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## Determination of individual hydrocarbons in automobile exhaust from gasoline-, methanol- and variable-fueled vehicles

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### SUMMARY

A method was developed for determining individual hydrocarbon (HC) emissions from gasoline-, methanol- and variable-fueled vehicles. The exhaust samples are collected in Tedlar<sup>®</sup> bags, and a portion of the sample is injected into a gas chromatograph, equipped with a DB-1 60 m × 0.32 mm I.D. (1.0 μm) fused-silica column. Methanol was well resolved from the gasoline HC species and did not interfere in the analysis. Validation, stability and intercomparison studies for total HC are also reported in this paper. In addition, an impinger-gas chromatography (GC) technique for determining unburned methanol emissions is also described. The detection limits of the GC methods for individual HCs and methanol was about 50 and 250 parts per billion (10<sup>9</sup>) C, respectively. This corresponds to a vehicular mass emission rate of 0.1 mg/mile HC and 1.3 mg/mile methanol, respectively, for the Federal Test Procedure emissions test.

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### INTRODUCTION

Recent reports show that many areas of the country are not in compliance with the National Ambient Air Quality Standard for ozone<sup>1–4</sup>. Consequently, one of the strategies that states and the federal government are considering for meeting the standards is the mandatory introduction of methanol-fueled vehicles. The rationale for this decision is that methanol-fueled vehicles have the potential for improving air quality because of the potentially lower photochemical reactivity of their exhaust emissions. Conversion from gasoline to methanol would replace a large portion of the reactive hydrocarbons (HCs) in gasoline exhaust with less reactive methanol, and thus lower the ozone-forming potential of the exhaust<sup>5,6</sup>.

Currently, the South Coast Air Quality Management District of California is adopting plans mandating methanol-fueled vehicles as an ozone-control strategy. Additionally, the California Energy Commission will purchase up to 5000 variable-fueled vehicles by 1993 for evaluation and demonstration purposes<sup>7</sup>.

In the past few years, General Motors has been involved in methanol technology development<sup>8-11</sup> and has assembled a fleet of prototype light-duty methanol vehicles<sup>12,13</sup>. More recently, General Motors has developed a variable-fueled vehicle capable of operating on any combination of methanol or gasoline fuels. In support of these developing technologies, General Motors Research Laboratories needs to identify and measure the emissions of exhaust components from these vehicles that can contribute to air pollution. These components include individual HCs, unburned methanol, and aldehyde emissions that are produced by burning gasoline, methanol, and methanol-gasoline blends in these vehicles. This detailed data then can be incorporated into photochemical models so that air quality benefits of methanol vehicles as compared to gasoline vehicles can be calculated.

The problem that the chromatographer faces is the separation of the unburned methanol from other HC species such as methane, ethylene, acetylene, butane, 1,3-butadiene, pentane, benzene, toluene and many other HCs which are present in the exhaust. Many of the previous gas chromatography (GC) methods developed for measuring individual HCs in exhaust utilized a complicated set-up involving three to four columns coupled with column switching and backflushing<sup>14-18</sup>. In addition HCs such as 1,3-butadiene were not adequately resolved by any of these methods<sup>19</sup>.

We develop a simple method based on a single capillary column for separating the alkanes, olefins and aromatic HCs from the unburned methanol present in the exhaust. This paper describes the methodology, the validation, and the application of the method to measuring individual HCs in gasoline-, methanol- and variable-fueled vehicle exhaust. In addition, we also describe a modified method for performing methanol measurements so that the methanol and HC emissions can be determined in a single vehicle test.

## EXPERIMENTAL

### *Apparatus*

All analyses were performed by using a Varian Vista 6000 gas chromatograph (Varian, Sunnydale, CA, U.S.A.) equipped with a direct capillary injector, gas sampling valve and flame ionization detector. Data collection was performed with a Varian Vista 401 data system. The analytical column for individual HC analysis was a J & W (J & W Scientific, Folsom, CA, U.S.A.) DB-1 60 m × 0.32 mm I.D. (1.0- $\mu$ m film) fused-silica capillary column. The analytical column for unburned methanol analysis was a Quadrex (Quadrex, New Haven, CT, U.S.A.) 007 methyl silicone 50 m × 0.53 mm I.D. (5.0- $\mu$ m film) Thickote fused-silica capillary column.

Exhaust emissions for HC analyses were collected in 10-l Tedlar<sup>®</sup> bags (SKC, Eight-Four, PA, U.S.A.) that contained both a dual hose/valve fitting and a septum injection port. Exhaust gases for unburned methanol analysis were collected in 25-ml midget impingers (Ace Glass, Vineland, NJ, U.S.A.) containing HPLC-grade water (Fisher Scientific, Pittsburgh, PA, U.S.A.). The exhaust gases were pumped into the Tedlar bags for HC analysis and were drawn through the midget impingers for methanol analysis with a Gilian Model HFS113UT (Gilian, Wayne, NJ, U.S.A.) portable air sampling pump.

### *Test vehicles*

The method was applied to measuring HCs and unburned methanol emissions from both production gasoline- and developmental methanol- end variable-fueled vehicles. As stated earlier, the variable-fueled vehicles were designed to operate on methanol, gasoline or any combination of the two fuels. All the vehicles tested were equipped with production three-way catalytic converters.

### *Total organics measurement*

Previous experience with methanol vehicles indicated that the standard non-heated flame ionization detector used in the emission test cell for gasoline vehicle exhaust HC analysis could not be used for methanol vehicles<sup>12</sup>. To minimize methanol losses, a heated flame ionization detector maintained at 125°C was used. Heated sample lines (125°C) from the constant-volume sampling (CVS) dilution system to the analyzer were also used. In addition, an insulated flex pipe was run from the vehicle tailpipe to the CVS dilution tunnel.

### *Exhaust sampling procedure*

Exhaust samples were collected as the vehicles were being tested by using the 1975 Federal Test Procedure (FTP) driving cycle<sup>15</sup>. The procedure consists of driving the vehicle on a chassis dynamometer over predescribed driving cycles.

The FTP uses the Urban Dynamometer Driving Schedule (UDDS), which is 1372 s in duration and is composed of two segments; a 505-s "cold start transient" phase and a 867-s "stabilized phase". The 1975 FTP consists of the 505-s cold start "transient" phase and the 867-s "stabilized" phase followed by a 505-s hot start "transient phase". Diluted exhaust samples were collected for both individual HCs and methanol from the CVS system for each of the cold, stabilized and hot phases of the test. The samples were collected at a point just upstream of the CVS heat exchanger. The sampling rate for both the Tedlar bags and midget impingers was 0.9 l/min.

A background air sample from the CVS tunnel dilution air was obtained in Tedlar bags before the test, and the results were subtracted from the results of each of the cold, stabilized, and hot bags.

The methanol samples were collected in single midget impingers that were immersed in an ice bath. After collection, the samples were transferred to 25-ml volumetric flasks and were diluted to volume with HPLC-grade water. Aliquots (1  $\mu$ l) of this solution were then injected on the Quadrex 007 methyl silicone column for the methanol analysis. By using this procedure, only methanol and other water-soluble exhaust gas species were collected, thus eliminating HC interference. The collection efficiency for methanol was in excess of 97% with a single impinger for both standard methanol calibration gases and diluted exhaust samples<sup>11,12</sup>.

### *Standard preparation*

Certified gas phase standards for many of the alkanes, olefins, and aromatics were purchased from Scott Specialty Gases (Troy, MI, U.S.A.) in Scotty IV cylinders. Serial dilutions were prepared in Tedlar bags by measuring known quantities of these gases with a mass flow meter (Tylan, Carson, CA, U.S.A.) and diluting with HC-free air. Other HC standards were prepared by injecting known quantities of pure HC liquids in a Tedlar bag and diluting with a known quantity of HC-free air.

Aqueous methanol standards for the GC methanol analysis were prepared by injecting known quantities of methanol in HPLC-grade water. Certified gas phase methanol standards in aluminum cylinders were also purchased from Scott Specialty Gases and were used in many of the validation experiments.

#### *Chromatographic conditions*

The individual HCs were separated on the DB-1 fused-silica capillary column by using the experimental conditions listed in Table I. These conditions were empirically selected to separate methanol from the C<sub>4</sub>-HC species and to provide resolution of as many other HCs as possible.

Unburned methanol was analyzed by a modification of the method of Smith and Urban<sup>16,17</sup>. In our scheme, exhaust methanol is sampled in a midget impinger at a lower sampling rate than in the previous procedure, with final analysis by direct injection onto a capillary column. The experimental conditions are listed in Table II. Other capillary columns that produced equivalent results to those of the Quadrex column were the J & W DB-WAX 30 m × 0.53 mm I.D. (1.0- $\mu$ m film) and the J & W DB-1 30 m × 0.53 mm I.D. (1.0- $\mu$ m film) fused-silica capillary columns.

#### *Compound identification*

Individual HCs were identified by comparing their retention times with those obtained with known HC standards. In addition, compounds for which we could not obtain standards were identified by comparing the relative retention times of those GC peaks to those obtained from an independent HC analysis of the fuel<sup>20</sup>.

#### *Fuels*

The gasoline used in these tests was Howell EEE, purchased from Howell (Howell, MI, U.S.A.). Howell EEE is a high-aromatic-content gasoline, similar to the indolene fuel used in emission certification testing.

The methanol used in these tests was purchased from Borden Chemicals and was of greater than 99% purity.

TABLE I  
CHROMATOGRAPHIC CONDITIONS OF INDIVIDUAL HYDROCARBON ANALYSIS

Column	DB-1 60 m × 0.32 mm I.D. fused-silica capillary (1.0- $\mu$ m film)
Carrier gas	He, 5.75 ml/min
Carrier gas make-up	He, 30 ml/min
Temperature program	- 50°C, hold for 4 min, 6°C/min to 110°C, 10°C/min to 140°C, hold for 10 min
Detector	Flame ionization detector (heated to 275°C)
Sample injection	Valco gas sampling valve, heated to 175°C
Sample size	0.5 ml

TABLE II  
CHROMATOGRAPHIC CONDITIONS OF UNBURNED METHANOL ANALYSIS

Column	Quadrex 007 methyl silicone, 50 m × 0.53 mm I.D. fused-silica (5.0- $\mu$ m film)
Carrier gas	He, 6.50 ml/min
Carrier gas make-up	He, 30 ml/min
Oven temperature	Isothermal, 75°C
Detector	Flame ionization detector
Sample injection	syringe
Sample size	1.0 $\mu$ l

## RESULTS

### *Quantitative aspects of this work*

One of the ultimate goals of this project was to compare our GC HC results to those obtained by the flame ionization detection (FID) analyzer in the Vehicle Emission Laboratory. To facilitate intercomparison of our GC results with the FID total-HC results obtained in the Vehicle Emission Laboratory, quantitation was performed by calibrating both detectors with propane calibration gas. Since the GC result is the sum of the individual HC results, the GC result and the FID result will agree if the responses of the two detectors are identical or if all HCs give identical responses. On the GC system, we measured the individual HC response factors by injecting known concentrations from the Scott calibration mixtures. The results in Table III show an

TABLE III  
CALIBRATION FACTORS FOR SELECTED HC SPECIES

Calibration factor expressed as area counts/ppm C.

<i>Species</i>	<i>Calibration factor</i>	<i>Species</i>	<i>Calibration factor</i>
Methane	1629	Pentane	1409
Ethylene	1392	<i>trans</i> -2-Pentene	1275
Ethane	1389	<i>cis</i> -2-Pentene	1275
Acetylene	1254	2,2-Dimethylbutane	1370
Propylene	1361	Cyclopentane	1375
Propane	1456	Isohexane	1358
Isobutane	1314	Hexane	1383
Isobutylene	1290	Methylcyclopentane	1297
1-Butene	1393	Benzene	1322
1,3-Butadiene	1311	Cyclohexane	1273
<i>trans</i> -2-Butene	1450	3-Methylhexane	1361
<i>cis</i> -2-Butene	1450	Heptane	1389
1-Butyne	1256	Methylcyclohexane	1268
Isopentane	1439	Toluene	1325
1-Pentane	1301		

Average calibration factor 1357  $\pm$  80

average calibration factor of  $1357 \pm 80$  area units per ppm of HC, expressed as ppm of carbon atoms. This corresponds to a relative standard deviation of 6.0%, which is well within the uncertainty (10%) of some of the Scott certified gas mixtures. Hence, the responses of all HCs are roughly equal, and the GC total-HC results should agree with the vehicle Emission Laboratory FID total-HC results.

#### *Chromatographic aspects of this work*

Fig. 1 shows a chromatogram of the Howell EEE fuel used in these studies, vaporized inside a Tedlar bag. The chromatogram shows the excellent resolution obtained for many of the gasoline constituents including butane, isopentane, pentane, isohexane, isooctane, benzene, toluene, *m/p*-xylene and *o*-xylene. Many of the species that we identified both in the fuel and in the exhaust are listed in Table IV.

For the analysis of individual HCs from methanol vehicles, the GC column must adequately resolve methanol from the gasoline HCs. Fig. 2 shows a chromatogram of the Howell EEE fuel, spiked with methanol to simulate exhaust from a methanol-gasoline-fueled vehicle. The non-polar DB-1 stationary phase allows methanol to be eluted early in the chromatogram in a region of relatively few gasoline HC peaks. In actuality, methanol would only interfere with *trans*-2-butene, *cis*-2-butene, 1-butyne and 2,2-dimethylpropane. Typically, the total amount of these four species is about 1% of the total HC emissions from a gasoline-fueled vehicle. In addition, as the percentage of methanol in the fuel was increased, the total concentration of these species decreased, thereby making their contribution to the total HC emission negligible. In short, the method allows excellent resolution of most of the HC species present in vehicle exhaust.

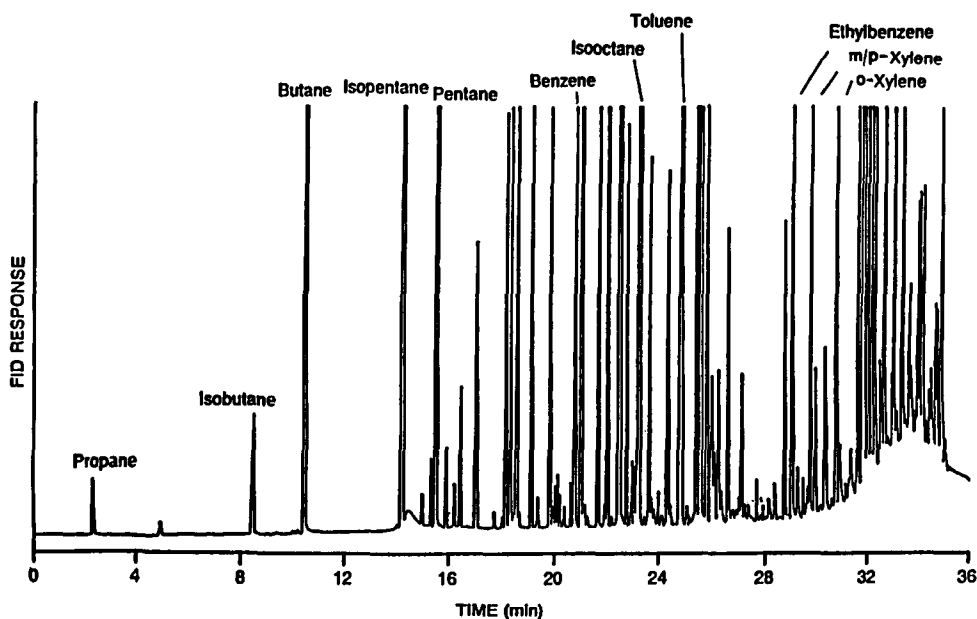


Fig. 1. Chromatogram of vaporized Howell-EEE fuel in a Tedlar bag.

TABLE IV  
RETENTION TIMES OF SELECTED HC SPECIES

<i>Species</i>	<i>Retention time (min)</i>	<i>Species</i>	<i>Retention time (min)</i>
Methane	2.33	2-Methyl-2-hexene	23.70
Ethylene	2.53	<i>cis</i> -2-Heptene	23.81
Ethane	2.63	2,3-Dimethyl-2-pentane	24.10
Acetylene	2.73	Methylcyclohexane	24.32
Propylene	4.73	2,5-Dimethylhexane	24.79
Propane	4.97	3,4-Dimethylhexane	24.86
Propyne	6.95	<i>cis</i> -1, <i>trans</i> -2,4-Trimethylcyclopentane	25.07
Isobutane	8.47	2,3,4-Trimethylpentane	25.41
Isobutylene	9.96	Toluene	25.54
1-Butene	10.01	2-Methylheptane	25.78
1,3-Butadiene	10.19	4-Methylheptane	25.97
Butane	10.44	3,4-Dimethylhexane	26.08
<i>trans</i> -2-Butene	11.08	3-Methylheptane	26.23
<i>cis</i> -2-Butene	11.57	<i>cis</i> -1, <i>trans</i> -2,3-Trimethylcyclopentane	26.35
1-Butyne	11.83	2,2,5-Trimethylhexane	26.61
2,2-Dimethylpropane	12.06	C <sub>8</sub> -Olefins	
3-Methyl-1-butene	13.67	1,1-Methylethylcyclopentane	26.69
Isopentane	14.25	C <sub>8</sub> -Olefins	26.77
1-Pentene	14.99	<i>trans</i> -4-Octene	26.81
2-Methyl-1-butene	15.32	<i>cis</i> -3-Octene	26.92
Pentane	15.50	Octane	27.11
Isoprene	15.62	2,3,4-Trimethylhexane	27.30
<i>trans</i> -2-Pentene	15.89	<i>cis</i> -1,2-Dimethylcyclohexane	28.00
<i>cis</i> -2-Pentene	16.22	2,4-Dimethylheptane	28.12
2-Methyl-2-butene	16.42	Propylcyclopentane	28.32
2,2-Dimethylbutane	17.00	Ethylbenzene	28.73
Cyclopentene	17.68	<i>m/p</i> -Xylene	28.99
4-Methyl-1-pentene	17.97	4-Methyloctane	29.23
Cyclopentane	18.12	2-Methyloctane	29.45
2,3-Dimethylbutane	18.28	3-Methyloctane	29.62
Isohexane	18.48	<i>o</i> -Xylene	29.73
3-Methylpentane	19.08	C <sub>9</sub> -Cycloalkanes	
1-Hexane	19.29	Nonane	30.30
2-Methyl-1-pentene	19.34	C <sub>9</sub> -Cycloalkanes	30.74
Hexane	19.80	2,2-Dimethyloctane	30.86
<i>trans</i> -2-Hexene	19.99	2,4-Dimethyloctane	31.29
<i>cis</i> -2-Hexene	20.34	Propylbenzene	31.59
2,2-Dimethylpentane	20.60	1-Methyl-4-ethylbenzene	31.79
Methylcyclopentane	20.76	C <sub>10</sub> -Cycloalkane	31.86
2-Methyl-2-pentene	20.91	C <sub>10</sub> -Cycloalkane	32.00
2,4-Dimethylcyclopentane	20.96	1-Methyl-2-ethylbenzene	32.17
2,2,3-Trimethylbutane	21.13	3-Ethyloctane	32.28
3-Methyl-1-hexene	21.24	C <sub>10</sub> -Cycloalkane	32.33
Benzene	21.66	1,2,4-Trimethylbenzene	32.67
3,3-Dimethylpentane	21.91	Isobutylbenzene	32.97
Cyclohexane	22.01	Decane	33.03
2-Methylhexane	22.47	C <sub>10</sub> -Aromatics	
2,3-Dimethylpentane	22.74	C <sub>11</sub> -Aromatics	
3-Methylhexane	22.95	Undecane	35.46
Isooctane	23.19	C <sub>12</sub> -Aromatics	
<i>trans</i> -3-Heptane	23.57	Dodecane	38.53
Heptane	23.64		

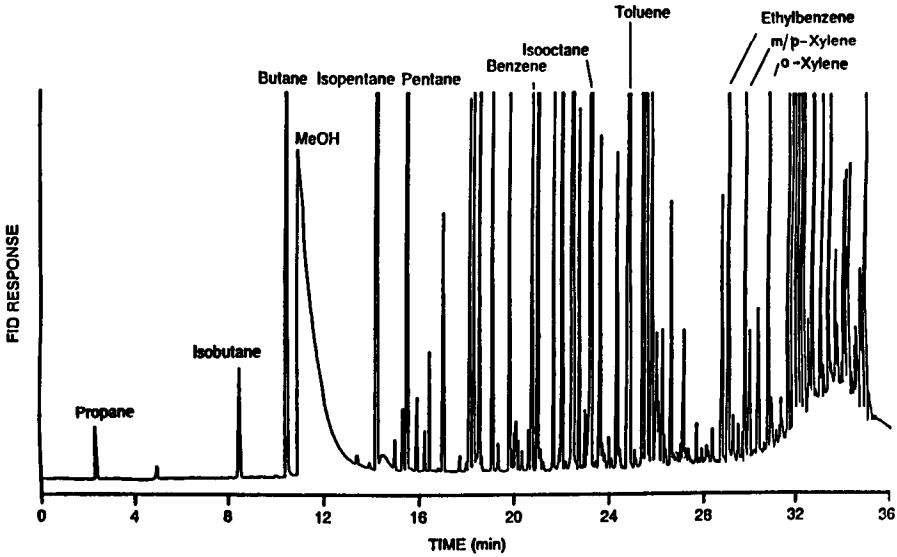


Fig. 2. Chromatogram of vaporized Howell-EEE fuel with methanol in a Tedlar bag. MeOH = Methanol.

Fig. 3 shows a typical chromatogram obtained by placing a HC standard mixture in a Tedlar bag. The elution order, as with all methyl silicone phases, is based on boiling point for members of a homologous series and therefore aids in determining

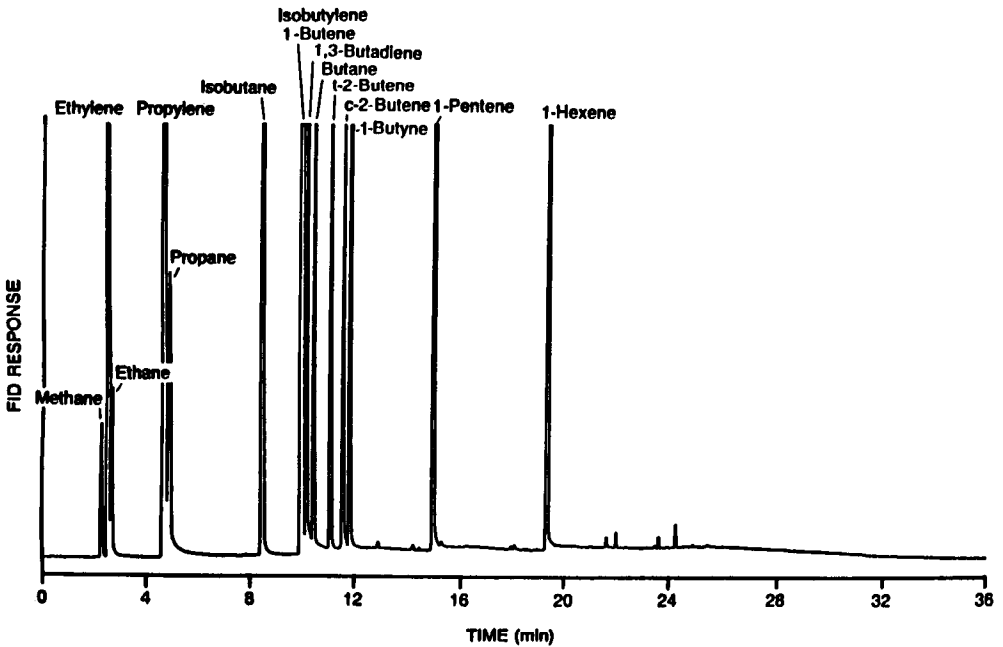


Fig. 3. Chromatogram of HC standards in a Tedlar bag. t = *trans*; c = *cis*.



the elution order for compounds in multicomponent mixtures. This effect is easily seen in the elution of 1-butene, 1-pentene, and 1-hexene in that mixture. The column does an excellent job of separating other olefins such as ethylene from ethane and methane, propylene from propane, and, even more importantly, 1,3-butadiene from butane and other  $C_4$ -HC species. This represents a marked improvement over previous attempts to separate 1,3-butadiene from other  $C_4$ -HC species.<sup>14</sup>

Unburned methanol, which was also collected in the Tedlar bags, was not quantitated by the above procedure because of adsorptive losses of methanol onto the walls of the Tedlar bags. We confirmed these adsorptive losses by placing a known quantity of methanol from a certified methanol calibration gas cylinder inside a bag and repeatedly analyzing gas samples from the bag over a 6-h period. From these experiments, we found that over 70% of the initial methanol disappeared over the 6-h period. In addition, the peak shape for methanol under the GC conditions for the HC analysis was quite poor and not ideal for quantitative integration. Therefore, it was decided that methanol should be collected and analyzed separately from the individual HCs.

Fig. 4 shows a chromatogram of the methanol analysis from one of the neat-methanol-fueled vehicles (M100). The methanol peak shape is very sharp and well resolved from any potential interferences. Acetonitrile, which is a potential interferent, may be present as a contaminant in the water impingers. This is because the aldehyde emission samples, which are collected concurrently with the methanol samples, are collected in impingers containing an acetonitrile solution of 2,4-dinitrophenylhydrazine.<sup>21</sup> Therefore, cross contamination of acetonitrile from the aldehyde to the methanol impingers can occur and should be avoided. The thick-film Quadrex column provides excellent resolution between methanol and acetonitrile and will eliminate this interference.

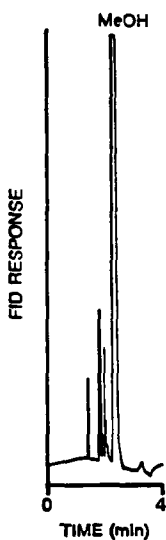


Fig. 4. Chromatogram of cold-start methanol emissions from a dedicated neat-methanol (M100) vehicle.

Fig. 5 is a typical chromatogram showing the cold-bag emissions from the variable-fueled vehicle running on M0 (*i.e.*, 100% Howell EEE). The major HC that was emitted was toluene, which accounted for over 17% of the HC emissions in the cold bag. This result was not unexpected because the toluene content of the Howell EEE fuel can range from 15 to 20%<sup>21</sup>. Ethylene, propylene, isobutylene, isopentane, pentane, benzene and isooctane are other major HCs species emitted, and they accounted for 7.6, 6.1, 4.7, 4.5, 3.1, 3.5 and 8.9% of the total, respectively. 1,3-Butadiene was well resolved from 1-butene and butane and it accounted for about 0.6% of the total HC emissions in the cold bag.

Fig. 6 shows a chromatograms of the cold-bag emissions from the variable-fueled vehicle running on M85 fuel (*i.e.*, 85% methanol and 15% Howel EEE). The methanol peak was completely resolved from the HC peaks. The HC peaks are mainly derived from the gasoline portion of the fuel as evidenced by the characteristic pattern of gasoline HC present in the exhaust. Toluene was the most abundant HC and accounted for over 13% of the total HC in the exhaust. Ethylene, propylene, isobutylene, isopentane, pentane, and benzene are also present, and these accounted for 11.7, 7.3, 5.0, 5.2, 3.7, and 3.8% of the total, respectively.

Fig. 7 shows a chromatogram of the cold-bag emissions from a developmental vehicle that was dedicated to run on neat methanol (M100). It was evident that the major organic species emitted in the cold bag from M100 combustion was methanol. Methane, ethylene, propylene, propane, propyne and isobutylene are other HCs that were present in the cold bag. These species comprise 35.8, 10.0, 3.2, 10.6, 31.1 and 3.1%, respectively, of the total HC emissions. The total HC emissions were about 6.5 ppm C which was about a factor of ten lower than the total HC emissions from a gasoline (M0) vehicle test.

#### GC column HC recovery experiments

Potential adsorption of HCs on the GC column was evaluated in a series of experiments in which we injected both known HC calibration standards and gasoline

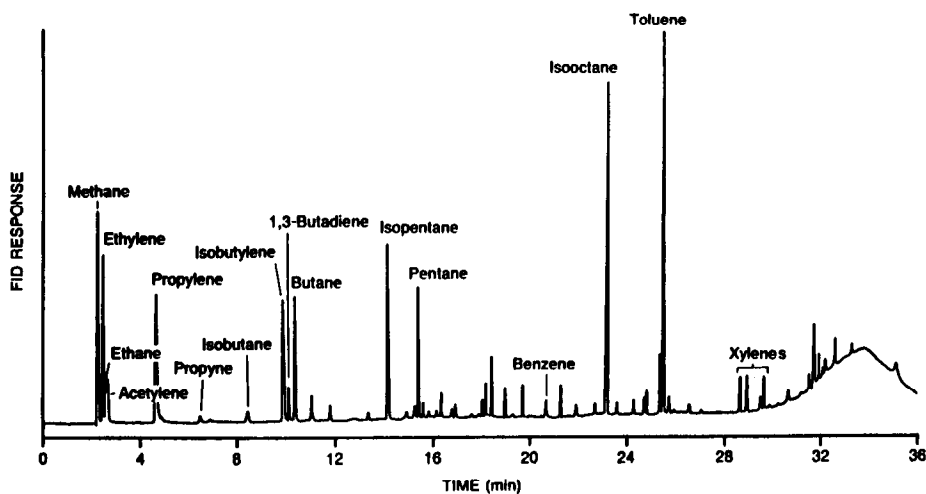


Fig. 5. Chromatogram of cold-bag emissions from a variable-fuel vehicle run on 100% Howell-EEE (M0).

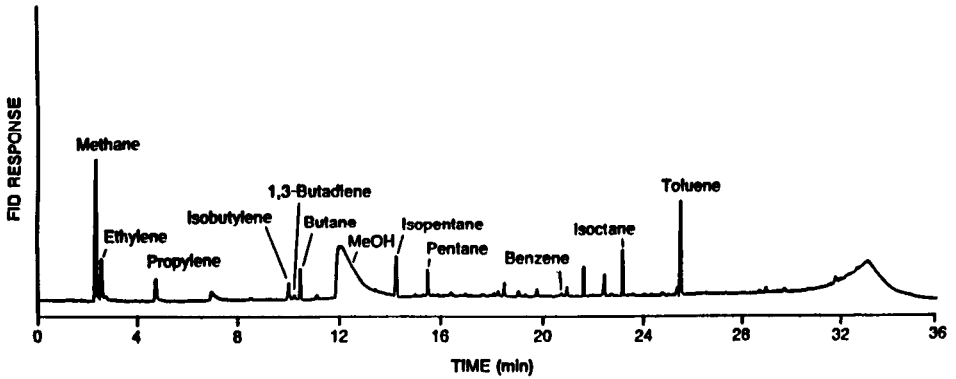


Fig. 6. Chromatogram of cold-bag emissions from a variable-fuel vehicle run on 85% methanol and 15% Howell-EEE (M85).

vehicle exhaust samples using the normal GC temperature program and an elevated isothermal temperature of 125°C. The high-temperature isothermal run was chosen so that all the exhaust HC components would be eluted into several large peaks in a short time period. The total area of the peaks was then compared without regard to resolution of the individual species, to the total area that was obtained by running the normal temperature program. These results, shown in Table V, indicated that the sum of the individual peak concentrations of the exhaust sample and standards agreed to within 97% of the total area obtained with the high-temperature isothermal run.

In another experiment, we replaced the analytical column with a 1 m × 0.53 mm I.D. piece of uncoated, deactivated fused-silica capillary tubing and reinjected the same gasoline exhaust and standard samples at the high-temperature conditions. In this case, the HCs were not separated, but eluted as one large sharp peak. As before, we found that the total area of both the exhaust and standard samples agreed to within 97% of the total area of the high-temperature runs.

These results suggested that no adverse adsorption effects of organics were

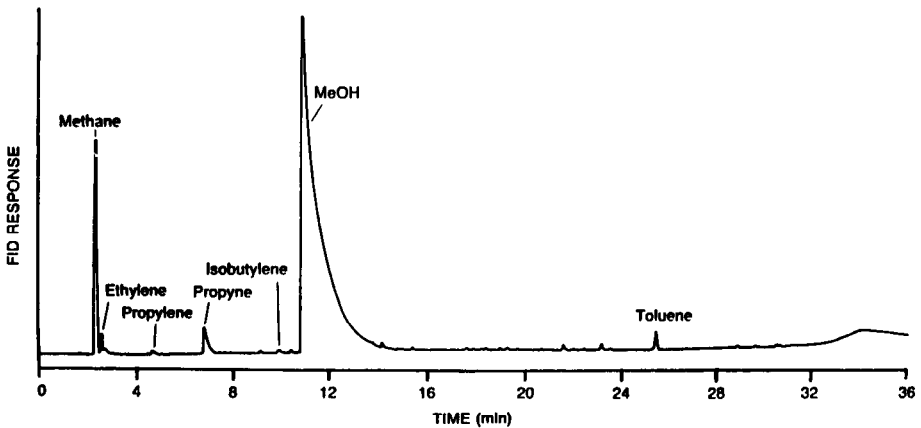


Fig. 7. Chromatogram of cold-bag emissions from a dedicated M100 vehicle.

TABLE V  
INTERCOMPARISON OF HC RECOVERY STUDIES

Species	Total concentration (ppm C)		
	DB-1 column, normal GC program	DB-1 column, 125°C isothermal	Uncoated fused-silica, 125°C isothermal
C <sub>1</sub> -C <sub>4</sub> Alkanes <sup>a</sup>	51.2	52.1	50.6
Toluene <sup>a</sup>	22.7	22.4	21.1
Cold bag (M0) <sup>b</sup>			
Gasoline vehicle	31.4	31.8	30.8

<sup>a</sup> Gas standards in a Tedlar bag.

<sup>b</sup> Vehicle exhaust.

occurring and that the individual HCs, including the higher-molecular-weight constituents, were being quantitatively eluted from the column during the normal GC temperature program.

#### Sample and standard stability studies

Because of the large number of samples that can be collected in a day, the analyst usually does not have sufficient time to analyze all the samples in a typical working day. Therefore, it is important that the exhaust HC samples are stable in the Tedlar bags and do not degrade with time. We examined the stability of both exhaust and standard HC calibration samples in Tedlar bags by periodically analyzing samples from the bags over a 48-h time period. The data in Table VI show that most of the alkanes and olefins are stable in the bag and that the variation in average concentration in the bag was about 1-6% over a 48-h time period. The average concentration for 1,3-butadiene, ethylbenzene, *m/p*-xylene, and *o*-xylene varied by about 40.0, 13.3, 10.5, and 10.7%, respectively over a 48-h time period. In addition, the concentration of 1,3-butadiene continually decreased by over 25% within 24 h and by over 70% within 48 h of sample collection. Although not shown in Table VI, the total integrated area for the cold bag of a gasoline vehicle test did not vary by more than 5% over 24 h, thereby indicating that the exhaust HCs are stable in the bag. In addition, we spiked another cold-bag exhaust sample from a gasoline vehicle test with methanol and monitored the total peak area over a 24-h time period, and again found that the total HC peak area did not vary by more than  $\pm 5\%$ . These results show that methanol does not have any adverse effects on the exhaust HC stability in the bag.

Similarly, HC standards prepared in Tedlar bags were analyzed over a 48-h period (Table VII). In these experiments, C<sub>1</sub>-C<sub>6</sub> normal alkanes, C<sub>4</sub> olefins, benzene, and toluene were prepared in separate bags and analyzed over a 48-h period. The data showed that the average concentration of these species varied from 0.6 to 2.5% over the 48-h period.

The exhaust sample bags were stored at room temperature under normal laboratory lighting. However, precautions were taken to avoid exposure to sunlight and possible photochemical effects during transport from the vehicle Emission Laboratory to the analytical laboratory. The most important sample, and therefore the first

TABLE VI

## EXHAUST HC STABILITY STUDY OF THE COLD-BAG EMISSIONS FROM THE VARIABLE-FUELED VEHICLE RUN ON M0

R.S.D. = Relative standard deviation.

<i>Species</i>	<i>Concentration (ppm C)</i>				<i>Average concentration (ppm C)</i>	<i>R.S.D. (%)</i>
	<i>Time (h)</i>					
	<i>0.2</i>	<i>4</i>	<i>24</i>	<i>48</i>		
Methane	5.44	5.19	5.14	5.32	5.27	2.66
Ethylene	2.59	2.58	2.56	2.55	2.57	0.78
Propylene	2.03	1.93	1.94	1.88	1.94	3.10
Propane	0.26	0.25	0.26	0.26	0.26	3.85
Isobutylene	1.92	1.96	1.75	1.92	0.25	6.25
1,3-Butadiene	0.22	0.17	0.14	0.07	0.15	40.00
Butane	1.49	1.44	1.44	1.43	1.45	2.07
Isopentane	2.23	2.21	2.25	2.19	2.22	1.35
Pentane	1.66	1.63	1.61	1.60	1.62	1.85
Isohexane	0.56	0.54	0.56	0.53	0.55	3.64
Benzene	1.46	1.45	1.44	1.36	1.43	2.80
Isooctane	2.45	2.41	2.44	2.35	2.41	1.66
Toluene	5.37	5.27	5.21	4.75	5.15	5.24
Ethylbenzene	0.32	0.27	0.27	0.34	0.30	13.33
<i>m/p</i> -Xylene	0.41	0.38	0.41	0.33	0.38	10.53
<i>o</i> -Xylene	0.27	0.24	0.26	0.19	0.24	16.67
Propylbenzene	0.54	0.48	0.52	0.53	0.52	5.77
Others	7.34	7.09	7.32	7.09	7.21	1.94

TABLE VII

## STABILITY STUDY OF HC STANDARDS PLACED IN TEDLAR BAGS

<i>Species</i>	<i>Concentration (ppm C)</i>				<i>Average concentration (ppm C)</i>	<i>R.S.D. (%)</i>
	<i>Time (h)</i>					
	<i>0.2</i>	<i>4</i>	<i>24</i>	<i>48</i>		
Methane	9.57	9.48	9.40	9.37	9.45	0.95
Ethane	9.62	9.42	9.49	9.50	9.51	0.84
Propane	10.33	10.42	10.20	10.22	10.29	0.97
Butane	10.68	10.42	10.66	10.50	10.56	1.23
Pentane	11.43	11.62	11.44	11.32	11.45	1.05
Isopentane	10.53	10.64	10.22	10.18	10.39	2.12
Propylene	8.40	8.50	8.10	8.15	8.29	2.20
1,3-Butadiene	6.39	6.28	6.31	6.16	6.28	1.59
Isobutylene	8.29	8.43	8.26	8.10	8.27	1.69
Benzene	18.82	18.93	18.65	17.89	18.57	2.53
Toluene	19.85	19.95	19.68	19.92	19.85	0.60

TABLE VIII  
 INTERCOMPARISON OF VEHICLE EMISSION LABORATORY FID AND GC EXHAUST HYDROCARBON METHOD MEASUREMENTS  
 Diff. means percentage difference of GC versus the FID value.

Vehicle	Fuel	Concentration (ppm C)		Cold bag		Stabilized bag		Hot bag	
		FID/GC	Diff. (%)	FID/GC	Diff. (%)	FID/GC	Diff. (%)	FID/GC	Diff. (%)
Gasoline A	Howell-EEE <sup>a</sup>	36.19/ 34.20	5.6	1.27/0.53	50.8	9.13/ 7.52	17.8		
Gasoline B	Howell-EEE	37.59/ 32.55	13.4	1.11/0.79	28.8	7.05/ 5.80	17.7		
Gasoline C	Howell-EEE	35.40/ 31.88	9.9	1.35/0.85	37.0	18.60/16.74	10.0		
Gasoline D	Howell-EEE	45.39/ 43.72	3.7	1.11/0.66	10.5	8.37/ 7.69	8.1		
Gasoline E	Howell-EEE	51.78/ 47.83	7.6	3.12/3.23	+3.5	14.85/12.44	16.2		
Variable fuel	Howell-EEE <sup>a</sup>	82.12/ 69.50	15.4	6.24/4.98	20.2	14.85/11.59	22.0		
Variable fuel	methanol <sup>a,b</sup>	143.91/163.76	+13.7	4.41/0.20	95.4	2.37/ 0.36	84.8		

<sup>a</sup> Average of two tests.

<sup>b</sup> Methanol means neat methanol.

bag analyzed, was the cold bag. Efforts were made to analyze the cold bag within 1 h after collection in the VEL.

The stability of the aqueous methanol samples and standards was also evaluated by repeated analysis over a two-week period. Similarly, we found that both the samples and standards stored in the laboratory at room temperature did not show any significant deterioration over two-week period, but refrigeration would assure good quality control. In actual practice, the samples, once received from the Vehicle Emission Laboratory, were transferred into graduated vials and stored at 4°C in a refrigerator.

#### *Linearity and detection limits*

The linearity of the GC method for HCs was evaluated by injecting known concentrations of propane, butane, isooctane, and toluene at concentrations ranging from 3 to 200 ppm C. At these concentrations, no deviation from linearity was observed.

The linearity of the methanol method was evaluated by injecting standard aqueous solutions ranging from 7.9 to 790 µg/ml methanol. Again no deviation from linearity was observed.

The detection limit of the GC method for individual HCs was about 50 parts per billion (10<sup>9</sup>) C based on a signal-to-noise ratio of three and a 0.5-ml sample size. This corresponds to a vehicular mass emission rate of about 0.1 mg/mile HC for the FTP test.

The detection limit of the aqueous methanol GC method was about 0.25 ppm methanol based on a 25-ml impinger sample and a 8-l exhaust gas volume. This corresponds to a vehicular mass emission rate of about 1.3 mg/mile methanol for the FTP test.

## DISCUSSION

#### *Method validation and application*

The method was validated by measuring the individual HC emissions and methanol emissions from vehicles running on M0 and M100, and then comparing the results to the total HC emissions measured with the FID analyzer in the Vehicle Emission Laboratory. By using this approach, the two methods should give equivalent results by using these two fuels. By using M0, the sum of the individual HC concentrations determined by GC should be equivalent to the total HC concentration reported by the FID analyzer. By using M100, the methanol determined by the GC method should be equivalent to that reported by FID if the FID analyzer is properly calibrated. Because of the lower FID response of methanol on a ppm C basis relative to propane, we calibrated the FID analyzer with methanol calibration gas and determined the overall methanol response factor. We then used the methanol response factor to calculate the concentration of methanol in the exhaust. The results should agree, assuming that the HC emitted by using M100 was negligible. Looking at Fig. 7, we can see that this assumption was valid, thus making additional intercomparisons meaningful.

Table VIII summarizes the intercomparison results. There was very good agreement in the cold-bag emissions between the Vehicle Emission Laboratory FID results

and the total GC HC results for both the M0 and M100 vehicles. The differences between the two methods for the cold-bag emissions ranged from 3 to 13%. There was also rather good agreement for the hot-bag emissions between the two methods for the gasoline test and the differences in this case ranged from 8 to 18%.

The differences in the stabilized-bag emissions results for the two methods appear large, but in fact, have little effect on the composite FTP results. The main reason is that both the methanol and the HC emissions are extremely low during the stabilized portion of the FTP and approach background-air levels of 3–4 ppm C. The inherent uncertainty of subtracting two very small numbers (*i.e.*, the stabilized and background air bags) is present in both the GC and FID analysis techniques, and thus gives rise to the imprecision. In addition, small changes in the background-air HC levels during the test could affect the results, especially at these extremely low levels. The background-corrected Vehicle Emission Laboratory FID HC emissions during the stabilized portion of the test ranged from 1.1 to 3.7 ppm C, while the background-corrected emissions for the GC HC emissions ranged from 0.29 to 3.23 ppm C for the stabilized portion of the test. Considering that the overall levels are barely above background, large variations are not surprising.

Similarly, attention should be given to the large discrepancy between the FID and GC results for the hot-start portion of the FTP for the M100 vehicle. As with the stabilized bag, the catalyst dramatically reduces unburned methanol emissions in the hot-start phase to near detection limit levels. As before, the uncertainties involved in subtracting these small background and sample levels exaggerate the variability.

We also assessed the accuracy of the impinger GC methanol method by collecting known volumes of Scott certified methanol calibration gas in dual impingers connected in series and analyzing these samples by GC. The results of these experiments, shown in Table IX, indicated that the GC methanol method results agreed very well with the Scott certification value, with the differences between the two methods ranging from 2.4 to 9.2%. Although not shown in Table IX, we found that more than 97% of the methanol was collected in the first impinger for both these laboratory tests and for preliminary exhaust emissions tests on an M100 vehicle. This reconfirmed our previous findings and ensured that methanol was effectively collected for these tests.

TABLE IX  
INTERCOMPARISON OF METHANOL MEASUREMENT METHODS

*Concentration (ppm methanol)*

<i>Scott certified value<sup>a</sup></i>	<i>GC method</i>	<i>Difference (%)</i>
29.2	31.9	9.2
47.6	50.4	5.9
93.8	96.1	2.4
496.0	464.6	6.3
Average 6.0 ± 2.8		

<sup>a</sup> Certification value ± 5%.



## CONCLUSION

We have developed a method for determining individual exhaust HCs from gasoline-, methanol- and variable-fueled vehicles. This method, in conjunction with an impinger-GC method for methanol, allows one to determine the methanol and non-methanol exhaust HC form methanol- and variable-fueled vehicles. The data that can be generated, along with detailed aldehyde data which are also collected during vehicle tests, should provide the necessary input for atmospheric models that assess the photochemical impact of methanol- and variable-fueled vehicles as compared to gasoline-fueled vehicles.

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## REFERENCES

- 1 *Business Week*, June 29 (1987) 100.
- 2 *Chem. Eng. News*, August 10 (1987) 19.
- 3 *Air Quality Benefits of Alternative Fuels, EPA Draft Report*, prepared by Interagency Task Force on Alternate Fuels, Office of Mobile Sources, Ann Arbor, MI, June 1987.
- 4 D. Moses and C. Saricks, *SAE Paper No. 872053*, Society of Automotive Engineers, Toronto, November 1987.
- 5 R. J. Nichols and J. M. Norbeck, *APCA Paper No. 85-35.3*, Air Pollution Control Association, Detroit, MI, June 1985.
- 6 J. W. Shiller, *Paper Presented at Specialty Workshop on Post 1987 Ozone Issues, San Francisco, CA, November 18, 1987*. Air Pollution Control Association-Golden West Chapter, San Francisco, CA.
- 7 *Proceedings of the APRAC Methanol Workshop, Atlanta, GA, April 19-21, 1988, CRC Report No. 564*. Coordinating Research Council, Atlanta, GA 1988.
- 8 D. L. Hilden and F. B. Packs, *SAE Paper No. 760378*, Society of Automotive Engineers, Detroit, MI, February 1976.
- 9 R. R. Toepel, J. E. Bennethum and R. E. Heruth, *SAE Paper No. 831744*, Society of Automotive Engineers, San Francisco, CA, November 1983.
- 10 J. E. Bennethum and N. Srinivasan, *Proceedings VI International Symposium on Alcohol Fuels Technology*, 1 (1984) 38.
- 11 F. Lipari and D. Keski-Hynilla, *SAE Paper No. 860307*, Society of Automotive Engineers, Detroit, MI, February 1986.
- 12 F. Lipari and F. L. Colden, *SAE Paper No. 872051*, Society of Automotive Engineers, Toronto, November 1987.
- 13 R. A. Potter, *Presented at Fourth Washington Conference on Alcohol Fuels, Washington, DC, November 1984*.
- 14 F. B. Black, L. E. High and J. E. Sigsby, *J. Chromatogr. Sci.*, 14 (1976) 257.
- 15 H. E. Dietzman, *Final Report EPA 600-1-79-017*, U.S. Environmental Protection Agency, Research Triangle Park, NC, February 1979.
- 16 L. R. Smith and C. Urban, *Final Report EPA 460/3-82-004*, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1982.
- 17 L. R. Smith, *Final Report Project CAPE-30-81*, Coordinating Research Council, Atlanta, GA, May 1985.

- 18 C. J. Raible and F. W. Cox, *SAE Paper No. 790690*, Society of Automotive Engineers, Detroit, MI, June 1979.
- 19 P. M. Carey, *Technical Report EPA-AA-TSS-PA-86-J*, U.S. Environmental Protection Agency Office of Mobile Sources, Ann Arbor, MI, June 1985.
- 20 B. E. Nagel, General Motors Research Laboratories, Warren, MI, personal communication, 1989.
- 21 F. Lipari and S. J. Swarin, *J. Chromatogr.*, 247 (1982) 297.