Air



# The Effect of Methanol on Evaporative Canister Charcoal Capacity

# Disclaimer

The data presented in this report should be viewed with care, and any possible conclusions based on these data should be considered tentative at best due to the inconsistent treatment of the charcoal samples during the test program. A more consistently performed extension of this study is underway at Southwest Research Institute, which may confirm the data in this report.

# DRAFT

# The Effect of Methanol on Evaporative Canister Charcoal Capacity

by

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Contract No. 68-03-3162 Work Assignment 12

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Prepared for

ENVIRONMENTAL PROTECTION AGENCY
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Emission Control Technology Division
2565 Plymouth Road
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January 1985

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Publication No. EPA 460/3-84-014

#### FORE WORD

This project was conducted for the U.S. Environmental Protection Agency by the Department of Emissions Research, Southwest Research Institute. The work was carried out between February and August 1984 under EPA Contract No. 68-03-3162, Work Assignment 12. It was identified within Southwest Research Institute as Project 03-7338-012. The EPA Project Officers were Mr. Robert J. Garbe and Mr. Craig A. Harvey of the Office of Mobile Source Air Pollution Control, Emission Control Technology Division, Environmental Protection Agency, 2565 Plymouth Road, Ann Arbor, Michigan. The Southwest Research Institute Project Manager was Charles T. Hare, and the Project Leader was Mary Ann Warner-Selph.

#### **ABSTRACT**

This program involved the evaluation of four types of unused evaporative canister charcoal with a hydrocarbon-only blend and a hydrocarbon-methanol blend. The HC blend consisted of 77% paraffins (butane), 18% olefins (isobutylene) and 5% aromatics (toluene) by weight. The HC-methanol blend was composed of 73% butane, 17% isobutylene, 5% toluene, and 5% methanol by weight. Tests were conducted on a bench-scale apparatus designed to load each blend onto separate sets of twelve reduced-size mini-canisters, and to subsequently purge off the hydrocarbons. The charcoals were evaluated by the measurement of retained charcoal weight gain after purging, time to hydrocarbon breakthrough, and charcoal working capacity. The mini-canisters which were loaded with the methanol blend, had shorter breakthrough times, retained less weight gain after purge, and had lower working capacities than did mini-canisters tested with the hydrocarbon blend only. These methanol blend mini-canisters also underwent less simulated aging than the hydrocarbon blend canisters in this program, since they were only exposed to 40% as much total vapor.



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#### I. INTRODUCTION

Evaporative emissions from gasoline vehicles are controlled by the use of charcoal canisters. The Sealed Housing for Evaporative Determinations (SHED) test was developed to measure vehicle evaporative emissions. This test is used to confirm canister effectiveness in controlling evaporative emissions during simulated vehicle operation. A study conducted by the Department of Energy in 1980<sup>(1)\*</sup> with 10 percent methanol in gasoline raised concerns over whether methanol in gasoline reduces canister effectiveness.

The purpose of this program was to design a laboratory bench-scale apparatus for evaluating the effects of a methanol-hydrocarbon blend on charcoal from evaporative emissions canisters. Two sets of mini-canisters were filled with activated charcoal from new evaporative canisters and aged by repetitively loading and purging with the hydrocarbon and the methanol-hydrocarbon blends, respectively. Hydrocarbon breakthrough times and charcoal weight gains (after purging) were monitored throughout the program. In addition, charcoal working capacity was also measured.

The first part of testing involved operation of the mini-canister apparatus with a gaseous hydrocarbon blend composed of butane, isobutylene, and toluene in nitrogen. After breakthrough times and weights were monitored for repetitive hydrocarbon loading and purging cycles, the mini-canisters were refilled with fresh charcoal. Methanol in nitrogen was added to the hydrocarbon blend, and the mini-canisters were once again subjected to repetitive load and purge cycles. The comparison of hydrocarbon and methanol-hydrocarbon blends using breakthrough times and charcoal weight gains provided a preliminary indication of the effect of methanol on canister performance.

<sup>\*</sup>Numbers in parentheses designate references at the end of this report.

#### IL PROCEDURES AND INSTRUMENTATION

The work plan called for the development of a bench scale apparatus to evaluate charcoal from evaporative canisters. The apparatus that was developed allowed delivery of hydrocarbon vapors to twelve mini-canisters containing fresh charcoal from standard-size evaporative canisters. After the HC vapors broke through the charcoal, the canister system was designed to permit hydrocarbon vapor purge by pulling room air in the reverse direction through the mini-canisters.

### A. Development of Procedure and Instrumentation

The goal of the program was to determine the effect of repetitive hydrocarbon loading and purging cycles (aging) on four types of canister charcoal. The variables that were measured during the aging process were: time to hydrocarbon breakthrough, retained weight gain of the canisters, and charcoal working capacity. Two feed gases were used for canister loading, a hydrocarbon blend of butane, isobutylene, and toluene vapors, and a hydrocarbon-methanol blend composed of the hydrocarbon blend mixed with methanol vapors.

# 1. Fuel Delivery

The original work plan called for the development of a fuel containment vessel equipped with a temperature programmer designed to deliver unleaded gasoline vapors and gasoline-methanol vapors to twelve minicanisters. As a result of discussions with the EPA project officer concerning safety, the plans for a fuel source were changed from a simulated gas tank filled with gasoline to hydrocarbons supplied by pressurized cylinders. The new fuel delivery system still satisfied the requirements for maintaining consistent fuel vapor composition and vapor volume per cycle while reducing the possibility of a fire hazard.

The hydrocarbon sources, as mentioned previously, were compressed gases and vaporized toluene and methanol. Butane and isobutylene were supplied from pressurized cylinders (both 99.0% pure), and toluene and methanol were delivered to the mini-canisters by bubbling nitrogen through the respective liquids. Gas flows were measured with soap bubble meters and monitored with flowmeters.

Several delivery systems for toluene and methanol were evaluated before a decision was made to use nitrogen saturated with toluene and methanol at room temperature. Initially, the liquids were heated to produce pure gas vapors. However, since the remainder of the canister system was not heated, the vapors condensed before reaching the canisters. A second method involved bubbling nitrogen through liquid toluene and methanol in a system heated to 30°C, but the same condensation problem occurred. To avoid vapor condensation, liquid methanol and toluene were placed in separate containers at room temperature, and separate flows of nitrogen were bubbled through each liquid. Toluene made up approximately 1.5% of the toluene-nitrogen flow (by volume) at a nitrogen flowrate of 38 milliliters /min, and methanol constituted about 6.8% of the methanol-nitrogen flow by volume with a nitrogen flowrate of 42 milliliters/min.

# 2. Composition of Hydrocarbon and Methanol Blends

The targeted composition of the simulated fuel was based upon a hydrocarbon speciation study performed by EPA-RTP in which hot soak evaporative emissions were measured on forty six 1975 to 1982 model year gasoline vehicles. Overall, the hot-soak emissions were composed of 70 percent paraffins, 21 percent olefins, and 9 percent aromatics by mass. The flowrates of the fuel gases were set with the goal of achieving these available hot soak weighting factors. Butane was chosen to represent paraffins, isobutylene for olefins, and toluene for aromatics. Feed gas flows were monitored continuously with flowmeters. Heavier hydrocarbons (also representative of hot-soak emissions) were not included in the simulated fuels because of the inability to accurately measure vaporization and delivery of such compounds to the canister system.

The targeted level of methanol in the methanol blend was based on data from two research projects. A study on the alcohol content of gasoline in the Houston area showed the fraction of methanol in one brand of methanol-containing fuel to be about 5% (by volume). Another study measured SHED methanol concentrations from vehicles fueled with methanol-gasoline blends. This study indicated that the mass fraction of methanol in hot soak evaporative emissions was approximately equivalent to the volume percent of methanol in the fuel. Thus, a 5% methanol concentration by mass was targeted for the simulated methanol fuel vapors.

# 3. Load and Purge Cycles

The laboratory procedure was loosely modeled after the Code of Federal Regulations SHED test, which measures evaporative emissions from vehicles. The SHED test cycle consists of a diurnal segment during which the fuel tank is heated from 60-84°F, an FTP driving cycle for purging fuel vapors from the evaporative canister, and a hot soak segment in which the carburetor, at temperatures of 150-200°F, emits fuel vapors to the canister.

The laboratory procedure developed for evaluating canister charcoal combined the two fuel loading segments of the SHED test into a single load cycle. An approach was to simulate and monitor fuel loading and purging cycles similar to the SHED test until hydrocarbons broke through the charcoal. However, the possibility that a SHED-type cycle might not ever show breakthrough became apparent. Therefore, the load cycle was redefined as the length of time until hydrocarbons broke through the mini-canisters. change was incorporated into the program with the approval of the project officer. After breakthrough, the canisters were purged until the rate of change of purge hydrocarbon concentrations became small in relation to that observed at the start of purging (from over 600ppmC/min to less than 10 ppmC/min). These revisions in the load and purge cycles still provided the opportunity to observe the change in canister weight as the charcoal was aged with repetitive loadings and purgings. In addition, cycle by cycle breakthrough times could be observed. The hydrocarbon blend was loaded onto each mini-canister for a cumulative total of about 155 g. This weight is roughly equivalent to the amount of hydrocarbons that a canister would be subjected to over 69 repetitive

SHED tests.<sup>a</sup> Due to time restrictions, a total of only 68 g of the methanol blend was loaded onto each mini-canister, an equivalent of about 29 SHED tests.<sup>a</sup> At the end of testing, a single load-purge cycle with the HC-only blend was conducted on the mini-canisters which had been previously exposed to the HC-methanol blend.

Prior to the decision to alter the load and purge cycles, vapor flow from the carburetor during the hot soak cycle was measured on two vehicles, a 1980 Mercury Cougar and a 1981 Chevrolet Monte Carlo. Vapor flowrate was measured using a 10 ml soap bubble meter attached to the carburetor bowl (where the carburetor vents to the evaporative canister). Vapor volumes produced by the Cougar were measured and found to be 0.1 ml, 0.3 ml, and 0.75 ml over approximately 10 minutes of the hot soak on three tests. Vapor flow was measured at 0.3 ml on the Monte Carlo within a period of about 10 minutes.b The carburetor bowl was found to produce negligible amounts of vapor from the carburetor during the hot soak. In addition, canister vacuum was monitored on the two vehicles during a hot FTP using a vacuum transducer teed into the line connecting the canister to the engine. The average vacuum was 4 in. Hg on the Cougar and 2 in. Hg on the Monte Carlo. The disparity in the amount of vacuum applied to the canisters appeared to be due to the relative size of the purge ports (Cougar purge port was larger than the Monte Carlo purge port) and to the engine size. To relate canister vacuum to the bench-scale apparatus it was necessary to determine purge flowrates. A bench evaluation of new Ford and GM canisters produced flowrates of 4 ft<sup>3</sup>/min (113 liters/min) and 2 ft<sup>3</sup>/min (57 liters/min) at applied vacuums of 4 in. Hg and 2 in. Hg, respectively. This range of flowrates is consistent with the Ford test procedures for testing the "Working Capacity" of Evaporative canisters. According to these procedures, canisters are purged at 2 ft<sup>3</sup>/min. The total flowrate of purge air through the mini-canister system was set at about 3.5 ft<sup>3</sup>/min (99 liters/min). Each mini-canister, which was approximately 1/12 the size of a standard-size canister, was purged at about 0.3 ft<sup>3</sup>/min (8.5) liters/min). This rate is within the flow range measured on the Ford and GM canisters on a proportional volume basis.

### 4. Mini-Canisters

The bench-scale apparatus was designed to test twelve minicanisters. With this setup, multiple positions could be used to evaluate each type of charcoal. Miniature canisters were used instead of standard size canisters in an effort to minimize total flow rates and apparatus size. Minicanisters were initially made of polypropylene tubing (about 6 in. long) with plastic caps on each end. The caps were modified to allow flow through the

aBased on two vehicles tested with four fuels, the average increase in canister weight during each SHED test was 27 g (sum of hot soak plus diurnal). The value is divided by twelve for mini-canister comparisons.

<sup>&</sup>lt;sup>b</sup>Vapor volume was also measured on a third vehicle, a 1981 Ford Mustang. This car produced 0.2 ml of vapor over 15 minutes.

mini-canisters. Preliminary experiments were performed using only butane and isobutylene to determine breakthrough times. During initial experimentation with the hydrocarbon blend (butane, isobutylene, and toluene in nitrogen), the mini-canisters were found to leak hydrocarbons at the cap. The plastic caps were apparently not sealing with the additional flow of nitrogen and toluene through the mini-canisters. A heavier mini-canister design with a threaded aluminum cap was used in all subsequent testing to prevent leaks. The all-plastic canisters were selected initially due to their low filled weight (70 g). The new mini-canisters, though heavier (220-250 g), could still be weighed accurately after hydrocarbon loading.

### B. Description of Charcoal Evaluation Apparatus

The bench scale apparatus for evaluating evaporative canister charcoal is shown in several views in Figure 1. The mini-canister system is composed of a hydrocarbon source (liquids and compressed gases); a series of valves, flowmeters, and tubing to direct equal flows to the mini-canisters; a vacuum pump for purging; and a hydrocarbon analyzer and recorder. schematic of the apparatus is shown in Figure 2. The fuel and delivery gases were set to 20 psig at the cylinder regulator and were individually controlled with needle valves to achieve the desired proportion of butane, isobutylene, toluene, and methanol (as needed). Load and purge cycles were controlled by a timer which automatically switched the purge pump and the fuel solenoid valves on and off. Total hydrocarbon concentrations could be monitored at the exit to individual canisters or in the purge manifold before the pump. A sample line to the HC analyzer allowed sequential hydrocarbon analyses to determine breakthrough time for each mini-canister. A second vacuum pump, which was manually operated, was used to remove hydrocarbons which broke through the mini-canisters.

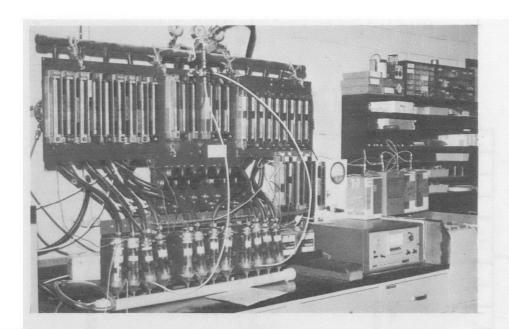
Background hydrocarbon levels were monitored in the lab and generally ranged from about 15 to 25 ppmC. Room temperature was 75°F 2°F, and relative humidity generally varied from a daily high of about 60 percent to a daily low of 50 percent.

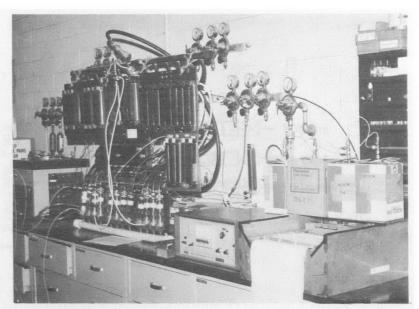
#### 1. Mini-Canisters

The mini-canisters that were used during experimentation were made of an acrylic tube (5 3/4 in. long, 1 in. diameter) with a threaded aluminum cap. The volume of each mini-canister was approximately 74 milliliters. The bottom of the canister was capped by a polypropylene cap with a large hole cut from the center. A metal screen was inserted into the cap to retain the charcoal while allowing vapors or air to pass freely. A large hole (5/8 in.) was drilled into the canister top for a purge outlet, and a smaller hole (1/16 in.) was drilled in the side of the canister top for fuel delivery. A screen was placed in the purge opening to prevent charcoal from being pulled off while under vacuum. In addition, glass wool was used at the purge opening and at the bottom cap to prevent the loss of charcoal dust.

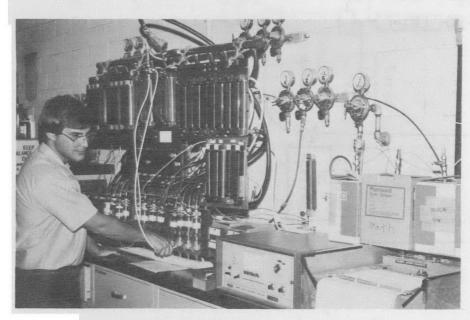
#### 2. Charcoal

Four types of activated charcoal were evaluated in the minicanisters. The charcoals were obtained from new evaporative canisters ordered

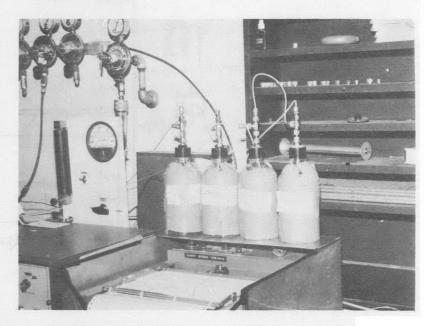




Charcoal Evaluation Apparatus



Measuring Hydrocarbon Breakthrough



Toluene and Methanol Delivery System

Figure 1. Several Views of the Charcoal Evaluation Apparatus

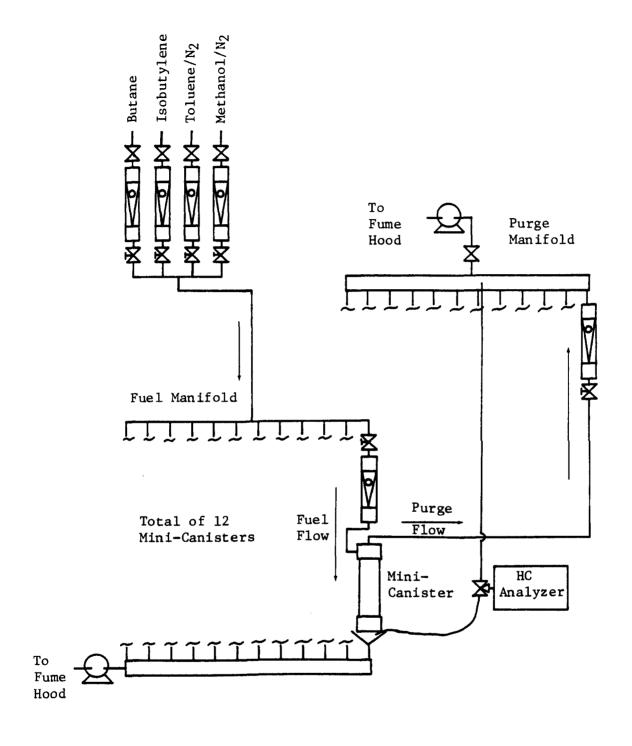


Figure 2. Flow schematic of charcoal evaluation apparatus

for four vehicle types. Charcoal weights and volumes contained in the canisters are listed as follows:

	Typical Standard Size Canister Charcoal Weight, g	Approximate Volume of Charcoal, ml	Approximate Density g/ml
1983 Chrysler Reliant K	344	1270	0.27
1983 Ford Escort	407	1030	0.40
1983 Chevrolet Monte Carlo	438	1500	0.29
1983 Toyota Corolla	362	870	0.42

Initially, charcoal samples were provided by some of the auto manufacturers' charcoal suppliers for use in the mini-canisters. A visual comparison to actual canister charcoal, however, showed differences in size and shape of the charcoal pieces. Because of these variations, the mini-canisters were tested with charcoal from actual evaporative canisters. The weights of fresh charcoal used in the mini-canisters are shown below:

Type of	Mini-Canister		coal Weight, g
Charcoal	Number	HC Blend	HC-Methanol Blend
Chrysler	1 2	19.7	18.9
Chrysler		19.7	17.2
Ford	3	27.9	74.5 <sup>a</sup>
Ford	4	27.5	28.4
Ford	5	27.9	31.1
Ford	6	27.9	26.5
GM	7	19.5	22.3
GM	8	18.5	20.5
GM	9	19.5	21.1
Toyota	10	29.1	34.1
Toyota	11	29.0	31.8
Toyota	12	28.8	29.1

aMini-canister number 3 was filled with Teflon chips (when using the HC-methanol blend) to measure breakthrough time of the mini-canister system. This breakthrough time was found to be less than one minute.

Charcoals from Ford and Toyota canisters are apparently denser than Chrysler or GM charcoals, since a greater mass fills the same mini-canister volume. In addition, Ford and Toyota charcoal particles were generally larger than Chrysler or GM charcoal particles.

# 3. Hydrocarbon and Methanol Blend Compositions

The composition of the hydrocarbon and methanol blends, (by volume) was about 16 percent butane, 4 percent isobutylene, 0.7 percent toluene, and for the methanol blend, 2 percent methanol. The remainder was nitrogen carrier gas. The flowrate of hydrocarbon vapors plus nitrogen carriers to the mini-canisters was on the order of 70 milliliters/min. The actual mass flowrates were determined using the weight of blend loaded onto the mini-canisters, volume percentages, molecular weights of the compounds, and the assumption that the gases obey the ideal gas law. Resulting mass flows are shown below. Due to the low vapor pressure of toluene, the fraction of toluene in the blends was only 5 percent by mass instead of the 9 percent initially desired.

	Mini-Cani	ster Flow, mg/min
Hydrocarbon Component	HC	HC-Methanol
Butane	. 31	29
Isobutylene	7	7
Toluene	2	2
Methanol	<u> </u>	2
Total	40	40

# 4. Hydrocarbon Breakthrough

Hydrocarbon vapors were delivered to the canisters at the above flowrates to establish hydrocarbon breakthrough times. The length of the load cycle was based on the longest breakthrough time of the four types of charcoal. The longest average breakthrough time with the HC blend was for Toyota charcoal, at 110 to 140 minutes. The load cycle for methanol blend testing was set at 120 minutes. The purge cycle with the HC blend was set with the intention of reaching a hydrocarbon concentration in the purge manifold of approximately 300 ppmC. The mini-canisters were purged for 108 to 143 minutes to achieve this level. This level of hydrocarbons represented a drop from over 10,000 ppmC at the beginning of the purge cycle. The purge cycle with the HC-methanol blend was set at 110 minutes. The slope of the logarithmic shaped hydrocarbon purge rate curve leveled out in the 300 ppmC range, as illustrated in Figure 3.

Initially, breakthrough was defined as the emission of hydrocarbons from the bottom of the mini-canisters in excess of 100 ppmC for 10 seconds. The increase in hydrocarbon concentration with time was observed on a recorder, and it appeared that 100 ppmC HC was an adequate indicator of breakthrough. During the preliminary evaluations, breakthrough times were defined at the 100 ppmC level; however, additional experiments were conducted which indicated that 1000 ppmC was a more appropriate definition of breakthrough. Traces of HC breakthrough on the 100 ppmC and 1000 ppmC ranges are illustrated in Figures 4 and 5, respectively. Comparison of the HC and HC-

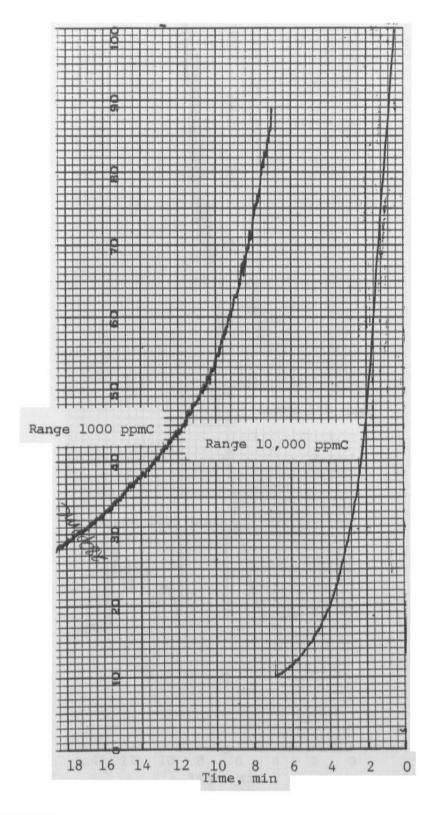


Figure 3. Purge cycle monitored on 10,000 ppmC and 1000 ppmC ranges

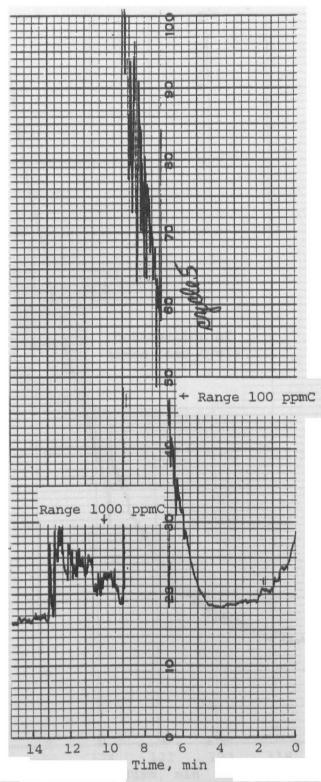


Figure 4. Hydrocarbon breakthrough at 100 ppmC

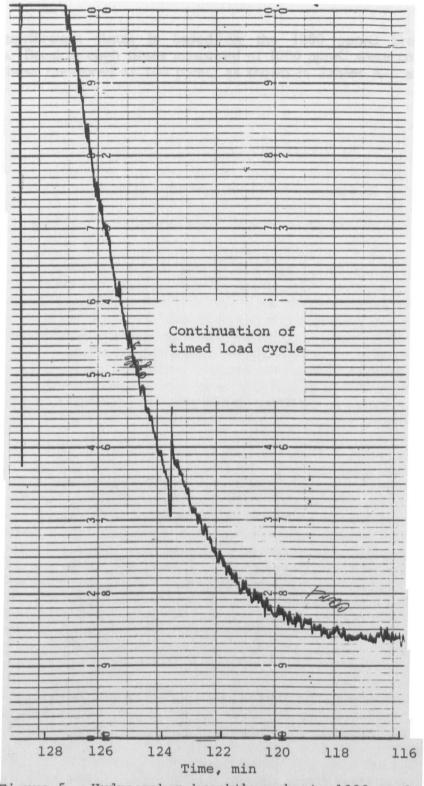


Figure 5. Hydrocarbon breakthrough at 1000 ppmC

methanol breakthrough times is based on the 1000 ppmC breakthrough concentration. Breakthrough times measured at 1000 ppmC were considerably longer than those measured at 100 ppmC as shown in Tables A-1 and A-2 of Appendix A.

# DRAFT

#### III. RESULTS

The effect of the repetitive loading and purging of a hydrocarbon blend and a hydrocarbon-methanol blend on evaporative canister charcoal was measured by canister weight gain and hydrocarbon breakthrough time. The mini-canisters were weighed after the last load-purge cycle of each day. From one to three load-purge cycles were accomplished each test day. Canister weight gain was calculated daily by subtracting the initial clean canister weight from the weight after the last load-purge cycle. Breakthrough time was defined as the length of time for hydrocarbons to break through the bottom of the mini-canisters at 1000 ppmC with a fuel blend flowrate of about 40 mg/min per canister. This loading was equivalent to approximately 5g of HC or HC-methanol per mini-canister.

Variations in canister weight gain and breakthrough times were noted between charcoal types and between fuel blends (HC, HC-methanol). However, canister weight gains and breakthrough times were relatively constant over the course of the program for each individual mini-canister. The only major exception to this finding was the increased weight gain after purge associated with the 110-minute loading on day 8 with the HC-only blend. The first set of mini-canisters received a cumulative hydrocarbon loading of about 155 g of hydrocarbons per canister, and the second set was loaded with about 65 g of the methanol blend and 23 g of the HC-only blend. Appendix A lists the load-purge cycles necessary to achieve these loading levels. Average charcoal weight gains after purge using the hydrocarbon fuel and the hydrocarbon-methanol fuel are compared in Table B-l of Appendix B and in Figure 6 for charcoal from Chrysler, Ford, GM, and Toyota mini-canisters. The canisters containing the smaller mass of lower-density Chrysler and GM charcoals retained greater amounts of hydrocarbons (and/or methanol) after purging than did the Ford and Toyota canisters for both fuels. In addition, all four charcoal types retained more weight after purge when only hydrocarbons were loaded than when the hydrocarbon-methanol blend was loaded to breakthrough. The effect was greater in the cases of the Ford and Toyota charcoals, for which the average weight gain after purge for the hydrocarbon blend was 3 to 7 times that for the methanol blend. The weight gains measured for the Chrysler and GM charcoals using the hydrocarbon blend were 54 and 25 percent higher than with the methanol blend, respectively. Retained weight gains for individual minicanisters using the HC and the HC-methanol blend are listed in Tables A-3 and A-5 of Appendix A.

Hydrocarbon breakthrough times were shorter with the methanol blend than with the hydrocarbon blend for all charcoal types. This finding is illustrated in Figure 7 and Table B-2 of Appendix B. Average breakthrough times for Chrysler, Ford, GM, and Toyota charcoals with the methanol blend were 44, 22, 29, and 20 percent lower, respectively, than with the hydrocarbon fuel. The denser Ford and Toyota charcoals had the longer breakthrough times. Breakthrough times are listed in Tables A-1, A-2 and A-4 of Appendix A for individual mini-canisters. At the end of testing, a single load-purge cycle with the HC blend was conducted on the mini-canisters which had been previously exposed to the HC-methanol blend. Breakthrough times as shown in Table A-4 of Appendix A did not return to the longer times experienced with the HC blend (working capacities were not measured).



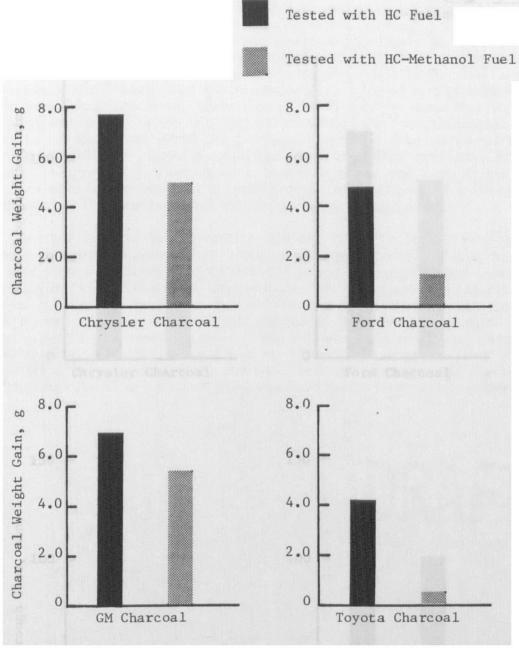
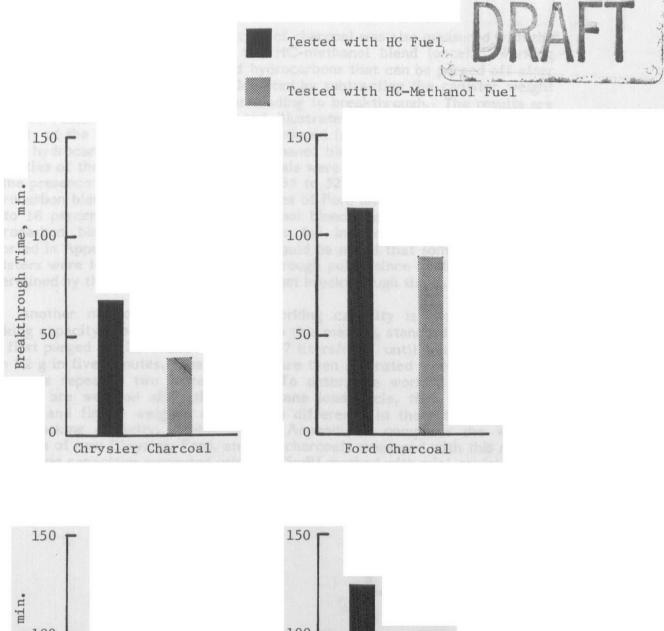


Figure 6. Average daily weight gain after purge of four types of evaporative canister charcoal



GM Charcoal

Toyota Charcoal

Figure 7. Average daily breakthrough time of four types of evaporative canister charcoal

The working capacity of each type of charcoal was also measured with the HC blend (three times) and with the HC-methanol blend (once). capacity is defined as the weight of hydrocarbons that can be purged off after loading to breakthrough. It was calculated by subtracting the canister weight after purging from the weight after loading to breakthrough. The results are shown in Table B-3 in Appendix B and illustrated in Figure 8. The working capacity of the four charcoal types was reduced from 10 to 52 percent relative to the hydrocarbon blend when the methanol blend was used. The working capacities of the Chrysler and GM charcoals were affected to a greater degree by the presence of methanol. They were 35 to 52 percent lower than with the hydrocarbon blend. The working capacities of Ford and Toyota charcoals were 10 to 16 percent lower when the methanol blend was used compared to the Working capacities for individual mini-canisters are hydrocarbon blend. reported in Appendix A, Table A-6. It should be noted that some of the minicanisters were loaded beyond the breakthrough point, since loading times were determined by the charcoals with the longest breakthrough times.

Another method for measuring working capacity is the Ford butane working capacity procedure. According to this method, standard size canisters are first purged at 120°F and 2 ft³/min (57 liters/min) until weight loss is less than 1.2 g in five minutes. The canisters are then saturated with butane. This process is repeated two more times. To determine working capacity, the canisters are weighed after the last butane load cycle, then purged for 20 minutes, and finally weighed again. The difference in these two weights is called working capacity. Table B-4 in Appendix B compares the working capacities of new Chrysler, Ford, and GM charcoals measured with this method and working capacities measured using the SwRI method with mini-canisters.





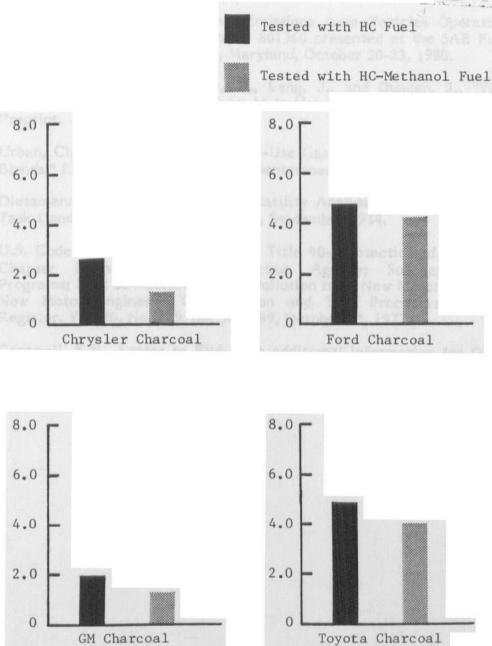


Figure 8. Average daily working capacity of four types of evaporative canister charcoal

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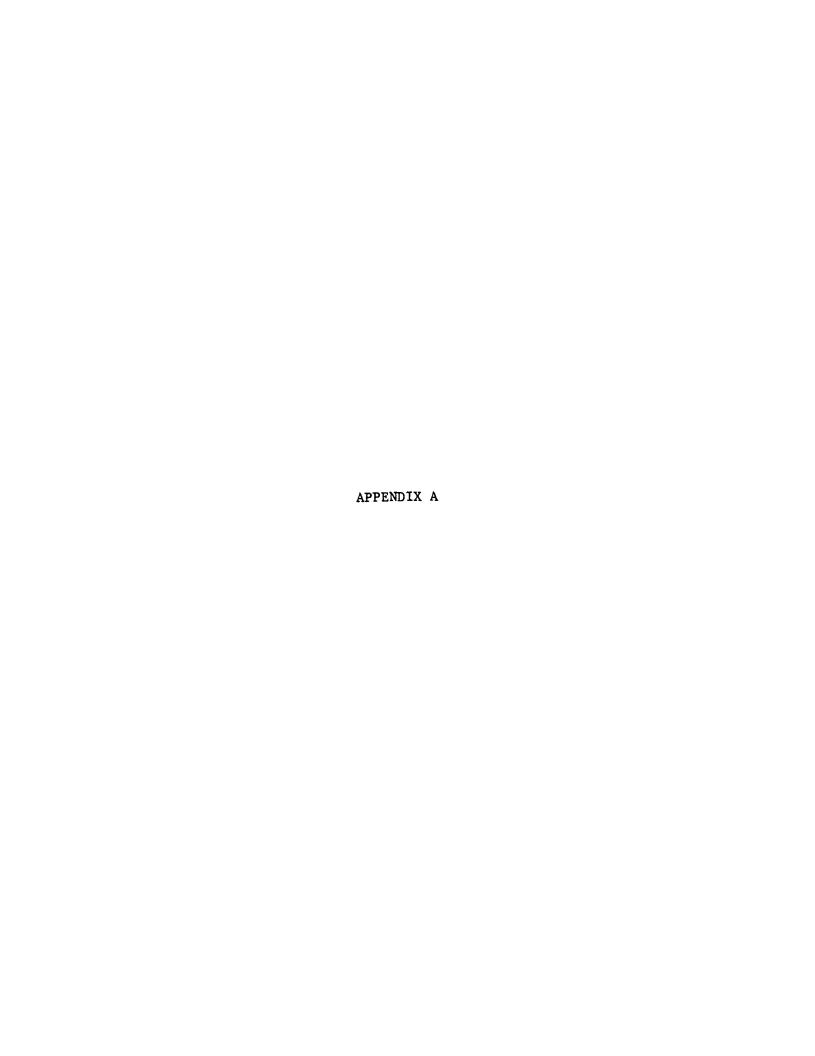






TABLE A-1. INDIVIDUAL MINI-CAMISTER BREAKTHROUGH TIMES WITH HC BLEND 100 ppmC BREAKTHROUGH LEVEL

	Cum	u-		Breakthrough :										
	lati	ve	Chry	sler		For	rd			GM		7	'oyota	
Day	Cyc1		1	2	3	4	5	6	7	8	9	10	11	12
	-	<del></del>												
1 <sup>a</sup>	5		7.25	6.75	10.75	11_	13.25	11.25	4.25	4.75	5.25	10	8.75	9
	6		6.5	6.5	9.5	11.5	14.25	12.25	4.5	4.5	4.75	10	9	9.5
	7		6.25	6.25	10	10.25		12	4.5	4.5	4.75	9.75	8.75	9.25
	8		6		11.5	10.25		11.75	5	4.75	5.25	10	6.25	9
	9		6.25		10.5	10.5	14	12	4.75	5.25	5.5	9.5	9	9.25
	10		6.5	6.5	11.5		14.75		5	5.75	4.75	9.5	9	9
	11		8.5	8.5	11		14.75		7.25	7.25	7.25	11.5	10.5	10.25
		Avg	6.			1.		13.73		5.2	7 . 2. 3	1110	9.4	10.23
		TAR	•	•						J • 2			7.4	
2 <b>a</b>	12		5.25	5.25	8.75	8.75	11	10	3.75	3.75	3.75	3.75	8.5	8.25
-	13		5.5	6			13.8	9	3.5	3.5	3.5	9.25	8.5	8.5
	14		5.25	5.1	9		13.7	13	4	3.8	4.1	9.2	8.2	8.2
	15		6.5	6.5	9.6	10.5	12.2	12	5	4.6	5.2	10.2	8.5	9.5
	20		6.2	7.1	10.5	10.5	13.1	11.7	6.2	5.7	6.2	11.2	9.4	10.25
	22		5.3	5.3	9.5	9.5	12.0	10.2	4.6	4.6	4.8	8.9	7.5	7.5
		Avg	5.		7,00		0.6	10.2	7.0	4.5	7.0	-0.7	8.9	
		Avg	٠,٠	,			0.0			7.3			0. 3	
3 <sup>a</sup>	24		5.2	5.3	10.4	10.2	13.9	13:1	3.9	3.8	4.3	9.2	7.7	7.9
•	31		6.5	6.6	10.6	10.4	12.4		4.4	4.5	4.7	9.8	8.8	8.7
		Avg	5.		10.0		1.5	_41,5		4.3	7.,		8.7	
				•						4.5			<b>5.</b> /	
4 <sup>a</sup>	36		6.4	6.4	11.2	9	10.5	11.2	4	3.4	4.7	9.5	9.1	8.5
·	37		5.4	5.8	11	11.5		.11.4	3.5	3.2	4	9.6	8	7.7
	٠.	Avg	6		==	1	1.3			3.8			8.7	
			•											
5 <sup>a</sup>	44		6.7	7.1	10.7	11.4	14.3	10.7	4.1	4.2	5.0	9.8	8.4	8.2
	49		6	5.9	12.4	8.9		.10.1	3.9	3.9	4.	8	7.4	7.2
	53		7.1	6.5	12.7	11.2	14.4	11.9	4.3	4.4	5.2	9.9	8.5	9.2
		Avg	6.		***************************************		1.6	·		4.3			8.5	<del></del>
			•											
6 <sup>a</sup>	54		5.2	5.4	10.1	8.6	12.7	10.6	3.6	3.7	4	8.9	7.9	8.1
	61		5.3	5.4	9.4	8.7	10.8	10.9	4.1	4.2	4.3	8.2	7.5	7.9
	64		5.6	6.1	10	8.8	10.4	9.9	4.1	4.4	4.2	8.3	7.8	8
		Avg	5.				0.1			4.1			8.1	
										. • -				
7 <sup>a</sup>	65		5.4	5.2	11.7	10.1	13.1	9.9	4.1	4.2	5	9.3	8.1	8.4
	74		4.7	4.4	9	9.3	10	9.6	3.6	3.6	3.8	8.2	7	7.1
	81	•	_5.5	5.5	8.5		8.5	.8.9	4.6	4.8	5	7.5	6.8	6.2
	_	Avg	5.	1			9.8			4.3			7.6	
-		•								_				
8 <sup>a</sup>	3	hours	of cont	inuou	s load:	ing wi	thout	purge	to chec	k flow	rates	3		
	83		6	6.3			9.8		4.4	4.4	5.4		7.9	8.8
		Avg	6.				9.2		***************************************	4.7			8.5	· · · · · · · · · · · · · · · · · · ·
		~												



TABLE A-1 (CONT'D). INDIVIDUAL MINI-CANISTER BREAKTHROUGH TIMES WITH HC BLEND 100 ppmC BREAKTHROUGH LEVEL

	Cumu-						Breakt	hrough	Time.	min				
	lative		Chry	sler	Ford					GM		Toyota		
Day	Cycles		1	2.	3	4	5	6	7	8	9	10	11	12
9 <sup>a</sup>	85		4.7	4.6	8.7	8.7	10	9.2	3.3	3.3	4 .		7.4	7.6
	89		4.1	4.4	8.7	9.4	9	8	2.8	2.9	3.8	7.5	6.8	7
	95		3.8	3.9	8.4		8.2	8.1	2.9	2.9	3	6.4	6.4	6.3
		Avg	4.	, 2		8	. 7			3.2			7.1	
10 <sup>a</sup>	97		4	4.1	8.5	8.4	10.2	8.4	2.8	2.9	3,6	6.7	6.4	6.5
	107		4.2	4.2	8.8		10.6	9.1	3	3	3.5	7.4	6.7	7.5
	114		4.8	4.7	8.7		9.8	_10	2.8	2.8	2.8	7.2	7	6.7
		Avg	4.			9	.1			3			6.9	
2					•									
11 <sup>a</sup>	116		4.6	4.5	8.5		10.7	8.8	2.5	2.6	3	7	6.5	6.7
	125		4.9	4.8	9.3		12.4	8.5	2.7	2.7	3	7.6	6.6	7
	131		4.1	4.6	9.2	8.7		8.3	2.7	2.6	3	7	6.5	6.7
		Avg	4.	, 6		9	.3			2.8			6.8	
12 <sup>a</sup>	133		4.7	4.6	8.3	8.3	11	8.9	2.5	2.6	3	6.9	6.1	6.6
	144		4.6	4.4	8.5		11.8	8.9	2.7	2.7	3.2	6.9	6.3	6.7
	±-7-7	Avg		6			•3	- 0,7		2.8	7,2		6.6	
			• •			_							•••	
13 <sup>a</sup>	151		4.7	4.7	8.7	8.7	b	8.6	2.6	2.8	3.5	7.8	7.3	7.5
. –	156		4.6	4	7.7	9.3	8		2.7	2.7	3	6.6	6.1	6.7
		,	4.				. 4			2.9			7.0	
	Overall	Avg	5.	4		10	.1			3.5			7.9	

aLoad Cycle = 15 min, purge cycle = 25 min No data

TABLE A-2. INDIVIDUAL MINI-CANISTER BREAKTHROUGH TIMES WITH HC BLEND 1000 ppmC BREAKTHROUGH LEVEL

		Breakthrough Time, min											
		Chrysler	Ford	GM	Toyota								
Day	Cumulative Cycles	1 2.	3 4 5 6	7 8 9	10 11 12								
16	179 cycles w/purge +280 min loading, purge 25 min to 3600 ppmC +216 min loading, purge 124 min to 410 ppmC												
17	111 min loading, purge 143 min to 300 ppmC Avg	63 52.5 58	108 101 100 100 102	43 42 46.5	109 111 111 110								
18	120 min loading, purge 120 min to 295 ppmC Avg	61 70.5	112 108 104,5 107.5 108	47 47 49	117.6 116.5 122.5 119								
	125 min loading, purge 120 min to 190 ppmC Avg	67 71 69	121 108 107 107 111	<u>51</u> <u>51</u> <u>55</u> <u>52</u>	126 122 126 125								
19	140 min loading, purge 108 min to 285 ppmC Avg	75 74 74	132.5 124 132 127 129	54 52 61 56	141 137.5 140 140								
	140 min loading, purge 122 min to 330 ppmC Avg	75 75 75	124 122 121 121 122	51 47 52	137 135 134 135								
	Overall Avg	68	114	50	126								

TABLE A-3. INDIVIDIAUL MINI-CANISTER RETAINED WEIGHT GAIN WITH HC BLEND

				Retained Weight Gain, g											
				Chr	ysler	rora					GM	M Toyota			
	Day	Cumulative Cy	cles	1	2	3	4	5	6	7	8	9	10	11	12
	1 <sup>b</sup>	11	Avg	2.75	2.71 .7	0.41	0.41	0.40	0.42	2.55	2,53	2.58	0.15	0.18	0.13
	2 <sup>b</sup>	22	Avg	$\frac{3.25}{3}$	3.17	0.47	0.48	0.47	0.50	3.01	3.00	2.95	0.18	0.23	0.17
	3 <sup>b</sup>	35	Avg	3.45	3.36	0.58	0.59	0.60	0.61	3.18	3,11	3.03	0.23	0.28	0.23
	4°	42			0				с			c			c
	5 <sup>b</sup>	53	Avg	$\frac{2.17}{2}$	2.02	0.32	0.32	0.29	0.31	1.86	1.75	1.67	0.18	0.20	0.17
A-5	6 <sup>b</sup>	64	Avg	2.36	2.18	0.37	0.34	0.34	0.36	1.98	1.85	1.82	0.20	0.23	0.18
	7 <b>b</b>	81	Avg	3.35	3.22	0.61	0.62	0.61	0.63	2.86	2.77	2.69	0.28	0.38	0.28
	8р	3 hours of 83	continue						neck f1 4.56			6.95	4.14	4.19 4.16	4.16
	9b	95	Avg	7.90	7.29 .60	4.68	4.69	4.61	4.59	7.22	6.87 7.01	6.93	4.16	4.20 4.19	4.21
	10 <sup>b</sup>	114	Avg	7.83	7.26 .55	4.67	4.68	4.60	4.60	7.24	6.96 7.07	7.00	4.18	4.18	4.22
	11 <sup>b</sup>	131	Avg	8.19	7.58 .89	4.78	4.80	4.74 .76	4.72	7.54	7.15 7.26	7.10	4.21	4.21	4.28
	12 <sup>b</sup>	150		7.28	6.64 .96	4.56	4.56	4.47 •51	4.45	6.54	6.14	6.09	4.13	4.11	4.19

				Reta	ained	Weight	Gain,	a g					
		Chrysler		Fo	rd			GM		Toyota			
Day	Cumulative Cycles	1 2	3	4	_5_	6	7	8	9	10	_11_	12	
13	b 160 Avg	$\frac{7.65}{7.35}$	4.69	4.69	4.61 65	4.60	6.98	6.65	6.68	4.18	4.17	4.24	
14	b	c	·			с			c			с	
15	b	C	:			с			C			c	
16	Total of 179 cycles with purge +280 min loading, purge 25 min to 3600 ppmC + 216 min loading, purge 124 min to 410 ppmC	8.07 7.42	4.88 <sup>.</sup>	4.86	4.79	4.79	7.36	6.97	7.07	4.29	4.26	4,37	
	Avg	8.07 7.42 7.75	<u></u>	4.	83			7.13		<del></del>	4.31	,	
å 17	d 111 min loading, purge 143 min to 300 ppmC Avg	8.41 7.87 8.14	5.27	5.21 5.	5.16 19	5.13	7.58	7.09 7.38	7.47	4.54	4.49	4.61	
18	120 min to 295 ppmC + 125 min load, purge	0.00 7.75	5 11	F 07	5 00	/ 00	7 20	6 72	7 10	<i>l.</i>	1	<i>l</i> . 52	
	120 min to 190 ppmC Avg	$\frac{8.28  7.75}{8.02}$	5.11	5.07	04	4.99	7.28	7.06	7.18	4.48	4.41	4.53	
19	d 140 min load, purge 108 min to 285 ppmC + 140 min load, purge 122 min to 330 ppmC	8.12 7.69	4.96	4.94	-4.88	4.87	7.26	6.75	7.12	4.36	4.29	4.42	
	Avg	$\frac{8.12}{7.91}$	***	4.	91			7.04			4.36		
	Overall Avg. from Day 8 to Day 19	7.6		4.	8			7.0	=		4.3	;	

a Retained weight gain = mini-canister weight after purging - clean mini-canister tare weight Breakthrough level 100 ppmC, load cycle = 15 min, purge cycle = 25 min



CNo weight measurement dBreakthrough level = 1000 ppmC

TABLE A-4. INDIVIDUAL MINI-CANISTER BREAKTHROUGH TIMES WITH HC-METHANOL BLEND 1000 ppmC BREAKTHROUGH LEVEL

			Breakthroug	gh Time, min		
		Chrysler	Ford		GM	Toyota
<u>Day</u>	Cumulative Cycles	1 2	3 4 5	6 7	8 9	10 11 12
	HC Blend	only for 2½ d	ays to establish	breakthrough	n times	
1	1 107 min load w/108 min purge to 270 ppmC . Avg	58 64.6 61	94.9 111.5	89.6 64.2	58.5 64 62	115.2 106.7 98.2 107
2	2 136 min load w/110 min purge to 300 ppmC Avg	b 50	121 139 124	112 44	48 45 46	144.5 138 124 136
	3 118 min load w/110 min purge to 300 ppmC Avg	58 58 58	104 121 109	103 58	58	123 120 110 118
	4 112 min load w/109 min purge to 320 ppmC Avg	55.5 54 55	102 116 104	95.4 53.5	52.3 52.3 53	121 111 105 112
3	5 140 min load w/114 min purge to 300 ppmC Avg	66 59	118 136 123	114 58	57	149 142 130 140
	Overall Avg	57	112	_	55	122
	•	HC	-Methanol Blend			

3 <sup>c</sup>	1	46	41	92.2		84	41		43 110		95.9
	2	40_	<u>38</u>	91.6	100.3	<u>79</u>	38	40	38 101.3	96.3	<u>95.6</u> 🛊
		Avg	41		91			40		100	
4 <sup>C</sup>	3	45	41,	92.7	107.3	83.4	43	41 45	115	106.5	101.6
	4		<sup>U</sup>	88.8	98.2	85			<sup>D</sup> 108.	1 95.4	89.9
	5	42	35	78.7		74.8	33.9		104.		88.7
		•	41		89			38		101	Ĭ

TABLE A-4 (CONT D). INDIVIDUAL MINI-CANISTER BREAKTHROUGH TIMES WITH HC-METHANOL BLEND 1000 ppmC BREAKTHROUGH LEVEL

						Bre	akthrou	igh Tin	e, min					
			Chi	rysler		Fo	ord			GM			Toyota	
Day		Cumulative Cycles	1	2	3	4	_5_	6	7	_8_	9	10	11	12
5 <sup>c</sup>	6		48	37		98.5	109.4	88.9	39.7	<b>3</b> 9	40.8	114.4	108.1	103.8
	7		41.4	35,2		86.5	103.3	81.8	34.9	31.1	32.8	113.3	91.1	91.1
	8		39.6	33.9		83.7	115_	79	33.3	31.3	32.7	114.3	94	84.1
		Avg		39			94			35			102	
6c	9		46.4	40		101.6	113.8	93.8	40	38	41.4	127.9	117.2	108.5
	10		28	25		75.2	87.7	62.9	22	22	24	96.3	85.7	78.8
	11		36.7	32.1		78.7	93.5	71.8	30.3	30	31.5	105.6	92.2	87.8
		Avg		35			87			31			100	
7 <sup>C</sup>	12		43	38,5		93.5	103.4	83.8	39.4	37	40.9	123.2	115	104
	13	•	40	34.5		82	90.5	73	32.5	30.8	33.1	112.4	96.6	91.8
	14		36	33		79.8	93.8	73.5	29.4	28.5	31	107.9	94.8	86.6
		Avg		38			86			34			104	
<b>!&gt;</b>		Overall Avg with	=	==			===							
A- 8		HC-Methanol Blend		39			89			36			101	
					Н	C-Blen	d							
8	1	Avg	39.7	47.5 44		88.8	93	79.6	29	30 31	33	109.9	104.5 101	90.9



<sup>&</sup>lt;sup>a</sup>Mini-canister 3 filled with Teflon chips to measure breakthrough time of mini-canister system bNo data
<sup>c</sup>Load cycle = 120 min, purge cycle = 110 min

TABLE A-5. INDIVIDUAL MINI-CANISTER RETAINED WEIGHT GAIN WITH HC-METHANOL BLEND

						Reta	ined W	eight	Gain,	a				
				Chrysler		For	d			GM		To	oyota	<del></del>
	Day	Cumulative Cycles		1 2	<del>-3b</del>	4	5	6	7	8	9	10	11	12
	20,7			<del></del>		<del></del>			<u></u>		<u> </u>	<del></del> -		
		HC Blend only	for 3	2 1/2 days t	o esta	blish l	reaktl	nrough	time					
	1	1 107 min load w/												
				2.09 1.90		0.63	0.67	0.56	1.93	1.83	1.85	0.23	0.24	0.22
		A A	VΩ	$\frac{2.09  1.90}{2.00}$			0.62			1.87			0.23	
			0	-										
	2	2 136 min load w/ 110 min purge 3 +118 min load w/ 110 min purge +118 min load w/ 110 min purge 4 +112 min load w/												
		109 min purge		4.19 3.75		0.95	1.04	0.85	4.18	3.88	3.84	0.33	0.35	0.39
		Too man barge	Avg	4.19 3.75 3.97			0.95			3.97		0.33	0.36	
			vB	3.77			0.75			3.37			0.30	
A-9		Overal1	A370	3.0			0.8			${2.9}$			$\frac{\overline{0.3}}{0.3}$	
<b>.</b> →.		Overdir	****	HC-Methan	ol Ble	nd								
<b>1</b>								,						
JRAL-	3 <sup>c</sup>	2	Avg	5.02 4.53 4.78		1.27	1.25	1.12	5.40	4.98 5.12	4.98	0.46	0.49	0.52
***	•													
	4 <sup>C</sup>	5		5.08 4.67 4.88		1.24	1,33	1.08	5.67	5.17	5.14	0.41	0.51	0.56
			Avg	4.88			1.22			5.33			0.49	
			•											
	5 <sup>C</sup>	8		5.25 4.88		1.38	1.44	1.23	5.99	5.57	5.52	0.42	0.60	0.68
	•		Avg	5.25 4.88 5.07			1.35			5.69		0.42	0.57	
I g			vB	3.07			1,33			3.03			• • • • • • • • • • • • • • • • • • • •	
	6 <sup>c</sup>	11		5 20 4 84		1 31	1 //3	1 16	5 91	5 42	5 36	0 39	0.54	0.70
ě	U		A	5.20 4.84 5.02		1. 11	1 30	1.10	J. J.	5 56	3.30	0.39	0.54	0.70
ť			Avg	3.02			1.30			٥٠.ر			0,54	•
<u>.</u>	7 <sup>C</sup>	7.4						1 /0	( 1)	E 01	F 06	0 60	0.04	0.04
	/	14		$\frac{5.54  5.17}{5.36}$		1.72	1./6	1.49	6.43	2.91	3.80	0.68	0.04	0.94
			Avg	5.36			1.66			6.07			0.82	•
										$\phantom{00000000000000000000000000000000000$			<del></del>	
		Overall	Avg	5.0			1.4			5.6			0.6	

aRetained weight gain = mini-canister weight after purging-clean mini-canister tare weight bMini-canister 3 filled with Teflon chips to measure breakthrough time of mini-canister system Load cycle = 120 min, purge cycle = 110 min

TABLE A-6. INDIVIDUAL MINI-CANISTER WORKING CAPACITY WITH HC BLEND

					Wo	rking	Capaci	ty, g					
		Chry	sler		For	ď			GM		T	'oyota	
Day	Cumulative Cycles	1_	2	3	_4	_5	_6_	7	_8_	9	10	11	12
16	179 load/purge cycles (load = 15 min, purge = 25 min) +280 min load, purge 25 min to 3600 ppmC	2.76	2.82	4.77	4.86	4.90	4.76	2.05	1.90	2.02	5.00	4.65	4.77
17	216 min load, purge 124 min to 410 ppmC	2.10	2.05	4.20	4.34	4.28	3.99	1.59	1.47	1.43	4.46	4452	4.35
18	111 min load, purge 143 min to 300 ppmC Avg	3.32	3.31 7	5,51	5.52 4.		5.43	2.66	2.54	2.67	5.61	5.50 4.9	5.58

#### INDIVIDUAL MINI-CANISTER WORKING CAPACITY WITH HC-METHANOL BLEND

		Chr	/8ler		For	(d			GM			Toyota	
		1	2	3	_4_	5	_6_	7_	8	9	10		12
7	14 load/purge cycles (load = 120 min, purge	=							1.0/	1.06	4 20	( 35	0.70
	110 min)	1.39	1.29		4.29	4.60	3.91	1.33	1.24	1.26	4.39	4.15	3.69
	Avg	1.	, 3		4.	. 3			1.3			4.1	

<sup>&</sup>lt;sup>a</sup>Working capacity is defined as the weight of hydrocarbons that can be purged after loading to breakthrough. It should be noted that due to the procedure used, some canisters were bloaded beyond the breakthrough point.

Mini-canister 3 filled with Teflon chips to measure breakthrough time to mini-canister system

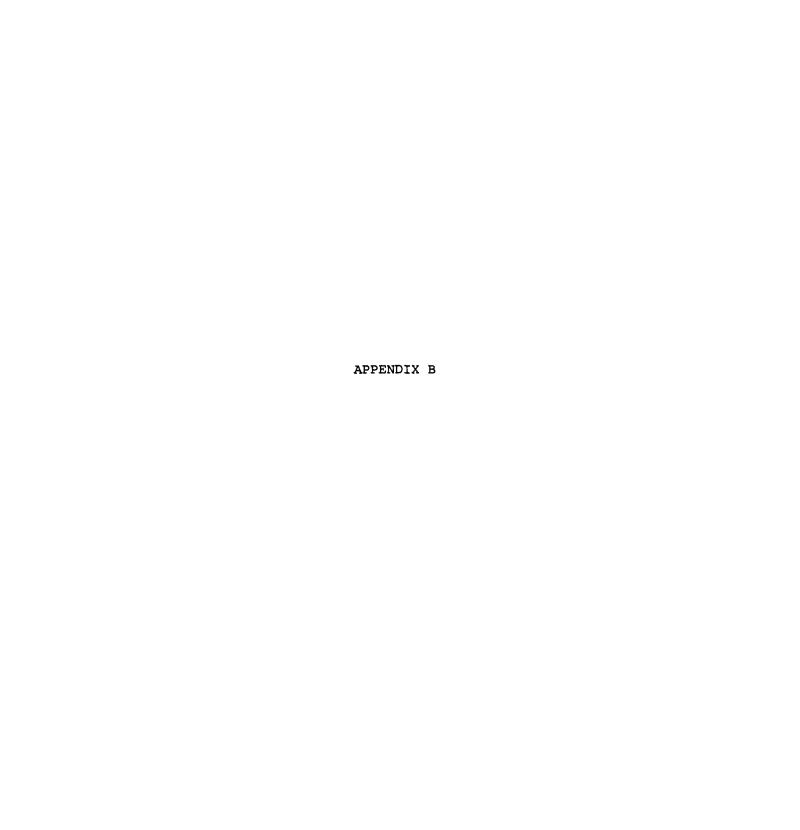


TABLE B-1. AVERAGE DAILY WEIGHT GAIN

		HC Blend		HC-Methanol Blend						
Type of Charcoal	Number of Mini- canisters	Weight Gain, g	Weight Gain as Percentage of Clean Charcoal Weight	Number of Mini- canisters	Weight Gain, g	Weight Gain as Percentage of Clean Charcoal Weight	Percent Difference in Weight Gains <sup>b</sup>			
Chrysler	2	7.7	41%	2	5.0	26%	-35%			
Ford	4	4.8	17%	3	1.4	5%	-71%			
GM	3	7.0	35%	3	5.6	28%	-20%			
Toyota	3	4.3	14%	3	0.6	2 %	-86%			

 $<sup>^{</sup>a}$ One mini-canister was filled with Teflon chips to measure breakthrough time of the mini-canister  $$^{\rm b}$$  Percent differences were calculated relative to weight gains using the HC blend

TABLE B-2. AVERAGE DAILY BREAKTHROUGH TIME<sup>a</sup> (minutes)

Type of Charcoal	HC Blend	HC-Methanol Blend	Percent Difference b
Chrysler	68	38	-44%
Ford	114	89	<del>-</del> 22%
GM	50	36	-28%
Toyota	126	101	<del>-</del> 20%

 $<sup>^{\</sup>rm a}_{\rm b}$  Loaded at about 40 mg/min with hydrocarbons or methanol blend bercent of differences were calculated relative to breakthrough times using the HC blend



Type of Charcoal	HC Blend	HC-Methanol Blend	Percent Differencea
Chrysler	2.7	1.3	-52%
Ford	4.8	4.3	-10%
G <b>M</b>	2.0	1.3	<del>-</del> 35%
Toyota	4.9	4.1	-16%

TABLE B-4. WORKING CAPACITIES OF STANDARD SIZE (NEW) CANISTERS USING THE BUTANE WORKING CAPACITY PROCEDURE AND OF MINI-CANISTERS USING THE SWRI PROCEDURE

Ε	Charcoal	Auto	HC Blend	HC-Methanol Blend
	Manufacturer Specified	Manufacturer Specified	SwRI Mini-canisters,	SwRI Mini-canisters,
Type of Charcoal	Virgin BWC, g/100 ml	Virgin BWC, g/100 ml	g/100 ml	g/100 ml
Chrysler - 14x35 Westvaco wood	9.0	8.2	3.9	1.8
Ford - 6x16 Calgon coal	6.8	a	6.8	6.1
GM - 10x25 Westvaco wood	8.5	8.5	2.9	1.9
Toyota - description unknown	a	a	6.8	5.7



<sup>&</sup>lt;sup>a</sup>Percent differences were calculated relative to working capacities using the HC blend.

a Data not available

(1	TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)								
1. REPORT NO. EPA 460/3-84-014	2.	3. RECIPIENT'S ACCESSIONNO.							
4. TITLE AND SUBTITLE The Effect of Methanol of	on Evaporative Canister	5. REPORT DATE January 1985							
Charcoal Capacity	6. PERFORMING ORGANIZATION CODE								
7. AUTHOR(S)  Mary Ann Warner-Selph	8. PERFORMING ORGANIZATION REPORT NO.								
9. PERFORMING ORGANIZATION NAME AN Southwest Research Inst	itute	10. PROGRAM ELEMENT NO.							
Department of Emissions 6220 Culebra Road Ann Arbor, Michigan 48	11. CONTRACT/GRANT NO. 68-03-3162								
12. SPONSORING AGENCY NAME AND ADI Environmental Protection 2565 Plymouth Road Ann Arbor, Michigan 48.		13. TYPE OF REPORT AND PERIOD COVERED Final (Feb. 1984 - Aug. 1984)  14. SPONSORING AGENCY CODE							

#### 15. SUPPLEMENTARY NOTES

#### 16. ABSTRACT

This program involved the evaluation of four types of unused evaporative canister charcoal with a hydrocarbon-only blend and a hydrocarbon-methanol blend. The HC blend consisted of 77% paraffins (butane), 18% olefins (isobutylene) and 5% aromatics (toluene) by weight. The HC-methanol blend was composed of 73% butane, 17% isobutylene, 5% toluene, and 5% methanol by weight. Tests were conducted on a bench-scale apparatus designed to load each blend onto separate sets of twelve reduced-size mini-canisters, and to subsequently purge off the hydrocarbons. The charcoals were evaluated by the measurement of retained charcoal weight gain after purging, time to hydrocarbon breakthrough, and charcoal working The mini-canisters which were loaded with the methanol blend, had capacity. shorter breakthrough times, retained less weight gain after purge, and had lower working capacities than did mini-canisters tested with the hydrocarbon blend only. These methanol blend mini-canisters also underwent less simulated aging than the hydrocarbon blend canisters in this program, since they were only exposed to 40% as much total vapor.

17.	KEY WORDS AND DOCUMENT ANALYSIS								
1.	DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group						
Air Poll	ution	Evaporative Canisters Methanol Charcoal Evaluation							
B. DISTRIBUTION S		19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 36						
Kelease	Unlimited	20. SECURITY CLASS (This page) Unclassified	22. PRICE						