United States
Environmental Protection
Agency

Office of Mobile Source Air Pollution Control
Emission Control Technology Division
2565 Plymouth Road
Ann Arbor, Michigan 48105

EPA 460/3-85-010
December 1985

Air

EPA

Additional Mini-Canister Evaluation

EPA 460/3-85-010

Additional Mini-Canister Evaluation

by

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Contract No. 68-03-3162
Work Assignment 29

EPA Project Officer: Craig A. Harvey

Prepared for

ENVIRONMENTAL PROTECTION AGENCY
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Publication No. EPA-460/3-85-010

FOREWORD

This project was conducted for the U.S. Environmental Protection Agency by the Department of Emissions Research, Southwest Research Institute. The program, authorized by Work Assignment 29 under Contract 68-03-3162, was initiated March 11, 1985 and completed in August 1985. This program was identified within Southwest Research Institute as Project 03-7338-029. The EPA Project Officer for the program was Mr. Craig A. Harvey of the Emission Control Technology Division, Ann Arbor, Michigan. The SwRI Project Leader and principal researcher for the project was Dr. Lawrence R. Smith. Mr. Charles T. Hare was Project Manager and was involved in the initial technical and fiscal negotiations and subsequent major program decisions.

ABSTRACT

This program involved the continuation of testing on charcoal mini-canisters that were developed and previously tested in Work Assignment 12 of this Contract. The results of the previous study are reported in EPA Report No. 460/3-84-014. In this study, additional testing was conducted both on mini-canisters previously exposed to a hydrocarbon-only blend, and on mini-canisters previously exposed to a hydrocarbon-methanol blend. Switching of exposure blends (between the hydrocarbon-only and the hydrocarbon-methanol blend) on the same set of mini-canisters was also undertaken to determine if any of the effects of the previous blend exposure were reversible. Breakthrough times, working capacities and canister weight gains were monitored for each of the mini-canisters during all testing. Laboratory humidity, temperature, and barometric pressure were also monitored to determine the effect of these parameters on mini-canister working capacity and weight gain. Hydrocarbon and methanol speciation were conducted on the vapors purged from eight of the canisters (four from the hydrocarbon-methanol blend exposures and four from the hydrocarbon-only blend exposures).

SUMMARY

Detailed testing was conducted on charcoal mini-canisters developed and previously tested in Work Assignment 12 of this Contract. The charcoals used in these studies had been obtained from new evaporative canisters ordered for four vehicle types: a 1983 Chrysler Reliant K, 1984 Ford Escort, a 1983 Chevrolet Monte Carlo, and a 1983 Toyota Corolla. The testing was conducted with a bench-scale apparatus designed to repeatedly load either a hydrocarbon-only blend (butane, isobutylene, and toluene) or a hydrocarbon-methanol blend (methanol, butane, isobutylene, and toluene) onto separate sets of twelve reduced size mini-canisters, and to purge off the hydrocarbons (and methanol) after each loading. The charcoals were evaluated by the measurements of retained charcoal weight after purging, time to hydrocarbon breakthrough, and charcoal working capacity.

The additional testing in this study was conducted in three tasks and involved both the mini-canister charcoal samples previously exposed to the hydrocarbon-only blend and those exposed to the hydrocarbon-methanol blend. In the first task, loading and purging of the mini-canisters previously exposed to the hydrocarbon-methanol blends in Work Assignment 12 were continued until the cumulative loading (this study and Work Assignment 12) was approximately equal to the cumulative loading of the mini-canisters exposed to the hydrocarbon-only blend in Work Assignment 12. (This had not been done in that work assignment due to time limitations.) In the second task, both sets of mini-canister charcoals were subjected to changes in exposure blends (charcoal previously exposed to the hydrocarbon-only blend was exposed to the hydrocarbon-methanol blend, and vice versa). During this task, daily humidity, temperature, and barometric pressure measurements were recorded. The third task involved the speciation of vapors purged from eight of the mini-canisters (four from the hydrocarbon-methanol blend exposures in the first task, and four from the hydrocarbon-only blend exposures in the second task). The procedures used to purge and analyze the vapors from the charcoal samples were developed at Southwest Research Institute (SwRI) in Work Assignment 27 of this contract. Both room temperature and elevated temperature purges were conducted on the samples.

The most significant observations made from the data in this study (not necessarily in order) are as follows:

- In general, on a per gram of charcoal basis, the working capacities were larger, the breakthrough times were shorter, and the weight gains larger for the mini-canisters exposed to the hydrocarbon-only blend as compared to the mini-canisters exposed to the hydrocarbon-methanol blend. However, when the day-to-day variations in the hydrocarbon-methanol blend values (this study) and the variations in test conditions are taken into consideration, it is difficult to quantify any meaningful difference between for the two blends on a per gram of charcoal basis.

- Ford and Toyota charcoal had longer breakthrough times and larger working capacities than either the GM or Chrysler charcoal on a per gram of charcoal basis for exposure to both blends.

- In general, the switch to the hydrocarbon-only blend after the Task 1 testing of the mini-canisters with the hydrocarbon-methanol blend produced lower working capacities, shorter breakthrough times (except for the Toyota charcoal), and less weight gain (except for the Toyota charcoal). It should be noted that in addition to the change in blend composition, the use of bypass valves was initiated during this portion of the testing, and that some of the differences in working capacity and weight gain may be related to the use of the bypass valves. However, this does not explain the apparent contradiction between the findings of lower working capacity and less weight gain for HC-only versus the HC-methanol blends.

- In comparing the three sets of average results for the switching of the exposure blend from hydrocarbon-only to hydrocarbon-methanol and back to hydrocarbon-only, there is in all cases an overlap of standard deviations for working capacity, breakthrough time, and weight gain values, which indicates that no significant difference was found due to the presence of methanol.

- In one segment of the testing, variations in laboratory humidity were found to have a high correlation with variations in mini-canister weight gain and working capacity. Linear regression plots of daily working capacities and weight gains versus daily laboratory humidity in grains of water per cubic foot of air gave r^2 values from 0.74 to 0.82 for weight gain and 0.63 to 0.78 for working capacity (excluding r^2 of 0.18 and 0.28 for Toyota working capacities). This observation indicates that variations in laboratory humidity must be taken into consideration when evaluating charcoal samples in this manner.

- Butane and isobutylene are removed for the most part from mini-canister charcoals during room temperature purging, however, only a small fraction of toluene is removed from the mini-canister charcoal during room temperature purging. This observation indicates that toluene plays a more important role in mini-canister weight gain than either butane or isobutylene.

- While all four charcoal types show similar purge characteristics for butane, isobutylene, and toluene, there are considerable differences in relation to methanol. For the Chrysler and GM mini-canisters, only one half of the detectable methanol can be purged from the charcoal during room temperature purging, while 85 to 94 percent of the methanol can be removed from the Ford and Toyota canisters, respectively, during the room temperature purges. This observation indicates that methanol may be more important in weight gain increases and working capacity decreases for the Chrysler and GM charcoals than for the Ford or Toyota charcoals. Excluding water, methanol amounted to 15-18 percent of the total weight from the Chrysler and GM mini-canisters and 4-5 percent of the weight from the Ford and Toyota mini-canisters. However, when the water weight was included, the methanol only amounted to 3-5 percent of the total weight purged from any of the canisters. When comparing the ratio of butane to methanol in the four types of charcoal, there is an enrichment of methanol in the Chrysler and GM charcoals and a slight depletion of methanol (small amount of methanol pass through?) in the Ford and Toyota charcoals.

- In the purging experiments, considerably more water was found in the Chrysler and GM charcoals than in the Ford and Toyota charcoals. This observation indicates a relation between the affinity of the four charcoal types for water and methanol, with the Chrysler and GM charcoals having a higher affinity for both methanol and water than the Ford and Toyota charcoals. The levels of water in the canisters do not appear to be a result of methanol, however, as both the charcoals exposed to the hydrocarbon-only and the hydrocarbon-methanol blends gave similar water levels for each charcoal type.

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I. INTRODUCTION

Southwest Research Institute (SwRI) has been involved in a number of projects for the Environmental Protection Agency (EPA) to determine the effects of alcohol fuels on vehicular fuel evaporative emission control systems.[1,2,3,4]* One of these programs (Work Assignment 12 of EPA contract 68-03-3162, EPA Publication 460/3-81-029) led to the development of miniature evaporative charcoal canisters and a prototype system for simulating evaporative charcoal canister operation.[1] In this previous study, the charcoals from four types of unused evaporative charcoal canisters were subjected to repeated loading and purging of either a hydrocarbon vapor blend containing methanol, or a hydrocarbon-only blend. The charcoals were evaluated by the measurement of retained weight, time to hydrocarbon breakthrough, and working capacity. This report describes further detailed testing of the charcoal mini-canisters developed and tested in Work Assignment 12.

A. Project Objective

The objective of this study was to continue Work Assignment 12 evaluations in order to provide additional information as to the effects of methanol on evaporative canister charcoal. Testing was carried out in order to investigate the effects of equivalent exposures of either hydrocarbon-only or hydrocarbon-methanol blends on two sets of mini-canisters, and to determine the effects of switching exposure blends (from hydrocarbon-only to hydrocarbon-methanol and vice versa) on the mini-canisters. Time to hydrocarbon breakthrough, retained weight gain, and charcoal working capacity were monitored daily during testing. Although not included in the original Scope of Work for the program, daily laboratory humidity, temperature, and barometric pressure were recorded during a portion of the testing to evaluate the effects of these parameters on the breakthrough time, weight gain, and working capacity measurements. In another phase of the program, mini-canister charcoal samples were subjected to room temperature and elevated temperature purges using equipment and procedures developed and qualified in another work assignment for this contract (Work Assignment 27)[2], which involved the evaluation of in-use evaporative charcoal canisters. The effluent purged from the canisters in this phase of the study was analyzed for methanol, individual hydrocarbons, and water to permit further evaluations as to the effect of methanol on evaporative canister charcoal.

B. Approach and Scope

To effectively accomplish the project objectives, the project was carried out in three tasks. In the first task, the eleven mini-canisters previously exposed to a hydrocarbon-methanol blend in Work Assignment 12 were subjected to additional blend loading and purging until approximately the same cumulative loading as that for mini-canisters exposed to the hydrocarbon-only blend in Work Assignment 12 was accomplished, and until stable breakthrough

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* Numbers in parenthesis designate references at the end of this report.

times, weight gains, and working capacities were achieved over a 3 to 4 day period. Breakthrough times were recorded for each mini-canister during each load cycle. Weight gain and working capacity were recorded daily for each mini-canister. At the completion of Task 1, the eleven mini-canisters were exposed to the hydrocarbon-methanol blend one more time to breakthrough; then the charcoal was removed from four of the mini-canisters and stored for subsequent speciation in Task 3.

Task 2 investigated the effect of switching exposure blends and consisted of two parts. In the first part the remaining seven Task 1 mini-canisters were subjected to additional exposures with a hydrocarbon-only blend. The second part of Task 2 involved the continued testing of charcoal previously exposed to a hydrocarbon-only blend in Work Assignment 12, and the subsequent switching of the exposure blends. Breakthrough times, weight gains, and working capacities were also monitored during Task 2 testing. In addition, laboratory humidity, temperature, and barometric pressure were recorded daily during Task 2. An additional four mini-canisters were stored for Task 3 speciation in Task 2.

In the third task, the eight charcoal samples saved from Tasks 1 and 2 were subjected to room temperature and high temperature purges with a stream of dry nitrogen, using procedures and apparatus developed in Work Assignment 27 of this contract. The effluent vapors from both the room temperature and high temperature purges of the charcoal samples were analyzed for butane, isobutylene, toluene, methanol, and water using analytical techniques also developed and/or applied in Work Assignment 27.

II. PROCEDURES AND INSTRUMENTATION

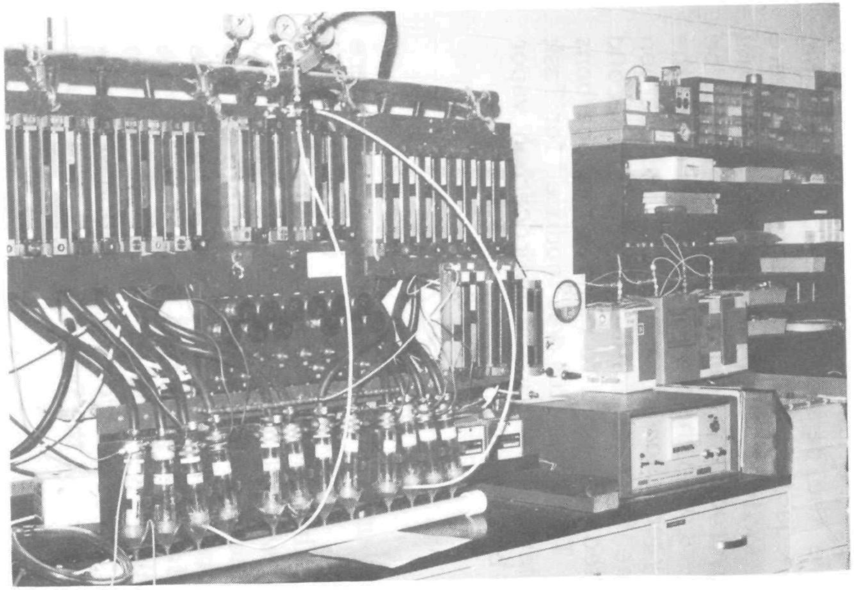
This section describes the procedures and instrumentation utilized in this project. The charcoal mini-canisters, the apparatus developed to allow repeated loading and purging of hydrocarbons from the mini-canisters, and the procedures used to measure hydrocarbon breakthrough times, weight gain retained on the mini-canisters, and the mini-canister working capacity, were all developed in Work Assignment 12 of this contract(1) and have been applied to the Task 1 and Task 2 testing conducted in this program. The apparatus and procedures used for the room temperature and high temperature purging of the mini-canister charcoal and the subsequent speciation of the effluent were developed in Work Assignment 27 of this contract(2) and have been used in Task 3 testing. The procedures and equipment as used in this study are described briefly in the following sections. A more in-depth description may be found in the cited references.

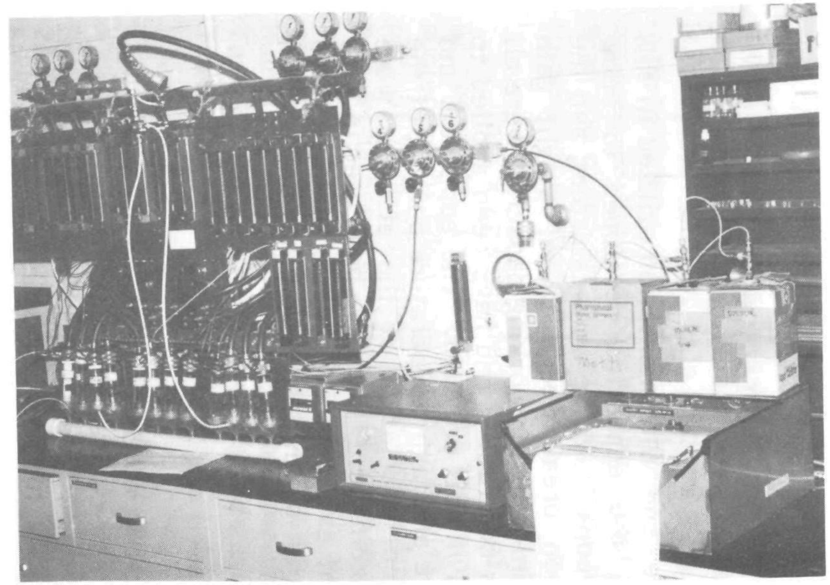
A. Equipment and Procedures used in Task 1 and 2 Testing

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 with room air; and a hydrocarbon analyzer and recorder. The flow 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 break-through time for each mini-canister. A second vacuum pump, which was manually operated, was used to remove hydrocarbons which broke through the mini-canisters. The apparatus was modified for Task 2 testing by the installation of bypass valves to allow the hydrocarbon vapor flow to bypass each canister as it reached breakthrough.

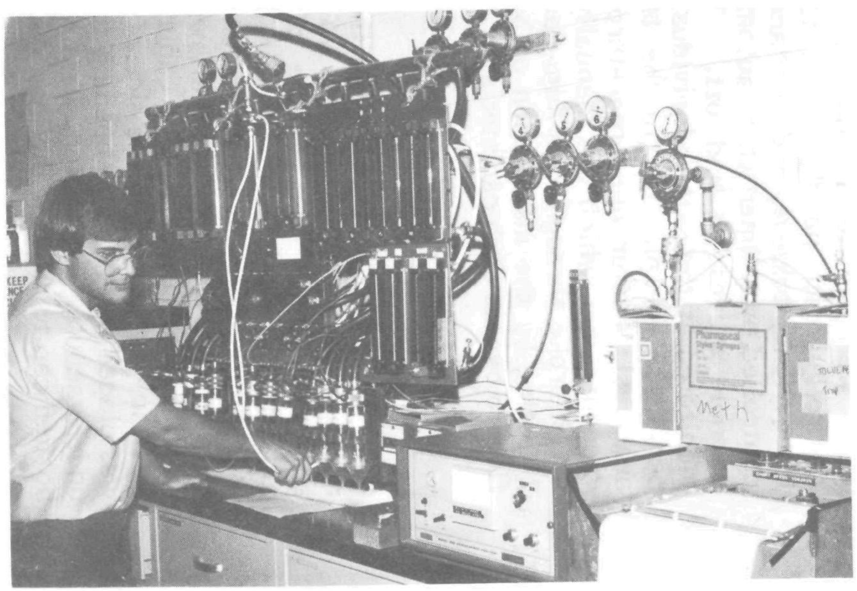
1. Mini-Canisters

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 each 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.

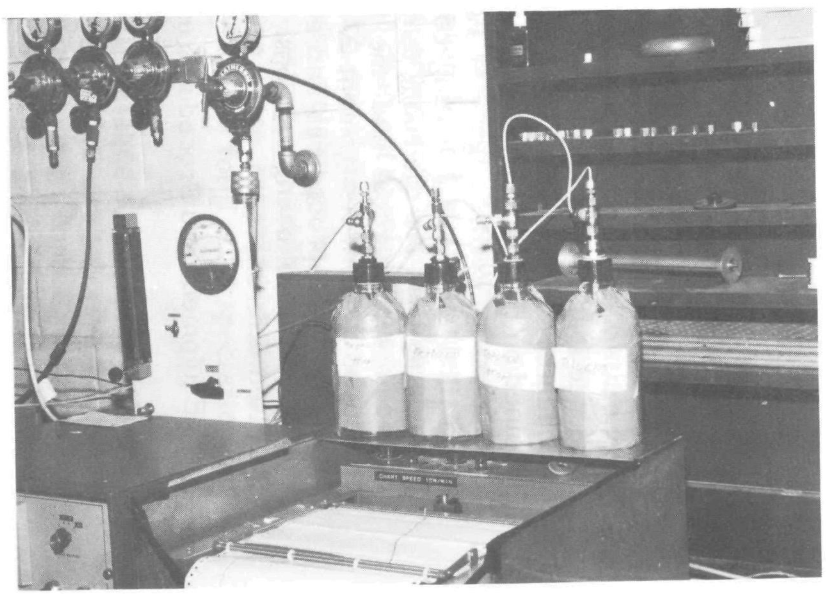




Charcoal Evaluation Apparatus



Measuring Hydrocarbon Breakthrough



Toluene and Methanol Delivery System

Figure 1. Several Views of the Charcoal Evaluation Apparatus

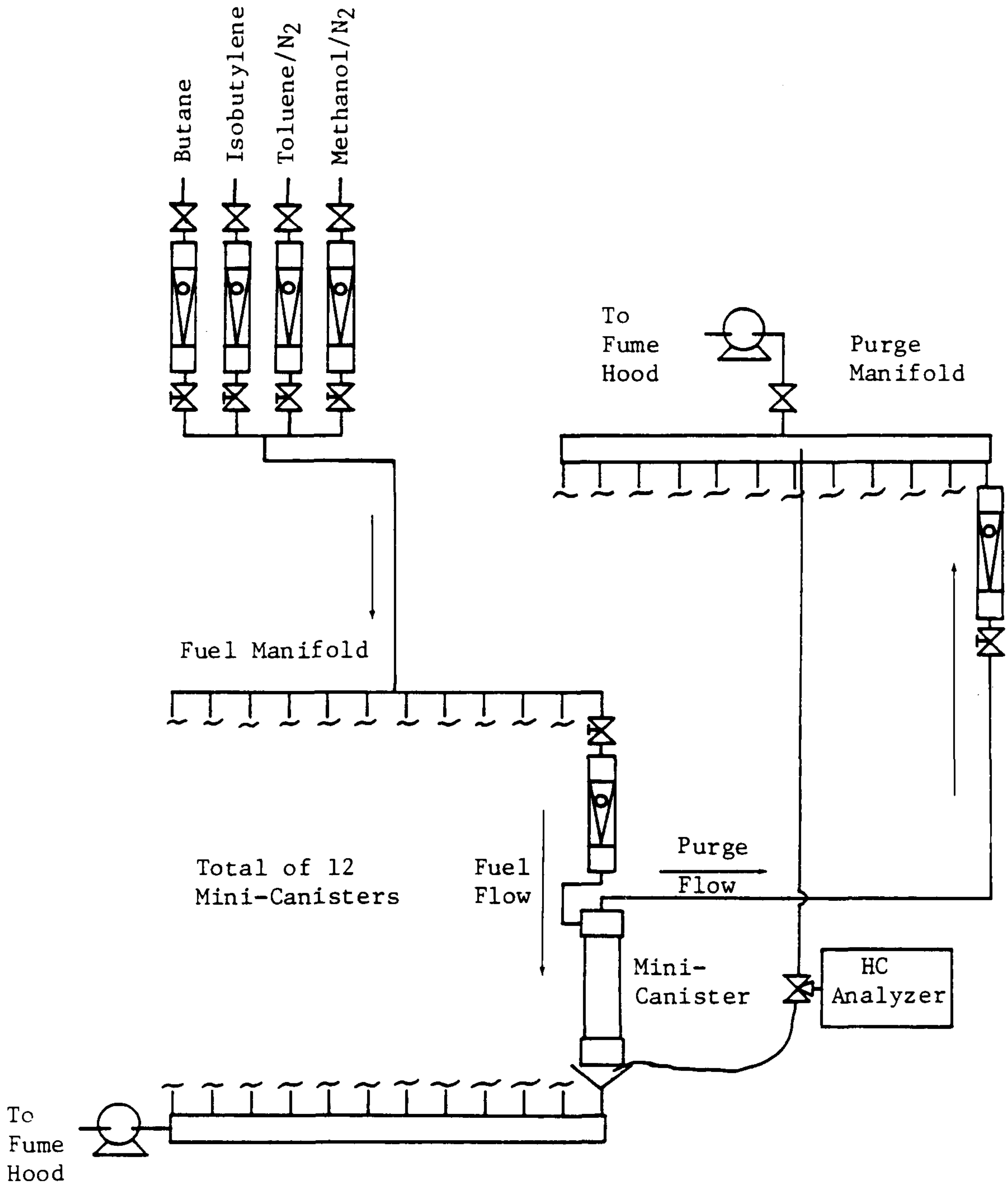


Figure 2. Flow schematic of charcoal evaluation apparatus

2. Charcoal

All charcoal used in this program had been previously tested in Work Assignment 12. The Work Assignment 12 charcoal consisted of four types of activated charcoal obtained from new evaporative canisters ordered 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[a] 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

[a] According to information from a charcoal supplier, Chrysler and GM charcoal are believed to be wood based, while Ford and Toyota charcoal are coal based. Different charcoal mesh sizes could also affect the density.

The clean charcoal weights (from Work Assignment 12) used in the mini-canisters are listed below:

	Charcoal Weight, g	
Charcoal	HC Blend	HC-Methanol Blend
Chrysler 1	18.9[a]	18.9
Chrysler 2	17.6[a]	17.2
Ford 1	27.9	28.4
Ford 2	27.5	31.1
Ford 3	27.9	26.5
Ford 4	27.9	
GM 1	19.5	22.3
GM 2	18.5	20.5
GM 3	19.5	21.1
Toyota 1	29.1	34.1
Toyota 2	29.0	31.8
Toyota 3	28.8	29.1

[a]As a result of variations in the mini-canister volumes, only 96% of Chrysler 1 and 89.5% of Chrysler 2 charcoal (by weight) used in Work Assignment 12 could be placed in the mini-canisters used in this Work Assignment. To permit comparisons between the two work assignments, the actual Work Assignment 12 values have been multiplied by 0.960 (Chrysler 1) and 0.895 (Chrysler 2).

3. Hydrocarbon and Methanol Blend Compositions

The compositon of the hydrocarbon and hydrocarbon-methanol blends as used in this study, and for comparison those used in Work Assignment 12, are presented below:

	This Work Assignment Mini-Canister Flow, mg/min		Work Assignment 12 Mini-Canister Flow, mg/min	
Hydrocarbon Component	HC	HC-Methanol	HC	HC-Methanol
Butane	29.4	27.0	31	29
Isobutylene	7.0	6.4	7	7
Toluene	2.0	2.0	2	2
Methanol	0.0	2.9	0	2
Total	38.4	38.3	40	40

The HC-methanol blend composition is based on calculated mass flow rates (butane and isobutylene), individual hydrocarbon speciation (butane, isobutylene, and toluene)* and wet chemistry collection with GC analysis (methanol).

4. Hydrocarbon Breakthrough

Hydrocarbon vapors were delivered to the canisters at the above flowrates to establish hydrocarbon breakthrough times. In Task 1, the length of the load cycle was based on the longest breakthrough time of the twelve mini-canisters. With the use of bypass valves in Task 2, the length of the load cycle varied with the length of the breakthrough time because the hydrocarbon flow was diverted at breakthrough. The purge cycle for all Task 1 and Task 2 testing was 110 minutes. Hydrocarbon breakthrough was determined to occur when the hydrocarbons passing through the mini-canisters reached a 1000 ppmC concentration. The hydrocarbons were monitored continuously during the load cycle to determine breakthrough, and during the purge cycle to monitor the hydrocarbon levels, by the use of a Beckman 402 Hydrocarbon Analyzer.

5. Breakthrough Time, Mini-Canister Weight Gain, and Working Capacity Measurements

Breakthrough time is the time lapse between the initiation of the mini-canister hydrocarbon loading and breakthrough, and is measured with a pre-programmed electronic timer. The hydrocarbon level emitted by the mini-canister is monitored continuously to breakthrough (defined as 1000 ppmC), at which point the timer reading is recorded. The hydrocarbon concentration is read from a strip chart recorder connected to a Beckman 402 Hydrocarbon Analyzer.

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* This method was developed in Work Assignment 27, and was not available for use in the Work Assignment 12 flow rate determinations.

Mini-canister weight gain is the gain in weight by the mini-canister after a designated purge cycle as compared to a predetermined cansister weight (clean weight, weight at the end of Work Assignment 12, etc.) For these determinations, the mini-canisters were weighed after designated purge cycles using a top-loading balance.

Working capacity is defined as the difference between the weight of the mini-canister after hydrocarbon loading to breakthrough and the weight of the mini-canister after the 110 minute purge cycle. The weight difference is the amount of fuel vapor that is adsorbed by the charcoal during the load cycle and removed by the purge cycle.

B. Equipment and Procedures Used in Task 3 Testing

The procedures and instrumentation required to sample and analyze alcohols, water, and hydrocarbons purged from mini-canister charcoal samples at room temperature and at high temperature (355-375°F, 180-190°C) are described in this section. The sampling system was designed to remove compounds retained on charcoal in a stream of nitrogen. Impingers were used to sample methanol, Drierite to sample water, and Tedlar bags for hydrocarbons (butane, isobutylene, and toluene). Gas chromatography was used to analyze methanol and hydrocarbons, and water content was measured by Drierite weight gain.

1. Sampling System

The charcoal from each mini-canister was transferred to a metal container that was screened on the bottom to secure the charcoal. A Swagelok fitting had been welded to the top of the container to allow nitrogen flow through the charcoal. A view of the canister is shown in Figure 3. Glass wool was also placed on the screen and at the fitting to minimize the loss of fine charcoal particles.

The system, which was designed to draw nitrogen through the canister, consisted of two chambers: one for room-temperature and one for heated purging. A schematic of the sampling system is shown in Figure 4, and views of the system are shown in Figure 5. Gaseous nitrogen from a liquid nitrogen cylinder was directed to a Boekel desiccator adapted to gas flow for cold (room temperature) purging, or to a Blue M oven adapted to gas flow for hot purging. The heated purge system was also equipped with a sleeve heater on the inlet line to the oven. Excess nitrogen flow was used to create a slight positive pressure in the system with the pump "on". This precaution reduced the possibility of room air being drawn into the purge system.

A Thomas dual-head pump, operating at approximately 42 ℓ/min (1.5 cfm), directed sample flow to a four-way manifold with a vent to the atmosphere for excess flow. Four smaller Thomas pumps withdrew samples of charcoal effluent from the manifold for methanol, water content, bag hydrocarbon, and continuous hydrocarbon analyses. Methanol was sampled in impingers, and water in a Drierite tube at sample flowrates of about 4 ℓ/min; and bag hydrocarbons were collected at approximately 1 ℓ/min. A continuous hydrocarbon analyzer, Beckman Model 400, was operated according to the manufacturer's specifications to monitor the sample stream for hydrocarbons.

Figure 3. Weighing metal charcoal holder

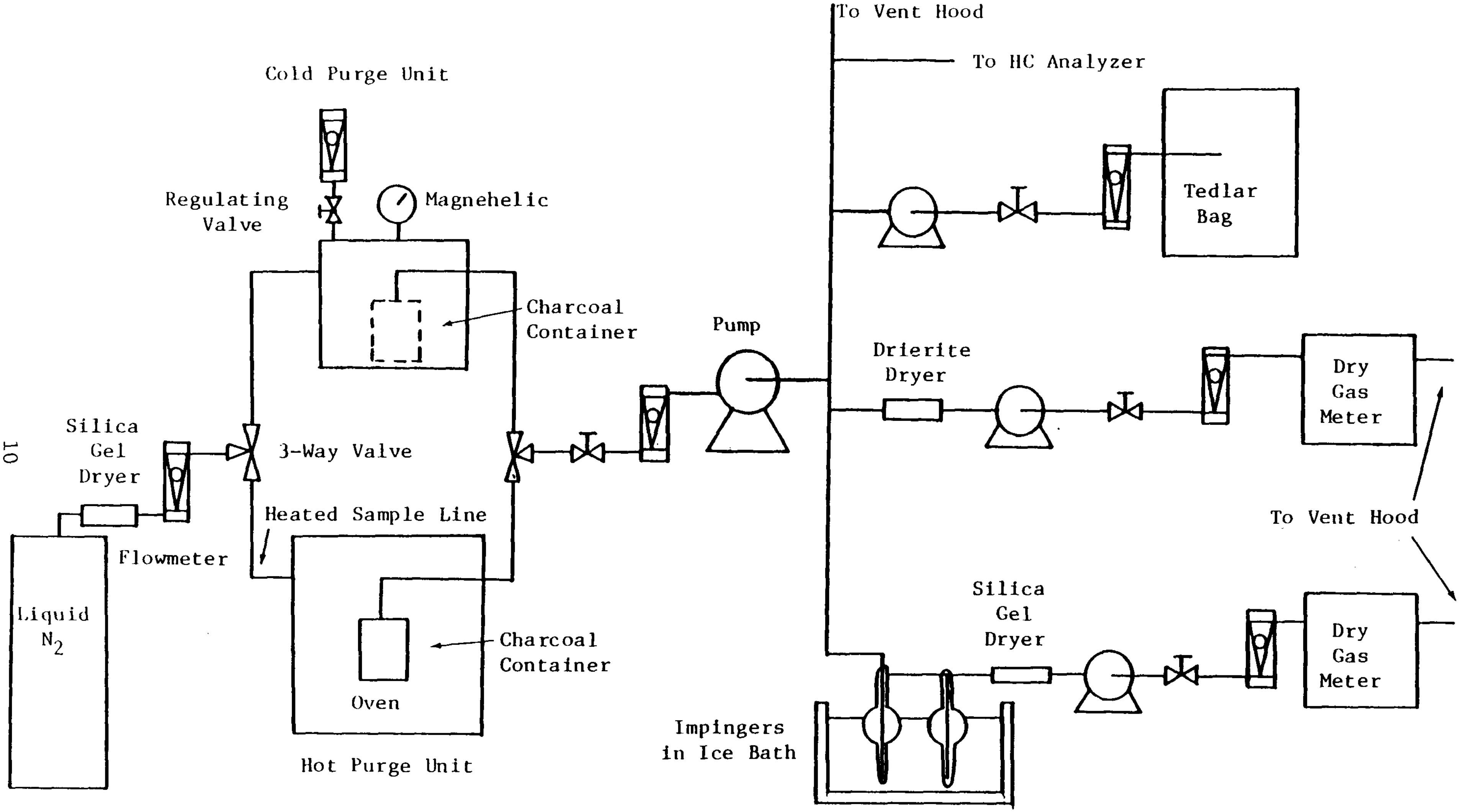
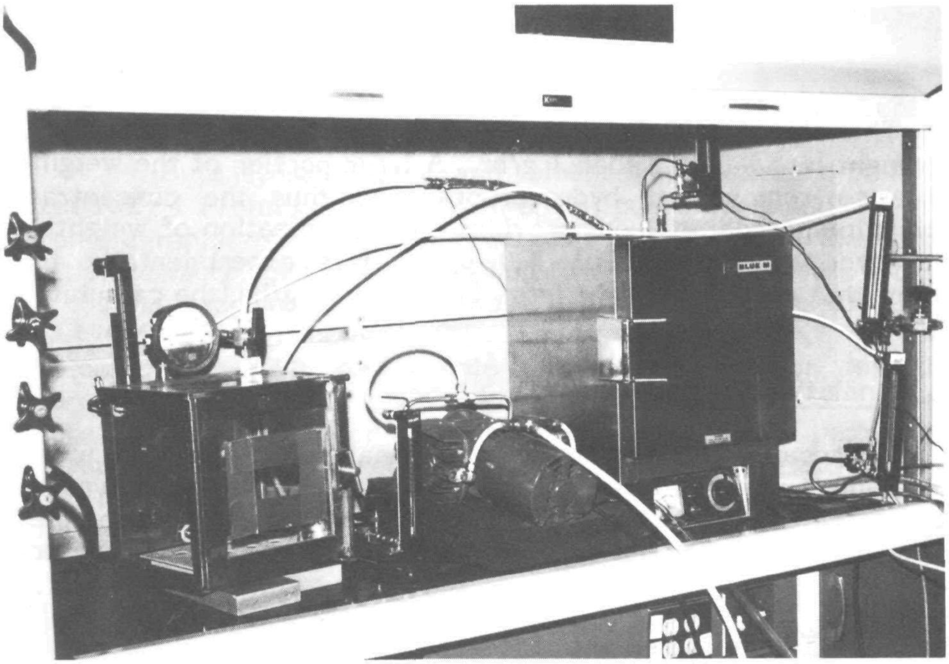
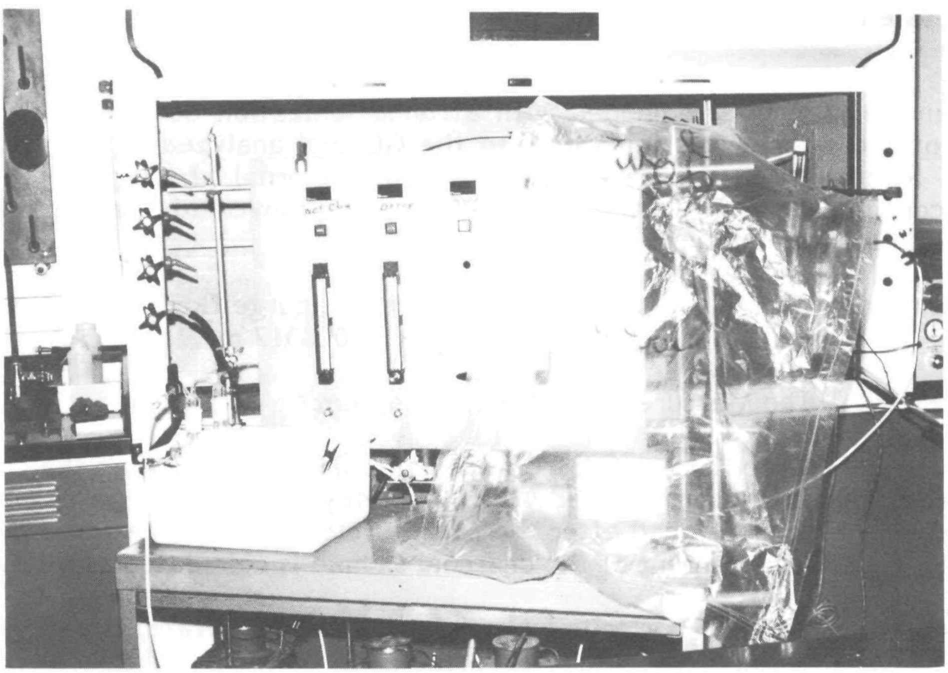


Figure 4. Schematic of charcoal purge and sampling system



Cold and Hot Purge Units



Sampling Cart

Figure 5. Charcoal purge and sampling system

The charcoal sample was cold or hot purged until the rate of charcoal weight loss was less than 1 g/hr. A large portion of the weight loss is attributable to removal of hydrocarbons, and thus the concentration of hydrocarbons in charcoal effluent provides a good indication of weight loss. A continuous hydrocarbon level of 300 ppmC was experimentally found to correspond with a charcoal weight loss of less than 1 g/hr (the calculated value was 0.4 g/hr).

2. Analytical Procedures

Charcoal effluent samples were analyzed by several procedures. Impinger samples were analyzed for methanol, a Drierite tube was weighed before and after testing to determine water content, and bag samples were analyzed for detailed individual hydrocarbons. The procedures are described in this section.

a. The Measurement of Methanol

Methanol was sampled by bubbling the charcoal effluent during a cold or hot purge cycle through two glass impingers in series, each containing 25 mℓ of deionized water. The temperature of the impingers was maintained at 0 to 5°C by an ice bath, and the flow rate through the impingers was maintained at 4 ℓ/min by a sample pump. The samples were transferred to polyethylene containers after completion of a cold or hot purge cycle.

The methanol samples were analyzed on a Perkin-Elmer 3920B gas chromatograph (GC) equipped with a flame ionization detector. A 5 $\mu\ell$ portion of the sample was injected into the GC and analyzed isothermally at 105°C. Sample peak areas were compared to external standards to obtain alcohol concentrations in $\mu g/m^3$. These values were converted to g of methanol using the following equation:

$$\text{grams methanol} = (\text{concentration, } \mu g/m^3) \times (\text{purge flowrate, } ft^3/min) \times (\text{purge time, min}) \times (0.028317\ m^3/ft^3) \times (10^{-6} g/\mu g)$$

b. The Measurement of Water Content

Water is sampled from the charcoal effluent during the cold or hot purge cycle using a preweighed 4 inch polyethylene drying tube filled with Drierite. The tube is weighed after the purge cycle to determine water weight gain to 0.01 g. Water content of the charcoal sample is calculated as follows:

$$\text{water content, grams} = (\text{Drierite wt. gain, g}) \times (\text{purge flowrate, } ft^3/min) \times (\text{purge time, min}) \times \frac{1}{\text{flow through Drierite tube, } ft^3} \times \frac{29.92 \text{ in Hg}}{\text{barometer, in Hg}} \times \frac{(\text{temperature, } ^\circ F + 460)\ ^\circ R}{528^\circ R}$$

c. The Measurement of Detailed Individual Hydrocarbons

Butane, isobutylene, and toluene were collected in Tedlar bags at approximately 1 ℓ/min during the cold or hot purge cycle and analyzed using a gas chromatographic (GC) system. The GC system permits the quantitative determination of more than 80 hydrocarbons with carbon numbers 4 to 10. The capillary column used to separate the compounds is a Perkin-Elmer F-50 versilube, 150 ft x 0.020 inch WCOT stainless steel column. The column is initially cooled to -95°C for sample injection. Upon injection, the temperature is programmed at a 4°C increase per minute to 85°C. The column temperature is held at 85°C for approximately 15 minutes to permit complete column flushing. A flow controller is used to maintain a 1.5 mℓ/min carrier flow rate. The 10 mℓ sample volume for C_4-C_{10} permits accurate determination of 0.1 ppmC with the flame ionization detector used (Perkin-Elmer 3920B). The baseline is re-established at about 60 minutes after injection, resulting in about 1 1/2 hours of analytical turn-around time. Calibration of the gas chromatograph is achieved using a benzene standard traceable to a NBS benzene standard, and the relative FID response factors for benzene, toluene, butane, and isobutylene.

III. MINI-CANISTER TESTING

Additional detailed testing was conducted on the charcoal mini-canisters developed and previously tested in Work Assignment 12 of this contract. This additional testing was conducted both on the mini-canister charcoal samples previously exposed to a hydrocarbon-only blend and on the mini-canister charcoal samples previously exposed to a hydrocarbon-methanol blend. In Task 1, loading and purging of the eleven mini-canisters that were previously exposed to the hydrocarbon-methanol blend in Work Assignment 12 was continued with the hydrocarbon-methanol blend. This loading and purging was continued until the cumulative loading (this study and Work Assignment 12) was approximately equal to the cumulative loading of the mini-canisters exposed to the hydrocarbon-only blend in Work Assignment 12, and until stable breakthrough times, working capacities, and weight gains were achieved. In Task 2, both sets of mini-canister charcoals were subjected to changes in exposure blends (charcoal previously exposed to the hydrocarbon-only blend was exposed to the hydrocarbon-methanol blend, and vice versa) to determine the resulting effects on the mini-canister breakthrough times, working capacities, and weight gains. During Task 2 testing, daily humidity, temperature, and barometric pressure measurements were initiated. Task 3 testing involved the hydrocarbon and methanol speciation of vapors purged from eight of the mini-canisters (four from the hydrocarbon-methanol blend exposures in Task 1 and four from hydrocarbon-only blend exposures in Task 2). The procedure used to purge and analyze the vapors from the charcoal samples was developed by SwRI in Work Assignment 27 of this contract. Both room temperature and elevated temperature purges were conducted on the samples. The remainder of this section describes in detail the testing conducted in these three tasks.

A. Task 1 - Continuation of Hydrocarbon-Methanol Blend Charcoal Testing

Each mini-canister previously exposed to the HC-methanol blend in Work Assignnment 12 was weighed (on 4/29/85) before testing was initiated in Task 1. These weights, along with the clean charcoal weights (Work Assignment 12) and the weights at the end of the 7th day of loading and purging with the HC-methanol blend in Work Assignment 12 are presented in Table 1. As can be seen in the table, all eleven of the mini-canisters lost a significant amount of the weight gained in Work Assignment 12. The HC-methanol blend composition used in this study, along with the composition of the blend as used in Work Assignment 12, was presented in Section II. A. 3.

The eleven mini-canisters were exposed to a 3-hour continuous loading of HC-methanol blend followed by a 110-minute purge (to 230 ppm) on April 30, and a 3-hour continuous loading of HC-methanol blend followed by a 25-minute purge (to 2800 ppm) on May 1. Breakthrough times were not recorded for these cycles, but weight gain and working capacities were recorded. The three-hour load followed by a 25-minute purge was carried out to expose the charcoal to a load-purge sequence of HC-methanol similar to that which occurred on Day 8 with the HC-only blend in Work Assignment 12.

TABLE 1. CHARCOAL WEIGHTS (HC-METHANOL EXPOSURES)

Type of Charcoal	Clean Charcoal Weight [a], g	Charcoal Weight, g, End of Work Assign. 12[b]	Charcoal Weight, g, 4/29/85
Chrylser 1	18.9	24.4	22.4
Chrysler 2	17.2	22.4	20.5
Ford 1	28.4	30.1	29.3
Ford 2	31.1	32.9	31.8
Ford 3	26.5	28.0	27.2
GM 1	22.3	28.7	26.7
GM 2	20.5	26.4	24.3
GM 3	21.1	27.0	25.1
Toyota 1	34.1	34.8	34.2
Toyota 2	31.8	32.6	32.0
Toyota 3	29.1	30.0	29.6

[a]Weights from Work Assignment 12, page 8 of EPA Report 460-3-84-014
[b]Clean charcoal weights plus weight gain for day 7, page A-9 of EPA report 460/3-84-014

The routine load/purge sequence as conducted in Work Assignment 12 was initiated on 5/1/85 using the 1000 ppmC breakthrough level. After discussions with the Project Officer, it was decided that the bypass valves installed at the initiation of this Work Assignment would not be used in Task 1 in order to more closely duplicate load/purge conditions used in Work Assignment 12. The valves, which were installed to allow diverting of the flow once breakthrough was observed, were used only in Task 2. For the remainder of the Task 1 testing, the load cycles were terminated after breakthrough had occurred for all eleven canisters, with the following purge cycle 110 minutes in duration. The working capacity and retained weight gain were recorded daily, while breakthrough times were measured during each cycle for each mini-canister.

Task 1 testing was terminated after 19 load/purge cycles (summarized in Appendix A-1). This number of cycles gave a cumulative loading of 129 grams per mini-canister in this Work Assignment and an overall cumulative loading of 197 grams when including the loading in Work Assignment 12. This compares to 155 grams of cumulative loading for the mini-canisters exposed to the HC-only blend in Work Assignment 12. The cumulative loading with the HC-methanol blend was allowed to exceed the cumulative loading with the HC-only blend in an attempt to 1) obtain stable breakthrough times, weight gains, and working capacities for the mini-canisters, and 2) attempt to compensate for some of the loss in weight gain between Work Assignment 12 and this Work Assignment.

At the completion of Task 1, the eleven canisters were exposed to the HC-methanol blend one more time to breakthrough (173 minutes, or 6.63 grams of blend per canister) and weighed. The charcoal was then removed from four of the mini-canisters (one representing each manufacturer), sealed in glass containers, and stored at 6°F for subsequent speciation in Task 3. The remaining seven mini-canisters were purged for 110 minutes (purge manifold concentration of 240 ppmC), weighed, and made ready for testing in Task 2.

B. Task 2 - Switching of Exposure Blends

In Task 2, the seven remaining mini-canisters from Task 1 were exposed to a HC-only blend to determine if any change in working capacity would result. The composition for the HC-only blend used for this additional exposure was given in Section II. A. 3. Butane and isobutylene rates were increased in the blend to give a total exposure rate similar to the rate with methanol present (38.3 mg/min). The use of the bypass valves was also initiated during this portion of the testing. The valves permit the vapor to be diverted once breakthrough has occurred thus limiting any additional loading or change in the proportions of adsorbed species following breakthrough. As a result, these mini-canisters were now exposed to varying amounts of HC-only blend depending on the breakthrough times. The purge time for each load/purge cycle was maintained at 110 minutes. The mini-canisters were exposed to a total of 14 load/purge cycles (summarized in Appendix A-2) after which the charcoal was removed from the mini-canisters and stored in sealed polyethylene bottles at room temperature.

During the next phase of Task 2 the mini-canisters were refilled with the charcoal that had previously been exposed to the HC-only blend in Work Assignment 12. These refilled mini-canisters were then subjected first to additional HC-only blend exposures, second to HC-methanol blend exposures, and finally to additional exposures with the HC-only blend. The compositions of the exposure blends were the same as used in Task 1 and in the initial phase of Task 2. All testing was conducted with the use of the bypass valves to divert the flow of the exposure vapor once breakthrough had occurred. Moisture content, barometric pressure, and room temperature were recorded daily during testing to determine what effect these parameters might have on variability in mini-canister working capacity, breakthrough time, and weight gain.

For this phase of Task 2, the weight of the charcoal in each of the twelve mini-canisters was recorded before testing was initiated. These charcoal weights, along with the clean charcoal weights (Work Assignment 12) and the weights at the end of the final day of loading and purging with the HC-only blend in Work Assignment 12 are presented in Table 2. As was the case with the charcoal samples exposed to the HC-methanol blend in Work Assignment 12, these charcoal samples had lost a significant amount of the weight that had been gained in Work Assignment 12. The discrepancy between the clean charcoal weight and the 5/24/85 charcoal weight for Toyota 3 can not be readily explained.

The exposure of the twelve mini-canisters to the HC-only blend was initiated on May 24 and continued until a total of 24 load/purge cycles (summarized in Appendix A-3) were completed on June 11. On June 12 the twelve canisters were exposed to the HC-only blend one more time to breakthrough and weighed. The charcoal was then removed from four of the

TABLE 2. CHARCOAL WEIGHTS (HC-ONLY EXPOSURES)

Type of Charcoal	Clean Charcoal Weight, g[a]	Charcoal Weight, g, End of Work Assign. 12[b]	Charcoal Weight, g, 5/24/85
Chrysler 1	18.9[c]	26.7[c]	23.8
Chrysler 2	17.6[c]	24.5[c]	22.1
Ford 1	27.9	32.9	29.7
Ford 2	27.5	32.4	29.1
Ford 3	27.9	32.8	29.7
Ford 4	27.9	32.8	29.7
GM 1	19.5	26.8	23.5
GM 2	18.5	25.3	21.5
GM 3	19.5	26.6	23.6
Toyota 1	29.1	33.5	30.1
Toyota 2	29.0	33.3	29.9
Toyota 3	28.8	33.2	28.6

[a] Weights from Work Assignment 12, page 8 of EPA Report 460/3-84-014
[b] Clean charcoal weights plus weight gain for day 19, page A-6 of EPA Report 460/3-84-014
[c] As a result of variations in the mini-canister volumes, only 96.0% of Chrysler 1 and 89.5% of Chrysler 2 charcoal (by weight) used in Work Assignments 12 could be placed in the mini-canisters used in this Work Assignment. To permit comparisons between the two Work Assignments, the actual Work Assignment 12 values have been multiplied by 0.960 (Chrysler 1) and 0.895 (Chrysler 2)

mini-canisters (one representing each manufacturer), sealed in glass containers and stored at 6°F for subsequent speciation in Task 3. The remaining eight mini-canisters were purged for 110 minutes (purge manifold concentration of 115 ppmC), weighed, and made ready for HC-methanol blend exposure. On June 13 the HC-only blend was altered to include methanol, and HC-methanol blend testing on the remaining eight mini-canisters was initiated. The HC-methanol blend testing was terminated on June 28 after a total of 20 load/purge cycles (summarized in Appendix A-4). At this time the blend was changed once again to exclude methanol, and the eight mini-canisters were made ready for additional exposure to the HC-only blend.

The additional HC-only exposures were initiated on July 1 and terminated on July 15 after 10 load/purge cycles (Appendix A-5). On the last cycle of the last day of testing with the HC-only blend, zero air from a compressed gas cylinder was used instead of room air for the 110 minute purge cycle for two of the mini-canisters. This experiment was carried out to investigate the effect of purging with air containing little or no water on the mini-canister working capacity and weight gain.

C. Task 3 - Purge/Speciation of Mini-Canister Charcoal

The eight charcoal samples saved from Tasks 1 and 2 were subjected to both cold (room temperature) and hot (180 to 190°C) purges with a stream of dry nitrogen using procedures and apparatus developed in Work Assignment 27 of this contract. The effluent vapors from both the cold and hot purges of the charcoal samples were analyzed for butane, isobutylene, toluene, methanol, and water using analytical techniques also developed and/or applied in Work Assignment 27. Humidity was found to be an important variable in Task 2 testing, therefore water was added to the list of compounds analyzed.

The clean charcoal weights, the weight of the charcoal after the last load cycle (in Task 1 or Task 2), the weight of the charcoal before cold purge/speciation, and the weight of the charcoal after the hot purge speciation are listed for each of the eight samples in Table 3. In general the weight of the charcoal after the last load cycle (in Task 1 or Task 2) agreed with the weight of the charcoal at the time of the Task 3 speciation (within 0.1 to 0.2 grams). There was, however, a 1.0 to 1.3 gram variation between the Ford charcoal weights after loading and at the time of the Task 3 speciation. For both Ford samples, condensation was noted on the sides of the mini-canisters after the last load cycle and on the walls of the glass storage bottle when the charcoal samples were transferred for speciation. The condensation remaining on the mini-canisters and on the glass storage bottles during sample transfer likely accounted for these weight variations. The 0.7 gram variation in the Toyota charcoal sample exposed to the HC-only blend can not be explained.

TABLE 3. CHARCOAL WEIGHTS FOR SAMPLES UNDERGOING TASK 3 SPECIATION

Type of Charcoal	Exposure Gas	Initial Sample Weight, g	Sample Weight After Last Load, g	Sample Weight Before Speciation, g	Sample Weight After Speciation, g
Chrysler	HC-Methanol	18.9	26.1	26.0	17.7
Chrysler	HC-Only	17.6[a]	25.7	25.5	16.7
Ford	HC-Methanol	28.4	36.6	35.6	26.8
Ford	HC-Only	27.9	35.7	34.4	26.0
GM	HC-Methanol	20.5	28.7	28.5	18.6
GM	HC-Only	19.5	27.3	27.1	17.6
Toyota	HC-Methanol	34.1	41.4	41.2	33.3
Toyota	HC-Only	29.1	35.5	34.8	28.4

[a]As a result of variations in the mini-canister volumes, only 89.5% of the charcoal (by weight) used in Work Assignment 12 could be placed in the mini-canister used in this Work Assignment. To permit comparisons between the two work Assignments, the actual Work assignment 12 value has been multiplied by 0.895

IV. RESULTS

This section describes the results for each of the three tasks conducted in this program. Task 1 includes breakthrough times, working capacity, and weight gain results for additional HC-methanol exposures of the mini-canisters previously exposed to a HC-methanol blend in Work Assignment 12. Breakthrough times and working capacities on a per gram of charcoal basis have been compared to Work Assignment 12 results for the HC-only blend exposures. Task 2 includes working capacity, breakthrough time and weight gain results related to switching between exposure blends for the two sets of charcoal. Daily laboratory humidity, temperature, and barometric pressure were recorded during Task 2. A discussion relating laboratory humidity to mini-canister working capacity and weight gain is presented. Task 3 includes analytical results for room temperature and elevated temperature purging of the charcoal from eight of the mini-canisters (four from hydrocarbon-methanol blend exposures in Task 1 and four from hydrocarbon-only blend exposures in Task 2). Discussions related to charcoal type, exposure blend, and type of purge (room or elevated temperature) are presented.

A. Task 1 - Continuation of Hydrocarbon-Methanol Blend Charcoal Testing

Working capacities, breakthrough times, and canister weight gains (relative to 4/29/85 canister weights) for the Task 1 testing are presented in Appendix B. In general, the working capacities (Appendix Table B-1) for the eleven canisters increased through May 3 (after 7 cycles), followed by a gradual decrease in working capacities (with the exception of the May 9 working capacities) with each subsequent load/purge cycle. Since the mini-canister working capacity is dependent on the weight of the charcoal in the mini-canister, and the weight of the charcoal in each of the mini-canisters varies from canister to canister, it is necessary to divide the working capacity for each mini-canister by its clean charcoal weight before manufacturer or blend comparisons can be made. The working capacities for the canisters exposed to the HC-methanol blend in this study have been averaged (Appendix Table B-1) and divided by their respective clean charcoal weights (Table 1 Section III). The resulting values are presented in Table 4. For comparison, the 18th day exposure working capacities for the twelve canisters exposed to the HC-only blend in Work Assignment 12 have also been divided by their respective clean charcoal weights with the resulting values also listed in Table 4. The load/purge cycle conditions on the 18th day of loading with the HC-only blend in Work Assignment 12 were found to more closely resemble the conditions used in this Work Assignment; therefore, working capacities from the 18th day were selected over working capacities determined on the 16th and 17th days of loading and over an average working capacity for the three days. The working capacity values determined on a per gram of charcoal basis were found to be slightly higher with the HC-only blend than with the HC-methanol blend for all four manufacturers (3 to 13 percent); however, when the day-to-day variability for the HC-methanol blend working capacity (this Work Assignment) and the variations in test conditions are taken into consideration, it is difficult to quantify any meaningful difference in the working capacity for the two blends on a per gram of charcoal basis. For both the HC-methanol and the HC-only blends, the Ford and Toyota charcoals had higher per gram of charcoal working capacities than either the Chrysler or the GM charcoal.

TABLE 4. COMPARISON OF WORKING CAPACITIES FOR CANISTERS EXPOSED TO A HC-METHANOL BLEND AND TO A HC-ONLY BLEND

	Working Capacity mg HC-Methanol Blend/g Charcoal	Working Capacity mg HC-Only Blend/g Charcoal
Chrysler 1	147 ± 22	196
Chrysler 2	153 ± 23	168
Ford 1	188 ± 8	197
Ford 2	187 ± 8	201
Ford 3	193 ± 8	197
Ford 4		195
GM 1	127 ± 24	136
GM 2	127 ± 24	137
GM 3	129 ± 24	137
Toyota 1	184 ± 7	193
Toyota 2	188 ± 3	190
Toyota 3	188 ± 4	194

Breakthrough times for Task 1 testing are tabulated in Appendix B-2. General trends in breakthrough times were difficult to determine from the data, therefore average values for the 17 load/purge cycles were calculated and have also been tabulated in Appendix Table B-2. Breakthrough times were calculated on a per gram of charcoal basis in an attempt to compare the results generated in this Work Assignment to those obtained in Work Assignment 12 for the HC-only blend. Average breakthrough times for the eleven mini-canisters divided by their respective clean charcoal weights are presented in Table 5. For comparison, average breakthrough times (days 17 to 19) for the mini-canisters exposed to the HC-only blend in Work Assignment 12 have also been divided by their clean charcoal weights and are presented in Table 5. The Work Assignment 12 values have also been multiplied by the ratio of the exposure rates (40/38.3) for the two sets of canisters to compensate for the differences in the exposure rates. This process is necessary since the breakthrough times are inversely related to the exposure rates.

Except for the two Chrysler samples, the breakthrough times for the mini-canisters exposed to the HC-methanol blend were slightly longer on a per gram basis than the breakthrough times for the mini-canisters exposed to the HC-only blend. However, as was the case with the working capacities, variations in the data make rigid comparisons difficult. Ford and Toyota charcoal had longer breakthrough times than either GM or Chrysler charcoal on a per gram basis for exposure to both blends.

Task 1 daily canister weight gains relative to charcoal weights at the start of this Work Assignment (4/29/85) are listed in Appendix Table B-3. Before the Task 1 testing was initiated, all eleven of the mini-canisters had lost a significant portion of the weight gain previously accumulated in Work

TABLE 5. COMPARISON OF BREAKTHROUGH TIMES FOR CANISTERS EXPOSED TO A HC-METHANOL BLEND AND TO A HC-ONLY BLEND

	HC-Methanol Breakthrough Times,[a] Minutes/g Charcoal	HC-Only Breakthrough Times,[b] Minutes/g Charcoal
Chrysler 1	2.8 ± 0.4	3.6 ± 0.4
Chrysler 2	3.4 ± 0.5	3.6 ± 0.5
Ford 1	4.7 ± 0.2	4.5 ± 0.4
Ford 2	4.7 ± 0.2	4.3 ± 0.4
Ford 3	4.7 ± 0.2	4.2 ± 0.5
Ford 4	--	4.2 ± 0.4
GM 1	2.8 ± 0.4	2.7 ± 0.2
GM 2	2.8 ± 0.4	2.7 ± 0.2
GM 3	2.9 ± 0.4	2.8 ± 0.3
Toyota 1	5.2 ± 0.2	4.5 ± 0.5
Toyota 2	4.8 ± 0.2	4.5 ± 0.4
Toyota 3	4.9 ± 0.1	4.6 ± 0.4

[a]Average breakthrough times from Table B-2 divided by respective clean charcoal weight in grams

[b]Average breakthrough times from Page A-4 of EPA Report 460/3-84-014 divided by respective clean charcoal weight in grams and then multiplied by a ratio of the exposure rates (40/38.3)

Assignment 12 testing. In the case of the GM, Toyota, and Ford charcoals, the mini-canisters regained this lost weight during the Task 1 testing (additional weight was gained by the Ford canisters). The Chrysler charcoal, however, did not regain the weight lost between the end of Work Assignment 12 and the start of Task 1. The weight gain in relation to the clean charcoal weights for the eleven mini-canisters is summarized in Table 6.

Table 7 presents the net charcoal weight gains for the mini-canisters exposed to both the HC-methanol blend and the HC-only blends divided by their respective clean charcoal weights. The weight gained per gram of charcoal is higher for the canisters exposed to the HC-only blend than for those exposed to the HC-methanol blend for all four types of charcoal. These differences can not be readily explained. Variations in daily laboratory humidity may have contributed in part to these differences. The relationship of laboratory humidity to mini-canister working capacity and weight gain is discussed in the next section of this report.

TABLE 6. SUMMARY OF WEIGHT GAIN FOR MINI-CANISTERS EXPOSED TO THE HC-METHANOL BLEND

Canister Contents	Weight Gain, g[a] At the End of Work Assignment 12	Retained from Work Assignment 12 on 4/29/85	Weight Gain at the end of Task 1
Chrysler 1	5.5	3.5	4.9
Chrysler 2	5.2	3.3	4.5
Ford 1	1.7	0.9	3.1
Ford 2	1.8	0.7	3.0
Ford 3	1.5	0.7	2.6
GM 1	6.4	4.4	6.6
GM 2	5.9	3.8	6.0
GM 3	5.9	4.0	6.1
Toyota 1	0.7	0.1	0.7
Toyota 2	0.8	0.2	0.7
Toyota 3	0.9	0.5	0.6

[a]Relative to the clean charcoal weights

TABLE 7. COMPARISON OF WEIGHT GAIN FOR CANISTERS EXPOSED TO A HC-METHANOL BLEND AND TO A HC-ONLY BLEND

	Weight Gain mg HC-Methanol Blend/g Charcoal	Weight Gain mg HC-Only Blend/g Charcoal
Chrysler 1	260	410
Chrysler 2	260	390
Ford 1	110	180
Ford 2	96	180
Ford 3	98	180
Ford 4	--	180
GM 1	300	370
GM 2	290	370
GM 3	290	360
Toyota 1	21	150
Toyota 2	22	150
Toyota 3	21	150

B. Task 2 - Switching of Exposure Blends

The results for this section are divided into two parts. The first part reports the results of testing the seven remaining Task 1 HC-methanol mini-canisters with a HC-only blend, and the second part reports results for continued testing of the charcoal previously exposed to the HC-only blend to establish a new baseline, followed by testing with the HC-methanol blend and once more with the HC-only blend.

1. Switching of HC-Methanol Blend to HC-only Blend - (Using Task 1 Mini-Canister Charcoals)

Working capacities, breakthrough times, and canister weight gains (relative to 4/29/85 canister weights) for the Task 2 testing of the seven remaining Task 1 HC-methanol mini-canisters with the HC-only blend are presented in Appendix C. In general, the switch to the HC-only blend produced lower working capacities, shorter breakthrough times (except for the Toyota charcoal), and less weight gain (except for the Toyota charcoal) for the mini-canisters. Table 8 presents a comparison of these properties for the seven mini-canisters. The decrease in working capacity and shorter breakthrough times seem inconsistent with the decrease in weight gain with additional exposure.

It should be noted that in addition to the change in blend composition, the use of the bypass valves was initiated during this portion of the testing, so some of the differences in working capacity and weight gain may be related to the use of the bypass valves. Additional exposure after breakthrough (as in Work Assignment 12 and Task 1 of this work assignment where no bypass valves were used) could result in preferential displacement of one type of hydrocarbon retained on the charcoal initially with another (i.e. butane displaced by toluene, resulting in an enrichment of toluene on the charcoal). If this enriched hydrocarbon species were more difficult to purge from the charcoal than the nominal blend mix, then an increase in weight gain and a corresponding decrease in working capacity would result with the additional exposure after breakthrough.

2. Switching of Exposure Blends - (Using Charcoal Exposed to the HC-Only Blend in Work Assignment 12)

Working capacities, breakthrough times, and canister weight gains (relative to 5/24/85 mini-canister weights) for the HC-only blend testing of charcoal previously exposed to the HC-only blend in Work Assignment 12 are presented in Appendix D. Despite some continued variability, working capacities, breakthrough times, and weight gains were found to stabilize after the third load/purge cycle; therefore average values for the working capacities and breakthrough times were calculated to include all data after the first three cycles. An attempt was made to correlate the daily working capacities and weight gain with the laboratory humidity level, but little or no correlation was observed (all mini-canisters gave linear regression r^2 values ≤ 0.05). However, the laboratory humidity did not vary greatly from day to day during this portion of the testing. Daily measurements of laboratory air specific humidity

TABLE 8. COMPARISON OF WORKING CAPACITIES, BREAKTHROUGH TIMES, AND WEIGHT GAIN FOR SEVEN MINI-CANISTERS WITH THE HC-METHANOL BLEND AND WITH THE HC-ONLY BLEND

	HC-Methanol Blend			HC-Only Blend		
Canister	Average working Capacity, grams	Average Breakthrough Times, Minutes	Weight Gain, grams[a]	Average Working Capacity, grams	Average Breakthrough Times, Minutes	Weight Gain, grams[a]
Chrysler 2	2.63 ± 0.39	58.8 ± 7.9	1.2	1.88 ± 0.35	55.5 ± 7.0	0.8
Ford 2	5.82 ± 0.25	146.8 ± 7.0	2.3	5.10 ± 0.33	139.5 ± 9.1	1.9
Ford 3	5.12 ± 0.22	125.8 ± 5.1	1.9	4.38 ± 0.32	123.5 ± 12.2	1.6
GM 1	2.84 ± 0.53	61.5 ± 9.7	2.2	1.95 ± 0.44	54.1 ± 7.9	1.8
GM 3	2.72 ± 0.52	60.2 ± 8.5	2.1	1.87 ± 0.43	53.0 ± 7.5	1.7
Toyota 2	5.98 ± 0.11	151.9 ± 7.0	0.5	5.52 ± 0.10	154.0 ± 6.5	0.5
Toyota 3	5.47 ± 0.12	141.7 ± 4.2	0.1	5.03 ± 0.14	143.8 ± 4.9	0.4

[a]Relative to 4/29/85 canister weights

(grains/ft^3), room temperature, and barometric pressure for Task 2 testing from May 27 to July 13 are reported in Appendix G. Much higher correlations between working capacities and weight gain with laboratory humidity were noted when the blend was switched to include methanol (r^2 from 0.18 to 0.82), however, day-to-day variations in humidity were more pronounced in this portion of the study. These correlations will be discussed in more detail in the following paragraphs.

Table 9 presents a comparison of the working capacities, breakthrough times, and weight gains on a per gram of charcoal basis for the twelve mini-canisters exposed to the HC-only blend in this Work Assignment and in Work Assignment 12. In general, the working capacities were larger, the breakthrough times longer, and the weight gains larger per gram of charcoal in the Work Assignment 12 exposures as compared to the exposures in this Work Assignment. The differences between these parameters for the two Work Assignments, however, does vary with charcoal type. The differences in parameters between the two Work Assignments may be a result of the additional HC-only blend exposure in this Work Assignment, and/or the use of the bypass valve to divert the vapor flow after breakthrough in this Work Assignment and not in Work Assignment 12. As previously explained, additional exposure after breakthrough (as in Work Assignment 12 with no bypass valve) could have resulted in preferential displacement of one type of hydrocarbon retained on the charcoal initially with another.

After removal of the four HC-only mini-canisters for Task 3 speciation, the remaining 8 mini-canisters were exposed first to the HC-methanol blend (20 load-purge cycles) and then once again to the HC-only blend (13 load-purge cycles). The working capacities, breakthrough times, and canister weight gains (relative to 5/24/85 canister weights) are presented in Appendix E for the HC-methanol blend testing and in Appendix F for the additional HC-only blend testing.

The switch first to the HC-methanol blend and then back to the HC-only blend gave similar working capacities, breakthrough times, and weight gains for each of the eight mini-canisters exposed to the two blends. Table 10 presents a comparison of the averages and standard deviations of these properties for the eight mini-canisters.

In comparing the three sets of average results, there is in all cases an overlap of standard deviations for working capacity, breakthrough time, and weight gain values. However, there were differences among the charcoal types. GM and Chrysler mini-canisters in general gave higher working capacities for the HC-methanol blend, compared with the HC-only blend, increasing breakthrough times with additional exposures (HC-only or HC-methanol), and decreasing weight gain with additional exposures. The Ford and Toyota mini-canisters in general gave similar average working capacities for the three exposures (largest difference between average values for a mini-canister, 0.22g) and decreasing breakthrough times with additional exposures. However, Ford mini-canister weight gains did decrease with additional exposures. Some of the differences between GM/Chrysler and Ford/Toyota trends may be related to the use of the bypass valves in this Work Assignment. In Work Assignment 12 the

TABLE 9. COMPARISON OF WORKING CAPACITIES, BREAKTHROUGH TIMES, AND WEIGHT GAINS FOR TWELVE MINI-CANISTERS EXPOSED TO A HC-ONLY BLEND IN WORK ASSIGNMENT 12 AND THIS WORK ASSIGNMENT

	Working Capacity, mg/g Charcoal		Breakthrough Times, Min/g Charcoal		Weight gain, mg/g Charcoal	
	This Work Assign.[a]	Work Assign. 12[b]	This Work Assign.[c]	Work Assign. 12[d]	This Work Assign.[e]	Work Assign. 12[f]
Chrysler	76 ± 11	196	2.4 ± 0.2	3.6 ± 0.4	370	410
Chrysler	75 ± 11	168	1.9 ± 0.4	3.6 ± 0.6	390	390
Ford 1	153 ± 9	197	4.4 ± 0.2	4.5 ± 0.4	150	180
Ford 2	147 ± 9	201	4.1 ± 0.2	4.3 ± 0.4	150	180
Ford 3	143 ± 9	197	4.1 ± 0.3	4.2 ± 0.5	140	180
Ford 4	146 ± 9	195	4.1 ± 0.2	4.2 ± 0.4	150	180
GM 1	56 ± 11	136	1.7 ± 0.2	2.6 ± 0.2	350	370
GM 2	54 ± 10	137	1.6 ± 0.2	2.7 ± 0.2	290	370
GM 3	58 ± 11	137	1.9 ± 0.2	2.8 ± 0.3	340	360
Toyota 1	169 ± 5	193	4.8 ± 0.1	4.5 ± 0.5	55	150
Toyota 2	164 ± 6	190	4.7 ± 0.2	4.5 ± 0.4	50	150
Toyota 3	165 ± 6	194	4.8 ± 0.3	4.6 ± 0.4	25	150

[a]Average working capacity values from Appendix Table A-1 divided by respective clean charcoal weight in grams

[b]Working capacity values from 18th day of exposure in Work Assignment 12, page A-10 EPA Report 460/3-84-014 divided by respective clean charcoal weight in grams

[c]Average breakthrough times from Appendix Table D-2 divided by respective clean charcoal weight in grams

[d]Average breakthrough times from page A-4 of EPA report 460/3-84-014 divided by clean charcoal weight in grams and then multiplied by a ratio of the exposure rates (40/38.4)

[e]Mini-canister weight on June 11 minus the clean charcoal weights and divided by the clean charcoal weights

[f]Mini-canister weights at completion of Work Assignment 12 minus the clean charcoal weights and divided by the clean charcoal weights

TABLE 10. COMPARISON OF AVERAGE WORKING CAPACITY, BREAKTHROUGH TIME, AND WEIGHT GAIN FOR EIGHT MINI-CANISTERS EXPOSED TO HC-ONLY, THEN HC-METHANOL, AND THEN TO HC-ONLY BLENDS

	HC-only Blend (May/June)	HC-methanol Blend	HC-only Blend (July)
	Average Working Capacity ± 1 Standard Deviation, grams		
Chrysler 1	1.44 ± 0.20	1.86 ± 0.54	1.66 ± 0.29
Ford 1	4.27 ± 0.25	4.28 ± 0.47	4.06 ± 0.30
Ford 2	4.04 ± 0.25	4.02 ± 0.43	3.85 ± 0.28
Ford 4	4.07 ± 0.25	4.16 ± 0.50	4.05 ± 0.30
GM 2	1.00 ± 0.18	1.26 ± 0.45	1.09 ± 0.25
GM 3	1.13 ± 0.21	1.50 ± 0.46	1.37 ± 0.26
Toyota 2	4.75 ± 0.17	4.55 ± 0.10	4.60 ± 0.12
Toyota 3	4.76 ± 0.18	4.64 ± 0.18	4.70 ± 0.10
	Average Breakthrough Time ± 1 Standard Deviation, Minutes		
Chrysler 1	44.8 ± 4.1	50.0 ± 8.7	49.6 ± 5.9
Ford 1	123.8 ± 5.5	119.2 ± 6.6	115.9 ± 8.1
Ford 2	112.9 ± 5.7	108.7 ± 7.2	107.2 ± 7.7
Ford 4	114.6 ± 6.5	115.6 ± 5.5	116.1 ± 7.0
GM 2	30.1 ± 3.5	32.6 ± 6.7	33.2 ± 3.5
GM 3	36.4 ± 3.8	41.0 ± 6.2	42.8 ± 4.8
Toyota 2	135.2 ± 4.4	130.3 ± 4.4	128.1 ± 6.7
Toyota 3	137.7 ± 7.4	137.0 ± 4.3	135.7 ± 3.5
	Average Weight Gain ± 1 Standard Deviation, grams		
Chrysler 1	1.95 ± 0.43	1.38 ± 0.96	1.36 ± 0.55
Ford 1	1.77 ± 0.55	1.74 ± 0.88	1.66 ± 0.56
Ford 2	1.92 ± 0.50	1.84 ± 0.79	1.73 ± 0.46
Ford 4	1.77 ± 0.53	1.63 ± 0.85	1.56 ± 0.58
GM 2	2.20 ± 0.37	1.76 ± 0.73	1.68 ± 0.44
GM 3	2.37 ± 0.39	1.85 ± 0.77	1.68 ± 0.45
Toyota 2	0.51 ± 0.20	0.72 ± 0.18	0.70 ± 0.07
Toyota 3	0.78 ± 0.22	0.96 ± 0.25	1.03 ± 0.09
	Average Mass of Water Vapor in air ± 1 Standard Deviation, grains/ft^3		
	6.17 ± 0.35	5.90 ± 0.85	5.96 ± 0.29

Chrysler and GM mini-canisters were exposed to considerably longer additional exposure times after breakthrough (no bypass valve) than either the Ford or Toyota mini-canisters. This additional exposure could have resulted in the preferential displacement of one type of hydrocarbon retained on the charcoal initially with another. Additional exposures in this Work Assignment (either with HC-only or HC-methanol) with the bypass valve in use may have slowly reversed this effect in the GM/Chrysler case resulting in different trends as compared to the Ford/Toyota mini-canisters.

The daily laboratory humidity also seems to play an important role in influencing the measured mini-canister parameters, especially working capacity and weight gain. A discussion of this relationship follows.

As can be seen in Table 10 and in Appendices D, E, and F, the day-to-day variations in the recorded parameters for the HC-methanol blend were much larger than those recorded for the HC-only blend exposures. It was also observed that the laboratory humidity in this portion of the testing showed more day-to-day variation than in either of the HC-only exposures. To determine the relationship of the laboratory humidity to the mini-canister weight gain and working capacities during the HC-methanol exposures, linear regressions of working capacities and weight gains versus humidity ($y = a+bx$, where y = weight gain or working capacity and x = moisture content in grains of water per cubic foot of air) were computed for each of the eight mini-canisters. The results of these regressions are presented in Table 11. The r^2 values represent the fraction of weight gain or working capacity variability than can

TABLE 11. LINEAR REGRESSION PLOTS OF HUMIDITY VERSUS WORKING CAPACITY AND WEIGHT GAIN FOR THE EIGHT MINI-CANISTERS EXPOSED TO THE HC-METHANOL BLEND

	Working Capacity			Weight Gain		
	r^2	a	b	r^2	a	b
Chrysler 1	0.78	5.06	-0.55	0.74	-4.17	0.96
Ford 1	0.75	6.99	-0.47	0.74	-3.39	0.89
Ford 2	0.64	6.63	-0.45	0.76	-2.79	0.80
Ford 4	0.64	6.83	-0.46	0.74	-3.28	0.85
GM 2	0.63	3.67	-0.42	0.79	-2.61	0.76
GM 3	0.66	3.99	-0.43	0.79	-2.67	0.78
Toyota 2	0.28	4.92	-0.06	0.79	-0.33	0.18
Toyota 3	0.18	5.15	-0.09	0.82	-0.56	0.28

be explained by changes in the laboratory humidity. The "a" values (y intercepts) represent the weight gains (relative to 5/24 canister weights) and working capacities at zero humidity, while the "b" values represent the slope of plotted lines or "regression coefficients" (change in working capacity or weight gain in relation to change in moisture content). As can be seen in the table, all four canister types give relatively high correlations of weight gain with laboratory humidity (r^2 = 0.74 to 0.82). Three of the four canister types (Chrysler, Ford, GM) also give relatively high correlations of working capacity with humidity (r^2 = 0.63 to 0.78), while the Toyota canisters give a much lower correlation (r^2 = 0.18 to 0.28). The negative "a" values for the weight gain regressions indicate that a significant amount of the weight previously gained in Work Assignment 12 could be due to moisture content. The negative working capacity "b" values in the table indicate a decrease in working capacity with increasing humidity, and the positive weight gain "b" values indicate an increase in weight gain with increasing humidity. The low "b" values for the Toyota canisters indicate that humidity influences the weight gain and working capacity of the Toyota canisters to a much lesser extent than the other three canister types.

C. Task 3 Purge/Speciation of Mini-Canister Charcoal

The results for the cold (room temperature) and hot (180 to 190°C) purges of the eight mini-canisters from Tasks 1 and 2 of this study are reported in Table 12. Several observations can be made from the data in the table. Butane and isobutylene for the most part are removed from the mini-canister charcoal during the cold purge cycle. From 86 to 99-plus percent of the butane and isobutylene purged from the mini-canisters is removed during the cold purge. The ratio of butane to isobutylene found in the charcoal (4.3 to 5.4 parts butane to 1 part isobutylene) was similar to the ratio of butane to isobutylene in the exposure blends (4.1 to 1).

TABLE 12. RESULTS PURGE/SPECIATIONS

		Weight of Compound Purged, grams									
		Butane		Isobutylene		Toluene		Methanol		Water	
Charcoal Type	Exposure Blend	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot	Cold	Hot
Chrysler	HC-methanol	0.80	0.06	0.18	0.01	0.02	0.63	0.19	0.19	2.53	3.00
Chrysler	HC-only	0.72	0.10	0.16	0.01	0.05	0.26	ND[a]	ND	2.04	4.50
Ford	HC-methanol	3.62	0.29	0.67	0.05	0.12	1.53	0.28	0.05	2.33	0.20
Ford	HC-only	3.40	0.15	0.73	0.03	0.15	1.77	ND	0.01	1.71	0.20
GM	HC-methanol	0.48	0.04	0.11	0.01	0.05	1.00	0.15	0.17	3.09	4.62
GM	HC-only	0.51	0.03	0.11	0.01	0.02	0.24	ND	ND	1.93	6.02
Toyota	HC-methanol	4.38	0.72	0.88	0.14	0.19	1.18	0.29	0.02	0.58	0.68
Toyota	HC-only	2.82	0.01	0.60	0.00	0.48	1.92	ND	0.01	0.69	0.51

[a] ND = not detectable

Unlike butane and isobutylene, only a small fraction of the toluene was removed from the mini-canisters during the cold purge (values ranged from 3 to 20 percent of the toluene). There was also a considerable enrichment of toluene in the mini-canisters as compared to the exposure blend compositions with the ratio of butane to toluene dropping from ~14 to 1 in the exposure blends down to 0.5 - 3.7 to 1 in the mini-canisters. This observation indicates that toluene (and probably any other heavy hydrocarbons that reach the canister) play an important role in increasing weight gain and decreasing working capacity with increasing exposures. However, in extrapolating these results to "real world" applications, it is uncertain how much difference there would be between the effects of actual gasoline vapor and the simulated (butane, isobutylene, toluene) vapor used in this study.

While all four charcoal types show similar purge characteristics for hydrocarbons, there are considerable differences in relation to methanol. For the Chrysler and GM mini-canisters, only half the detectable methanol can be purged from the charcoal during the cold purge, while 85 to 94 percent of the methanol can be removed from the Ford and Toyota canisters, respectively, during the cold purge. This observation indicates that methanol may be more important in weight gain increase and working capacity decrease for the Chrysler and GM charcoals than for the Ford and Toyota charcoals. The enrichment of methanol in the GM and Chrysler mini-canisters substantiates this observation. The ratio of butane to methanol drops from 9.3 to 1 in the exposure blend to 2.3 to 1 and 1.6 to 1 in the Chrysler and GM charcoals respectively. The Ford and Toyota charcoals do not show this enrichment, and even indicate there may be a small amount of methanol pass-through for these two charcoals. The ratio of butane to methanol is higher in the Ford (11.5 to 1) and Toyota (16.5 to 1) charcoals than in the exposure blend (9.3 to 1). Excluding water weight, methanol amounts to 15-18 percent of the total purged weight from the Chrysler and GM mini-canisters and 4-5 percent of the total weight purged from the Ford and Toyota mini-canisters. However, when the weight of the water is included, the methanol only amounts to 3-5 percent of the total weight purged from any of the mini-canisters.

While water measurements were not originally included in the project scope of work, the observation of a relationship between day-to-day laboratory humidity levels and mini-canister weight gain and working capacity indicated the need for these measurements. Considerably more water was found in the Chrysler and GM charcoals (5.5 to 8.0 grams) than in the Ford and Toyota charcoals (1.2 to 2.9 grams). Ford charcoal was found to differ from the other three charcoal types in that more than 90 percent of the water could be removed during the cold purge, while the remaining three charcoal types had only 24 to 58 percent of the water removed during the cold purge. The affinity of the four types of charcoal for water appears to be related to that for methanol, with Chrysler and GM charcoals having a higher affinity for both methanol and water than do the Ford and Toyota charcoals. The levels of water in the canisters do not appear to be a result of the methanol, however, because both the charcoals exposed to the HC-only and the HC-methanol blends gave similar water levels for each charcoal type.

V. QUALITY ASSURANCE

The Quality Assurance (QA) guidelines addressed in the QA report for this Work Assignment and for Work Assignment 27 were followed in performing the work for this program. Calibrations were performed on the analytical instruments, balances and timers, and daily sampling system leak checks were conducted on the charcoal purge and sampling system used in Task 3. The data are available for inspection if desired.

The program objectives for precision, accuracy, and completeness for the measurement of breakthrough time, weight gain, and working capacity are listed in Table 13. The objective of > 95 percent completeness was obtained

TABLE 13. PRECISION, ACCURACY, AND COMPLETENESS OBJECTIVES FOR BREAKTHROUGH TIME, WEIGHT GAIN, AND WORKING CAPACITY ANALYSIS

Analytical Procedure	Precision Std. Dev.	Accuracy, %	Completeness, %
Breakthrough Time	9	±10	>95
Weight Gain	0.00	±0.01	>95
Working Capacity	0.04	±0.02	>95

with 99+ percent of the breakthrough times, 100 percent of the weight gains, and 97+ percent of the working capacities successfully recorded during the course of the program. An eight ounce standard weight (226.80 grams), weighed daily along with the mini-canisters, gave an average wieght of 226.82 ± 0.04 grams. This average value is accurate to within 0.01 percent of the actual weight and can be assumed to be the accuracy of the weight gain and working capacity values during the course of the program. It should be noted, however, that initial weight gain values were recorded to one tenth of a gram, while the remainder of the weight gain values were recorded to one hundredth of a gram. The timers used to record the breakthrough times were checked periodically during the program and found to agree within 5 percent with a precision stopwatch.

Test to test variations in weight gain and working capacity were found to exceed the objectives for precision, 0.00 grams for weight gain and 0.04 grams for working capacity (i.e., the standard deviations for working capacity values ranged from 0.10 to 0.54 grams over the range of mini-canisters and test conditions). However, during the course of the program, it was found that day to day variations in laboratory humidity produced corresponding variations in mini-canister weight gain and working capacity (refer to Section IV. B. 2.). This relationship had not been determined previously and the effect on the weight gain and working capacity measurements was not anticipated. The standard deviations for the mini-canister breakthrough times fell below the 9 minute objective in most instances (96%) despite the variations in laboratory humidity.

The objectives for precision, accuracy, and completeness for methanol, water content and selected HC speciation (from Work Assignment 27) are presented in Table 14. All scheduled analyses were conducted in the study with 100 percent completeness. Accuracy and precision values in Table 14 were determined in Work Assignment 27 validation experiments.

TABLE 14. PRECISION, ACCURACY, AND COMPLETENESS OBJECTIVES FOR METHANOL, WATER, AND SELECTED HC SPECIATION ANALYSIS

Measurement	Analytical Procedure	Precision Std. Dev.[a]	Accuracy, %	Completeness
Methanol	Gas Chromatograph (FID)	2[b]	91[c]	>95
Water Content	Gravimetric	0.00	105[c]	>95
Selected HC Speciation	Gas Chromatograph (FID)	10[b]	70[d]	>95

[a] Standard deviation except where indicated
[b] Coefficient of variation
[c] Based on recovery experiments conducted on the sampling system
[d] Based on the recovery of gasoline as THC. Recoveries of individual HC species will vary.

REFERENCES

1. Warner-Selph, M.A., "The Effect of Methanol on Evaporative Canister Charcoal Capacity", Final Report EPA 460/3-84-014.

2. Warner-Selph, M.A., "In-Use Evaporative Canister Evaluation", Draft Report Work Assignment 27, EPA Contract 68-03-3162.

3. Smith, L.R., "Blend Vapor Analysis", Program in Progress, Work Assignment 12, EPA Contract 68-03-3192.

4. Dietzmann, H.E., "Gasoline Volatility Analysis", Letter Reports to EPA, Work Assignments 4 and 7, EPA Contract 68-03-3192.

APPENDIX A

Exposure Summaries for Tasks 1 and 2

TABLE A-1. TASK I CONTINUATION OF METHANOL BLEND CHARCOAL TESTING

Date	Cycle	Load Time, min.	HC-Methanol Blend Exposure for Each Canister, g	Purge Time, min.	Purge Manifold Concentration at 110 Min., ppmC
4/30	1	180	6.89	110	230
5/1	1	180	6.89	25	2800
	2	171	6.55	110	330
5/2	1	184	7.05	110	350
	2	183	7.01	110	360
5/3	1	178	6.82	110	370
	2	170	6.51	110	380
5/6	1	180	6.89	110	340
	2	163	6.24	110	370
5/7	1	182	6.97	110	340
	2	180	6.89	110	350
5/8	1	179	6.86	110	340
	2	175	6.70	110	360
5/9	1	177	6.78	110	320
	2	168	6.43	110	320
5/10	1	178	6.82	110	360
	2	176	6.74	110	310
5/13	1	182	6.97	110	300
	2	184	7.05	110	300
Totals	19	3370	129.06	2005	--

TABLE A-2. TASK 2 TESTING, SWITCHING OF HC-METHANOL BLEND TO HC-ONLY BLEND[a]

Date	Cycle	Load Time Range[b], min.	HC Blend Exposure Range[c],g	Purge Time, min	Purge Manifold Concentration, ppmC
5/15	1	54.8 to 154.8	2.10 to 5.94	110	200
	2	63.0 to 149.0	2.42 to 5.72	110	200
5/16	1	64.3 to 161.5	2.47 to 6.20	110	220
	2	68.0 to 161.0	2.61 to 6.18	110	190
5/17	1	56.5 to 168.5	2.17 to 6.47	110	190
	2	53.0 to 153.3	2.04 to 5.89	110	160
5/20	1	50.7 to 151.8	1.95 to 5.83	110	170
	2	47.7 to 151.0	1.83 to 5.80	110	150
5/21	1	44.4 to 153.4	1.70 to 5.89	110	160
	2	45.7 to 152.0	1.75 to 5.84	110	160
5/22	1	49.4 to 157.5	1.90 to 6.05	110	170
	2	47.2 to 153.0	1.81 to 5.88	110	180
5/23	1	49.9 to 146.3	1.88 to 5.62	110	150
	2	46.0 to 143.2	1.77 to 5.50	110	160

[a]Charcoal previously exposed to HC-Methanol blend in Work Assignment 12 and Task 1 of this Work Assignment

[b]Load time for each canister is the same as the breakthrough time, refer to Appendix Table C-2

[c]HC-only Blend Exposure in grams can be calculated for each canister by multiplying the exposure rate, 38.4 mg/min., times the breakthrough time (Appendix Table C-2) and dividing by 1000

TABLE A-3. TASK 2 SUMMARY OF TESTING, CONTINUATION OF HYDROCARBON-ONLY BLEND CHARCOAL TESTING[a]

Date	Cycle	Load Time Range[b], min.	HC-Blend Exposure Range[c],g	Purge Time, min.	Purge Manifold Concentration, ppmC
5/24	1	46.8 to 148.0	1.80 to 5.68	110	130
5/27	1	51.6 to 150.3	1.98 to 5.77	110	200
	2	45.8 to 152.8	1.76 to 5.88	110	190
5/28	1	35.8 to 147.0	1.37 to 5.64	110	210
	2	30.0 to 146.0	1.15 to 5.61	110	220
5/29	1	31.9 to 149.0	1.22 to 5.72	110	200
	2	32.2 to 148.0	1.24 to 5.68	110	180
5/30	1	29.9 to 140.1	1.15 to 5.38	110	--
	2	32.7 to 141.9	1.26 to 5.45	110	200
5/31	1	34.1 to 146.2	1.31 to 5.61	110	210
6/3	1	33.2 to 139.0	1.27 to 5.34	110	190
	2	27.9 to 137.3	1.07 to 5.27	110	160
6/4	1	32.9 to 141.7	1.26 to 5.44	110	170
	2	33.5 to 135.0	1.29 to 5.18	110	180
6/5	1	31.9 to 135.2	1.22 to 5.19	110	100
	2	29.1 to 140.7	1.12 to 5.40	110	100
6/6	1	30.5 to 144.0	1.17 to 5.53	110	110
	2	26.5 to 137.8	1.02 to 5.29	110	100
6/7	1	22.1 to 141.0	0.85 to 5.41	110	100
	2	24.6 to 138.1	0.94 to 5.30	110	100
6/10	1	26.3 to 141.6	1.01 to 5.44	110	110
	2	27.3 to 140.2	1.05 to 5.38	110	110
6/11	1	25.7 to 145.5	0.99 to 5.59	110	100
	2	23.6 to 142.2	0.91 to 5.46	110	100
6/12[d]	1	31.3 to 141.1	1.20 to 5.42	110	115

[a]Charcoal previously exposed to HC-Only blend in Work Assignment 12
[b]Load time for each canister is the same as the breakthrough time, refer to Appendix Table D-2
[c]HC-only blend exposure in grams can be calculated for each canister by multiplying the exposure rate, 38.4 mg/min., times the breakthrough time (Appendix Table D-2)and dividing by 1000
[d]After HC-blend loading, the charcoal was removed from four of the mini-canisters (one from each manufacturer) for subsequent speciation in Task 3

TABLE A-4. TASK 2 TESTING, SWITCHING OF HC-ONLY BLEND TO HC-METHANOL BLEND[a]

Date	Cycle	Load Time[b], min.	HC-Methanol Blend Exposure Range[c], g	Purge Time, min.	Purge Manifold Concentration, ppmC
6/13	1	33.9 to 148.0	1.30 to 5.67	110	150
	2	45.1 to 137.3	1.77 to 5.26	110	165
6/14	1	46.6 to 137.7	1.78 to 5.27	110	200
	2	43.0 to 135.1	1.65 to 5.17	110	185
6/17	1	42.0 to 135.4	1.61 to 5.19	110	160
	2	30.7 to 128.8	1.18 to 4.93	110	155
6/18	1	32.2 to 139.7	1.23 to 5.35	110	145
6/20	1	32.9 to 139.0	1.26 to 5.32	110	140
	2	33.2 to 141.4	1.27 to 5.42	110	140
6/21	1	33.6 to 139.7	1.29 to 5.35	110	145
	2	30.0 to 141.6	1.15 to 5.42	110	130
6/24	1	29.1 to 138.0	1.11 to 5.29	110	120
	2	25.1 to 135.0	0.96 to 5.17	110	130
6/25	1	24.6 to 129.8	0.94 to 4.97	110	110
6/26	1	29.1 to 134.5	1.11 to 5.15	110	115
	2	27.6 to 134.7	1.06 to 5.16	110	140
6/27	1	27.1 to 137.5	1.04 to 5.27	110	120
	2	26.4 to 138.2	1.01 to 5.29	110	130
6/28	1	28.5 to 133.0	1.09 to 5.09	110	125
	2	30.2 to 135.0	1.16 to 5.17	110	155

[a]Charcoal previously exposed to HC-only blend in Work Assignment 12
[b]Load time for each canister is the same as the breakthrough time, refer to Appendix Table E-2
[c]HC-Methanol blend exposure in grams can be calculated for each canister by multiplying the exposure rate, 38.3 mg/min., times the breakthrough time (Appendix Table E-2) and dividing by 1000

TABLE A-5. TASK 2 TESTING, SWITCHING OF HC-METHANOL BLEND BACK TO HC-ONLY BLEND[a]

Date	Cycle	Load Time[b], min.	HC-Methanol Blend Exposure Range[c], g	Purge Time, min.	Purge Manifold Concentration, ppmC
7/1	1	38.2 to 139.8	1.47 to 5.37	110	165
	2	38.4 to 136.6	1.47 to 5.25	110	185
7/2	1	38.6 to 130.1	1.48 to 5.00	110	150
	2	34.0 to 137.3	1.31 to 5.27	110	150
7/3	1	31.7 to 136.8	1.22 to 5.25	110	160
	2	30.7 to 133.0	1.18 to 5.11	110	160
7/10	1	33.5 to 130.8	1.29 to 5.02	110	135
	2	27.4 to 133.0	1.05 to 5.11	110	140
7/11	1	29.1 to 140.0	1.12 to 5.38	110	120
	2	33.8 to 134.6	1.30 to 5.17	110	145
7/12	1	33.3 to 139.3	1.29 to 5.35	110	120
	2	32.6 to 140.9	1.25 to 5.41	110	135
7/15	1	30.9 to 133.0	1.19 to 5.11	110	155

[a]Charcoal previously exposed to HC-only blend in Work Assignment 12
[b]Load time for each canister is the same as the breakthrough time, refer to Appendix Table F-2
[c]HC-Only blend exposure in grams can be calculated for each canister by multiplying the exposure rate, 38.4 mg/min., times the breakthrough time (Appendix Table F-2) and dividing by 1000

APPENDIX B

Daily Working Capacities, Breakthrough Times,
and Weight Gains for Task 1 Testing

TABLE B-1. TASK 1 WORKING CAPACITIES, CONTINUATION OF METHANOL BLEND CHARCOAL TESTING

	Working Capacity, grams[a]									
Canister	5/1	5/2	5/3	5/6	5/7	5/8	5/9	5/10	5/13	Average
Chrysler 1	2.9	3.34	3.41	2.95	2.70	2.46	2.63	2.38	2.23	2.78 ± 0.41
Chrysler 2	2.8	3.16	3.28	2.68	2.51	2.34	2.49	2.24	2.20	2.63 ± 0.39
Ford 1	5.6	5.56	5.62	5.29	5.26	5.15	5.40	5.09	5.01	5.33 ± 0.23
Ford 2	6.2	6.05	6.10	5.69	5.75	5.61	5.90	5.57	5.50	5.82 ± 0.25
Ford 3	5.5	5.27	5.35	5.05	5.06	4.92	5.17	4.92	4.87	5.12 ± 0.22
GM 1	2.9	3.48	3.79	3.03	2.73	2.38	2.62	2.34	2.26	2.84 ± 0.53
GM 2	2.7	3.22	3.51	2.75	2.45	2.17	2.38	2.14	2.17	2.61 ± 0.49
GM 3	2.8	3.38	3.67	2.89	2.56	2.28	2.44	2.25	2.19	2.72 ± 0.52
Toyota 1	6.6	6.23	6.12	5.76	6.38	6.31	6.35	6.20	6.55	6.28 ± 0.25
Toyota 2	6.2	5.92	5.95	5.82	6.02	5.99	5.90	5.92	6.09	5.98 ± 0.11
Toyota 3	5.6	5.40	5.44	5.38	5.47	5.40	5.37	5.40	5.73	5.47 ± 0.12

[a] Working capacity is defined as the weight of hydrocarbons that can be purged after hydrocarbon loading

TABLE B-2. TASK 1 BREAKTHROUGH TIMES, CONTINUATION OF METHANOL BLEND CHARCOAL TESTING

	Breakthrough Times, minutes								
Canister	5/1 Cycle 2	5/2 Cycle 1	5/2 Cycle 2	5/3 Cycle 1	5/3 Cycle 2	5/6 Cycle 1	5/6 Cycle 2	5/7 Cycle 1	5/7 Cycle 2
Chrysler 1	55.3	57.9	66.8	68.8	68.2	58.2	54.8	55.2	51.0
Chrysler 2	43.7	56.7	62.5	68.4	67.8	70.1	69.2	68.8	60.7
Ford 1	120.4	140.2	143.3	137.4	140.3	143.1	142.3	136.3	135.9
Ford 2	133.3	158.0	153.0	144.3	157.6	152.3	146.1	153.3	149.4
Ford 3	119.1	131.0	136.2	133.9	129.5	125.2	125.2	118.7	130.3
GM 1	45.1	59.0	65.6	69.3	75.7	72.5	77.0	73.6	66.4
Gm 2	45.4	55.0	61.1	67.3	68.0	66.9	68.1	68.3	59.0
GM 3	45.8	58.7	61.0	66.9	70.8	68.5	73.1	72.8	66.5
Toyota 1	170.1	183.8	182.6	177.0	169.5	179.0	162.7	181.1	179.7
Toyota 2	141.8	142.9	145.2	139.3	152.8	143.4	147.6	157.6	161.3
Toyota 3	138.2	139.0	143.1	138.4	140.5	142.2	131.8	137.4	139.6

Canister	5/8 Cycle 1	5/8 Cycle 2	5/9 Cycle 1	5/9 Cycle 2	5/10 Cycle 1	5/10 Cycle 2	5/13 Cycle 1	5/13 Cycle 2	Average
Chrysler 1	52.1	46.1	46.9	43.0	46.7	46.6	47.5	47.7	53.7 ± 8.1
Chrysler 2	58.5	54.8	56.0	52.8	$<$54.8	53.8	50.9	50.7	58.8 ± 7.9
Ford 1	132.4	131.2	129.9	122.6	132.6	130.6	126.3	128.5	133.7 ± 7.0
Ford 2	150.5	148.9	144.0	140.5	144.4	138.8	138.4	142.1	146.8 ± 7.0
Ford 3	125.8	124.4	127.9	120.7	119.8	125.4	122.4	122.8	125.8 ± 5.1
Gm 1	62.5	59.6	52.8	50.6	$<$54.8	56.0	53.4	52.0	61.5 ± 9.7
GM 2	57.5	51.2	60.0	55.8	57.5	46.8	46.9	45.9	57.7 ± 8.3
GM 3	62.5	56.2	58.4	54.6	$<$54.8	51.5	51.4	49.0	60.2 ± 8.5
Toyota 1	178.6	174.3	176.8	167.7	177.4	175.9	181.0	183.0	176.5 ± 5.9
Toyota 2	153.8	157.4	157.7	$<$ 156.3	154.4	155.4	156.0	159.1	151.9 ± 7.0
Toyota 3	141.7	145.4	148.7	140.8	143.8	144.1	147.5	146.2	141.7 ± 4.2

TABLE B-3. TASK 1 WEIGHT GAINS, CONTINUATION OF METHANOL BLEND CHARCOAL TESTING

Canister	Weight Gain, grams[a]								
	5/1	5/2	5/3	5/6	5/7	5/8	5/9	5/10	5/13
Chrysler 1	0.5	-0.8	-1.6	-0.9	-0.2	1.0	0.7	0.9	1.4
Chrysler 2	0.6	-0.7	-1.3	-0.7	-0.1	0.4	0.5	0.7	1.2
Ford 1	1.1	0.5	0.3	0.8	1.2	1.5	1.5	1.7	2.2
Ford 2	1.1	0.9	0.3	0.8	1.2	1.6	1.6	1.7	2.3
Ford 3	0.9	0.4	0.3	0.7	1.0	1.3	1.3	1.4	1.9
GM 1	1.0	-0.4	-1.3	-0.7	0.2	1.1	1.3	1.6	2.2
GM 2	1.1	-0.3	-1.1	-0.5	0.4	1.2	1.5	1.7	2.2
GM 3	0.9	-0.5	-1.4	-0.7	0.2	1.0	1.3	1.6	2.1
Toyota 1	0.4	0.3	0.2	0.3	0.4	0.5	0.4	0.5	0.6
Toyota 2	0.3	0.2	0.1	0.2	0.3	0.3	0.4	0.4	0.5
Toyota 3	0.2	0.1	0.1	0.2	0.2	0.3	0.3	0.3	0.1

[a]Weight gain relative to April 29, 1985 canister weights

APPENDIX C

Daily Working Capacities, Breakthrough Times, and Weight Gains for Task 2 Testing (HC-Methanol Mini-Canisters Exposed to HC-Only Blend)

TABLE C-1. TASK 2 WORKING CAPACITIES, SWITCHING OF HC-METHANOL BLEND TO HC-ONLY BLEND[a]

Canister	Working Capacity, grams,[b]									
	5/15 Cycle 1	5/15 Cycle 2	5/16 Cycle 1	5/16 Cycle 2	5/17	5/20	5/21	5/22	5/23	Avg.
Chrysler 1	--	--	--	--	--	--	--	--	--	--
Chrysler 2	2.46	2.33	1.79	1.92	1.73	1.39	1.98	1.52	1.77	1.88 ± 0.35
Ford 1	--	--	--	--	--	--	--	--	--	--
Ford 2	5.78	5.27	5.23	5.08	4.88	4.79	5.25	4.88	4.70	5.10 ± 0.33
Ford 3	4.88	4.86	4.39	4.41	4.14	4.05	4.44	4.00	4.29	4.38 ± 0.32
GM 1	2.63	2.59	1.87	2.08	1.77	1.33	1.94	1.51	1.82	1.95 ± 0.44
GM 2	--	--	--	--	--	--	--	--	--	--
GM 3	2.59	2.48	1.77	1.96	1.71	1.27	1.92	1.43	1.73	1.87 ± 0.43
Toyota 1	--	--	--	--	--	--	--	--	--	--
Toyota 2	5.60	5.47	5.66	5.57	5.62	5.40	5.50	5.45	5.37	5.25 ± 0.10
Toyota 3	5.18	5.16	4.97	5.04	4.73	5.01	5.19	4.97	5.05	5.03 ± 0.14

[a]Charcoal previously exposed to HC-methanol blend in Work Assignment 12 and in Task 1 of this Work Assignment
[b]Working capacity is defined as the weight of hydrocarbons that can be purged after hydrocarbon loading

TABLE C-2. TASK 2 BREAKTHROUGH TIMES, SWITCHING OF HC-METHANOL BLEND TO HC-ONLY BLEND[a]

	Breakthrough Times, minutes									
Canister	5/15 Cycle 1	5/15 Cycle 2	5/16 Cycle 1	5/16 Cycle 2	5/17 Cycle 1	5/17 Cycle 2	5/20 Cycle 1	5/20 Cycle 2	5/21 Cycle 1	5/21 Cycle 2
Chrysler 1	--	--	--	--	--	--	--	--	--	--
Chrysler 2	55.5	66.2	64.8	70.0	59.0	57.3	53.0	49.3	48.2	52.0
Ford 1	--	--	--	--	--	--	--	--	--	--
Ford 2	127.7	146.5	152.5	1455.3	143.2	133.8	143.5	144.0	135.9	138.0
Ford 3	124.9	173.0	130.2	155.9	133.0	118.3	119.6	117.3	112.8	118.7
GM 1	55.8	67.2	65.3	69.0	57.0	53.0	52.0	48.7	46.5	45.7
GM 2	--	--	--	--	--	--	--	--	--	--
GM 3	54.8	63.0	64.3	68.0	56.5	53.8	50.7	47.7	44.4	46.0
Toyota 1	--	--	--	--	--	--	--	--	--	--
Toyota 2	154.8	149.0	161.5	161.0	168.5	153.3	151.8	151.0	153.4	152.0
Toyota 3	144.8	139.0	140.9	154.0	147.0	132.7	143.2	144.7	145.5	145.3

Canister	5/22 Cycle 1	5/22 Cycle 2	5/23 Cycle 1	5/23 Cycle 2	Average
Chrysler 1	--	--	--	--	--
Chrysler 2	52.0	51.8	50.0	48.5	55.5 ± 7.0
Ford 1	--	--	--	--	--
Ford 2	136.8	137.7	137.2	120.8	139.5 ± 9.1
Ford 3	121.8	116.2	111.2	112.0	123.5 ± 12.2
GM 1	51.0	50.4	49.5	46.0	54.1 ± 7.9
GM 2	--	--	--	--	--
GM 3	49.4	47.2	49.0	47.0	53.0 ± 7.5
Toyota 1	--	--	--	--	--
Toyota 2	157.5	153.0	146.3	143.2	154.0 ± 6.5
Toyota 3	148.5	143.0	143.5	141.0	143.8 ± 4.9

[a]Charcoal previously exposed to HC-methanol blend in Work Assignment 12 and in Task 1 of this Work Assignment

TABLE C-3. TASK 2 WEIGHT GAINS, SWITCHING OF HC-METHANOL BLEND TO HC-ONLY BLEND[a]

Canister	Weight Gain, grams[b] 5/15 Cycle 1	5/15 Cycle 2	5/16 Cycle 1	5/16 Cycle 2	5/17	5/20	5/21	5/22	5/23
Chrysler 1	--	--	--	--	--	--	--	--	--
Chrysler 2	-0.5	-0.7	0.0	0.1	0.5	1.2	0.6	0.9	0.8
Ford 1	--	--	--	--	--	--	--	--	--
Ford 2	0.9	0.7	1.3	1.5	1.7	2.3	1.6	1.9	1.9
Ford 3	0.8	0.6	1.1	1.2	1.4	1.9	1.4	1.6	1.6
GM 1	0.4	0.0	0.7	0.8	1.4	2.2	1.5	1.9	1.8
GM 2	--	--	--	--	--	--	--	--	--
GM 3	0.2	-0.2	0.6	0.7	1.3	2.1	1.4	1.8	1.7
Toyota 1	--	--	--	--	--	--	--	--	--
Toyota 2	0.3	0.0	0.4	0.4	0.4	0.6	0.3	0.5	0.5
Toyota 3	0.3	0.0	0.3	0.4	0.4	0.5	0.3	0.5	0.4

[a]Charcoal previously exposed to HC-methanol blend in Work Assignment 12 and in Task 1 of this Work Assignment

[b]Weight gain relative to April 29, 1985 canister weights

APPENDIX D

Daily Working Capacities, Breakthrough Times, and Weight Gains for Task 2 Testing (Continuation of HC-Only Blend Exposures for HC-Only Mini-Canisters)

TABLE D-1. WORKING CAPACITIES, CONTINUATION OF HYDROCARBON-ONLY BLEND CHARCOAL TESTING[a]

Canister	Working Capacity, grams[b] 5/24	5/27 Cycle 1	5/27 Cycle 2	5/28 Cycle 1	5/28 Cycle 2	5/29 Cycle 1	5/29 Cycle 2	5/30	5/31
Chrysler 1	0.99	1.69	1.14	1.40	1.37	1.48	1.47	1.79	1.33
Chrysler 2	0.78	1.21	1.17	1.24	1.29	1.34	1.37	1.69	1.19
Ford 1	2.86	4.27	4.31	4.45	4.42	4.38	4.26	4.78	4.22
Ford 2	2.93	4.22	4.00	4.20	4.16	4.13	3.97	4.55	4.04
Ford 3	2.52	4.14	3.91	4.41	3.97	4.18	3.99	4.46	--
Ford 4	2.70	4.20	4.01	4.43	4.21	4.00	4.22	4.48	4.04
GM 1	0.49	0.93	0.72	0.96	1.00	1.05	1.14	1.46	0.98
GM 2	0.49	0.80	0.68	0.88	0.94	1.00	1.03	1.33	0.85
GM 3	0.56	0.94	0.85	1.01	1.06	1.11	1.17	1.51	0.92
Toyota 1	3.01	4.93	4.89	4.97	4.92	4.96	5.05	5.11	4.97
Toyota 2	2.85	4.85	4.69	4.82	4.92	4.79	4.96	4.88	4.59
Toyota 3	2.80	4.86	4.85	4.96	4.76	4.96	4.87	4.89	4.57

Canister	6/3	6/4	6/5	6/6	6/7	6/10	6/11	6/12[c]	Average 12 Determinations 5/28 to 6/11
Chrysler 1	--	1.53	1.43	1.00	1.27	1.69	1.54	1.32	1.44 ± 0.20
Chrysler 2	--	1.43	1.33	0.90	1.18	1.54	1.38	--	1.32 ± 0.20
Ford 1	--	4.15	4.24	3.81	4.00	4.36	4.11	3.77	4.27 ± 0.25
Ford 2	--	3.96	4.09	3.48	3.83	4.03	3.99	3.67	4.04 ± 0.25
Ford 3	--	3.90	3.86	3.58	3.82	3.79	3.94	--	3.99 ± 0.26
Ford 4	--	3.95	3.89	3.61	3.81	4.16	4.01	3.75	4.07 ± 0.25
GM 1	--	1.19	1.07	0.70	0.97	1.42	1.21	--	1.10 ± 0.21
GM 2	--	1.06	1.00	0.64	0.91	1.28	1.05	0.91	1.00 ± 0.18
GM 3	--	1.24	1.15	0.75	1.01	1.44	1.21	1.05	1.13 ± 0.21
Toyota 1	--	4.80	4.87	4.77	4.66	5.10	4.88	--	4.92 ± 0.14
Toyota 2	--	4.73	4.67	4.39	4.70	4.94	4.66	4.60	4.75 ± 0.17
Toyota 3	--	4.73	4.61	4.52	4.48	4.95	4.78	4.69	4.76 ± 0.18

[a] Charcoal previously exposed to HC-only blend in work assignment 12
[b] Working capacity is defined as the weight of hydrocarbons that can be purged after hydrocarbon loading
[c] The charcoal from four of the canisters was removed before purging for speciation in Task 3

TABLE D-2. BREAKTHROUGH TIMES, CONTINUATION OF HYDROCARBON-ONLY BLEND CHARCOAL TESTING[a]

Breakthrough Times, Minutes

Canister	5/24	5/27 Cycle 1	5/27 Cycle 2	5/28 Cycle 1	5/28 Cycle 2	5/29 Cycle 1	5/29 Cycle 2	5/30 Cycle 1	5/30 Cycle 2	5/31	6/3 Cycle 1	6/3 Cycle 2	6/4 Cycle 1
Chrysler 1	76.0	72.6	59.2	51.8	46.5	47.7	44.5	45.3	50.8	49.5	46.8	45.0	46.5
Chrysler 2	61.0	61.3	49.5	48.0	45.5	42.1	37.0	36.2	36.4	37.8	37.3	38.4	37.7
Ford 1	130.0	136.5	140.8	131.5	127.6	128.1	123.5	120.0	127.0	131.5	127.0	127.7	126.4
Ford 2	129.0	135.8	127.2	124.5	119.0	118.0	116.5	120.3	114.3	123.5	113.0	111.2	114.4
Ford 3	112.3	134.6	--[b]	140.0	117.0	123.0	116.5	--[c]	119.5	117.6	114.3	112.7	107.3
Ford 4	120.3	139.7	130.1	127.4	124.5	113.0	122.5	121.3	119.8	124.5	113.7	115.1	111.7
GM 1	52.0	54.4	45.8	38.2	35.0	32.8	36.8	35.7	37.4	39.2	35.7	35.0	37.3
GM 2	46.8	51.6	45.8	35.8	30.0	31.9	32.2	29.9	32.7	34.1	33.2	27.9	32.9
GM 3	50.3	57.8	49.5	45.0	40.0	39.1	37.9	36.2	37.2	40.3	38.2	36.5	38.5
Toyota 1	143.5	145.6	148.3	143.5	142.9	144.6	146.0	140.1	141.9	146.2	137.5	137.3	137.5
Toyota 2	135.8	140.1	138.1	135.0	139.6	140.5	145.0	130.0	134.5	132.7	132.8	130.0	141.7
Toyota 3	148.0	150.3	152.8	147.0	146.0	149.0	148.0	137.5	139.8	132.7	139.0	129.0	131.1

Canister	6/4 Cycle 2	6/5 Cycle 1	6/5 Cycle 2	6/6 Cycle 1	6/6 Cycle 2	6/7 Cycle 1	6/7 Cycle 2	6/10 Cycle 1	6/10 Cycle 2	6/11 Cycle 1	6/11 Cycle 2	6/12	Average 21 Cycles 5/28 to 6/11
Chrysler 1	46.7	46.6	44.3	47.8	40.7	36.5	38.7	39.9	38.4	44.4	42.9	48.3	44.8 ± 4.1
Chrysler 2	38.6	32.0	29.5	35.7	29.4	26.4	26.9	26.7	27.6	25.7	23.6	28.5	34.2 ± 6.8
Ford 1	119.8	124.6	122.5	125.0	120.8	133.5	116.1	115.3	118.4	117.4	115.8	112.3	123.8 ± 5.5
Ford 2	109.3	106.5	111.0	110.5	110.7	106.3	110.6	108.1	103.5	107.9	112.3	110.5	112.9 ± 5.7
Ford 3	107.2	106.2	109.4	117.7	113.8	116.6	110.4	104.0	96.2	112.9	112.9	116.0	113.8 ± 8.7
Ford 4	111.4	105.9	109.9	109.8	112.0	106.0	112.8	109.2	105.7	117.0	113.5	111.0	114.6 ± 6.5
GM 1	35.0	32.2	29.3	34.6	27.5	24.4	25.9	29.5	29.6	33.5	32.7	32.1	33.2 ± 4.1
GM 2	33.5	31.9	29.1	30.5	26.5	22.1	24.6	26.3	27.3	32.7	27.1	31.3	30.1 ± 3.5
GM 3	38.3	36.2	36.8	38.5	32.8	27.7	31.0	31.6	31.9	35.2	34.4	33.3	36.4 ± 3.8
Toyota 1	135.0	135.1	140.7	134.5	137.8	141.0	138.1	141.6	140.2	144.0	141.1	141.1	140.3 ± 3.5
Toyota 2	134.5	134.5	136.7	134.9	128.5	141.0	133.9	133.2	133.5	137.4	128.4	139.3	135.2 ± 4.4
Toyota 3	135.0	135.2	129.5	144.0	135.8	141.0	127.2	122.7	134.9	145.5	142.2	137.5	137.7 ± 7.4

[a] Charcoal previously exposed to HC-only blend in Work Assignment 12
[b] Atypical breakthrough time observed, 162.5 minutes
[c] Atypical breakthrough time observed, 153.5 minutes

TABLE D-3. WEIGHT GAINS, CONTINUATION OF HYDROCARBON-ONLY BLEND CHARCOAL TESTING[a]

Canister	Weight Gains, grams[b]								
	5/24	5/27 Cycle 1	5/27 Cycle 2	5/28 Cycle 1	5/28 Cycle 2	5/29 Cycle 1	5/29 Cycle 2	5/30	5/31
Chrysler 1	-0.30	0.29	1.28	1.56	1.73	1.76	1.76	1.50	1.79
Chrysler 2	-0.07	0.89	1.57	1.85	2.02	2.03	2.05	1.83	2.09
Ford 1	-0.12	0.57	1.06	1.26	1.38	1.42	1.43	1.24	1.47
Ford 2	0.00	0.74	1.21	1.42	1.56	1.59	1.62	1.45	1.67
Ford 3	-0.09	0.66	1.14	1.35	1.45	1.49	1.47	1.25	1.47
Ford 4	-0.11	0.61	1.08	1.25	1.39	1.43	1.46	1.29	1.52
GM 1	0.07	1.04	1.80	2.09	2.29	2.33	2.31	2.12	2.37
GM 2	-0.07	0.87	1.58	1.83	2.00	2.02	2.00	1.80	2.03
GM 3	-0.07	0.92	1.64	1.97	2.15	2.20	2.18	1.96	2.18
Toyota 1	-0.16	0.19	0.37	0.40	0.42	0.42	0.43	0.31	0.39
Toyota 2	-0.18	0.12	0.37	0.40	0.40	0.42	0.40	0.29	0.38
Toyota 3	0.07	0.37	0.56	0.59	0.64	0.61	0.66	0.58	0.69

Canister	6/3[c]	6/4	6/5	6/6	6/7	6/10	6/11	6/12[c]
Chrysler 1	1.66	1.63	2.01	2.75	2.81	2.25	2.08	2.23
Chrysler 2	1.99	1.93	2.30	2.97	2.99	2.52	2.40	--
Ford 1	1.46	1.41	1.79	2.54	2.79	2.47	2.33	2.40
Ford 2	1.67	1.61	1.89	2.65	2.87	2.53	2.37	2.44
Ford 3	1.45	1.38	1.46	2.38	2.64	2.27	2.16	--
Ford 4	1.49	1.43	1.79	2.51	2.81	2.38	2.27	2.33
GM 1	2.33	2.33	2.63	3.35	3.38	2.87	2.79	--
GM 2	1.99	1.99	2.27	2.93	2.92	2.44	2.37	2.45
GM 3	2.13	2.13	2.43	3.10	3.15	2.65	2.55	2.60
Toyota 1	0.32	0.40	0.58	0.92	0.94	0.64	0.58	--
Toyota 2	0.38	0.44	0.55	0.91	0.92	0.61	0.50	0.58
Toyota 3	0.61	0.73	0.87	1.21	1.22	0.91	0.86	0.88

[a]Charcoal previously exposed to HC-only blend in Work Assignment 12
[b]Weight gain relative to May 24, 1985 canister weights
[c]The charcoal from four of the canisters was removed before purging for speciation is Task 3.

APPENDIX E

Daily Working Capacities, Breakthrough Times, and Weight Gains for Task 2 Testing (HC-Only Mini-Canisters Exposed to HC-Methanol Blend)

TABLE E-1. WORKING CAPACITIES, SWITCHING OF HC-ONLY BLEND TO HC-METHANOL BLEND[a]

Canister	Working Capacity, grams[b] 6/13 Cycle 1	6/13 Cycle 2	6/14 Cycle 1	6/14 Cycle 2	6/17	6/18	6/20	6/21
Chrysler 1	2.86	2.78	1.92	2.18	1.38	1.57	1.56	1.40
Chrysler 2	--	--	--	--	--	--	--	--
Ford 1	5.06	5.14	4.31	4.53	3.98	3.94	4.03	3.89
Ford 2	4.88	4.70	3.95	4.25	3.85	3.76	3.82	3.78
Ford 3	--	--	--	--	--	--	--	--
Ford 4	5.05	5.04	4.21	4.38	3.65	3.70	3.84	3.83
GM 1	--	--	--	--	--	--	--	--
GM 2	2.20	1.98	1.12	1.46	0.77	1.01	0.92	0.97
GM 3	2.36	2.30	1.37	1.64	1.07	1.28	1.19	1.18
Toyota 1	--	--	--	--	--	--	--	--
Toyota 2	4.75	4.58	4.67	4.60	4.41	4.48	4.41	4.60
Toyota 3	5.02	4.68	4.73	4.80	4.40	4.63	4.51	4.68

Canister	6/24	6/25	6/26	6/27	6/28	Average
Chrysler 1	1.36	1.52	1.67	1.48	2.47	1.86 ± 0.54
Chrysler 2	--	--	--	--	--	--
Ford 1	3.89	3.95	4.06	3.94	4.88	4.28 ± 0.47
Ford 2	3.39	3.83	3.93	3.66	4.40	4.02 ± 0.43
Ford 3	--	--	--	--	--	--
Ford 4	3.90	3.84	3.99	3.92	4.78	4.16 ± 0.50
GM 1	--	--	--	--	--	--
GM 2	0.99	1.02	1.05	1.07	1.77	1.26 ± 0.45
GM 3	1.21	1.23	1.36	1.22	2.13	1.50 ± 0.46
Toyota 1	--	--	--	--	--	--
Toyota 2	4.58	4.54	4.47	4.46	4.66	4.55 ± 0.10
Toyota 3	4.50	4.43	4.45	4.69	4.78	4.64 ± 0.18

[a]Charcoal previously exposed to HC-only blend in Work Assignment 12)
[b]Working capacity is defined as the weight of hydrocarbons that can be purged after hydrocarbon loading

TABLE E-2. BREAKTHROUGH TIMES, SWITCHING OF HC-ONLY BLEND TO HC-METHANOL BLEND[a]

Canister	Breakthrough Times, Minutes												
	6/13 Cycle 1	6/13 Cycle 2	6/14 Cycle 1	6/14 Cycle 2	6/17 Cycle 1	6/17 Cycle 2	6/18	6/20 Cycle 1	6/20 Cycle 2	6/21 Cycle 1	6/21 Cycle 2	6/24 Cycle 1	6/24 Cycle 2
Chrysler 1	48.5	58.7	67.5	71.4	61.5	53.6	50.3	51.0	50.0	50.6	45.6	45.4	39.3
Chrysler 2	--	--	--	--	--	--	--	--	--	--	--	--	--
Ford 1	115.3	131.1	132.4	123.4	128.0	127.6	119.0	121.4	124.2	120.1	117.4	110.1	114.1
Ford 2	114.7	115.4	118.1	111.6	114.7	122.8	111.6	111.0	111.4	112.3	109.6	105.8	91.2
Ford 3	--	--	--	--	--	--	--	--	--	--	--	--	--
Ford 4	118.0	123.9	130.5	118.7	116.0	118.5	107.8	116.1	119.7	118.3	117.1	114.2	112.5
GM 1	--	--	--	--	--	--	--	--	--	--	--	--	--
GM 2	33.9	46.1	46.6	43.0	42.0	30.7	32.2	32.9	33.2	33.6	30.0	29.1	25.1
GM 3	40.0	52.6	57.4	46.8	49.3	43.3	41.4	40.7	39.4	40.0	36.1	38.1	34.1
Toyota 1	--	--	--	--	--	--	--	--	--	--	--	--	--
Toyota 2	139.6	131.7	131.8	124.5	125.0	128.2	131.0	125.8	136.0	126.4	136.6	134.3	127.8
Toyota 3	148.0	137.3	137.7	135.1	135.4	128.8	139.7	139.0	141.4	139.7	141.6	138.0	135.0

Canister	6/25	6/26 Cycle 1	6/26 Cycle 2	6/27 Cycle 1	6/27 Cycle 2	6/28 Cycle 1	6/28 Cycle 2	Average
Chrysler 1	41.7	43.0	42.4	46.2	43.8	43.8	46.8	50.0 ± 8.7
Chrysler 2	--	--	--	--	--	--	--	--
Ford 1	114.1	113.5	114.8	116.4	112.5	112.5	115.6	119.2 ± 6.6
Ford 2	106.8	103.3	107.0	102.7	101.2	102.0	101.5	108.7 ± 7.2
Ford 3	--	--	--	--	--	--	--	--
Ford 4	107.9	109.6	114.0	108.9	112.0	115.3	113.1	115.6 ± 5.5
GM 1	--	--	--	--	--	--	--	--
GM 2	24.6	29.1	27.6	27.1	26.4	28.5	30.2	32.6 ± 6.7
GM 3	36.5	35.9	36.4	36.7	36.5	36.5	42.4	41.0 ± 6.2
Toyota 1	--	--	--	--	--	--	--	--
Toyota 2	129.3	--[b]	130.3	135.0	125.1	128.5	128.4	130.3 ± 4.4
Toyota 3	129.8	134.5	134.7	137.5	138.2	133.0	135.0	137.0 ± 4.3

[a]Charcoal previously exposed to HC-only blend in Work Assignment 12
[b]Atypical breakthrough time observed, 116.4 minutes

TABLE E-3. WEIGHT GAINS, SWITCHING OF HC-ONLY BLEND TO HC-METHANOL BLEND[a]

	Weight Gains, grams[b]								
Canister	6/13 Cycle 1	6/13 Cycle 2	6/14 Cycle 1	6/14 Cycle 2	6/17	6/18	6/20	6/21	6/24
Chrysler 1	0.73	-0.16	0.22	0.12	1.36	1.58	1.63	2.13	2.65
Chrysler 2	--	--	--	--	--	--	--	--	--
Ford 1	1.09	0.36	0.74	0.61	1.65	1.85	1.97	2.50	2.95
Ford 2	1.21	0.62	0.98	0.87	1.83	1.96	2.06	2.53	2.96
Ford 3	--	--	--	--	--	--	--	--	--
Ford 4	1.01	032	0.70	0.59	1.60	1.75	1.85	2.39	2.82
GM 1	--	--	--	--	--	--	--	--	--
GM 2	1.14	0.51	0.96	0.91	1.93	2.04	2.05	2.38	2.71
GM 3	1.31	0.55	1.01	0.93	2.01	2.11	2.11	2.48	2.86
Toyota 1	--	--	--	--	--	--	--	--	--
Toyota 2	0.39	0.49	0.58	0.61	0.75	0.81	0.77	0.85	1.00
Toyota 3	0.56	0.59	0.71	0.67	0.98	1.01	1.03	1.15	1.29

Canister	6/25	6/26	6/27	6/28
Chrysler 1	2.46	2.19	2.30	0.79
Chrysler 2	--	--	--	--
Ford 1	2.77	2.50	2.53	1.11
Ford 2	2.73	2.48	2.51	1.18
Ford 3	--	--	--	--
Ford 4	2.62	2.35	2.32	0.90
GM 1	--	--	--	--
GM 2	2.52	2.29	2.36	1.13
GM 3	2.66	2.43	2.50	1.12
Toyota 1	--	--	--	--
Toyota 2	0.92	0.79	0.84	0.62
Toyota 3	1.24	1.10	1.19	0.93

[a]Charcoal previously exposed to HC-only blend in Work Assignment 12
[b]Weight gain relative to May 24, 1985 canister weights

APPENDIX F

Daily Working Capacities, Breakthrough Times, and Weight Gains for Task 2 Testing (Re-exposure of HC-Only Mini-Canisters to HC-Only Blend)

TABLE F-1. WORKING CAPACITIES, SWITCHING OF HC-METHANOL BLEND TO HC-ONLY BLEND[a]

Canister	Working Capacity, grams[b]										
	7/1 Cycle 1	7/1 Cycle 2	7/2 Cycle 1	7/2 Cycle 2	7/3 Cycle 1	7/3 Cycle 2	7/10	7/11	7/12	7/15	Average
Chrysler 1	1.86	2.25	1.51	1.83	1.22	1.57	1.49	1.57	1.83	1.48	1.66 ± 0.29
Chrysler 2	--	--	--	--	--	--	--	--	--	--	--
Ford 1	4.20	4.69	4.06	4.25	3.65	3.84	3.84	3.93	4.22	3.89	4.06 ± 0.30
Ford 2	4.06	4.23	3.98	3.99	3.51	3.41	3.71	3.61	4.14	3.88	3.85 ± 0.28
Ford 3	--	--	--	--	--	--	--	--	--	--	--
Ford 4	4.21	4.56	4.05	4.23	3.56	3.78	3.93	3.86	4.25	6.62[c]	4.05 ± 0.30
GM 1	--	--	--	--	--	--	--	--	--	--	--
GM 2	1.17	1.50	0.89	1.22	0.63	1.00	1.05	1.06	1.31	6.06[c]	1.09 ± 0.25
GM 3	1.47	1.82	1.15	1.49	0.89	1.22	1.27	1.25	1.56	1.53	1.37 ± 0.26
Toyota 1	--	--	--	--	--	--	--	--	--	--	--
Toyota 2	4.49	4.52	4.59	4.66	4.55	4.44	4.83	4.73	4.71	4.52	4.60 ± 0.12
Toyota 3	4.79	4.76	4.56	4.74	4.50	4.68	4.76	4.70	4.77	4.70	4.70 ± 0.10

[a]Charcoal previoiusly exposed to HC-only blend in Work Assignment 12
[b]Working capacity is defined as the weight of hydrocarbons that can be purged after hydrocarbon loading
[c]Zero air from compressed gas cylinder was used as purge air for the 110 minute purge cycle for these two mini-canisters, values not used in averages

TABLE F-2. BREAKTHROUGH TIMES, SWITCHING OF HC-METHANOL BLEND TO HC-ONLY BLEND[a]

	Breakthrough Times, Minutes									
Canister	7/1 Cycle 1	7/1 Cycle 2	7/2 Cycle 1	7/2 Cycle 2	7/3 Cycle 1	7/3 Cycle 2	7/10 Cycle 1	7/10 Cycle 2	7/11 Cycle 1	7/11 Cycle 2
Chrysler 1	55.5	55.8	59.0	54.6	54.1	50.5	49.0	42.2	42.9	46.2
Chrysler 2	--	--	--	--	--	--	--	--	--	--
Ford 1	117.0	128.3	129.7	122.3	122.5	114.5	108.3	105.8	110.4	113.4
Ford 2	113.1	112.4	119.3	114.0	113.0	98.9	107.6	96.4	103.5	97.8
Ford 3	--	--	--	--	--	--	--	--	--	--
Ford 4	118.5	124.1	128.7	121.7	116.7	111.9	120.3	108.0	109.8	110.7
GM 1	--	--	--	--	--	--	--	--	--	--
GM 2	38.2	38.4	38.6	34.0	31.7	30.7	33.5	27.4	29.1	33.8
GM 3	49.1	46.7	51.3	47.1	46.2	43.0	41.8	37.6	36.9	37.3
Toyota 1	--	--	--	--	--	--	--	--	--	--
Toyota 2	122.6	124.6	127.5	133.3	132.8	115.0	128.0	128.6	129.9	126.8
Toyota 3	139.8	136.6	130.1	137.3	136.8	133.0	130.8	133.0	140.0	134.6

Canister	7/12 Cycle	7/12 Cycle 2	7/15 Cycle 1	Average
Chrysler 1	47.9	47.6	40.0	49.6 ± 5.9
Chrysler 2	--	--	--	--
Ford 1	117.6	114.1	103.3	115.9 ± 8.1
Ford 2	110.8	110.1	96.5	107.2 ± 7.7
Ford 3	--	--	--	--
Ford 4	118.3	116.5	103.7	116.1 ± 7.0
GM 1	--	--	--	--
GM 2	33.0	32.6	30.9	33.2 ± 3.5
GM 3	40.0	40.2	39.6	42.8 ± 4.8
Toyota 1	--	--	--	--
Toyota 2	139.3	136.7	120.0	128.1 ± 6.7
Toyota 3	138.0	140.9	133.0	135.7 ± 3.5

[a]Charcoal previously exposed to HC-only blend in Work Assignment 12

TABLE F-3. WEIGHT GAINS, SWITCHING OF HC-METHANOL BLEND TO HC-ONLY BLEND[a]

Canister	Weight Gains, grams[b]									
	7/1 Cycle 1	7/1 Cycle 2	7/2 Cycle 1	7/2 Cycle 2	7/3 Cycle 1	7/3 Cycle 2	7/10	7/11	7/12	7/15
Chrysler 1	0.79	0.41	0.94	0.91	1.56	1.62	2.10	1.89	1.61	1.76
Chrysler 2	--	--	--	--	--	--	--	--	--	--
Ford 1	1.08	0.75	1.22	1.19	1.82	1.90	2.43	2.24	1.99	2.01
Ford 2	1.21	0.97	1.40	1.39	1.89	1.96	2.41	2.22	1.98	1.87
Ford 3	--	--	--	--	--	--	--	--	--	--
Ford 4	0.97	0.73	1.13	1.14	1.71	1.86	2.37	2.20	1.92	-0.73[c]
GM 1	--	--	--	--	--	--	--	--	--	--
GM 2	1.21	0.97	1.45	1.40	1.93	1.98	2.27	2.07	1.84	-3.01[c]
GM 3	1.20	0.89	1.42	1.37	1.95	1.99	2.29	2.15	1.87	1.66
Toyota 1	--	--	--	--	--	--	--	--	--	--
Toyota 2	0.69	0.70	0.70	0.70	0.82	0.72	0.74	0.55	0.64	0.76
Toyota 3	0.94	0.91	1.00	0.98	1.11	1.09	1.17	1.01	0.99	1.12

[a]Charcoal previously exposed to HC-only blend in Work Assignment 12
[b]Weight gain relative to May 24, 1985 canister weights
[c]Zero air from a compressed gas cylinder was used as purge air during the 110 minute purge cycle for these two mini-canisters

APPENDIX G

Mini-Canister Daily Environment

TABLE G-1. MINI-CANISTER DAILY ENVIRONMENT - MASS OF WATER VAPOR IN AIR, ROOM TEMPERATURE, AND BAROMETRIC PRESSURE

Day	Room Temperature, °F	Mass of Water Vapor in Air, grains/ft^3	Barometric Pressure, inches Hg
5/27	73	5.78	29.05
5/28	76	6.05	29.08
5/29	76	6.05	28.99
5/30 (am)	75	5.87	29.01
5/30 (pm)	75	6.25	28.99
5/31	76	6.05	29.10
6/3	76	7.13	29.09
6/4	75	6.25	29.03
6/5	76	6.06	29.04
6/6	75	6.25	29.18
6/7 (am)	73	6.13	29.25
6/7 (pm)	73	6.40	29.18
6/10 (am)	74	5.96	29.13
6/10 (pm)	74	6.33	29.05
6/11 (am)	74	6.32	29.14
6/11 (pm)	73	5.51	29.14
6/12	74	5.68	29.27
6/13 (am)	73	4.62	29.29
6/13 (pm)	76	4.20	29.25
6/14 (am)	74	5.32	29.13
6/14 (pm)	74	5.04	29.04
6/17 (am)	76	6.73	29.14
6/17 (pm)	74	5.32	29.12
6/18	73	5.78	29.13
6/20	75	6.53	29.18
6/21	75	6.53	29.03
6/24 (am)	76	7.52	29.27
6/24 (pm)	75	6.91	29.25
6/25	75	5.87	29.16
6/26 (am)	74	5.68	29.12
6/26 (pm)	75	6.25	29.14

TABLE G-1 (CONT'D). MINI-CANISTER DAILY ENVIRONMENT - MASS OF WATER VAPOR IN AIR, ROOM TEMPERATURE, AND BAROMETRIC PRESSURE

Day	Room Temperature, °F	Mass of Water Vapor in Air, grains/ft^3	Barometric Pressure, inches Hg
6/27 (am)	75	6.33	29.24
6/27 (pm)	75	6.91	29.27
6/28 (am)	75	5.58	29.37
6/28 (pm)	75	5.30	29.36
7/1 (am)	75	5.58	29.37
7/1 (pm)	76	5.47	29.35
7/2 (am)	74	5.96	29.31
7/2 (pm)	75	5.87	29.40
7/3 (am)	75	6.25	29.31
7/3 (pm)			29.21
7/10 (am)	75	6.53	29.23
7/10 (pm)	74	5.96	
7/11	76	6.05	29.20
7/12 (am)	76	5.76	29.23
7/12 (pm)	76	6.05	29.19
7/15	76	6.05	29.39

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1. REPORT NO. EPA 460-3-85-010	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Additional Mini-Canister Evaluation		5. REPORT DATE December 1985
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Lawrence R. Smith		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Southwest Research Institute Department of Emissions Research 6220 Culebra Road San Antonio, Texas 78284		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 68-03-3162
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Protection Agency 2565 Plymouth Road Ann Arbor, Michigan 48105		13. TYPE OF REPORT AND PERIOD COVERED Final(3/85 - 8/85)
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This program involved the continuation of testing on charcoal mini-canisters that were developed and previously tested in Work Assignment 12 of this Contract. The results of the previous study are reported in EPA Report No. 460/3-84-014. In this study, additional testing was conducted both on mini-canisters previously exposed to a hydrocarbon-only blend, and on mini-canisters previously exposed to a hydrocarbon-methanol blend. Switching of exposure blends (between the hydrocarbon-only and the hydrocarbon-methanol blend) on the same set of mini-canisters was also undertaken to determine if any of the effects of the previous blend exposure were reversible. Breakthrough times, working capacities and canister weight gains were monitored for each of the mini-canisters during all testing. Laboratory humidity, temperature, and barometric pressure were also monitored to determine the effect of these parameters on mini-canister working capacity and weight gain. Hydrocarbon and methanol speciation were conducted on the vapors purged from eight of the canisters (four from the hydrocarbon-method blend exposures and four from the hydrocarbon-only blend exposures).

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Evaporative Canisters Methanol Charcoal Evaluation	

18. DISTRIBUTION STATEMENT Release Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 77
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