EPA-460/3-76-026
August 1976

ACCELERATED DECAY OF NON-FUEL EVAPORATIVE EMISSIONS

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Mobile Source Air Pollution Control
Emission Control Technology Division
Ann Arbor, Michigan

EPA-460/3-76-026

ACCELERATED DECAY OF NON-FUEL EVAPORATIVE EMISSIONS Task No. 1

by

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Contract No. 68-03-2413

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
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ABSTRACT

The purpose of this program was to determine if driving a vehicle on a dynamometer or baking a vehicle in a paint oven could accelerate the normal decay of background hydrocarbon evaporative emissions from new vehicles. A series of daily background evaporative emission tests were performed on two groups of three identical Ford LTD's. The tests were performed in accordance with the procedures outlined in SAE J171a. All fuel system components were either removed or plugged. The carburetors were removed and the intake manifolds covered with a plate. An auxiliary fuel system was used when running each vehicle on the dynamometer.

Daily testing was begun on each vehicle within nine days after manufacturing. One vehicle in each group was a control vehicle which soaked between daily tests. After each daily test, the second vehicle in each group was driven on the dynamometer for five series of two LA-4 driving schedules, with a 30-minute soak with the engine off following each series. It was then soaked until the next test. The third vehicle in each group was placed in a bake oven at 125°F for 12 hours after each test and then soaked until the next test.

All initial background emission levels were below 1.5 gms per test. The cars tested were manufactured in California where the California Air Resources Board has a rule governing the use of photochemical reactive solvents. The implementation of this rule has resulted in the use of paints, sound deadening materials, body fillers, etc., which are non-photochemically reactive. Compliance to this rule may have contributed to lower vehicle background emissions levels.

The first group of three vehicles had no vinyl roofs, whereas the second group of three vehicles were equipped with vinyl roofs. The results tend to indicate that the background emission levels were not affected by the presence of the vinyl roofs.

The "dyno" and "oven" vehicles showed more rapid declines in background emissions than the control vehicles. The daily background emission reductions in "dyno" vehicles were comparable to the daily reductions experienced in the "oven" vehicles. The results indicate that background emission decay rates can be accelerated by driving the vehicles on a dynamometer or by baking the vehicle.

Gas chromatography (GC) and mass spectrometry (GCMS) were used to attempt to identify and quantify the constituents of the background hydrocarbon emissions in the enclosure. Toulene was the most prominent constituent ranging from 5% to 56% by weight. Benzene, xylene, methylethylbenzene, and trimethylethylbenzene were consistently identified and quantified in these California built vehicles, however, this may not typify nationwide results.

1.0 INTRODUCTION

The testing project described in this report was undertaken as Task 1 of EPA Contract No. 68-03-2413. The purpose of this project was to attempt to accelerate the decay of vehicular non-fuel evaporative emissions. The background emission levels of new vehicles typically decay very rapidly during the days following production until eventually a stabilization level is reached. In order to perform evaporative emission tests on new vehicles, it is important that the background emissions be reduced to the stabilization level as rapidly as possible.

In addition to measuring the total hydrocarbon emissions, it was decided to attempt to use mass spectrometry and gas chromatography (GC and GCMS) to identify and quantify the constituents of the enclosure atmosphere. The identification of the constituents could assist in determining the sources of background emissions.

Initially one group of three vehicles was to be tested for thirteen consecutive days. But after seven days of testing, the background levels were so low it was decided to check the results by testing a second set of three vehicles for seven days.

2.0 SUMMARY

Non-fuel evaporative emission tests were performed on two groups of three full size passenger cars to determine if driving and baking the vehicles would accelerate the decay of non-fuel evaporative emissions.

It would appear, as illustrated in Figures 2-1 and 2-2, that the greatest decay by mass of non-fuel hydrocarbons was in the first 9 to 10 days after production. Another observation would be that vinyl interiors and roof do not significantly contribute to hydrocarbon emissions, as vehicles D, E and F were so equipped while vehicles A, B and C were not.

The task performed for EPA originally called for the testing of three identical full-size vehicles, produced at the same assembly plant on the same day and equipped without vinyl interiors or roofs. These vehicles were built as requested by Ford Motor Company's Pico Rivera, California assembly plant and delivered to AESi's test facilities. However, since initial tests produced hydrocarbon levels much lower than the expected 4 to 6 grams per test, a second set of three vehicles was requested by EPA to confirm the result of the initial tests. As illustrated by Figures 2-1 and 2-2, the next series of tests produced comparable HC concentrations.

An investigation was made in an attempt to find a reason for the low evaporative hydrocarbon emissions experienced with these test vehicles. Previous background emissions tests were performed by EPA and Ford Motor Company on vehicles produced in the Detroit area. However, in this program all the test vehicles were built in California. After extensive research, AESi discovered that the California Air Resources Board (CARB) has Rule 442 governing the use of photochemically reactive solvents in Los Angeles County. In automobile assembly this rule applies to paints, sound deadening materials, body fillers, etc. which must be non-photochemically reactive solvents. The CARB Rule 442 is presented in Appendix A.

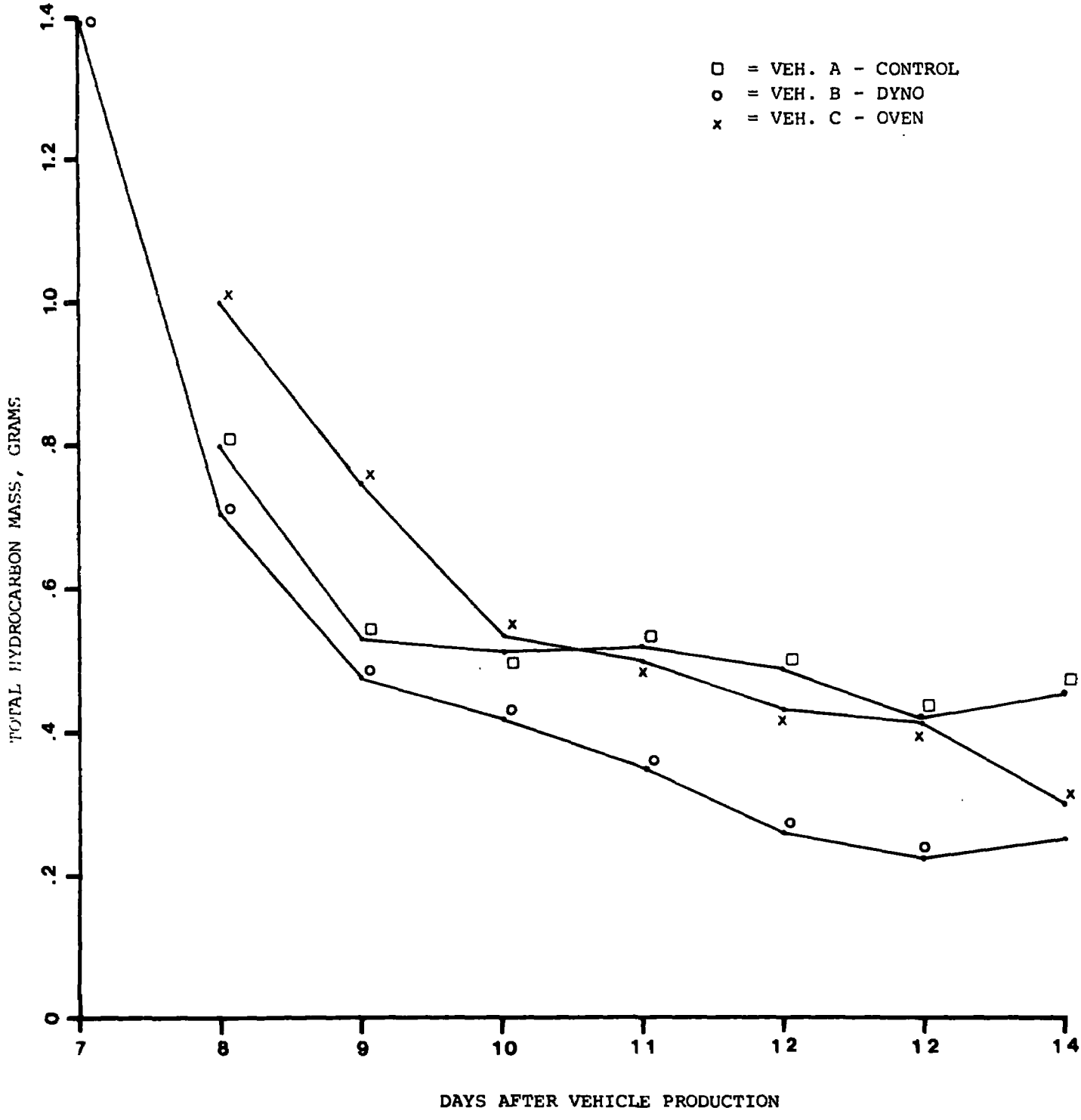

Figure 2-1. NON-FUEL EVAPORATIVE EMISSION TEST
VEHICLE TOTAL MASS HYDROCARBONS PER DAY

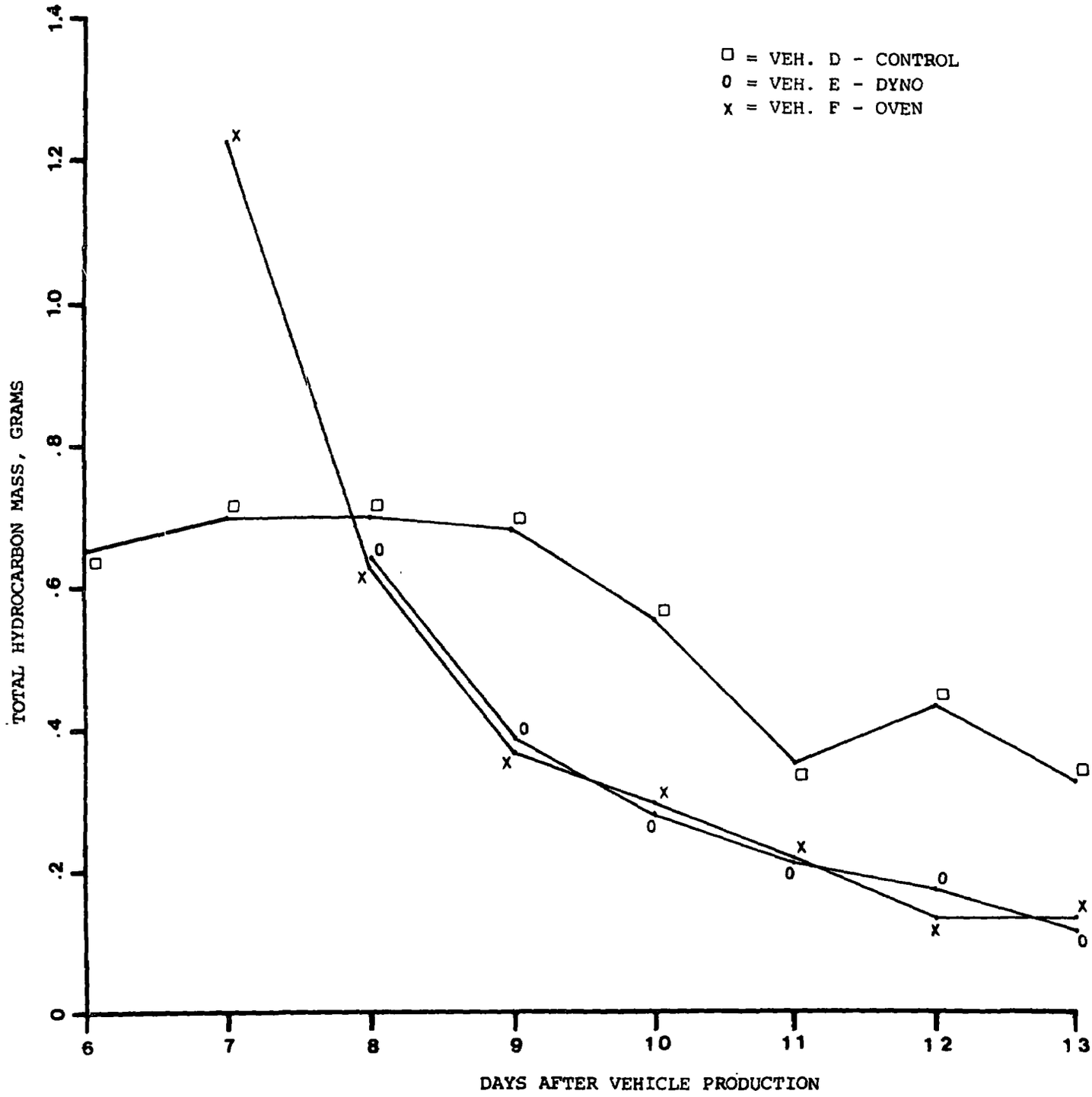

Figure 2-2. NON-FUEL EVAPORATIVE EMISSION TEST
Vehicle Total Mass Hydrocarbons per Day

3.0 TECHNICAL DISCUSSION

3.1 PROGRAM OBJECTIVE

The primary objective of this program was to attempt to find a means of accelerating the decay of new vehicle background emissions.

Typically a new vehicle must stand for 60 to 90 days before the background emissions reach acceptable levels. This program was designed to evaluate two alternate methods of accelerating the decay of these non-fuel background emissions. The first method involved placing the test vehicle in a paint bake room. The second method involved accumulating mileage on a vehicle by operating it on a chassis dynamometer.

A secondary objective of this program was to identify the hydrocarbon constituents of the background emissions. The plan was to enable source identification by quantifying the hydrocarbon compounds present in the background emissions. Gas chromatography and mass spectrometry were used to attempt to identify and quantify the constituents of the background hydrocarbon emissions.

3.2 PROGRAM DESIGN

This program was designed to compare the background emission degradation rates of three identical vehicles receiving different treatments. One vehicle was randomly selected to be the control vehicle which was only soaked between tests. Another vehicle was driven on the dynamometer between tests. It was driven using a series of LA-4 driving schedules. The test sequence consisted of 2 LA-4's followed by a 30 minute soak. This procedure was replicated five consecutive times each day. The final vehicle was baked in a paint shop bake oven for 12 hours between tests. Each vehicle was tested daily using the SHED method of measuring background hydrocarbon emissions.

The data was plotted using "days after vehicle production" as the X axis and "total hydrocarbon mass emissions" as the Y axis. The degradation rates were compared to determine if one or both of the treatments would significantly accelerate the reduction in background emissions.

Samples of the enclosure atmosphere were taken during selected tests and were analyzed using GCMS and GC. These samples were collected using a variety of methods. One of the program goals was to evalute various methods of GCMS sample collection. A calibration procedure was developed for the GCMS sampling work.

3.3 TEST VEHICLES

3.3.1 Selection and Preparation

The test vehicles selected for this program were three, 1976 Ford LTD 2-door automobiles without vinyl roofs. Each vehicle was equipped with a 351-2V engine (belonging to the 351m/400 catalyst, EGR/Air family), automatic transmission, air conditioning, power steering and brakes with cloth interiors. All three vehicles were assembled at Ford Motor Company's Pico Rivera, California plant on the following dates and times:

Vehicle	VIN	Assembly Date	Time
A (control)	6J62H169231	6/7/76	08:00
C (oven)	6J62H169232	6/7/76	16:00
B (dyno)	6J62H169233	6/8/76	08:00

The vehicles were randomly assigned to the treatments they were to receive.

The vehicles were received at AESi test facilities in Westminster, California on June 11, 1976 at which time it was noticed that one of the vehicles (VIN: 6J62H169233) was equipped with a vinyl interior. This car was returned to Ford on June 14 to have the vinyl exchanged for a cloth interior. The mileage on these vehicles when received were as follows:

VIN: 6J62H169231 - 34.0 miles
VIN: 6J62H169232 - 45.5 miles
VIN: 6J62H169233 - 34.4 miles

Each vehicle underwent the same preparation procedure prior to the beginning of testing. This preparation included the removal or plugging of the items as follows.

Items Removed	Items Plugged
- Fuel tank	- Valve cover vent
- Carburetor	- Fuel pump
- Evap. Canister	- All vacuum hoses
- Evap. Hoses	- Vapor hoses
- Spare tire	- Fuel lines
- Trunk mats	- PCV
	- Intake manifold
	- Tailpipe
	- Dipstick tubes - engine
	- Dipstick tubes - transmission
	- Dipstick tubes - P/S
	- Radiator over-flow tube
	- Differential vent
	- Transmission vent

All fuel and vapor lines were purged with nitrogen at 5 psi for 15 minutes. The windshield washer containers were checked, but not removed since all units were found to contain water. A check for oil leaks and spills was made. All leaks were repaired and all spills were cleaned. The catalytic converters and mufflers were inspected for possible drainholes which would require plugging, however, none were found.

Vehicle preparation for the LA-4 driving cycle prior to the hot soak evaporative emission test included reinstalling the vehicle's carburetor and connecting to an external fuel supply consisting of a long flexible fuel hose and a Chevrolet Vega fuel tank with integral fuel pump. Electric choke connector, vacuum advance, EGR and PCV were all reconnected to the carburetor, and the plug in the valve cover vent was removed. The same procedure was followed for the dyno vehicle when being prepared for its series of daily LA-4 cycles. In addition the air cleaner was installed complete with EGR back-pressure valve. The plugs in the differential and transmission vents and power steering filler tube were also removed.

After the LA-4 Cycle the vehicle was re-prepared for the hot soak by removing the carburetor, sealing the intake manifold opening, and plugging the various hoses and vents before being moved to the SHED. An elapsed time of 6 minutes was allowed for this operation. A sniff test was made with the enclosure FID to identify any fuel spills. The vehicle was then moved into the enclosure, and after the enclosure was sealed the initial readings were taken. This 6 minute time period was maintained throughout the the duration of the task. The allowed time of 6 minutes was a nominal value derived by a series of practice runs on a non-test vehicle.

A thermocouple was taped to the inside of the oven vehicle so interior temperatures could be recorded during the 12-hour bake period.

Midway into the testing program and at the request of EPA, three more vehicles were procured from a Ford dealer. The dealer acted immediately on our request and located three more nearly identical vehicles. The only changes from the first three vehicles were that these new vehicles had vinyl roofs and that they were produced on three consecutive days. A description of these vehicles is as follows: Three 1976 Ford LTD 2 doors with vinyl roofs. Each was equipped with 400-2V engines (belonging to the 351m/400 catalyst, EGR/air family), automatic transmissions, air conditioning, power steering and brakes with vinyl interior. All these vehicles were assembled at Ford Motor Company's Pico Rivera, California plant on the following dates and times:

Vehicle	VIN	Assembly Date	Time
E (dyno)	6J68S167818	6/16/76	15:00
F (oven)	6J68S167836	6/17/76	17:00
D (control)	6J68S167817	6/18/76	08:00

The mileage on these vehicles as received are as follows:

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VIN:	6J68S167817	-	3.3 miles
VIN:	6J68S167818	-	2.2 miles
VIN:	6J68S167836	-	3.4 miles

It can be noted that vehicle D (VIN: 6J68S167817) was equipped with a full vinyl roof while vehicles E & F had half vinyl roofs.

These vehicles underwent the same preparation procedures as the first 3 vehicles including both driving and testing preparations.

3.4 FACILITIES AND EQUIPMENT

3.4.1 Evaporative Emissions Enclosure

An AESi designed and fabricated SHED (Sealed Housing for Evaporative Determinations), as illustrated by Fig. 3-1, was used to perform the Evaporative Emission Test Program. The SHED was constructed of light-gauge aluminum panels providing good heat dissipation. Panels were bolted together at formed flanges, and the SHED was fitted with windows, doors, and a ceiling of DuPont Tedlar Polyvinyl Fluoride Film. The SHED interior dimensions are approximately 10 feet wide by 21 feet long by 8 feet high, having a total volume of 1695.3 $ft.^3$. Specially designed doors seal completely upon closing, rendering the enclosure leakproof. Specifications for the SHED were in agreement with all requirements stipulated in the SAE J171a Evaporative Emission Test Procedure. A Beckman Model 400 Flame Ionization Detector was used in conjunction with the SHED to measure hydrocarbon evaporative emissions. A Leeds and Northrup Speedomax Temperature Recorder was used to record ambient temperature inside the SHED.

3.4.2 Bake Oven

The Oven used for the required baking of vehicles C and F is located at P & R Auto Painting Center, 7601 Garden Grove Blvd., Garden Grove, California, which is a distance of 2.3 miles from the AESi test facilities. It was manufactured by West Coast Spray Booth of Bell Gardens, California and heated by a 200,000 BTU Gaffers & Sattler, Inc. Gas Fired Furnace. As illustrated by Fig. 3-2, the oven dimensions are 25 ft x 14 ft. x 9 ft. The oven is equipped with one drive-in door and one personnel door, a 12" purge fan, one cut-off microswitch located on each door to control the fan and heater. The heater is pre-set (stipulated by prevailing safety requirements) to approximately 125°F. The ambient temperature inside the oven and inside the test vehicle were continuously recorded. A typical temperature recording during the vehicle bake period is illustrated by Figure 3-3, showing the oven ambient temperature and temperatures recorded in the vehicle interior.

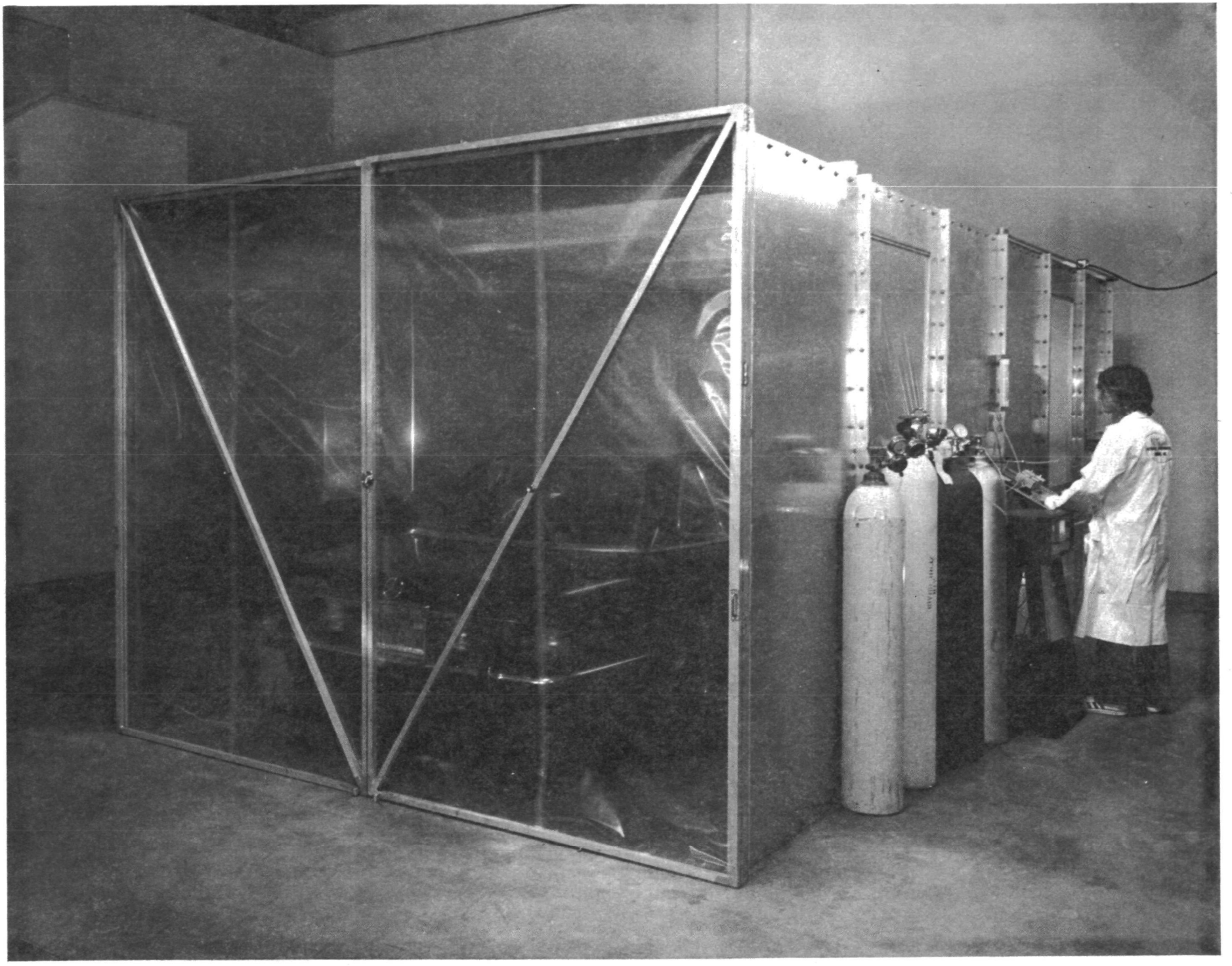

FIGURE 3-1. AESi SEALED HOUSING FOR EVAPORATIVE DETERMINATIONS (SHED)

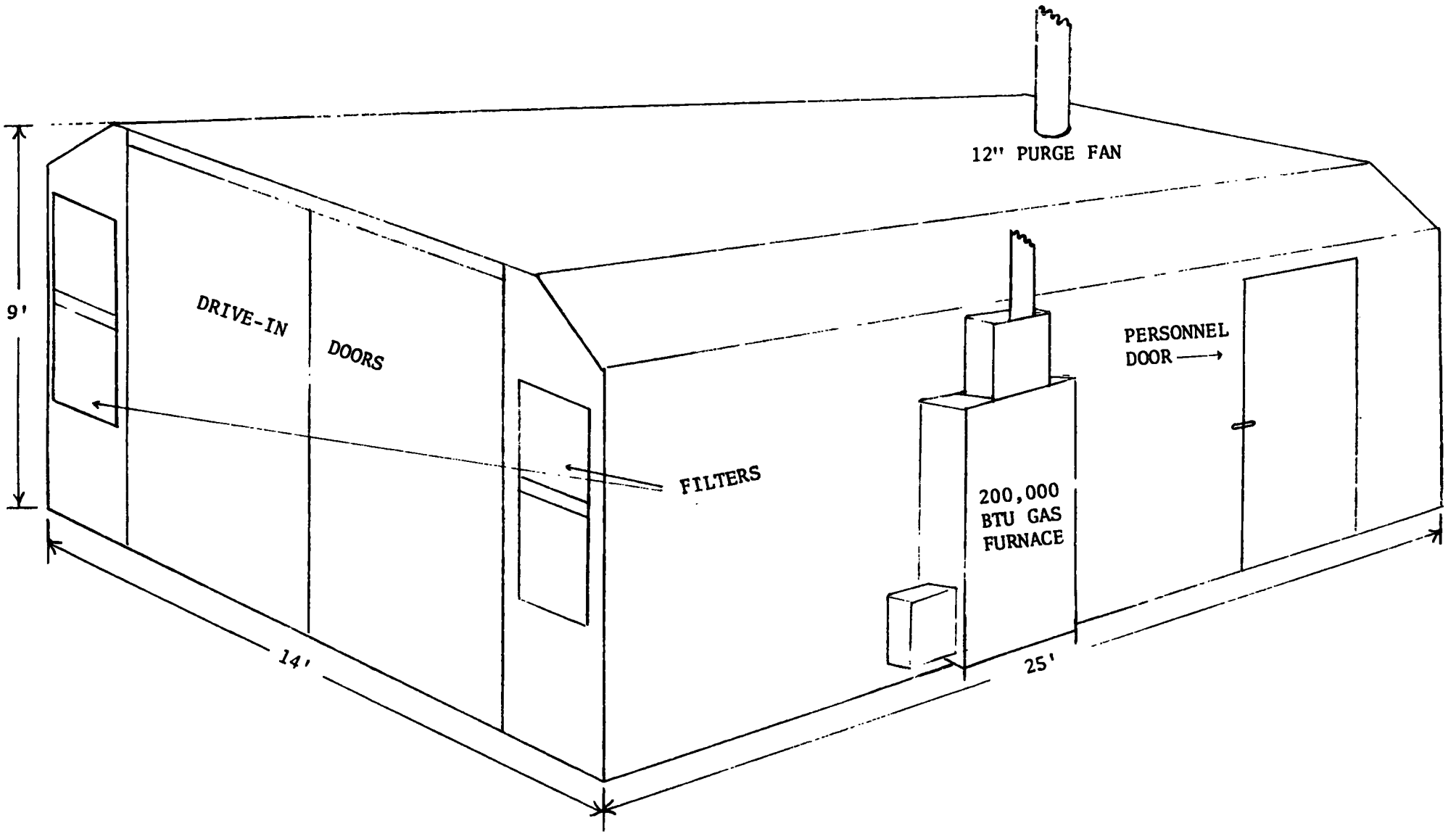

Figure 3-2. Vehicle Bake Oven

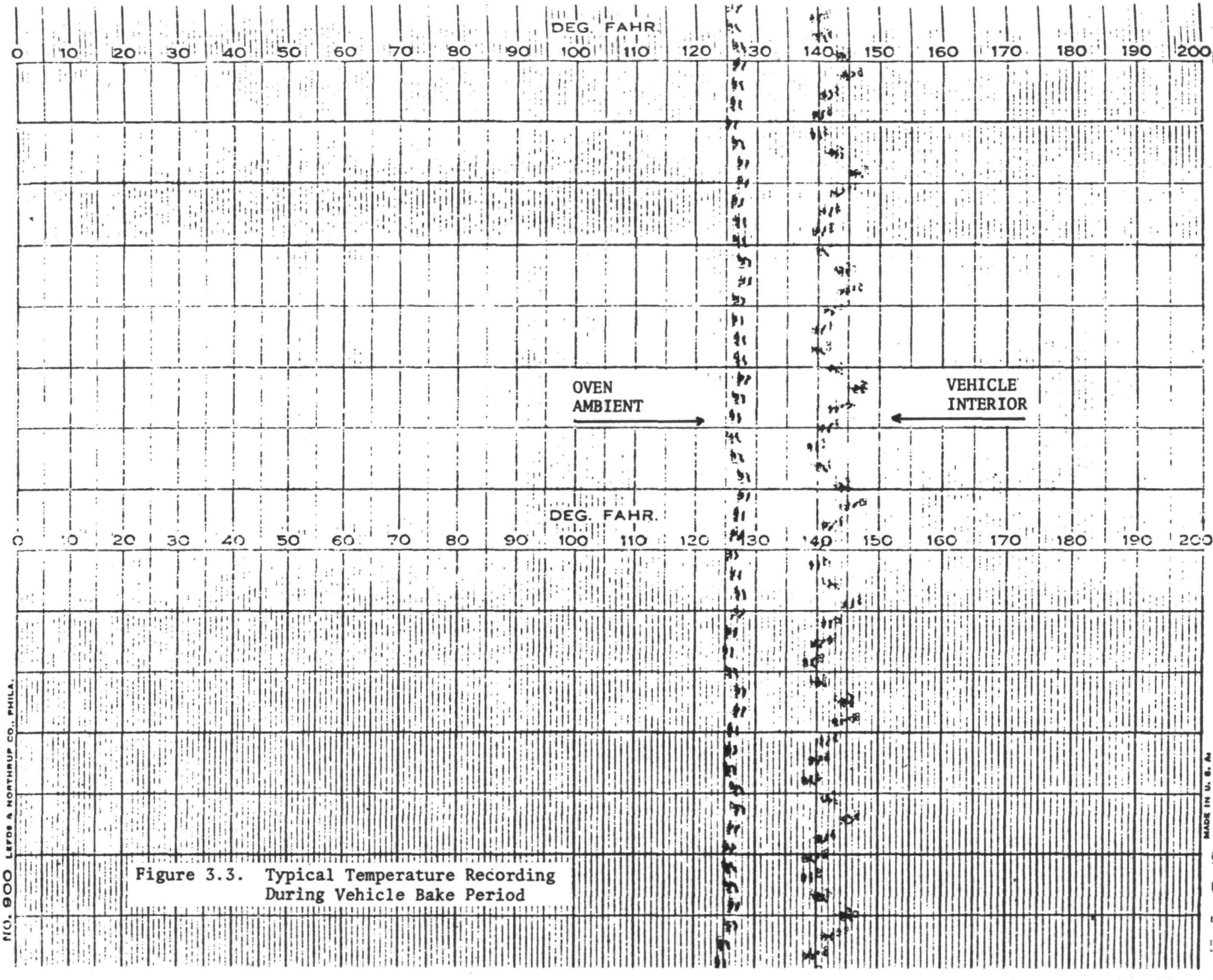

Figure 3.3. Typical Temperature Recording During Vehicle Bake Period

3.4.3 Gas Chromatography/Mass Spectrometry

The Gas Chromatography/Mass Spectrometry Tests of new car non-fuel evaporative emissions was conducted by West Coast Technical Service, Inc., of Cerritos, California. Founded in 1965 as a mass spectrometry laboratory, WCTS is a versatile analytical service organization. WCTS' 3000 ft^2 laboratory space is fully equipped for chemical analysis with special instrument capabilities as follows:

- Mass Spectrometry
  Gas - Liquid - Solid capability
  Mass Range: m/e 1-1800
  Resolution: maximum of 1 part in 2500
  Detectability: 1 ppb ultimate
  Direct Ion Introduction

- Gas Chromatography
  Sample: Gas, liquid or solid
  Injector Temperature control for flash vaporization
  Column Capabilities: Glass or metal columns, capillary or packed columns
  Detectors: Differential flame ionization and thermal conductivity
  Isothermal and Temperature Programming to 350° C.
  Direct Integration

- Combined Gas Chromatography - Mass Spectrometry
  Sensitivity: 1×10^{-9} grams/second
  Minimum scan time: 1 second
  Capillary and SCOT columns
  Peak detection by total ion monitor

- Thermal Analysis

  Temperature Ranges:

  Thermogravimetric Analysis 25°C to 1200°C.

  Differential Thermal Analysis- 150°C to 1600°C.

  Differential Scanning Calorimetry - 150°C to 600°C.

  Heating Rates - 0.5°C to 100°C per minute

  Pressure Ambient to High Vacuum

  Any noncorrosive or nonexplosive atmospheres

- Infrared Spectrophotometry

  Spectral Range - 4000 CM^{-1} to 625 CM^{-1}

  (2.5 to 15 microns)

  Scale Expansion - 2.5 and 10

  Micro sample capability

- Atomic Absorption

  Percent to parts per billion range

  Lamps for most metals on hand

  Flame emission

- UV-Visible Spectrophotometry

  Range: 200nm to 975 nm

  Resolution: Maximum of 1 part in 2500

3.5 TEST PROCEDURES

3.5.1 Evaporative Emissions Test Procedure

In this program only non-fuel evaporative emissions were measured using the SAE Sealed Housing for Evaporative Determination (SHED) method and in accordance with SAE J171a Appendix C entitled "Measurement Procedure for Car Background HC Emission." Vehicle preparation for this test included removal of the fuel tank and carburetor, purging the fuel, vapor lines, and fuel pump with nitrogen and then plugging all entrances and exits. All other exits from the engine and exhaust system which could supply a source of hydrocarbons were plugged.

Prior to each test, the enclosure was purged, instrumentation checked, and the mixing blower was turned on. A visual check of the test vehicle was made to ensure all required plugs were installed and no oil leaks existed. Two or three minutes before the scheduled start time of the cold test, the Flame Ionization Detector (FID) was zeroed and spanned and the test vehicle was pushed to the front of the enclosure. Then the temperature recorder was started, the vehicle pushed into the enclosure, and the enclosure sealed. At this point the initial FID, temperature and barometric pressure readings were taken and recorded on the Evaporative Emission (SHED) Data Sheet - EPA (XAA-502) 12-74. This data sheet was supplied by EPA and was completed for each vehicle test. It included cold/hot soak readings in addition to vehicle I.D., model, model year, inertia, actual dyno hp, engine information, odometer reading, operator, test date, wet bulb (°F), dry bulb (°F), test time, evaporative test number, etc. During the 60 minute cold soak, the SHED enclosure temperatures and hydrocarbon emission levels were recorded as well as the barometric pressure at 10 minute intervals. At 50 minutes into the test, gas samples were drawn from the enclosure for the Gas Chromatography/Mass Spectrometry Analysis. At the end of the cold soak period, final enclosure readings were taken and recorded, the vehicle was removed from the enclosure and pushed onto the chassis dynamometer. The dynamometer was previously warmed up with a non-test vehicle

and inertia set at 4500 lbs and horsepower at 12.7. At this point, the carburetor connected to an external fuel supply was reinstalled and the tailpipe unplugged along with all other atmospheric openings required for engine operation. While the test vehicle ran the single LA-4 cycle, which was recorded on a driver's aid, the enclosure was being purged for the hot soak. Upon completion of the driving cycle, the vehicle was moved off the dynamometer where the engine was then shutdown. The time was recorded at this point and at the point of initial enclosure atmosphere readings after enclosure sealing. A six minute elapsed time for this operation was allowed by EPA. During this allowed time the carburetor was removed and inlet block-off plate installed, the tailpipe was plugged along with all unplugged atmospheric openings that were necessary for engine operation. The vehicle was then pushed to the front of the enclosure where a 15 second (approximately) sniff sample of the engine compartment was taken with the FID. At 5 minutes 15 seconds the vehicle was pushed into the enclosure, and then the enclosure was sealed. The initial readings of hydrocarbon, temperature and barometric pressure were recorded at this time. As in the cold soak, enclosure atmopsheric conditions were taken and recorded at 10 minute intervals and at 50 minutes into the test, gas samples were taken for the Gas Chromatography/Mass Spectrometry. At 60 minutes the final hydrocarbon emission level, temperature and barometric pressure were recorded and the vehicle removed from the enclosure. The test procedure is illustrated in Figures 3-4 and 3-5.

An Enclosure Qualification Test was performed before both series of tests were made in accordance with EPA's Recommended Practice, dated April, 1976.

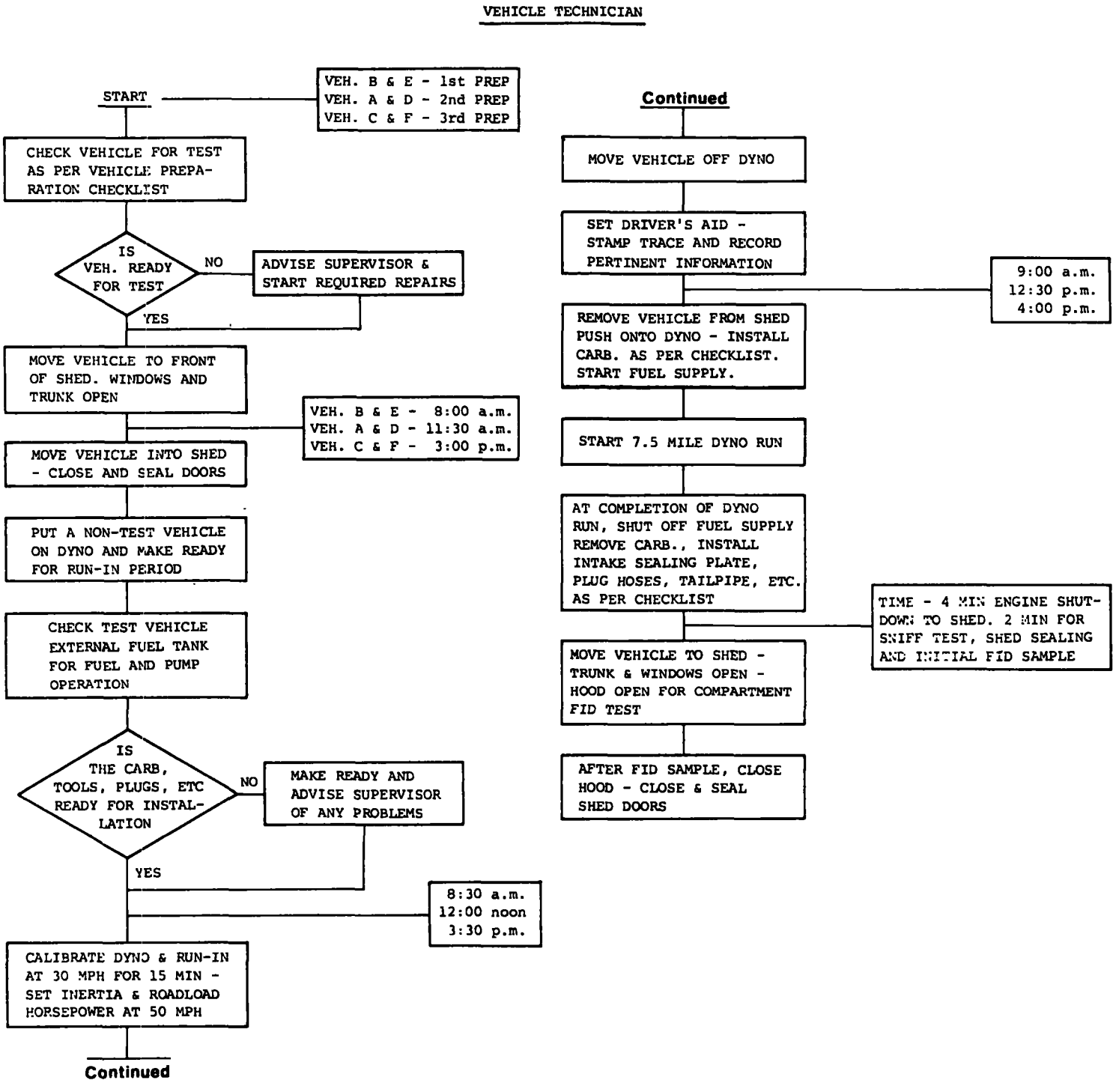

Figure 3-4. Non-Fuel Evaporative Emission Procedure – Vehicle Technician

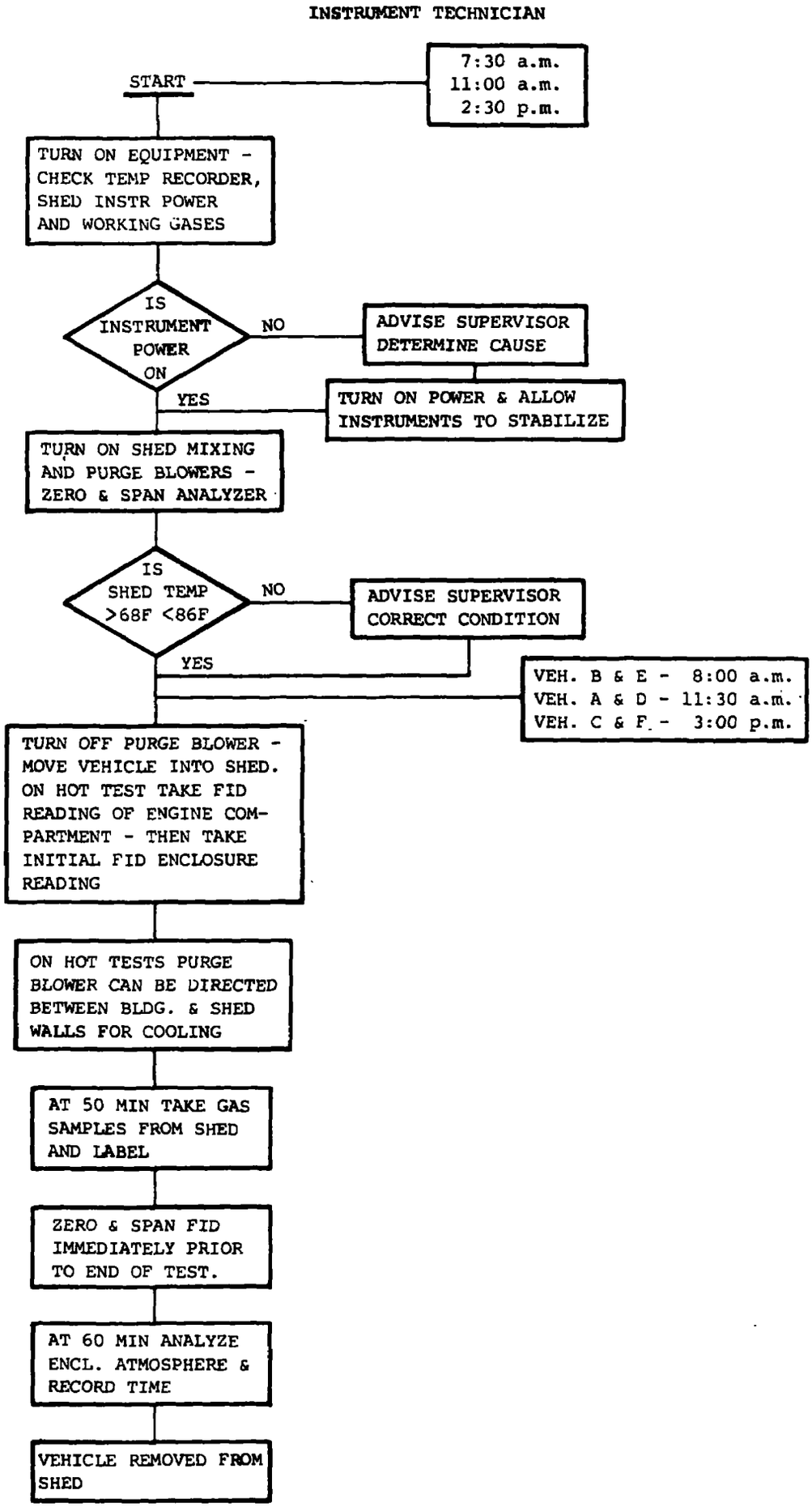

Figure 3-5. Non-Fuel Evaporative Emission Procedure — Instrument Technician

3.5.2 Gas Chromatograph Test Procedure

To study the feasibility of getting quantitative data, a standard gas mixture was prepared containing equal parts by weight of methylene chloride, methy ethyl ketone, 1,1,1-trichloroethane, p-xylene, and an aliphatic hydrocarbon mixture containing primarily n-decane, n-undecane, and n-dodecane. Three separate samples were taken at the concentration levels equivalent to 1, 3 and 6 grams given by EPA as the expected levels to be found during the testing program. This was accomplished by weighing these amounts (1, 3 and 6 grams) of the gas standard into beakers. For each sample, a beaker was placed on a hot plate inside the enclosure, a corresponding shot of propane in weights of 0.2, 0.6 and 1.2 grams was introduced through an external port. The circulation fan inside the enclosure was turned on when the doors were sealed. After 15 minutes the FID showed a stable reading. Samples were taken from the enclosure with glass bottles and tenax tubes containing a porous organic polymer. During the first few tests several different sized samples were taken ranging from 0.1 to 1.0 liters using a hand operated 100 milliliter Drager Model 31 pump. One stroke of this bellows type pump equals 100 milliliters. The grab samples were pulled through 125 and 250 milliliter bottles for 3 minutes at 5 CFH and then capped. All samples were labeled as to test number, initial and final FID readings; temperature and barometric pressure at time of sample. A 500 milliliter background sample was also taken for identification purposes by purging the enclosure, sealing it, and allowing it to sit with the mixing blower on for 15 minutes before taking sample. In a further attempt to identify the hydrocarbon vapors, three additional tests were run where one hour samples were taken by using a pump flow rate of 8 CFH to pull the sample through a large drying column filled with "Drierite" (calcium sulfate), then passing the gasses through a small impinger trap cooled in a dry ice-acetone slush bath. Other tenax samples were taken at the rate of 1 liter/min. for the last 50 minutes of the soak. Gas samples were discontinued after June 25 at the request of EPA due to the low total hydrocarbon concentrations inside the enclosure.

3.5.3 Scheduling

The following is a summary of the daily scheduling of each vehicle as illustrated by Fig. 3-6.

The "dyno" vehicle (designated B & E) started the daily tests since it required a technician for the entire working day. It was given a visual inspection to ensure all necessary plugs were in place and that there was no evidence of oil leaks. Each day at 0800 hours, the vehicle was pushed into the enclosure for the cold soak portion of the evaporative emission test. Upon completion of the cold soak, the vehicle was pushed from the enclosure onto the dynamometer where the auxiliary fuel system was connected by installing the carburetor. Then an LA-4 cycle was run. Within six minutes after the completion of the LA-4, the auxiliary fuel system was removed and the vehicle was sealed in the enclosure for the beginning of the hot soak portion of the test. After the hot soak, the vehicle was prepared for its series of LA-4 cycles which started at 1130 hours and lasted 6 hours, or until 1730 hours. After running on the dyno, the auxiliary fuel system was removed, the vehicle lines were plugged as required for testing, and the vehicle was moved to the soak area.

The "control" vehicle (designated A & D) was visually inspected and then placed in the enclosure at 1130 hours to undergo an evaporative emission test. At the conclusion of the complete tests, (approx. 1415 hours) the control vehicle was returned to the vehicle soak area. This vehicle received no other treatment and was only driven for the one LA-4 (required prior to the hot soak test) each day.

The "oven" vehicle (designated C & F) received the same visual inspection and at 1500 hours was moved into the enclosure for the evaporative emission

test which was completed at approximately 1745 hours. At 1800 hours, a tow truck picked up the vehicle and delivered it to the bake oven location at P & R Auto Painting Center, 7601 Garden Grove Blvd., Garden Grove, California (a distance of 2.3 miles), where at 1830 hours the vehicle began its 12 hour bake period. At 0630 hours the following day, the tow truck picked up the vehicle and delivered it back to the AESi facility where it entered the vehicle soak area for the remainder of the soak period. This vehicle was only driven during the evaporative emission tests.

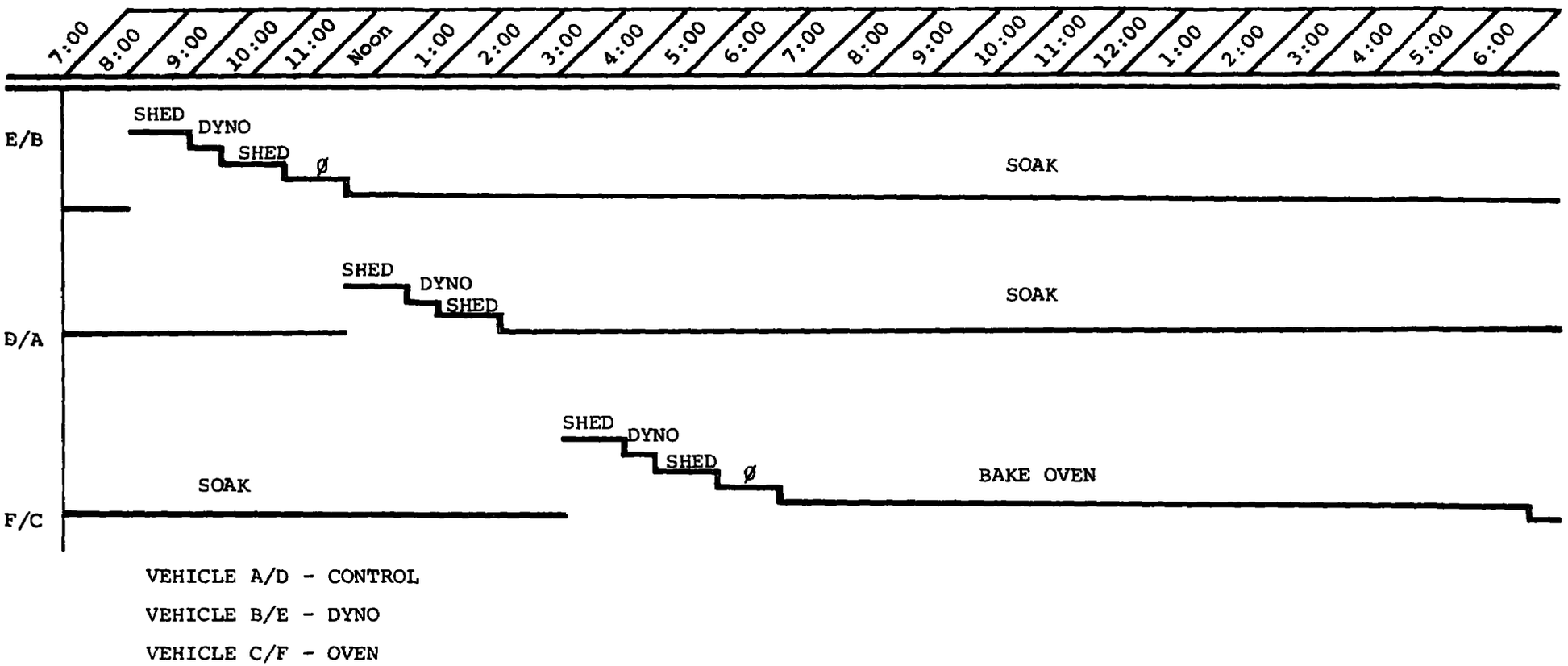

Figure 3-6. EPA Non-Fuel Evaporative Emission Test — Vehicle Schedule

4.0 TEST RESULTS

4.1 EVAPORATIVE EMISSION RESULTS

The non-fuel evaporative emission test results for the two groups of test vehicles are presented in Tables 4-1 and 4-2 as well as Figures 2-1 and 2-2. Tables 4-1 and 4-2 present the mass hyrdrocarbons measured in both the cold and hot soak portions of the tests as well as the total mass hydrocarbons per test. Figures 2-1 and 2-2 present the total measured mass hydrocarbons plotted by number of days after being built.

Every vehicle tested experienced a reduction in total hydrocarbons with the passing of time. The "dyno" vehicles and the "oven" vehicles both showed a more rapid decline than the "control" vehicles. All of the SHED test results were relatively low compared to what was expected by EPA.

Table 4.1. Non-Fuel Evaporative Emission Test

DAILY MASS HYDROCARBONS PER VEHICLE

Date	Test #	Veh.	Cold Soak	Hot Soak	Total
6/15	1	B	.337	1.058	1.395
6/15	2	A	.161	.631	.792
6/15	3	C	.234	.765	.999
6/16	4	B	.193	.521	.714
6/16	5	A	.101	.429	.530
6/16	6	C	.182	.560	.742
6/17	7	B	.133	.343	.476
6/17	8	A	.117	.393	.510
6/17	9	C	.117	.413	.530
6/18	10	B	.103	.313	.416
6/18	11	A	.088	.431	.519
6/18	12	C	.102	.394	.496
6/19	13	B	.104	.241	.345
6/19	14	A	.088	.399	.487
6/19	15	C	.094	.340	.434
6/20	16	B	.074	.184	.258
6/20	17	A	.076	.342	.418
6/20	18	C	.102	.310	.412
6/21	19	B	.058	.164	.222
6/21	20	A	.087	.369	.456
6/21	21	C	.073	.222	.295
6/22	22	B	.044	.205	.249

Table 4.2. Non-Fuel Evaporative Emission Test

DAILY MASS HYDROCARBONS PER VEHICLE

Date	Test #	Veh.	Cold Soak	Hot Soak	Total
6/24	23	E	.139	.500	.639
6/24	24	D	.115	.536	.651
6/24	25	F	.220	1.002	1.222
6/25	26	E	.047	.338	.385
6/25	27	D	.130	.566	.696
6/25	28	F	.115	.509	.624
6/26	29	E	.050	.229	.279
6/26	30	D	.130	.564	.694
6/26	31	F	.043	.321	.364
6/27	32	E	.043	.169	.212
6/27	33	D	.123	.557	.680
6/27	34	F	.058	.233	.291
6/28	35	E	.043	.131	.174
6/28	36	D	.101	.451	.552
6/28	37	F	.043	.166	.209
6/29	38	E	.021	.097	.118
6/29	39	D	.058	.295	.353
6/29	40	F	.014	.123	.137
6/30	41	D	.072	.359	.431
6/30	42	F	.022	.110	.132
7/1	43	D	.021	.303	.324

4.2 GAS CHROMATOGRAPHY RESULTS

The results from gas chromatography and gas chromatography/mass spectrometry analyses are summarized in Table 1. The relative concentrations and identity of each component is listed. The composition of the gas does not appear to change very much with time or between test vehicles. The identity for each component was obtained from GCMS analysis of large volume samples. In addition to the aromatic compounds which predominated the mixture, alkanes and some alkenes, primarily in the range of C_{10} through C_{12}, were observed. However, these were not present in high enough concentration to fully characterize. Samples analyzed using a DC-200 column gave excellent separation of the major components. "Grab" samples showed that there were no detectable C_1 through C_6 hydrocarbons produced. The detection limit was less than 0.1 grams of propane in the SHED. Typical gas chromatograph and graphs are illustrated by Figures 4-5 through 4-9.

The following table relates the test number to the vehicle and test date:

Test No.	Date Tested	Vehicle Code	Type
4	6/16	B	Dyno
5	6/16	A	Control
6	6/16	C	Oven
7	6/17	B	Dyno
8	6/17	A	Control
9	6/17	C	Oven
21	6/21	C	Oven
23	6/24	E	Dyno
24	6/24	D	Control
25	6/24	F	Oven
26	6/25	F	Dyno
27	6/25	D	Control
28	6/25	F	Oven

Table 1 Weight Percent

	Test #4 Cold	Test #4 Hot	Test #5 Cold	Test #5 Hot	Test #6 Cold	Test #6 Hot
Benzene	6.3	8.5	------	3.1	5.7	6.5
Toluene	28.9	25.6	43.0	56.0	33.0	35.7
Xylene	8.8	8.0	9.6	10.9	10.8	11.6
Xylene + Styrene + Alkane *	6.8	5.6	5.5	4.5	5.9	4.0
Methylethylbenzene	5.8	3.2	4.1	5.2	3.9	4.0
Trimethylbenzene	1.6	2.2	2.4	3.1	2.1	2.2
C_4 Substituted Benzene	0.6	------	1.1	1.5	1.6	0.6
Dimethylethylbenzene	0.8	------	1.1	1.3	1.2	0.7
Total Other Components	40.4	46.9	33.2	14.4	35.8	34.7

	Test #7 Cold	Test #7 Hot	Test #8 Cold	Test #8 Hot	Test #9 Cold	Test #9 Hot
Benzene	1.1	1.1	2.0	4.6	0.3	3.8
Toluene	33.1	22.2	31.1	34.1	29.1	34.8
Xylene	15.6	11.4	16.9	17.0	15.2	17.6
Xylene + Styrene + Alkane *	16.2	14.5	14.8	8.8	10.0	7.3
Methylethylbenzene	6.4	12.5	7.9	7.3	7.5	5.9
Trimethylbenzene	2.5	10.3	5.4	5.1	6.4	3.4
C_4 Substituted Benzene	------	5.4	3.9	2.6	3.2	1.5
Dimethylethylbenzene	------	2.0	2.6	2.7	3.2	1.9
Total Other Components	25.1	20.6	15.4	17.8	25.1	23.8

* Probably a C_{10} or C_{11} alkane

	Test #21 Hot (1)	Test #23 Hot (1)	Test #24 Hot (1,2)	Test #25 Hot (1)
Benzene	0.2	1.5	------	1.6
Toluene	11.4	13.8	------	12.8
Xylene	25.1	16.0	2.4	27.4
Xylene, Styrene, Alkane *	11.1	10.4	------	8.8
Methylethylbenzene	15.1	13.4	12.1	12.3
Trimethylbenzene	7.6	16.0	17.7	12.2
C_4 Substituted Benzene	8.3	8.1	21.2	6.6
Dimethylethylbenzene and alkane	8.9	8.8	22.1	7.5
Total Other Components	12.3	12.0	24.5	10.8

(1) large sample analyzed by GCMS
(2) bad sample

	Test #26 Hot	Test #27 Hot	Test #28 Hot	Back-ground on 6/16/76	Back-ground on 6/25/76
Benzene	------	1.5	------	3.2	------
Toluene	4.9	17.1	22.8	14.3	------
Xylene	6.9	18.2	16.7	5.4	------
Xylene, Styrene, Alkane *	8.0	7.2	8.7	6.6	------
Methylethylbenzene	7.6	9.2	6.7	------	------
Trimethylbenzene	10.8	9.2	6.8	------	------
C_4 Substituted Benzene	12.3	6.6	5.5	------	------
Dimethylethylbenzene	11.5	8.5	4.4	------	------
Total Other Components	38.0	22.5	28.4	70.5	100

* Probably a C_{10} or C_{11} alkane

The chromatograms are enclosed for your reference. If we can be of any further service, please do not hesitate to contact us.

Respectfully submitted,

WEST COAST TECHNICAL SERVICE INC.

D.J. Northington

D.J. Northington, Ph.D.
Assistant Technical Director

DJN/kd

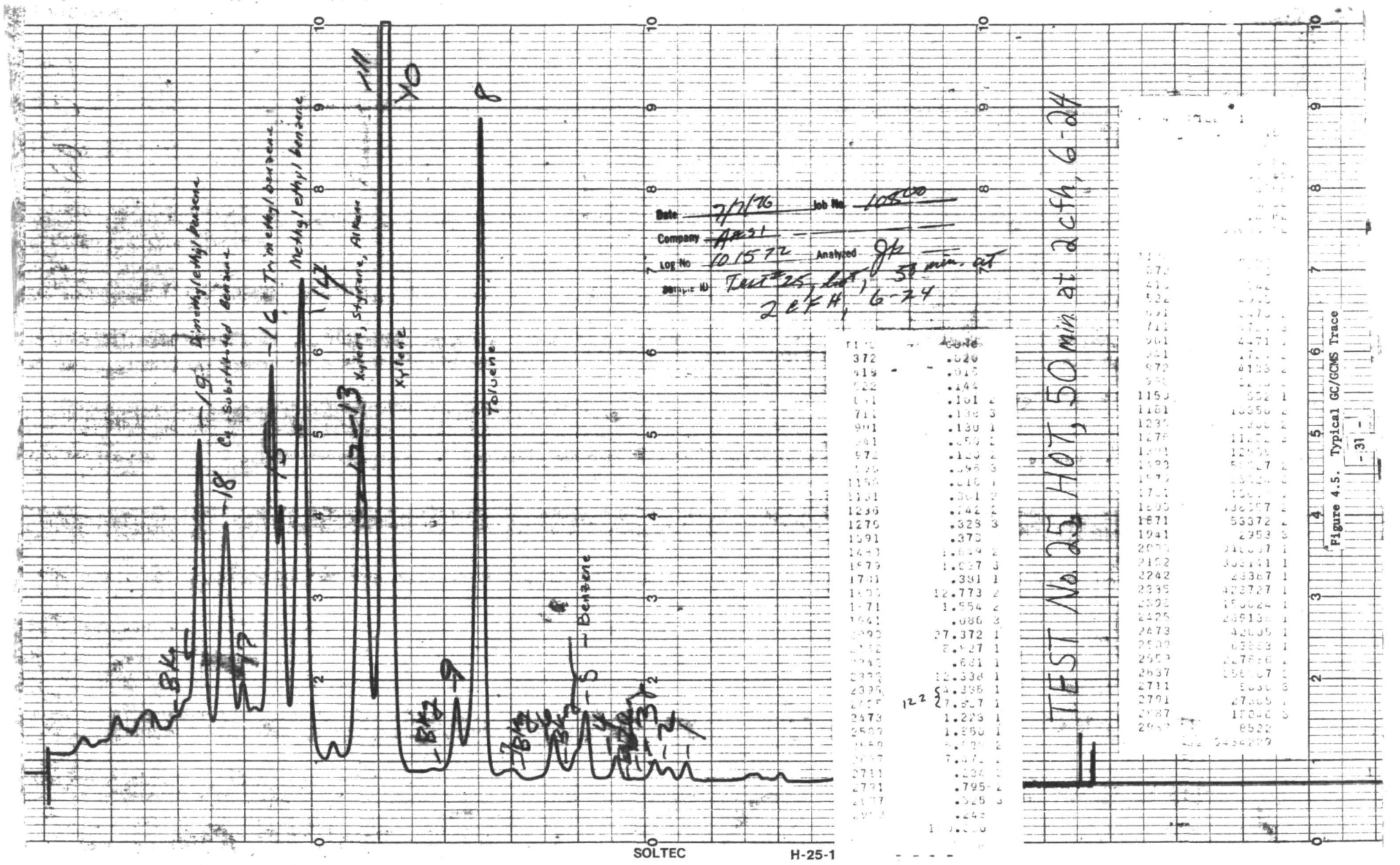

Figure 4.5. Typical GC/GCMS Trace

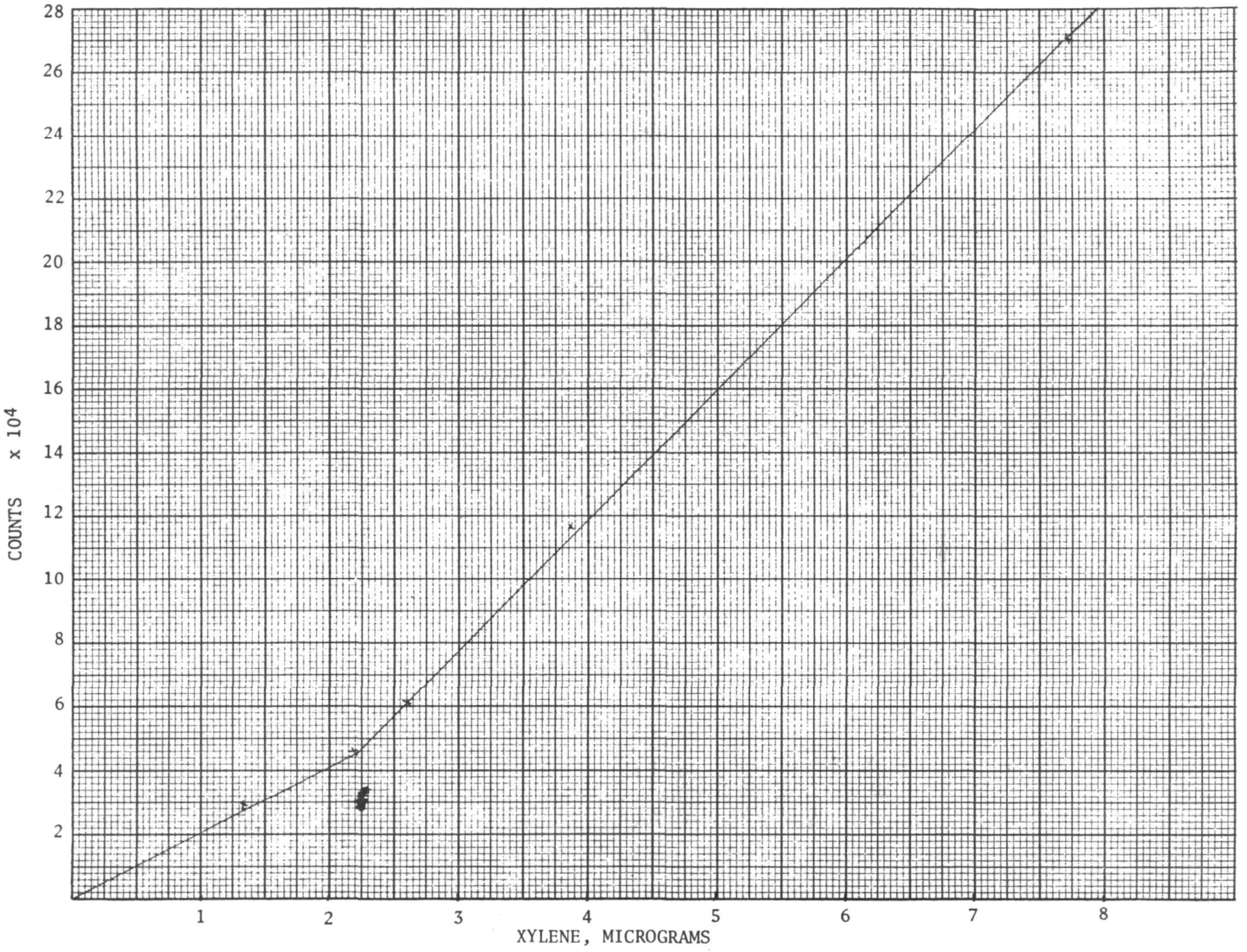

Figure 4-6. Xylene (Gas Standard Calibration Curve)

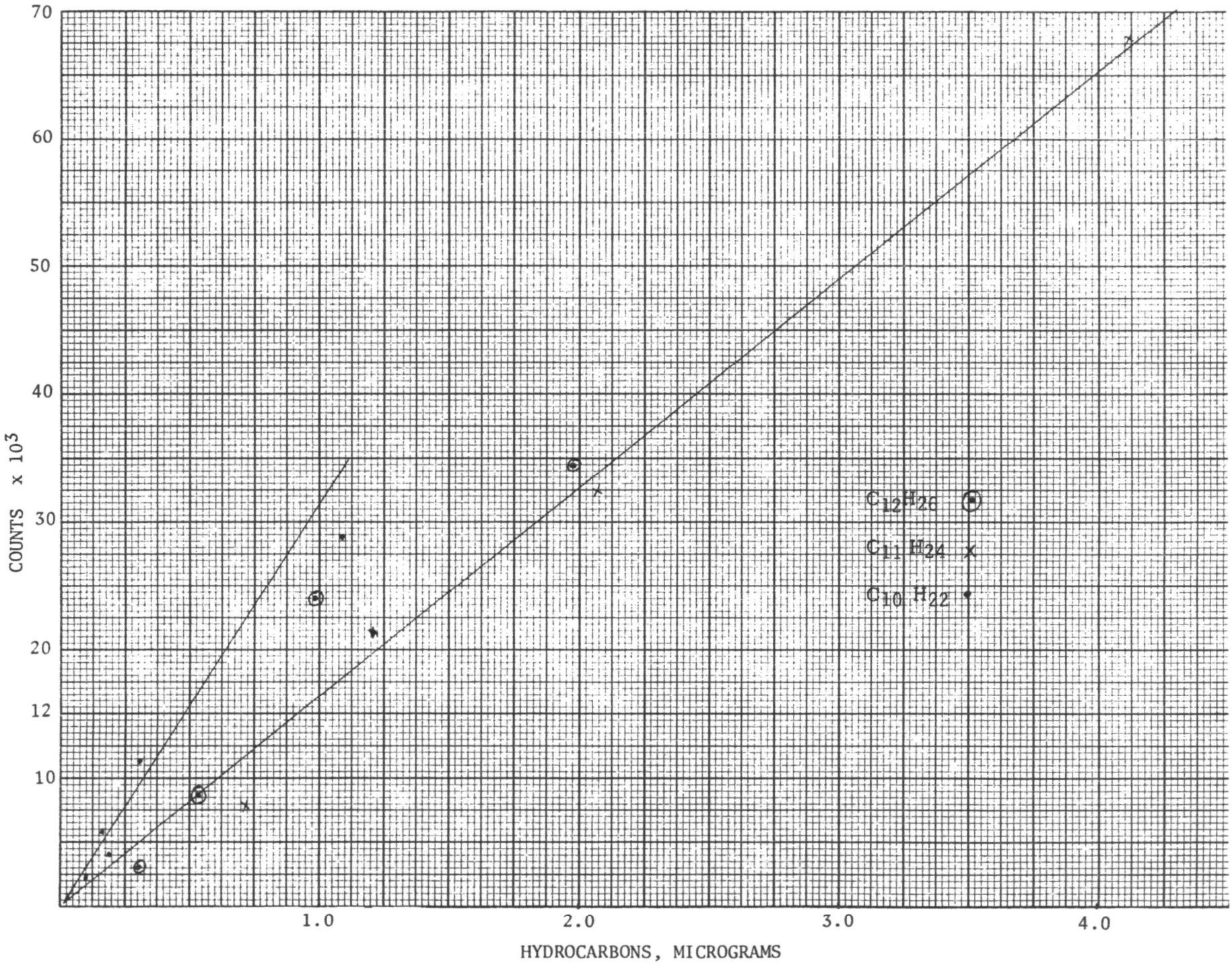

Figure 4-7. Hydrocarbon (Gas Standard Calibration Curve)

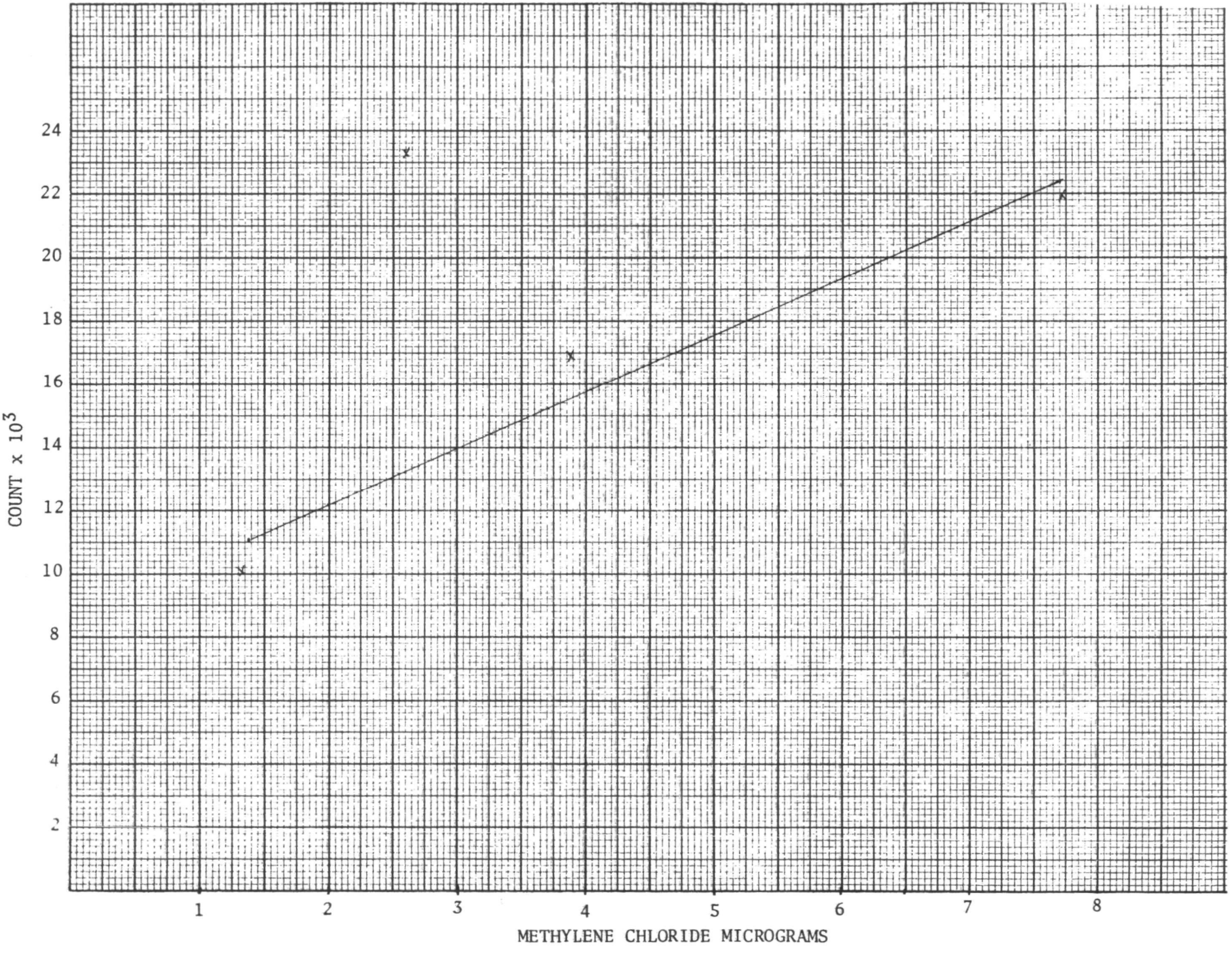

Figure 4-8. Methylene Chloride (Gas Standard Calibration Curve)

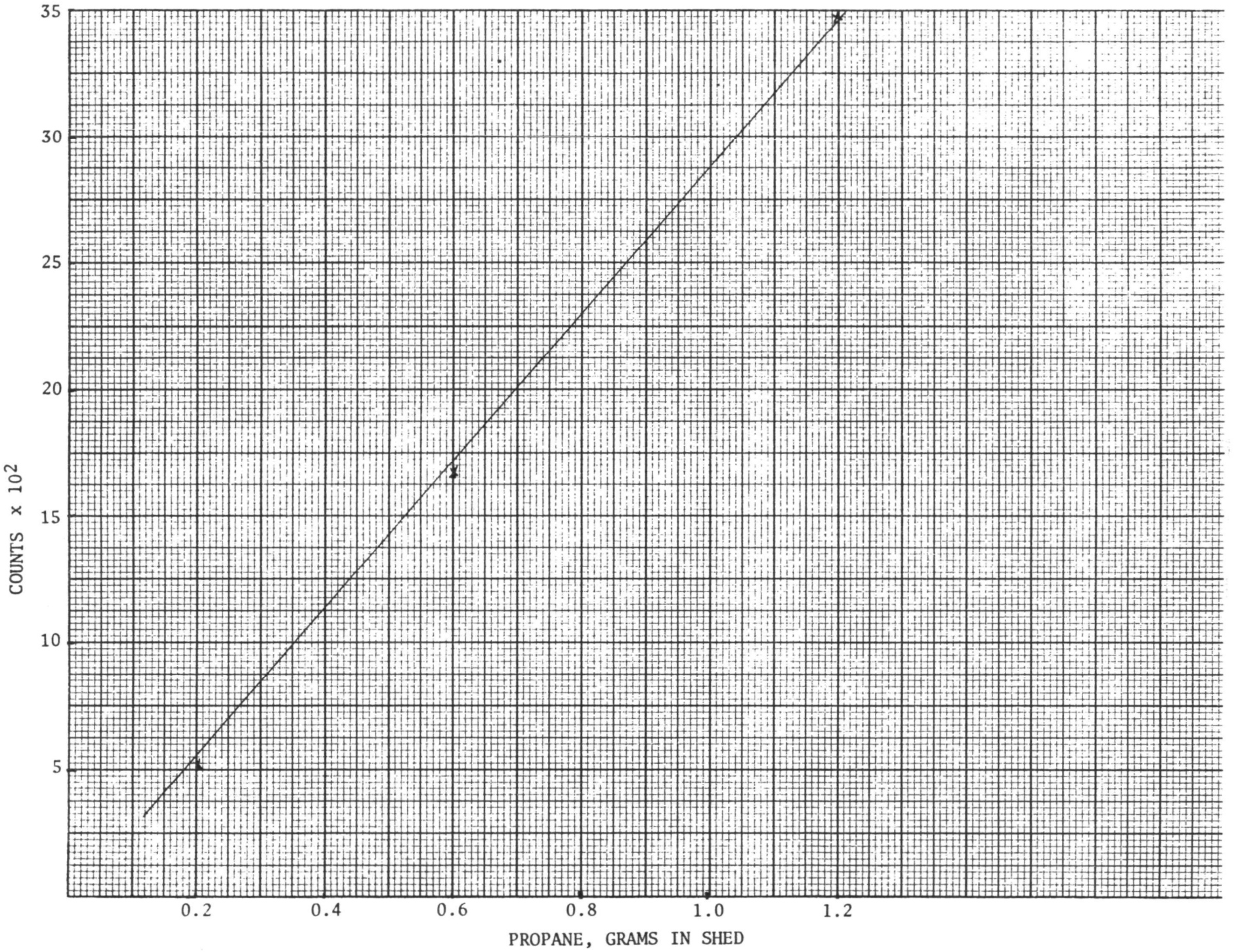

Figure 4-9. Propane (Gas Standard Calibration Curve)

APPENDIX A

RULE 442. Usage of Solvents

(a) A person shall not discharge organic materials into the atmosphere from equipment in which organic solvents or materials containing organic solvents are used, unless such emissions have been reduced by at least 85% or to the following:

(1) Organic materials that come into contact with flame or are baked, heat cured or heat polymerized, are limited to 1.4 kilograms (3.1 pounds) per hour not to exceed 6.5 kilograms (14.3 pounds) per day.

(2) Organic materials emitted into the atmosphere from the use of photochemically reactive solvents are limited to 3.6 kilograms (7.9 pounds) per hour, not to exceed 18 kilograms (39.6 pounds) per day, except as provided in subsection (a) (1). All organic materials emitted for a drying period of 12 hours following their application shall be included in this limit.

(3) Organic materials emitted into the atmosphere from the use of non-photochemically reactive solvents are limited to 180 kilograms (396 pounds) per hour not to exceed 1350 kilograms (2970 pounds) per day, except as provided in subsection (a) (1). All organic materials emitted for a drying period of 12 hours following their application shall be included in this limit.

(b) Equipment designed for processing a continuous web, strip or wire which emit organic materials shall be collectively subject to the limitations stated in subsection (a).

(c) Emissions of organic materials into the atmosphere required to be controlled by subsection (a) shall be reduced by:

(1) Incineration, provided that 90 percent or more of the carbon in the organic material being incinerated is oxidized to non-organic materials, or

(2) Incineration, provided that the concentration of organic material following incineration is less than 50 ppm, calculated as carbon and with no dilution or

(3) Absorption, or

(4) Processing in a manner determined by the Air Pollution Control Officer to be not less effective than (1) or (3) above.

(d) A person shall not use any organic solvent containing a total of 4 percent or more by volume of the materials described in Rule 102 under PHOTOCHEMICALLY REACTIVE SOLVENT for the commercial cleaning of garments and fabrics unless the emission of organic materials into the atmosphere has been reduced by at least 90 percent by weight.

(e) A person shall not use photochemically reactive solvent to thin, reduce or dilute industrial and commercial metal surface coatings unless the emission of organic materials into the atmosphere has been reduced by at least 85 percent by weight.

(f) A person shall not use photochemically reactive solvent in industrial and commercial surface cleaning or degreasing operations unless the emission of organic materials into the atmosphere has been reduced by at least 85 percent by weight.

(g) A person shall not during any one day dispose of a total of more than 5 liters (1.3 gallons) of any photochemically reactive solvent, or of any material containing more than 5 liters (1.3 gallons) of any photochemically reactive solvent by any means which will permit the evaporation of such solvent into the atmosphere.

(h) A person shall not use, sell or offer for sale for use in the District, in containers of 0.94 liter (one quart) capacity or larger, any architectural coating containing photochemically reactive solvent.

(i) A person shall not thin or dilute any architectural coating with a photochemically reactive solvent.

(j) The provisions of this rule shall not apply to:

(1) The manufacture of organic solvents, or the transport or storage of organic solvents, or the transport or storage of materials containing organic solvents.

(2) The use of equipment for which other requirements are specified by Rules 461, 462, 463, or 464 or which are exempt from air pollution control requirements by said rules.

(3) The spraying or other employment of organic solvents as insecticides, pesticides or herbicides.

(4) The use of water reducible materials, provided that:

(A) the volatile content of such material is not photochemically reactive and consists of at least 80 percent water by volume, and

(B) more than 50 percent by volume of such volatile material is evaporated before entering a chamber heated above ambient application temperature, and

(C) the organic solvent or any material containing organic solvent does not come into contact with flame.

(6) The use of ultra high solid materials, provided that:

(A) the volatile content of such material is not photochemically reactive and does not exceed 5 percent by volume of said material, and

(B) the organic solvent or any material containing organic solvent does not come into contact with flame.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-460/3-76-026	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Accelerated Decay of Non-Fuel Evaporative Emissions		5. REPORT DATE August 1976
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Automotive Environmental Systems, Inc. 7300 Bolsa Ave. Westminster, California 92683		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 68-03-2413
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency 2565 Plymouth Road Ann Arbor, Michigan 48105		13. TYPE OF REPORT AND PERIOD COVERED Final Report
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This program was designed to determine whether driving a vehicle on a dynamometer or baking a vehicle in a paint oven could accelerate the normal decay of background hydrocarbon evaporative emissions from new vehicles. Daily background evaporative emission tests were performed on two groups of three identical Ford LTD's in accordance with the procedures outlined in SAE J171a. All fuel system components were either removed or plugged. The carburetors were removed and the intake manifolds covered with a plate. An auxiliary fuel system was used when running each vehicle on the dynamometer. Daily testing was begun on each vehicle within nine days after manufacturing. One vehicle in each group was a control vehicle, which soaked between daily tests. After each daily test, the second vehicle in each group was driven on the dynamometer for five series of two LA-4 driving schedules, with a 30-minute soak with the engine off following each series. It was then soaked until the next test. The third vehicle in each group was placed in a bake oven at 125°F for 12 hours after each test and then soaked until the next test.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Motor Vehicles	Evaporative Emissions	

18. DISTRIBUTION STATEMENT UNLIMITED	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 46
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)