak areas, and factors were calculated. A second set of factors was also calculated using 10 vol% of the four alcohols as directed by the method. Table 20 lists the factors for each oxygenate using both techniques of calibration. The values found in the GC analysis of these four alcohols blends in the same gasoline are shown in Table 21. Both sets of factors were used for each oxygenate. Values were also found for

TABLE 19. RETENTION TIMES OBTAINED USING UOP METHOD

Component	RT, min
MeOH	12.31
EtOH	13.15
IPA	13.98
TBA	14.85
MTBE	16.18

TABLE 20. COMPARISON OF CALIBRATION FACTORS FROM UOP METHOD TO MULTIPLE STANDARDS CURVE

	Factors	
Component	UOP Method	Multiple Stds Curve
MeOH	8.29×10^{-5}	1.07×10^{-4}
EtOH	4.52×10^{-5}	6.08×10^{-5}
IPA	3.61×10^{-5}	*
TBA	2.52×10^{-5}	4.20×10^{-5}
MTBE	3.75×10^{-5}	5.19×10^{-5}

*Used for internal standard evaluation; therefore, response factor not applicable.

ethanol in two different gasolines using both factors for ethanol. Table 22 shows these values. The factors which were calculated as directed in the method give values closer to the known volume percent of the oxygenated fuel blends.

TABLE 21. GC ANALYSIS OF ALCOHOL/AL-10155-G BLENDS BY UOP METHOD

Component	Concentration, Vol.% Known	Found UOP Method	Found Multiple Std Curve
MeOH	0.5	0.23	0.29
	1.0	0.33	0.43
	5.0	4.81	6.21
	10.0	12.79	16.51
EtOH	0.5	0.62	0.83
	1.0	1.92	2.59
	5.0	6.33	8.52
	10.0	11.13	14.97
TBA	0.5	0.32	0.53
	1.0	1.41	2.35
	5.0	4.58	7.64
	10.0	7.56	12.60
MTBE	0.5	0.59	0.82
	1.0	1.91	2.65
	5.0	3.67	5.08
	10.0	10.79	14.93

TABLE 22. COMPARISON OF ETHANOL VALUES OBTAINED BY UOP METHOD AND MULTIPLE STANDARDS MODIFICATION

Ethanol Concentration, Vol%

Known	Found AL-10155-G UOP	Found AL-10155-G Mutiple Std Curve	Found AL-9253-C UOP	Found AL-9253-C Multiple Std Curve
0.5	0.62	0.83	0.50	0.67
1.0	1.92	2.59	3.62	4.87
5.0	6.33	8.52	8.01	10.77
10.0	11.13	14.97	10.52	14.15

An internal standard is not used in this method; therefore, it is essential that the same volume of sample be injected each time. Ethanol standards with an internal standard of IPA were analyzed, and a calibration curve was prepared. The factor obtained was used to calculate the amount of ethanol present in blends with two different gasolines. The values found are listed in Table 23. No significant improvement was made by using an internal standard.

TABLE 23. ANALYSIS OF ETHANOL/GASOLINE BLENDS BY THE UOP METHOD MODIFIED TO USE INTERNAL STANDARDS

Ethanol Concentration, Vol%			
	Found		
Known	Toluene	AL-10155-G	AL-9253-G
0.5	1.21	0.55	0.42
1.0	1.37	1.72	3.01
5.0	4.44	4.33	6.37
10.0	10.24	8.11	11.77

V. SUMMARY AND CONCLUSIONS

The results of this study have shown that the quantitative analysis of the commonly used oxygenated gasoline extenders is a difficult task. Obstacles like hydrocarbon interferences, solubility differences, and gasoline composition must be overcome. Therefore, none of the six methods evaluated stood out as being the ultimate procedure.

Figures 4 through 6 graphically present the analytical error of the appraised methods for three different alcohols. The accuracy of the Standard Oil of Indiana method suffered from light hydrocarbon interferences. The U.S. Army Energy and Water Resources Laboratory method was laborious in that new standards were required for each fuel to be analyzed and only in the analysis of TBA was this method significantly more accurate (see Figure 6).

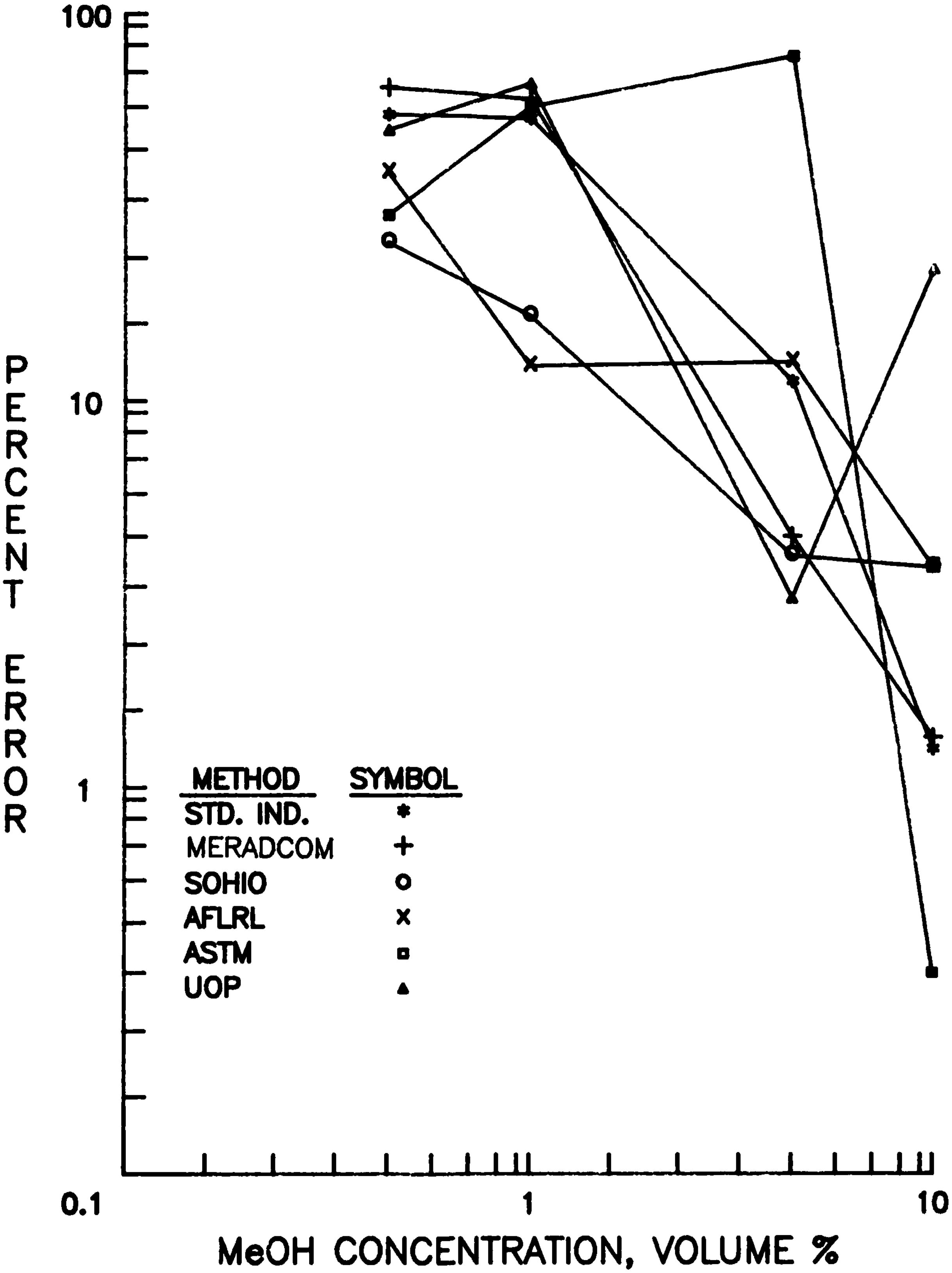


FIGURE 4. COMPARISON OF ACCURATE MeOH ANALYSIS
FOR SIX ANALYTICAL METHODS

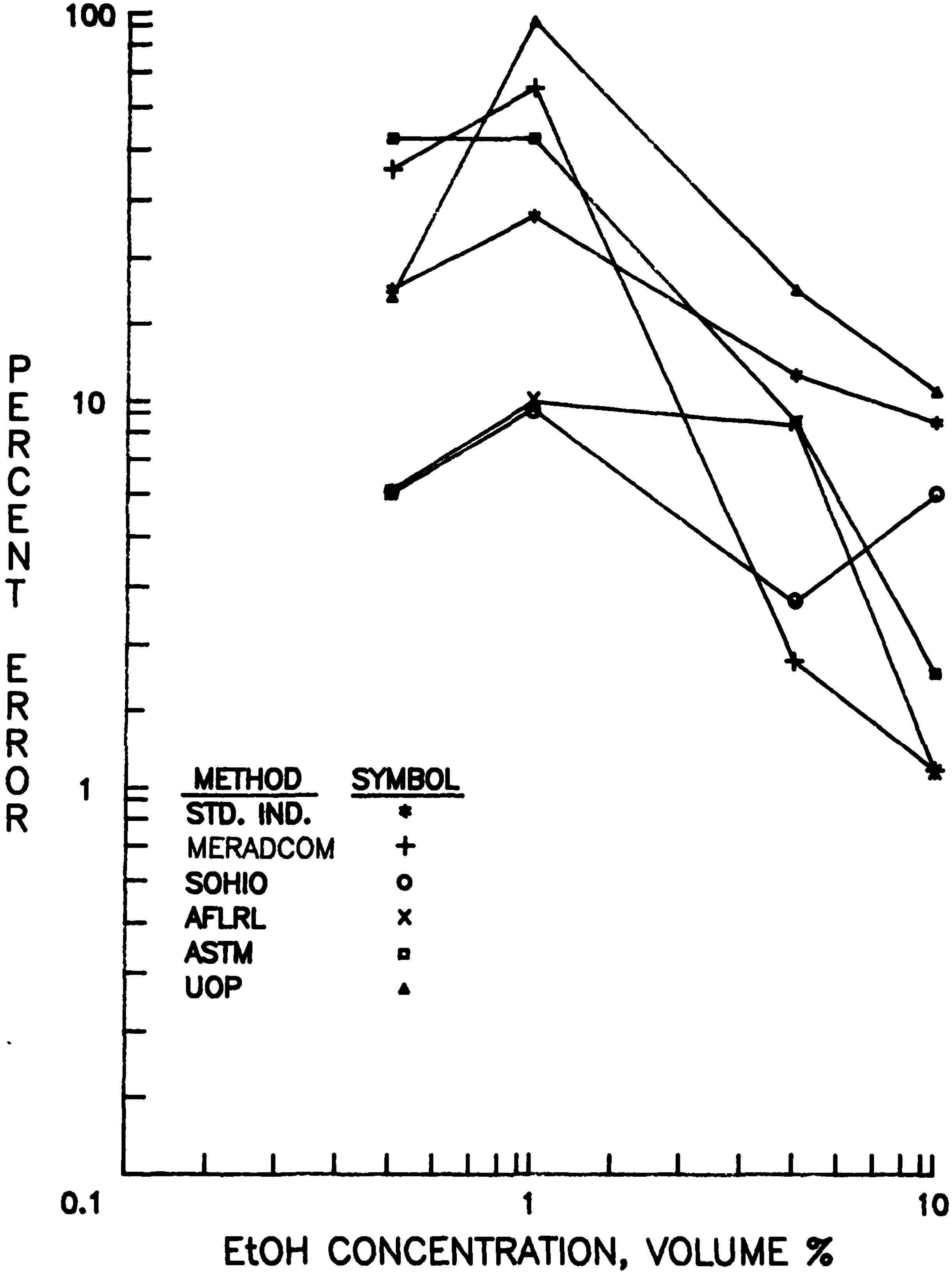


FIGURE 5. COMPARISON OF ACCURATE EtOH ANALYSIS FOR SIX ANALYTICAL METHODS

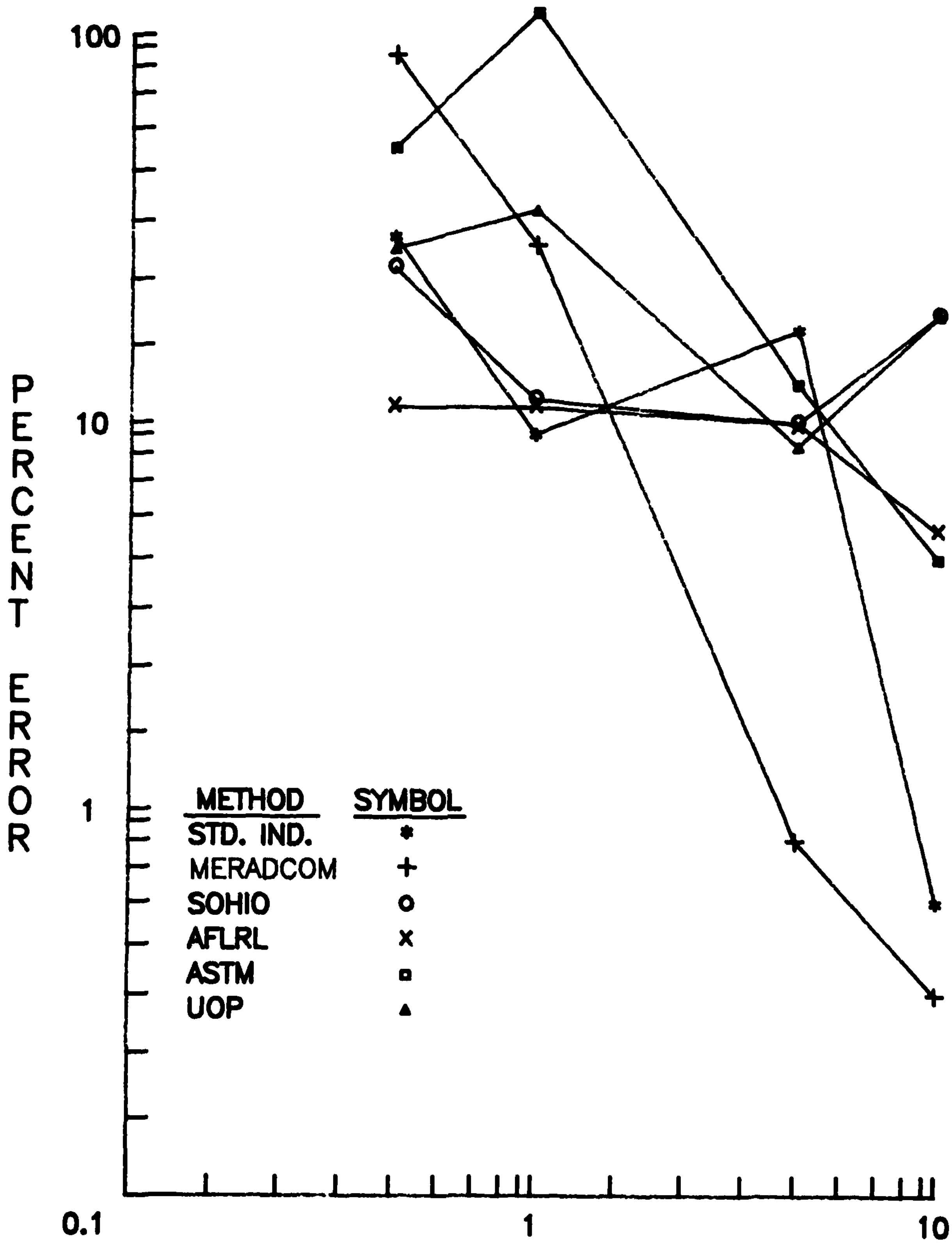


FIGURE 6. COMPARISON OF ACCURATE TBA ANALYSIS FOR SIX ANALYTICAL METHODS

Of the water extraction methods, the AFLRL method and the SOHIO method showed the best overall accuracy. The AFLRL modifications of the parent SOHIO method were simply an effort to expedite and streamline the analysis while maintaining accuracy. The evaluation shows that the AFLRL method is preferred for the analysis of C_1-C_4 alcohols.

The recovery efficiency of alcohols was investigated using the AFLRL method of water extraction. As the water-to-sample extraction ratio was increased, the percent recovery of the alcohols also increased. However, the amount of recovered alcohol never did reach 100 percent. In addition, the extraction efficiencies of different alcohols in a given fuel are different, and the recovery efficiency of an alcohol varies in different fuels. Since the extraction efficiencies of all alcohols in all fuels are not known, the use of an internal standard is essential for accurate analysis.

Two methods, from the ASTM Technical Division A-1 and UOP, Inc., are direct injection techniques which are attempts to reduce sample preparation time and effort as well as analyze the non-water extractable extenders such as MTBE. The ASTM procedure lacked the ability to adequately resolve MTBE from the hydrocarbons which reduced the accuracy. There are also significant interferences with low levels of TBA as shown in Figure 6. The UOP method, even with its extensive hardware requirement, has the most overall promise of the six methods evaluated. Even though Figures 4 through 6 show this method to be the least accurate, with sufficient refinement, this direct injection method could probably be improved to an acceptable level of accuracy. It should be noted that this method could be best employed by a laboratory which can afford to dedicate an instrument to the procedure. Table 24 summarizes the evaluation determined by this work.

VI. RECOMMENDATIONS

- A rapid and accurate analytical method for oxygenated gasoline extender compounds is urgently needed to meet supplier and user demands. New methods are currently being developed both in the United States and Europe. The ASTM is actively seeking to standardize a method. There-

TABLE 24. SUMMARY RATING OF SIX ANALYTICAL METHODS FOR THE DETERMINATION OF ALCOHOLS IN GASOLINE

Procedure	Features	Considerations
Standard Oil of Indiana	• Water extraction method • Internal standard • Standard GC hardware requirement • Single column/isothermal • Developed for TBA analysis, but can be expanded to determine methanol and ethanol	• Developed for TAB analysis • Accuracy diminishes below 10% concentration
U.S. Army MERADCOM	• Water extraction method • Internal standard • Standard GC hardware • Single column/temp. programmed • Good analyte resolution	• Developed for ethanol analysis • Excessive sample prep and analysis time • Accuracy diminishes below 10% concentration • Water extraction affected by gasoline hydrocarbon composition • Least accurate for TBA analysis
Standard Oil of Ohio	• Water extraction method • Internal standard • Standard GC hardware • Single column/isothermal • Good analyte resolution • Applicable for C_1-C_6 alcohols	• Developed for methanol analysis • Laborious sample prep procedure • Water extraction affected by gasoline hydrocarbon composition
U.S. Army Fuels and Lubricants Research Lab	• Water extraction method • Internal standard • Standard GC hardware • Single column/isothermo • Good overall accuracy • Good analyte resolution • Applicable for C_1-C_6 alcohols	• Water extraction affected by gasoline hydrocarbon composition
ASTM Tech Div. A-1	• Direct injection technique • Internal standard • Standard GC hardware • Single column/temp. programmed • Applicable for MTBE within limits	• Developed for ethanol analysis • Long analysis time • Extensive interferences of the gasoline sample • Poor overall accuracy
UOP, In.	• Direct injection method • External standard • Applicable to all common gasoline extenders • Good analyte resolution	• Complicated hardware requirements • Extensive set-up procedure • Poor overall accuracy

fore, additional investigation is recommended to obtain better separation/resolution and accurate quantitation in the analysis of oxygenated gasoline blends by gas chromatography.

- As a result of the work performed in this study, it is recommended that the AFLRL method be used for the analysis of water-extractable oxygenates such as C_1-C_4 alcohols.

- The UOP method is also a recommended procedure, especially for the analysis of the nonwater-extractable oxygenates such as MTBE.

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4. "Alcohol Content of Gasohol by Gas Liquid Chromatography (Water Extraction Method), Appendix X6, Information Document on Gasohol (Motor Fuel Containing 10% Volume of Denatured Ethanol in Gasoline)," 1980 Annual Book of ASTM Standard, Vol 23, p 928.

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7. "Procedure for Determining Absolute Ethyl Alcohol (200°) in Gasohol by Gas Chromatography," U.S. Army Mobility Equipment Research and Development Command, Energy and Water Resources Laboratory (DRDME-GL), Ft. Belvoir, VA, November 1979.

8. "Methanol in Gasoline and Diesel Fuel Chromatographic Method," The Standard Oil Company (Ohio), Cleveland, OH, 1966, Revised 1970, 1977.

9. "Alcohols in Gasoline and Diesel Fuel by Gas Chromatography," modification of Standard Oil Company (Ohio) method by U.S. Army Fuels and Lubricants Research Laboratory, Southwest Research Institute, San Antonio, TX, 1981.

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APPENDIX A

DETERMINATION OF t-BUTYL ALCOHOL IN GASOLINE

STANDARD OIL OF INDIANA

1978

Standard Oil Company (Indiana)
Research Department
Naperville, Illinois

DETERMINATION OF t-BUTYL ALCOHOL IN GASOLINE

Summary

The t-butyl alcohol concentration in gasoline is determined by gas chromatography. The samples are extracted with water and the aqueous layer is analyzed for the alcohol. Water bottoms can be analyzed under the same chromatographic conditions.

Apparatus

5 ml pipets
Hamilton 10 μl syringe
Screw-cap vials capable of holding 10 ml
A gas chromatograph equipped with a flame ionization detector

Operating Conditions

GC column: 5' x 1/8" stainless steel column packed with 80/100 mesh Porpak R
Carrier flow rate: 25 ml/min.
Column oven temperature: 160°C
Injector temperature: 200°C
Detector temperature: 200°C
Sample size: 1 μl

Procedure

A standard is prepared by first pipetting 5 ml of water into a vial. Then about 0.2g each of isopropanol (internal standard) and t-butyl alcohol (TBA) are weighed into the vial. Finally, 5 ml of gasoline free of TBA are pipetted into the vial and the vial is shaken. The alcohols are rapidly extracted into the water layer. A 10 μl syringe should be filled with 3 to 5 μl of water. While sampling the standard, the water in the syringe should be slowly expelled as the syringe passes through the top gasoline layer. Once the syringe is in the water layer, the remaining water in the syringe should be expelled and after a few seconds, a microliter of standard should be drawn up into the syringe. The sample is then injected onto the column. The analysis time is about eight minutes. After the peaks have eluted, a response factor should be calculated as shown below.

Samples are prepared by pipetting 5 ml of water into vial and weighing in 0.2g of internal standard. Five ml of sample are pipetted into the vial and weighed. The samples are analyzed as described for the standard. The weight percent t-butyl alcohol is then calculated as described below.

Aqueous solutions can be analyzed directly on the same column. A separate standard containing the two alcohols in water should be prepared to determine the response factor for these samples. If the water bottom samples are highly contaminated with organic compounds, they can be extracted with octane and the water layer analyzed as before.

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Other water soluble alcohols in gasoline can be analyzed using this extraction procedure and column. For example, the concentration of ethyl alcohol in "gasohol" has been determined using this procedure. It may be necessary to adjust the column temperature for these other alcohols.

Calculations

The response factor is calculated by

$$\text{RF} = \frac{\text{wt. t-butyl alcohol}}{\text{wt. isopropanol}} \times \frac{\text{area isopropanol}}{\text{area } \underline{\text{t}}\text{-butyl alcohol}}$$

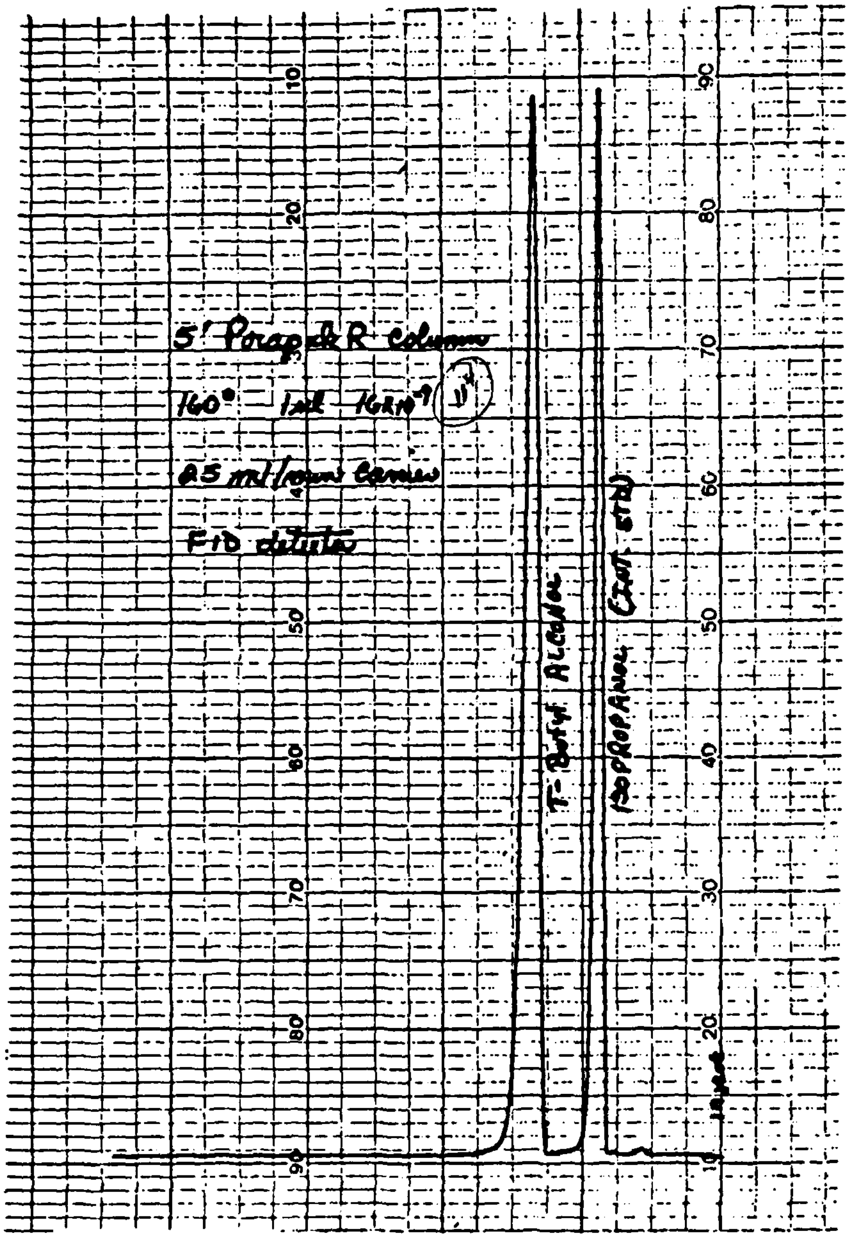
and the weight percent t-butyl alcohol in gasoline by

$$\text{wt\% TBA} = \frac{\text{wt isopropanol}}{\text{wt sample}} \times \frac{\text{area t-butyl alcohol}}{\text{area isopropanol}} \times 100$$

Peak heights can be substituted for areas, if necessary.

R. E. Pauls

REP/ch
6/22/78


5' Porapak R column
160° 1x1 16x10⁻⁹
25 ml/min carrier
FID detector
T-Butyl Alcohol
Isopropanol (Int. Std)
Inject
10
20
30
40
50
60
70
80
90

APPENDIX B

PROCEDURE FOR DETERMINING ABSOLUTE ETHYL ALCOHOL (200°) IN GASOHOL BY GAS CHROMATOGRAPHY

U.S. ARMY MOBILITY EQUIPMENT RESEARCH
AND DEVELOPMENT COMMAND

(Energy and Water Resources Laboratory, DRDME-GL)

NOVEMBER 1979

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PROCEDURE FOR DETERMINING ABSOLUTE ETHYL ALCOHOL (200°) IN GASOHOL BY GAS CHROMATOGRAPHY

1. Scope - This method covers the determination of absolute ethyl alcohol (200°) in concentrations of 8.0 to 25.0 percent. The results are reported to the third decimal place.

2. Summary of Method - The sample of GASOHOL is initially exposed to a water extraction procedure which quantitatively removes all the ethyl alcohol. Following this one to one GASOHOL to water separation, the water ethyl alcohol solution is introduced into a gas chromatographic column containing a porous polymer. Outstanding separations of volatile compounds are achieved, notably sharp symmetrical peaks and low retention volumes are found for water and alcohols. Calibration is performed by using laboratory blends of the gasoline, alcohol and water mixtures and analyzing the sample. Table I - Absolute Methanol is used as the Internal Standard.

3. Apparatus - Chromatograph - Hewlett Packard 5834A equipped with a micro-processor 18815OA GC Terminal.

4. Reagents and Materials

   a. Porous Polymer

   b. Carrier Gas

   c. Absolute Methanol and Ethanol

   d. Distilled Water

   e. Separatory Funnel, 500° ml capacity

   f. 1 and 10 ml Syringe

   g. Erlenmeyer Flask, 50 ml capacity

5. Calibration - Prepare a blend of gasoline and ethyl alcohol. Weigh nine grams to one gram of gasoline and 1 gram to one mg of ethyl alcohol and place in a separatory funnel, add ten grams to one mg of distilled water, shake for 15 seconds and let it settle until it turns clear (5 min). Remove the water layer into a tared 50 ml erlenmeyer flask and accurately weigh. Add ten percent by weight of absolute methanol to the water. Then inject 0.5 µl into the gas chromatograph using conditions listed in Table II. Typical retention times are found in Table III.

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Procedure for Determining Absolute Ethyl Alcohol (200^{o}) in GASOHOL by Gas Chromatography

6. Procedure - Ten grams weighed to the nearest one mg of the GASOHOL is put into a separatory funnel. Add ten grams distilled water weighed to the nearest one mg to the funnel and shake for 15 seconds. Let settle until clear, accurately remove the water layer and retain in a tared 50 ml erlenmeyer flask. Weigh and add ten percent by weight internal standard. Swirl and follow instructions in Table II for column and instrument conditions. After injection, allow chromatogram to develop until peak at 9.13 retention time elutes (Fig 1A & B). Then terminate the analysis, the total time for this test procedure is 25 minutes.

7. Calculations - The 5834A Gas Chromatograph with micro-processor electronically prints out the internal standard method and automatically applies the detector response factor in the printed results. The results are given in weight percent. In order to convert them to volume percent multiply by 0.945.

TABLE I

COMPOSITION OF STANDARD BLENDS, ABSOLUTE ETHYL ALCOHOL (200°) CONTENT

KNOWN % WT VALUES	FOUND % WT VALUES	AVG % WT VALUES	% VOL VALUES
8.725	8.786,8.627	8.706	8.227
11.530	11.516,11.499	11.507	10.874
16.931	16.924,17.039	16.981	16.047
25.749	25.650,25.705	25.527	24.123

Field Samples of GASOHOL:

Charlottesville, VA
Area A - 11.609,11.625, Avg 11.617 % wt 10.978% vol
Area B - 11.366,11.337, Avg 11.353 % wt 10.728% vol

Alexandria, VA
No Lead - 11.290,11.314, Avg 11.302% wt 10.680% vol
Regular - 12.627,12.630, Avg 12.628% wt 11.933% vol

TABLE II - TYPICAL COLUMN & CONDITIONS

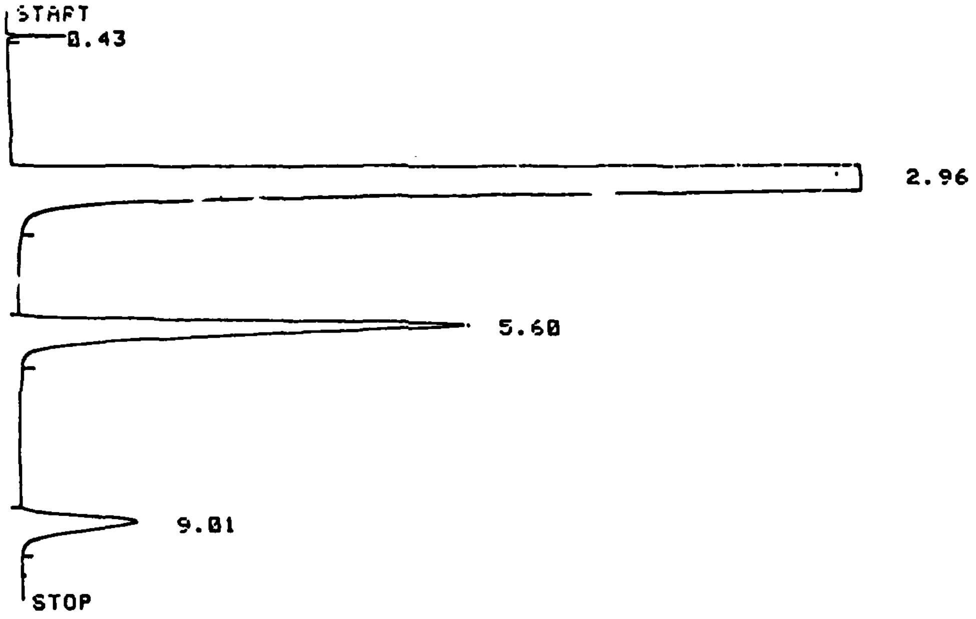
Column - On Column Glass
Material - Chromosorb 101
Length, ft - 6' - 1.8
Inside dia, mm - 4 mm

Temperature	
Sample Inlet System, deg, C	250
Detector, Thermal Conductivity, °C	295
Column	
Programmed, °C/Min	6
Initial Temperature °C	60
Final Temperature °C	125
Carrier Gas Material	Helium
Flow Rate, Cm^3/Min	60
Sample Size, μl	0.6
Speed In/Min	1

TABLE III - TYPICAL RETENTION TIME, MINUTES

Compound	Retention Time (Min.)
Water	2.97
Methanol	5.67
Ethyl Alcohol (200°)	9.13

FIGURE 1-A



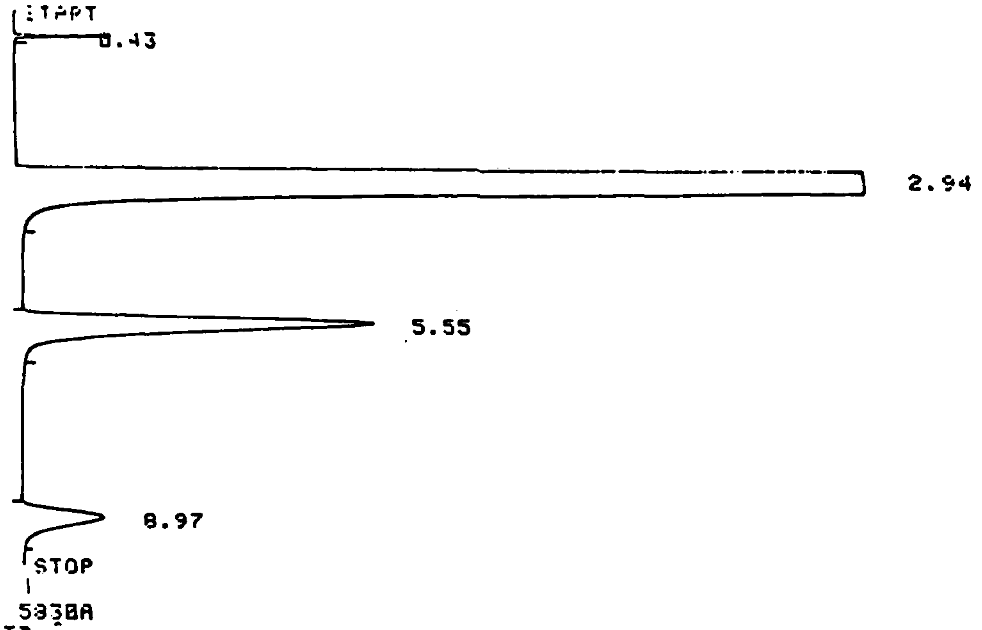
```
hp 5830A
ISTD
  RT       EXP RT         AREA          CAL #     AMT

 5.60       5.61          79020      R       1
 9.01       8.99          21720              2     8.786

              XF:  1.0000 E+ 0      ISTD AMT: 9.7580 E+ 0

XF: 0                ISTD AMT: 9 . 7 5 8 0
READY
```

FIGURE 1-B



```
5830A
ISTD
 RT      EXP RT       AREA       CAL #    AMT

 5.55     5.61       60910     R   1
 8.97     8.91       16440         2    8.627
         XF:  1.0000 E+ 0     ISTD AMT: 9.7580 E+ 0
```

APPENDIX C

METHANOL IN GASOLINE AND DIESEL FUEL GAS CHROMATOGRAPHIC METHOD

STANDARD OIL COMPANY (OHIO)
STANDARD TEST METHOD R6-77

ISSUED 1966
REVISED 1970, 1977

METHANOL IN GASOLINE AND DIESEL FUEL
Gas Chromatographic Method

SCOPE

1.1 This method is intended for the determination of methanol in gasoline and diesel fuel by gas chromatography.

1.2 The range of applicability for methanol is 0.01 to 1.0 vol%.

1.3 This method may be used for the determination of isopropanol or any other alcohol lower than n-hexanol if the extraction efficiency is known and a different alcohol is used as an internal standard.

SUMMARY OF METHOD

2.1 An internal standard, isopropanol, is added in known concentration to the gasoline or diesel fuel sample. All the alcohols present in the gasoline or diesel fuel are then extracted with distilled water and the water extract is introduced into a gas chromatographic column packed with glycerol on firebrick. The eluted alcohols are detected by a hydrogen flame ionization detector and recorded on a conventional strip chart. The peak areas or heights are measured and applied to the appropriate calibration curve from which the volume percent is obtained.

SAMPLE SIZE

3.1 A sample size of 100 ml is required.

APPARATUS

4.1 Chromatograph--Any chromatographic instrument having a flame ionization detector wth an overall sensitivity sufficient to detect the lowest concentration level of the methanol calibration standard.

4.2 Column--A 1.8 m (6-ft.) length of 3.2 mm (1/8-in.) O.D., 2.2 mm (0.085 in.) I.D. stainless steel tubing.

4.3 Recorder, strip chart--A recording potentiometer with a full scale deflection of 0 to 1 mV or less should be used. The full scale response of the recorder should not exceed 1 second and a maximum noise rate of ± 0.3% of full scale.

4.4 Microsyringe, 5-μl capacity--Precision Sampling Corp., P.O. Box 15119, Baton Rouge, LA, Pressure Lok Series "CG-130", Cat. No. 130021 or equivalent.

4.5 Vibrator, electric--The Alltech Associates, Inc., GC column vibrator, Model 4012, is recommended.

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4.6 Vacuum Source.

4.7 Evaporator, vacuum, rotary. Curtin-Matheson Catalog No. 086-850 or equivalent.

4.8 Flask, boiling, round bottom, short neck, with 24/40 ₮ joint, 500-ml capacity. Modify as shown in Figure STM R 6.1.

4.9 Funnels, separatory, 250-ml capacity, pear-shaped, equipped with stoppers and greaseless stopcocks.

4.10 Automatic Buret, with integral reservoir for dispensing 0.25 ml of internal standard, 5 ml capacity. Fisher Scientific Cat. No. 20-112B or equivalent.

4.11 Micro Buret, Koch, with integral reservoir, 0.01 ml subdivisions, 1-ml capacity. VWR Scientific Cat. No. 17477-002 or equivalent.

4.12 Lamp, infrared.

4.13 Pipets, 25-ml, volumetric.

4.14 Funnel, short stem.

4.15 Filter Paper, Whatman No. 2.

4.16 Sample Vial, 10-ml capacity. Supelco, Inc., Cat. No. 03-3105.

4.17 Septum, 20 mm neoprene, for 10-ml vial. Supelco, Inc., Cat. No. 03-3203.

4.18 Seals, aluminum, for 10-ml vial. Supelco, Inc., Cat. No. 03-3251.

4.19 Hand Crimper, for sealing 10-ml vial. Supelco, Inc., Cat. No. 03-3280.

4.20 Flasks, volumetric, 100-ml capacity.

4.21 Tubing, tygon, hydrocarbon resistant, orange color, 1/4-in. I.D. x 1/16-in. wall. Fisher Scientific F-4040 or equivalent.

MATERIALS

5.1 For carrier gas; either of the following:

5.1.1 Nitrogen Gas, 99.999% pure.

5.1.2 Helium Gas, 99.999% pure.

When helium is used as the carrier gas the analysis time is shortened. However, nitrogen is the preferred carrier gas because the column efficiency is higher, the thermal noise level in the detector is lower, and it is much cheaper.

5.2 For flame detector:

5.2.1 Air, zero grade.

5.2.2 Hydrogen Gas, 99.999% pure.

5.3 For column packing:

5.3.1 Stationary Phase.--Glycerol, reagent grade.

5.3.2 Support Phase.--Chromosorb P, non acid-washed, 60 to 80 mesh.

5.4 For calibration standards:

5.4.1 Methanol, 99+ mol. %.

5.4.2 Gasoline Base, containing no alcohols.

Sohio gasoline fill STA 091 has proved satisfactory.

5.4.3 Water, distilled.

5.5 For the internal standard:

5.5.1 Isopropanol, 99+ mol. %.

5.6 For cleaning column:

5.6.1 Chloroform.

5.6.2 Acetone.

5.7 Glass Wool, silanized.

PREPARATION OF PACKING

6.1 Weigh 80 g. of the dry Chromosorb P and pour into the 500-ml boiling flask (4.8).

6.2 Dissolve 20 g of glycerol in approximately 100 ml of methanol and pour into the flask containing Chromosorb P.

6.3 Attach the flask to the Rotovac and start the Rotovac.

6.4 Allow the packing to mix thoroughly in order to insure uniform coating of the support material.

6.5 Near the end of the evaporation step, turn on the infrared lamp to drive off any of the residual methanol.

PREPARATION OF COLUMN

7.1 Cleaning of Column.--Clean the stainless steel tubing as follows:

7.1.1 Attach a glass funnel to one end of the stainless steel tubing, using a short length of the tygon tubing (4.21) to make the connection.

7.1.2 Hold or mount the stainless steel tubing in an upright position and place a drain beaker under the outlet end of the tubing.

7.1.3 Pour about 50 ml of chloroform into the funnel and allow it to drain through the stainless steel tubing and into the drain beaker.

> CAUTION: Chloroform is a toxic material and inhalation must be avoided. The chloroform washing step should be carried out in a fume hood or well-ventilated room.

7.1.4 Pour about 50 ml acetone into the funnel and allow it to drain through the stainless steel tubing and into the drain beaker.

> Steps 7.1.1 through 7.1.4 can be performed without the glass funnel and vinyl tubing if fine-tipped wash bottles are available.

7.1.5 Remove the glass funnel and attach the stainless steel tubing to an air line, using the tygon tubing to make the connection.

7.1.6 Remove all solvent from the stainless steel tubing by blowing air through or pulling a vacuum.

> The air stream should be free of particulate matter. Use a filter on the air stream if necessary.

7.2 Packing of Column.

7.2.1 Preform the stainless steel tubing to fit the chromatograph.

7.2.2 Close one end of the tubing with a small glass wool plug (5.7) and connect this end to the vacuum source by means of a glass wool packed tube.

7.2.3 To the other end connect a small funnel by means of a short length of tygon tubing.

7.2.4 Start the vacuum and pour the packing (Section 6) into the funnel until the column is full.

> While filling the column gently vibrate the column with the electric vibrator (4.5) to settle the packing.

7.2.5 Remove the funnel and shut off the vacuum; when the column reaches atmospheric pressure, disconnect the vacuum source.

7.2.5 Remove the funnel and shut off the vacuum; when the column reaches atmospheric pressure, disconnect the vacuum source.

7.2.6 Remove the top ½-inch of packing and insert a glass wool plug in this end of the column.

7.3 Conditioning of Column.

7.3.1 Connect the column inlet to the injection port of the chromatograph.

7.3.2 Pass carrier gas (5.1) through the column at approximately 30 cc/min.

7.3.3 Condition the column at 60° C for one hour followed by 30 minutes at 90° C.

Do not exceed the maximum temperature limit of 100° C.

7.3.4 Cool the column to room temperature with the carrier gas flowing through it.

CALIBRATION CURVES

8.1 Standard Samples.--Using the gasoline base (5.4.2) prepare 6 known blends covering the concentration range from 0.01 vol. % to 1.0 vol. % methanol as given in the following table:

	Blend 1 Vol. % ml	Blend 2 Vol. % ml	Blend 3 Vol. % ml	Blend 4 Vol. % ml	Blend 5 Vol. % ml	Blend 6 Vol. % ml
Isopropanol	0.25	0.25	0.25	0.25	0.25	0.25
Methanol	0.01	0.05	0.10	0.20	0.50	1.00

Use burets or pipets of appropriate sizes to measure the volumes.

8.1.1 Add approximately 25-50 ml of the gasoline base into each of the 100-ml volumetric flasks.

8.1.2 Accurately measure by means of a buret (4.11) the indicated quantities of each component into the individual 100-ml volumetric flasks (8.1.1) containing the gasoline base. Then dilute to the mark with the gasoline base and mix well.

8.1.3 Extract each standard sample blend in duplicate as directed in Section 9.2.

8.2 Chromatographic Analysis.--Chromatograph each standard as directed in Section 10.2. Measure the peak area or height as directed in 11.1.2 and calculate peak area or height ratio as directed in 11.2.

8.3 Curves.--Determine the relationship between peak area or height ratio and concentration of methanol. Prepare calibration curves by means of the graphical procedure or the calculation procedure.

> Calibration points should lie on a straight line. With methanol some deviation from linearity is to be expected at concentrations lower than 0.05 vol. %; however, no point should deviate by more than ± 2% relative.

8.3.1 Graphical Procedure.--On arithmetic graph paper, plot peak area or height ratios (vertical axis) versus concentration of methanol (horizontal axis) and draw the best line.

> Group the standards so that concentration can be read to the nearest 0.005 vol. %.

8.3.2 Calculation Procedure.--To determine the best line mathematically calculate the slope and intercept of the calibration curve by means of the linear regression equation.

> Follow steps 1 through 10 on the worksheet shown in Figure STM R 6.2.

8.4 Check the column against a standard of low and high range at least once per week; recalibrate if the analysis differs from the original concentration by more than ± 3% relative.

PREPARATION OF SAMPLE

9.1 Measurement of Sample.

9.1.1 Add approximately 25-50 ml of gasoline or diesel fuel to the 100-ml volumetric flask, then accurately measure by means of a buret (4.10) 0.25 ml of isopropanol into the flask, dilute to the mark with the sample, stopper, and mix thoroughly.

9.2 Extraction of Sample.

9.2.1 Pipet 25 ml of sample plus internal standard (9.1.1) into the separatory funnel.

9.2.2 Add 25 ml of distilled water to the separatory funnel.

9.2.3 Stopper the funnel, invert, release the pressure immediately after inverting. Shake for one minute and release the pressure every fifteen seconds.

9.2.4 Allow the layers to separate and draw off 5 to 10 ml of the aqueous (lower) layer through a filter funnel into a clean dry sample vial. Seal with septum and aluminum seal by crimping.

PROCEDURE

10.1 Preparation of Chromatograph.

10.1.1 Connect the cooled, conditioned column (Section 7) to both the injection port and the flame ionization detector port.

10.1.2 Adjust the operating conditions to those listed in Table STM R 6.1.

10.1.3 Allow the chromatograph to run at the required maximum sensitivity (Table STM R 6.1) until a straight baseline is obtained.

10.1.4 Optimize the chromatographic detector system as directed in the manufacturer's instruction manual.

10.2 Injection of Sample.

10.2.1 Flush the 5 μl microsyringe 3 times with the aqueous extract and then fill with about 3 μl of the extract.

10.2.2 Slowly eject the extract until 1.0 μl remains in the syringe; wipe the needle with a tissue and draw back the plunger to admit 1 to 2 μl of air into the syringe.

10.2.3 Insert the needle of the syringe through the septum cap of the chromatograph and push until the barrel of the syringe is resting against the septum cap; then push the plunger to the hilt and remove the syringe immediately from the chromatograph.

> This injection technique is necessary so that sharp, symmetrical peaks are obtained.

10.2.4 Attenuate the peaks so that they are all on scale when measuring peak heights.

> See Table STM R 6.1 for approximate attenuation.

CALCULATIONS AND REPORT

11.1 Interpretation of Chromatogram.

11.1.1 Identify on the chromatogram the methanol and the internal standard (isopropanol) peaks to be measured from the retention times of the standards.

The typical chromatogram (Figure STM R 6.3) will contain 2 main peaks. In order of elution they are isopropanol and methanol.

11.1.2 Measure peak height or area of the component peak and the internal standard peak.

Measurement may be accomplished by any method that meets the precision requirements of Section 12. Acceptable methods of area measurement are by computer or integrator. Other methods such as by planimeter and triangulation (multiplying peak height by width at half height) should only be used if the prior are not available.

11.1.3 Convert the area measurement of all areas to a common base by using the following formula if necessary.

Corrected Area to Common Base = Area X Attenuation

11.2 Calculations.

11.2.1 Peak Area or Height Ratio.--Calculate the ratio of the peak area or height of methanol to the peak area or height of internal standard (isopropanol).

$$\text{Ratio} = \frac{P_c}{P_i}$$

where:

P_c = peak area or height of component (methanol)
P_i = peak area or height of internal standard (isopropanol).

11.2.2 Concentration of Component.--Determine the concentration of component in the sample by one of the following:

11.2.2.1 Graphical Procedure.--Read from the appropriate calibration curve the concentration of the methanol corresponding to the peak area or height ratio.

11.2.2.2 Calculation Procedure.--Calculate the concentration of the methanol corresponding to peak height or area ratio from the slope and intercept of the appropriate calibration curve from the equation

$$\text{MeOH , Vol. \%} = \frac{As - a}{b}$$

where:

As = peak area or height ratio (11.2.2)
a = intercept (8.3.2)
b = slope (8.3.2)

11.3 Report.

11.3.1 Report the methanol content in volume percent.

Report concentrations of less than one volume percent to the nearest 0.01 vol. %; report concentrations greater than one percent to the nearest 0.05 vol. %.

PRECISION

12.1 The following criteria should be used for judging the acceptability of results (95 percent confidence).

12.1.1 Repeatability.--Duplicate results by the same operator shall be considered suspect if they differ by more than 0.03 vol. %.

12.1.2 Reproducibility.--Undetermined.

Issued: 1966
Revised: 1970, 1977

INSTRUMENT PARAMETERS

Detector	Flame Ionization
Column	
Length, meters	1.8
Outside Diameter, mm	3.2
Stationary Phase, wt. %	20% Glycerol
Support Material, mesh size	Chromosorb P(NAW); 60 to 80 mesh
Temperature:	
Sample Inlet System, °C	150
Detector, °C	200
Column, °C	90
Carrier Gas	Nitrogen or Helium
Flow Rate, cc/min.	30
Detector	
Hydrogen Flow Rate, cc/min.	30
Air Flow Rate, cc/min.	300
Recorder Range, mV	0 to 1
Chart Speed, cm/min.	1
Sample Size, μl	1
Total Cycle Time, min.	
Nitrogen Carrier Gas	8
Helium Carrier Gas	7
Gas Hold-up Time (Methane), sec.	18 ± 5
Linear Gas Rate (Methane), cm/sec.	
Nitrogen Carrier Gas	10
Helium Carrier Gas	10.5
Range, amps/mV[a]	10^{-9}
Attenuation[a]	2

a) The sensitivity and attenuation setting required will vary with each chromatograph. These settings were used on a Varian Aerograph Series 2700 and are intended as a guide only.

Table STM R 6.1

MODIFIED BOILING FLASK

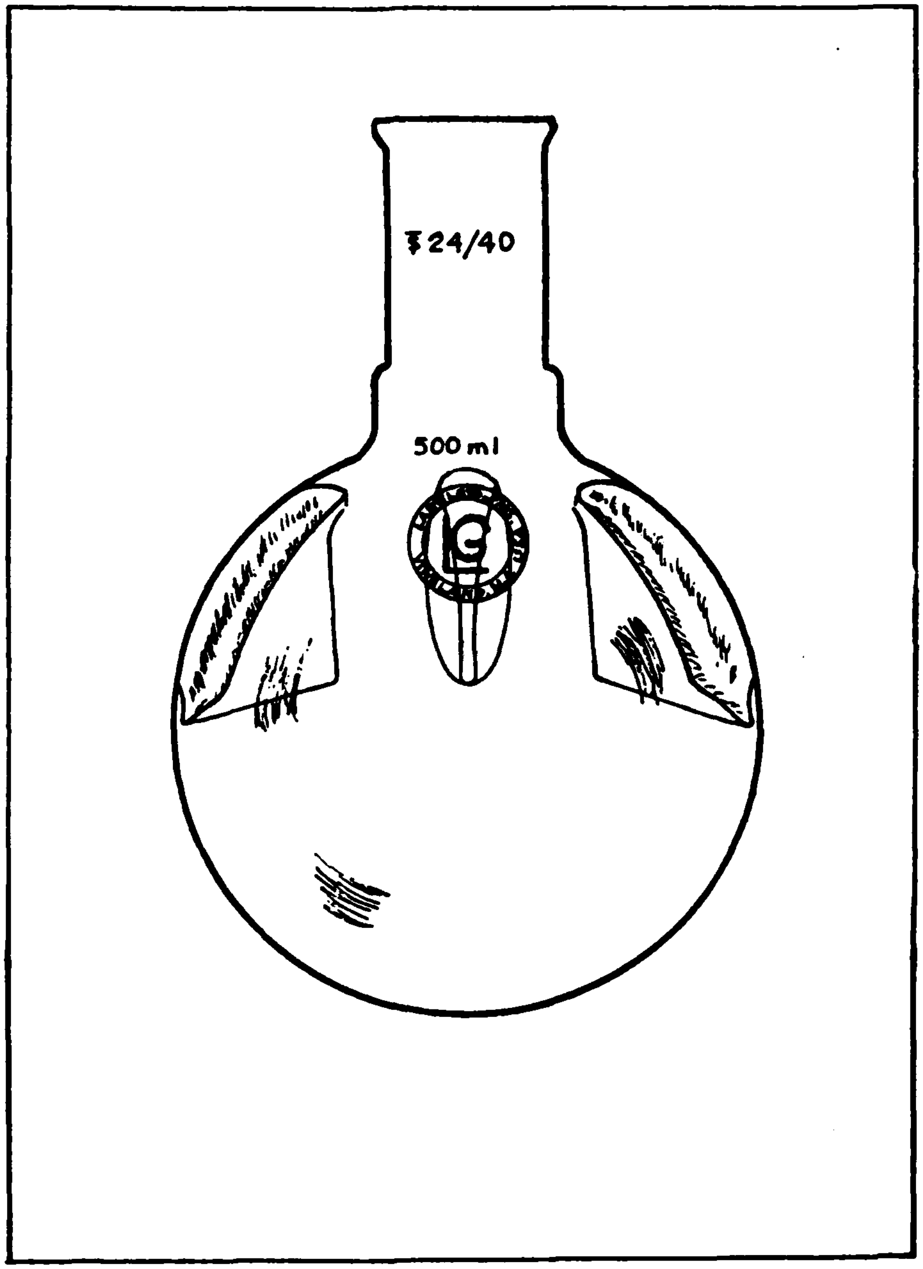

Figure STM R 6.1

WORKSHEET FOR
CALCULATION OF CALIBRATION CURVE

C denotes Concentration   A denotes Peak Area (or Height) Ratio

Standard #	C	C^2	A	CA
1				
2				
3				
4				
5				
6				

Sum: $\Sigma C =$ _____ $\Sigma C^2 =$ _____ $\Sigma A =$ _____ $\Sigma CA =$ _____

Average: $\bar{C} =$ _____ $\bar{A} =$ _____

Number of Points: $n =$ _____

Step

(1) $\Sigma CA =$ _____

(2) $(\Sigma C)(\Sigma A) \div n =$ _____

(3) Step (1) - Step (2) = _____

(4) $\Sigma C^2 =$ _____

(5) $(\Sigma C)^2 \div n =$ _____

(6) Step (4) - Step (5) = _____

(7) Slope: $b =$ Step (3) ÷ Step (6) = _____

(8) $\bar{A} =$ _____

(9) $b\,\bar{C} =$ _____

(10) Intercept: $a =$ Step (8) - Step (9) = _____

(11) Peak Area (or Height) of sample: $A_s =$ _____

(12) $A_s - a =$ Step (11) - Step (10) = _____

(13) Concentration in Sample: $C_s =$ Step (12) ÷ Step (7) = _____

Figure STM R 6.2

CHROMATOGRAM

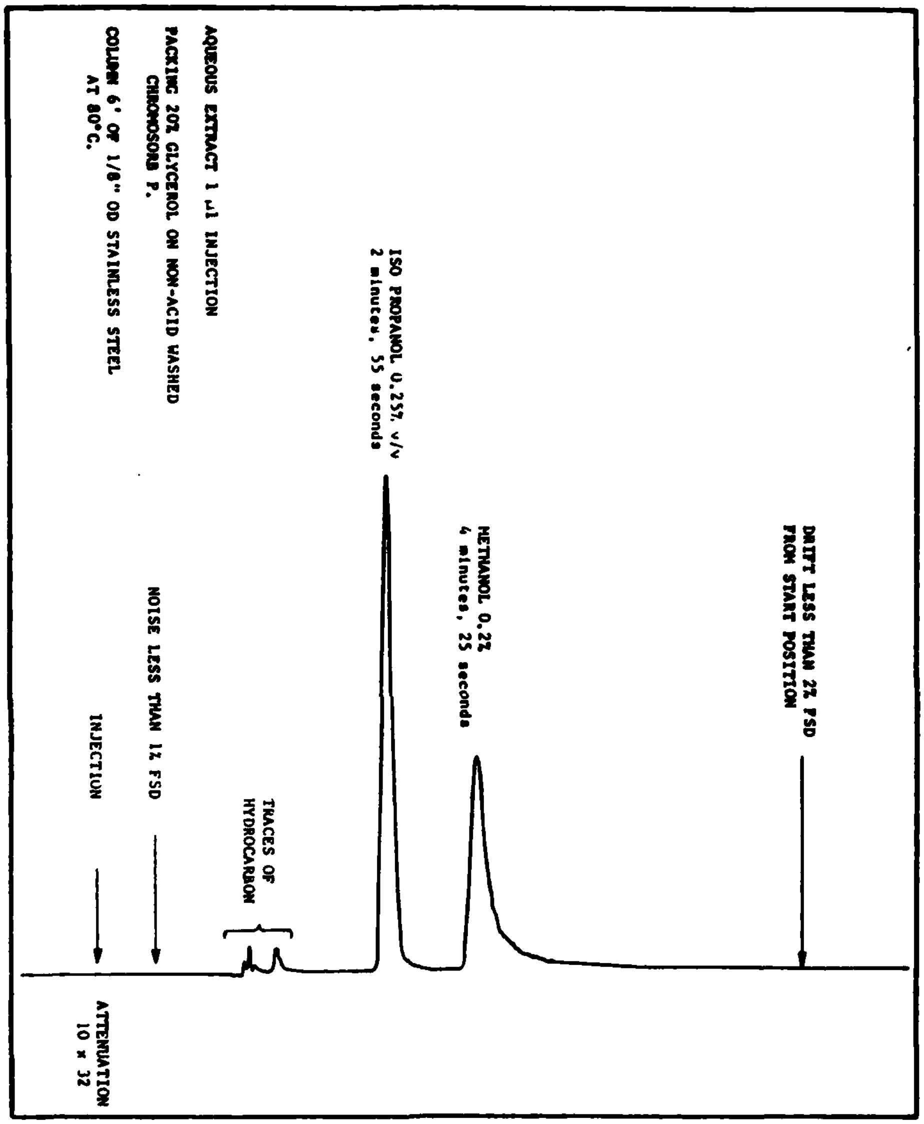

FIGURE STM R 6.3

APPENDIX D

ALCOHOLS IN GASOLINE AND DIESEL FUEL BY GAS CHROMATOGRAPHY

U.S. ARMY FUELS AND LUBRICANTS RESEARCH LABORATORY

(Modified from Standard Oil Company (Ohio)
Standard Test Method R6-77, Appendix C)

1981

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ALCOHOLS IN GASOLINE AND DIESEL FUEL
Gas Chromatographic Method

SCOPE

1.1 This method is in a developmental stage and is intended for the gas chromatographic determination of methanol or ethanol in gasoline and diesel fuel.

1.2 The range of applicability for methanol is 0.01 to 15 vol%.

1.3 This method may be used for the determination of isopropanol or any other alcohol lower than n-hexanol if the extraction efficiency is known and a different alcohol is used as an internal standard.

SUMMARY OF METHOD

2.1 An internal standard, isopropanol, is added in known concentration to the gasoline or diesel fuel sample. All the alcohols present in the gasoline or diesel fuel are then extracted with distilled water and the water extract is introduced into a gas chromatographic column packed with Chromosorb 101. The eluted alcohols are detected by a hydrogen flame ionization detector and recorded on a conventional strip chart. The peak areas or heights are measured and applied to the appropriate calibration curve from which the volume percent is obtained.

SAMPLE SIZE

3.1 A sample size of 100 ml is required.

APPARATUS

4.1 Chromatograph--Any chromatographic instrument having a flame ionization detector with an overall sensitivity sufficient to detect the lowest concentration level of the methanol calibration standard.

4.2 Column--A 1.8-m (6-ft) length of 3.2 mm (1/8-in.) O.D., 2.2 mm (0.085 in.) I.D. stainless steel tubing.

4.3 Recorder, strip chart. A recording potentiometer with a full scale deflection of 0 to 1 mV or less should be used. The full scale response of the recorder should not exceed 1 second and a maximum noise rate of ±0.3% of full scale.

4.4 Microsyringe, 5-microliter capacity. Precision Sampling Corp., P.O. Box 15119, Baton Rouge, LA, Pressure Lok Series "CG-130," Cat. No. 130021 or equivalent.

4.5 Vibrator, electric. The Alltech Associates, Inc., GC column vibrator, Model 4012, is recommended.

4.6 Vacuum Source.

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4.7 Evaporator, vacuum, rotary. Curtin-Matheson Catalog No. 086-850 or equivalent.

4.8 Flask, boiling, round bottom, short neck, with 24/40 joint, 500-ml capacity. Modify as shown in Figure STM R 6.1.

4.9 Funnels, separatory, 250-ml capacity, pear-shaped, equipped with stoppers and greaseless stockcocks.

4.10 Flasks, volumetric, 100-ml capacity.

4.11 Tubing, Tygon, hydrocarbon resistant, orange color, 1/4-in. I.D. x 1/16-in. wall. Fisher Scientific F-4040 or equivalent.

MATERIALS

5.1 For carrier gas:

5.1.1 Helium Gas, 99.999% pure.

5.2 For flame detector:

5.2.1 Air, zero grade.

5.2.2 Hydrogen Gas, 99.999% pure.

5.3 For column packing:

5.3.1 Support Phase. John-Mansville Century series Chromasorb 101 80/100 mesh.

5.4 For calibration standards:

5.4.1 Methanol, 99+ mol. %.

5.4.2 Gasoline Base, containing no alcohols.

5.4.3 Water, deionized.

5.5 For the internal standard:

5.5.1 Isopropanol, 99+ mol. %.

5.6 For cleaning column:

5.6.1 Chloroform.

5.6.2 Acetone.

5.7 Glass Wool, silanized.

PREPARATION OF COLUMN

6.1 Cleaning of Column--Clean the stainless steel tubing as follows:

6.1.1 Attach a glass funnel to one end of the stainless steel tubing, using a short length of the Tygon tubing (4.21) to make the connection.

6.1.2 Hold or mount the stainless steel tubing in an upright position and place a drain beaker under the outlet end of the tubing.

6.1.3 Pour about 50 ml of chloroform into the funnel and allow it to drain through the stainless steel tubing and into the drain beaker.

> CAUTION: Chloroform is a toxic material and inhalation must be avoided. The chloroform washing step should be carried out under a fume hood or in a well-ventilated room.

6.1.4 Pour about 50 ml acetone into the funnel and allow it to drain through the stainless steel tubing and into the drain beaker.

> Steps 6.1.1 through 6.1.4 can be performed without the glass funnel and vinyl tubing if fine-tipped wash bottles are available.

6.1.5 Remove the glass funnel and attach the stainless steel tubing to an air line, using the Tygon tubing to make the connection.

6.1.6 Remove all solvent from the stainless steel tubing by blowing air through or pulling a vacuum.

> The air stream should be free of particulate matter. Use a filter on the air stream if necessary.

6.2 Packing of Column.

6.2.1 Perform the stainless steel tubing to fit the chromatograph.

6.2.2. Close one end of the tubing with a small glass wool plug (5.7) and connect this end to the vacuum source by means of a glass wool packed tube.

6.2.3 To the other end connect a small funnel by means of a short length of Tygon tubing.

6.2.4 Start the vacuum and pour the packing into the funnel until the column is full.

6.2.5 Remove the funnel and shut off the vacuum; when the column reaches atmospheric pressure, disconnect the vacuum source.

6.2.6 Remove the top 1/2-inch of packing and insert a glass wool plug in this end of the column.

6.3 Conditioning of Column.

6.3.1 Connect the column inlet to the injection port of the chromatograph.

6.3.2 Pass carrier gas (5.1) through the column at approximately 33 cc/min.

6.3.3 Condition the column at 125°C for one hour followed by 30 minutes at 230°C.

6.3.4 Cool the column to room temperature with the carrier gas flowing through it.

CALIBRATION CURVES

7.1 Standard Samples--Using the gasoline base (5.4.2), prepare six known blends covering the concentration range from 0.01 vol% to 1.0 vol% methanol as given in the following table.:

	Blend 1 vol% ml	Blend 2 vol% ml	Blend 3 vol% ml	Blend 4 vol% ml	Blend 5 vol% ml	Blend 6 vol% ml
Isopropanol	0.25	0.25	0.25	0.25	0.25	0.25
Methanol	0.01	0.05	0.10	0.20	0.50	1.00

Use burets or pipets of appropriate sizes to measure the volumes.

7.1.1 Add approximately 25-50 ml of the gasoline base into each of the 100-ml volumetric flasks.

7.1.2 Accurately measure by means of a pipette (4.11) the indicated quantities of each component into the individual 100-ml volumetric flasks (7.1.1) containing the gasoline base. Then dilute to the mark with the gasoline base and mix well.

7.1.3 Extract each standard sample blend in as directed in Section 8.2.

7.2 Chromatographic Analysis--Chromatograph each standard as directed in Section 9.2. Measure the peak area or height as directed in 10.1.2 and calculate peak area or height ratio as directed in 10.2.

7.3 Curves--Determine the relationship between the peak area or height ratio and concentration of methanol. Prepare calibration curves by means of the graphical procedure or the calculation procedure.

> Calibration points should lie on a straight line. With methanol some deviation from linearity is to be expected at concentrations lower than 0.05 vol%; however, no point should deviate by more than ±2% relative.

7.3.1 Graphical Procedure--On arithmetic graph paper, plot peak area or height ratios (vertical axis) versus concentration of methanol (horizontal axis) and draw the best line.

Group the standards so that concentration can be read to the nearest 0.005 vol%.

7.3.2 Calculation Procedure--To determine the best line mathematically, calculate the slope and intercept of the calibration curve by means of the linear regression equation.

Follow Steps 1 through 10 on the worksheet shown in Figure STM R 6.2.

7.4 Check the column against a standard of low and high range at least once per week; recalibrate if the analysis differs from the original concentration by more than ±3% relative.

PREPARATION OF SAMPLE

8.1 Measure of Sample

8.1.1 Add approximately 25-50 ml of gasoline or diesel fuel to the 100-ml volumetric flask, then accurately measure by means of pipette (4.10) 0.5 ml of isopropanol into the flask, dilute to the mark with the sample, stopper, and mix thoroughly.

8.2 Extraction of Sample.

8.2.1 Pipet 25 ml of sample plus internal standard (8.1.1) into the 4-oz. sample bottle.

8.2.2 Add 50 ml of distilled water to the sample bottle.

8.2.3 Stopper the bottle, invert, release the pressure immediately after inverting. Shake for one minute and release the pressure every fifteen seconds.

8.2.4 Allow the layers to separate and take the extracted alcohol in water sample (bottom layer) directly from bottle with micro syringe. That is, fill microsyringe with 2-3 microliter of air, put syringe into the bottom water layer, dispel the air and take a bubble-free sample of the water layer.

PROCEDURE

9.1 Preparation of Chromatograph.

9.1.1 Connect the cooled, conditioned columns to both the injection port and the flame ionization detector port.

9.1.2 Adjust the operating conditions to those listed in Table STM R 6.1.

9.1.3 Allow the chromatograph to run at the required maximum sensitivity (Table STM R 6.1) until a straight baseline is obtained.

9.1.4 Optimize the chromatographic detector system as directed in the manufacturer's instruction manual.

9.2 Injection of Sample.

9.2.1 Flush the 5 microliter microsyringe three times with the aqueous extract and then fill with about 3 microliters of the extract (while in the bottom layer).

9.2.2 Slowly eject the extract until 0.5 microliters remains in the syringe; wipe the needle with a tissue and draw back the plunger to admit 1 to 2 microliter of air into the syringe.

9.2.3 Insert the needle of the syringe through the septum cap of the chromatograph and push until the barrel of the syringe is resting against the septum capl then push the plunger to the hilt and remove the syringe immediately from the chromatograph.

> This injection technique is necessary so that sharp, symmetrical peaks are obtained.

9.2.4 Attenuate the peaks so that they are all on scale when measureing peak heights.

> See Table STM R 6.1 for approximate attenuation.

CALCULATIONS AND REPORT

10.1 Interpretation of Chromatogram.

10.1.1 Identify on the chromatogram the methanol and the internal standard (isopropanol) peaks to be measured from the retention times of the standards.

> The typical chromatogram (Figure STM R 6.3) will contain two main peaks. In order of elution they are methanol, ethanol, and isopropanol.

10.1.2 Measure peak height or area of the component peak and the internal standard peak.

> Measurement may be accomplished by any method that meets the precision requirements of Section 11. Acceptable methods of area measurement are by computer or integrator. Other methods such as by planimeter and triangulation (multiplying peak height by width at half height) should only be used if the prior are not available.

10.1.3 Convert the area measurement of all areas to a common base by using the following formula if necessary.

> Corrected Area to Common Base = Area x Attenuation

10.2 Calculations

10.2.1 Peak Area or Height Ratio. Calculate the ratio of the specific detector response for methanol to that of internal standard (isopropanol).

$$\text{Ratio} = A_M \times \%_I \ / \ A_I \times \%_M$$

where:

A_M = peak area of methanol
A_I = peak area of internal standard (isopropanol)

10.2.2 Concentration of Component--Determine the concentration of component in the sample by one of the following:

10.2.2.1 Graphical Procedure--Read from the appropriate calibration curve the concentration of the methanol corresponding to the peak area or height ratio.

10.2.2.2 Calculation Procedure--Calculate the concentration of the methanol corresponding to peak height or area ratio from the slope and intercept of the appropriate calibration curve from the equation

$$\%_m = A_M \times \%_I \ / \ A_I \times \text{Ratio}$$

10.3 Report

10.3.1 Report the methanol content in volume percent.

Report concentrations of less than one volume percent to the nearest 0.01 vol%; report concentrations greater than one percent to the nearest 0.05 vol%.

PRECISION

11.1 The following criteria should be used for judging the acceptability of results (95 percent confidence).

11.1.1 Repeatability--Duplicate results by the same operator shall be considered suspect if they differ by more than 0.03 vol%.

11.1.2 Reproducibility--Undetermined.

TABLE STM R 6.1
INSTRUMENT PARAMETERS

Detector	Flame Ionization
Columns	
Length, meters	1.8
Outside Diameters, mm	3.2
Support Material, mesh size	Chromosorb 101 80/100 mesh
Temperature:	
Sample Inlet System, °C	water cooled/on-column
Detector, °C	200
Column, °C	125
Carrier Gas	
Flow Rate, cc/min.	30
Detector	
Hydrogen Flow Rate, cc/min.	30
Air Flow Rate, cc/min.	300
Recorder Range, mV	0 to 1
Chart Speed, cm/min.	1
Sample Size, microliter	0.5
Total Cycle Time, min.	
Nitrogen Carrier Gas	8
Helium Carrier Gas	7
Gas Hold-up Time (Methane), sec.	18 ± 5
Linear Gas Rate (Methane), cm/sec.	
Helium Carrier Gas	10.5
Range, amps/mV[a]	10^{-9}
Attenuation[a]	2

---

a) The sensitivity and attenuation setting required will vary with each chromatograph.

APPENDIX E

ALCOHOL CONTENT OF GASOHOL BY GAS-LIQUID CHROMATOGRAPHY

Appendix X6, Information Document on Gasohol
(Motor Fuel Containing 10% Volume of Denatured
Ethanol in Gasoline)
1980 Annual Book of ASTM Standards, Vol. 23, p 928

APPENDIX XI

ALCOHOL CONTENT OF GASOHOL BY GAS-LIQUID CHROMATOGRAPHY*

Direct method using methanol as an internal standard.

This procedure is applicable for the determination of ethanol in gasohol using either a flame ionization or thermal conductivity gas-liquid chromatographic detector. Operating conditions are listed for the two instruments employed.

EQUIPMENT:

A) Perkin - Elmer 881 temperature programmed gas chromatograph, or equivalent, with flame ionization detector. Column: 1/8 inch glass, 6 foot long, packed with Supelco 80/100 carbopack C 0.1% SP-1000. Cat No. 1-1820.

B) Varian Series 1800 temperature programmed gas chromatograph, or equivalent, with thermal detector. Column: 1/8 inch stainless steel, 6 foot long, packed with Supelco 80/100 carbopack C 0.1% SP-1000. Cat No. 1-1820. Source: Supelco Inc., Supelco Par, Bellefonte, PA 16823.

OPERATING CONDITIONS

A) PERKIN-ELMER 881

Flow rate: 6 ml N_2/min.
Adjust air and hydrogen flow to optimum detector performance.
Injector temperature: 200°C
Attenuator: X500
Sample size: 0.5 μl
Program: 85°C for 1.5 min. after injection to 190°C at 12°C/min.
Plateau at 190°C for 22 min. Cool down for 10 min.

B) VARIAN SERIES 1800

Flow rate: 6 ml He/min
Injector temperature: 200°C
Detector temperature: 200°C
Attenuator: 16
Filament current: 100 mA
Sample size: 3.0 μl

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* Information Document on Gasohol ASTM Committee D-2 on Petroleum Products Appendix 6 Revised June 23, 1980 Chicago.

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Program : 85°C for 1.5 min after injection to 190°C at 15°C / min. Plateau at 190°C for 22 min. Cool down for 10 min.

PROCEDURE:

Into a 100 ml volumetric flask pipette 50 ml of gasohol and 5 ml of methanol respectively and mix. Inject a 0.5 μl sample (3.0 μl for the Varian 1800) and analyze by the G.C. procedure. Determine the area of ethanol and methanol peaks. (The first peak to elute is the methanol followed by the ethanol peak.) Prepare a calibration curve by plotting the ratio of the ethanol/methanol areas vs the percent ethanol in the standard. Determine the concentration by 1) direct reading from the calibration curve or 2) determine the slope of the calibration curve.

$$\text{CONCENTRATION} = \left[\frac{1}{\text{SLOPE}}\right]\left[\frac{\text{AREA OF ETHANOL}}{\text{AREA OF METHANOL}}\right]$$

3) A close approximation to the percent composition can be obtained by multiplying the ratio of ethanol/methanol areas by ten, when the thermal conductivity detector instrument is employed.

CALIBRATION CURVE

REAGENTS AND EQUIPMENT

1) Ethanol absolute (certified A.C.S.)

2) Methanol (certified A.C.S.)

3) Lead free gasoline

4) 12 - 100 ml volumetric flasks

5) 50 ml burette

6) 50 ml pipette

7) 5 ml pipette

PROCEDURE :

To a series of six 100 ml volumetric flasks add 4, 6, 8, 10, 12, and 14 ml of ethanol using the 50 ml burette. Dilute to volume with gasoline and mix. Into a second series of six 100 ml flasks pipette 50 ml of each standard previously prepared. Next pipette 5 ml of methanol to each sample and mix. Continue with the G.C. procedure.

COMMENTS :

Accuracy obtained routinely was within ± 0.1 % of the true value for the amount of ethanol in the gasohol sample. Thus a sample having a true value of 10.0 % would analyze to 10 ± 0.1 %.

The accuracy obtained using the flame ionization detector instrument was within ± 0.05 %.

The G.C. pattern will reflect the changes in gasoline composition throughout the year. If methanol is suspected to be present in the sample, either run an adulterant test for methanol or run a gasohol sample to which no methanol has been added to see whether methanol is present.

APPENDIX F

STANDARD TEST METHOD FOR OXYGENATES IN GASOHOLS BY GAS CHROMATOGRAPHY

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Standard Test Method for Oxygenates in Gasohols by Gas Chromatography

1. SCOPE

1.1 This method covers the determination of specific alcohols and ethers in hydrocarbon mixtures.

1.2 The components determined include methanol, ethanol, isopropyl alcohol, *tert*-butyl alcohol and methyl *tert*-butyl ether.

2. APPLICABLE DOCUMENTS

2.1 ASTM Standards

D 270 Sampling Petroleum and Petroleum Products

E 260 Recommended Practice for General Gas Chromatography

E 355 Recommended Practice for Gas Chromatography Terms and Relationships

3. SUMMARY OF METHOD

3.1 A two-column chromatographic system connected to a thermal conductivity detector is used. A reproducible volume of sample is injected

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into the column containing a polar liquid phase. The light hydrocarbons through methylcyclopentane are vented to the atmosphere as they elute. The column is backflushed immediately after the elution of methylcyclopentane, and the components remaining in the column are directed into the second column containing an active solid. In this column, the oxygenates elute before the remaining hydrocarbons. Immediately after the oxygenates of interest have eluted, the flow through the active solid column is reversed to backflush the remaining hydrocarbons from the column. Quantitative results are obtained from the measured areas of the recorded oxygenate peaks by utilizing factors obtained from the analyses of blends of known oxygenate content.

4. PRECAUTIONS

4.1 This standard may involve the use of hazardous materials, operations and equipment. It is the responsibility of whoever uses this standard to establish appropriate safety practices and to determine the applicability of regulatory limitations prior to use.

5. SIGNIFICANCE AND USE

5.1 This test is suitable for determining the concentration of oxygenates commonly used as octane improvers and extenders in gasoline (gasohol).

6. APPARATUS

6.1 Gas chromatograph - A gas chromatograph equipped with a dual thermal conductivity detector with provision for installing a valve in the column oven or other heated zone. Provision must also be made, either within the chromatograph or externally, to operate the second column at a higher temperature than the first column and the valve.

6.2 Valve - Eight port rotary or equivalent

6.3 Integrator - Electronic integration is recommended.

6.4 Recorder - A 1-mV recorder with a 1-rec. full scale response. If Electronic integration is not used, a minimum chart width of 250 mm and a minimum chart speed of 1-cm/minute is required

6.6 Column 1 - A stainless steel column 2.4-m long, 3.5-mm ID (3/16" OD) packed with 80-100 mesh Chromosorb P coated to a 25 wt-% level with tetracyanoethylated pentaerythritol (TCEPE)

6.7 Column 2 - A stainless steel column 4.6-m long, 3.5-mm ID (3/16" OD) packed with 80-100 mesh Porapak P.

7. REAGENTS AND MATERIALS

7.1 Carrier gas - Chromatographic grade helium (Hydrogen should be tried before the method is finalized).

7.2 Pure compounds for calibration - shall include methanol, ethanol, isopropyl alcohol, *tert*-butyl alcohol, methyl *tert*-butyl ether, methylcyclopentane and toluene. The purity of all the reagents shall be 99% or greater.

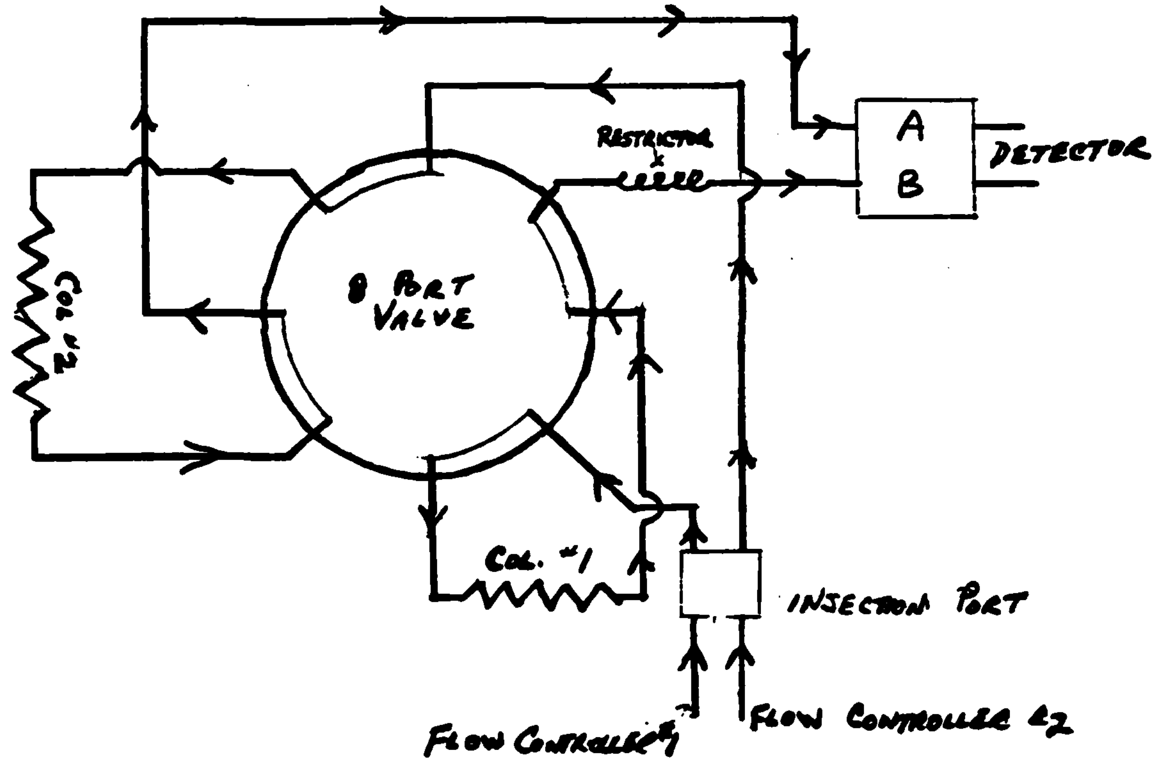
8. PREPARATION OF APPARATUS

8.1 Install the valve and the columns as shown in Figure 1.

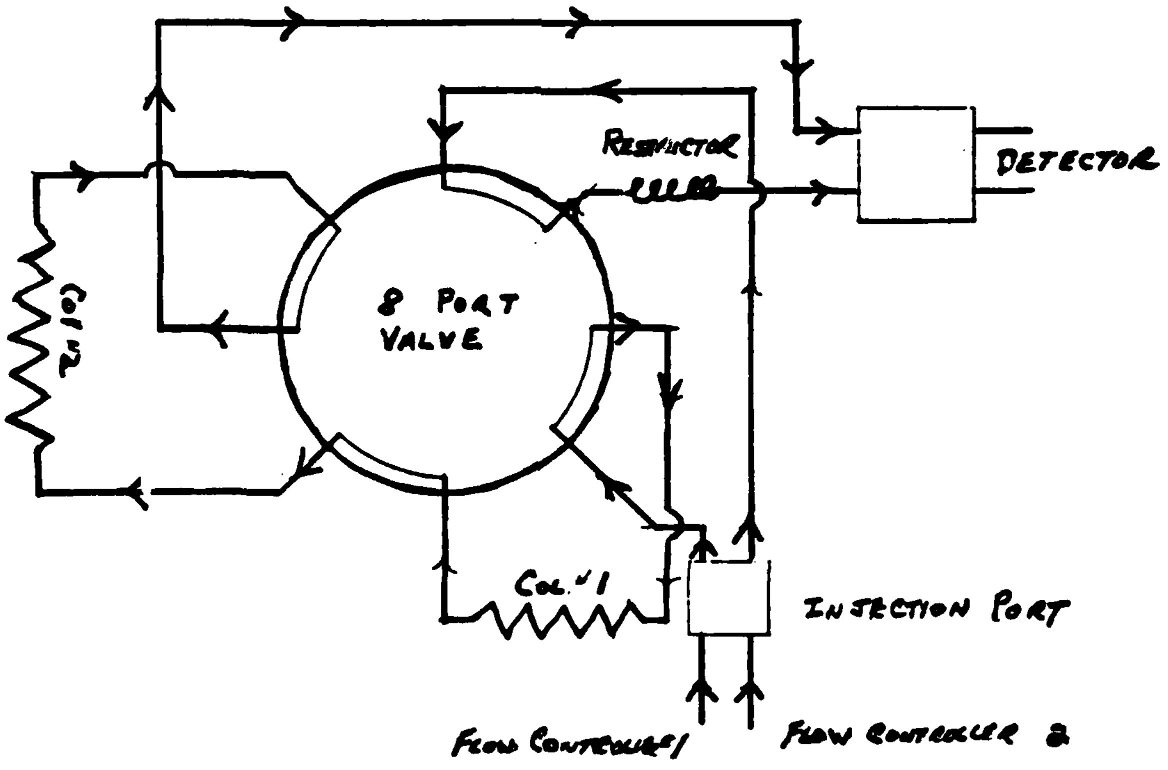
8.2 Column 2 is placed in a separate heated zone. Any necessary connecting lines should be of minimum diameter and length and should be heated.

8.3 The restrictor shown is optional and is used to reduce baseline disruption when the position of the valve is changed. It consists of a short length of 0.25-mm ID stainless steel capillary tubing and approximates the restriction of Column 2.

8.4 Establish the instrument parameters shown in Table 1.



INJECT POSITION



ANALYZE POSITION

Figure 1

Table 1

Operating Conditions

Carrier gas	helium
Carrier gas flow rate	60 mL/minute
Detector type	thermal conductivity
Detector temperature	200 C
Injection port temperature	170 C
Column 1 temperature	115 C isothermal
Valve temperature	115 C
Column 2 temperature	170 C isothermal
Sample size	2.5 μL (reproducible)

9. CALIBRATION

9.1 Prepare, by precise weighing, a calibration blend of oxygenates in toluene at levels approximating those in the samples to be analyzed. This blend should also contain 10% methylcyclopentane. Using densities, convert the calculated weight-% to liquid volume-%.

9.2 Chromatograph this blend with the valve in the inject position with the detector on polarity "B". Determine the time in seconds at which methylcyclopentane has completely eluted. Call this time T1.

9.3 Chromatograph the blend with the detector on polarity "A". At time T1 switch the valve to the analyze position. When the last oxygenate of interest has eluted, switch the valve to the inject position. Call this time T2. See Figure 2.

9.3.1 Referring to Figure 2, acetone elutes at the isopropyl alcohol site, n-propyl alcohol elutes between tert-butyl alcohol and methyl tert-butyl ether. sec-Butyl alcohol and n-butyl alcohol elute separately after methyl tert-butyl ether, but hydrocarbons begin to elute in this region and may prevent quantitation.

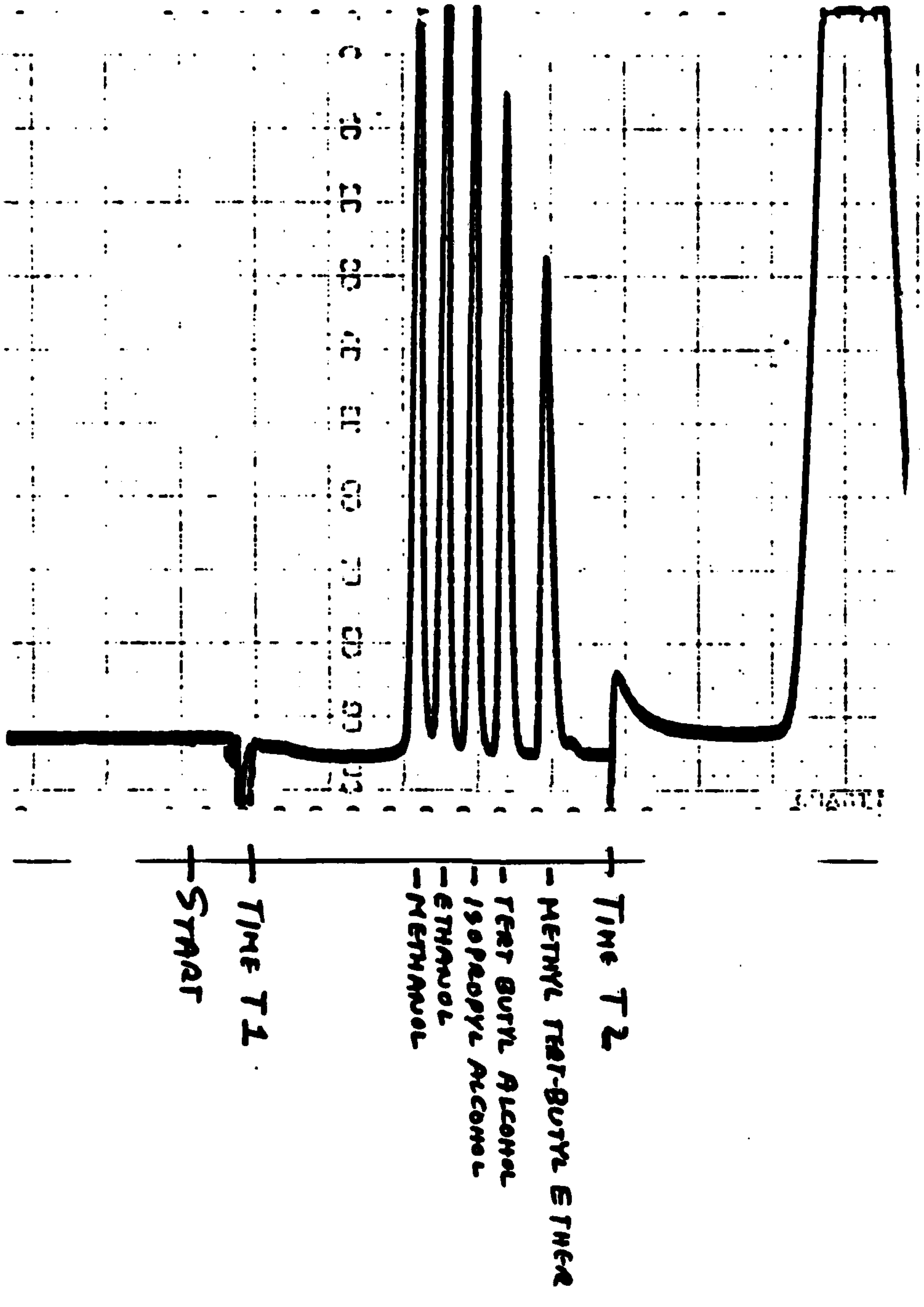

START
TIME T1
METHANOL
ETHANOL
ISOPROPYL ALCOHOL
TERT BUTYL ALCOHOL
METHYL TERT-BUTYL ETHER
TIME T2

Figure 2

9.4 Measure the areas of the oxygenates. Calculate the response factor (volume-percent per unit of area) for each of these components from the following formula:

$$F = \frac{L}{A}$$

Where:

A = peak area of the component

F = response factor of the component

L = concentration of the component, liquid volume-%

9.5 Calculate the response factors to at least three significant figures.

9.6 The blend prepared in 9.1 above contains very volatile components and may not be stable for an extended period. Because of this, an alternative calibration procedure may be used.

9.6.1 Prepare and analyze the blend as described in 9.1 to 9.5. Use the response factors (F) to determine the response of each oxygenate relative to tert-butyl alcohol as follows:

$$R_c = \frac{F_c}{T}$$

where:

F_c = response factor for an oxygenate

R_c = relative response of that component

T = relative response of _tert_-butyl alcohol

9.6.2 Prepare a blend (Blend 2) containing _tert_-butyl alcohol in toluene as described in 9.1. Use this blend as the daily calibration blend, determining response factors for the other oxygenates as follows

$$F_d = F_t R_c$$

where:

F_d = daily response factor for each oxygenate

F_t = response factor for _tert_-butyl alcohol from Blend 2, calculated as described in 9.4

R_c = relative response of the individual oxygenate, previously determined in 9.6.1

9.6.3 Redetermine relative response factors monthly or after any apparatus change by preparing a new blend as described in 9.1

10. PROCEDURE

10.1 Chromatograph the samples using the technique described for the blend in 9.3. The volume of sample injected must be exactly the same as the volume of blend injected.

10.2 Measure the areas of the oxygenates. Units must be consistent with 9.4 above.

11. CALCULATION

11.1 Calculate the liquid volume-percent (LV-%) of each oxygenate present in the sample using the following equation:

$$\text{Component, LV-\%} = FC$$

where:

C = peak area for that component

F = response factor, previously defined (F_d if the alternative calibration is used)

12. REPORT

12.1 Report the concentration of the individual oxygenates on an absolute basis to the nearest 0.1%.

13. PRECISION

To be determined.

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