SwRI-1816

MEASUREMENTS OF TOXIC EXHAUST EMISSIONS FROM GASOLINE-POWERED LIGHT-DUTY VEHICLES

By
Mary Ann Warner-Selph

FINAL REPORT

Prepared for
California Air Resources Board
1800 15th Street
Sacramento, California 95814

Under Contract No. A6-198-32
ARB Contract Manager: Manjit Ahuja
ARB Technical Monitor: Joseph De Vita

November 1989

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SAN ANTONIO HOUSTON

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Approved:

Charles T. Hare

Charles T. Hare, Director
Department of Emissions Research
Automotive Products and Emissions
Research Division

DISCLAIMER

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FOREWORD

This project was conducted for the California Air Resources Board (ARB) by the Department of Emissions Research, Southwest Research Institute. The report is submitted in fulfillment of ARB Contract Number A6-198-32, "Measurements of Toxic Exhaust Emissions From Gasoline-Powered Light-Duty Vehicles" by Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas. The program was initiated July 18, 1987, and completed March 1989. It was identified within Southwest Research Institute as Project 08-1816. The ARB Contract Manager was Mr. Manjit Ahuja of the Research Section, Sacramento, California. The ARB Project Technical Monitor was Dr. Joseph DeVita of the Mobile Source Division, El Monte, California. SwRI Project Manager was Dr. Lawrence Smith, and SwRI principal researcher was Mary Ann Warner-Selph.

Dr. Jong-Pyng Hsu of the Chemistry and Chemical Engineering Division, SwRI, was responsible for the mass spectral analyses; and Mr. Dave Cadena of the Fuels and Lubricants Research Division, SwRI, was responsible for radionuclide measurements. Analyses for nitrosamines were conducted by Thermedics, Inc. under the direction of Ms. Ulku Goff; and trace metal and elemental analyses were performed by the Environmental Protection Agency, Research Triangle Park, North Carolina, under the direction of Mr. Frank Black. Mr. Steve Welstand of Chevron Research Company provided the gasoline test fuel used in the program.

ABSTRACT

Exhaust emission rates of selected toxic substances were determined for two late model gasoline-powered passenger cars. These substances, which have appeared on California Air Resources Board Toxic Air Contaminant lists or have been candidates for the lists, included volatile and semi-volatile halogenated hydrocarbons, 1,3-butadiene, acrolein, phenols, nitrobenzene, dialkylnitrosamines, and a number of other unregulated emissions. Regulated gaseous emissions and fuel economy were also measured. A literature search was performed to determine if any of these compounds had previously been measured in the exhaust of gasoline-powered vehicles and if appropriate analytical procedures were available. When unavailable, procedures were developed for sampling and analyzing the unregulated toxic emissions compounds. The two vehicles were then tested to determine the emission rates of the targeted compounds. In the tests, a 1987 Ford Taurus equipped with a 3-way plus oxidation catalyst and a 1986 Toyota Camry equipped with a 3-way catalyst only were operated over the Federal Test Procedure, the Highway Fuel Economy Test, and the New York City Cycle. The test fuel was a regular unleaded gasoline without ethanol or methanol, and was obtained from California.

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SUMMARY

Two vehicles were tested over several driving cycles for the measurement of regulated emissions and several unregulated substances that appear on California Air Resources Board Toxic Air Contaminant list or have been candidates for the list. The first vehicle was a 1987 California-certified Ford Taurus equipped with a three-way plus oxidation catalyst. The second test vehicle was a 50-state certified Toyota Camry equipped with a three-way catalyst only. Both vehicles had electronic fuel injection and closed-loop feedback control. The test fuel was a regular unleaded gasoline without ethanol or methanol. The fuel was donated by Chevron Research Company and shipped from California to Southwest Research Institute.

The test vehicles were operated over three driving cycles: the Federal Test Procedure Urban Dynamometer Driving Schedule, the Highway Fuel Economy Test, and the New York City Cycle. The Taurus and Camry were evaluated for regulated and unregulated emissions. Regulated emissions included hydrocarbons, carbon monoxide, and oxides of nitrogen. Unregulated emissions measurements included volatile and semi-volatile halogenated hydrocarbons, 1,3-butadiene, acrolein, phenols, nitrobenzene, dialkylnitrosamines, and a number of other substances.

Several observations were made in the program. Discussions of these observations are listed below, not necessarily in order of importance.

- Regulated emissions were within the California Emission Standards for both vehicles operated over the FTP.

- In FTP tests, benzene, toluene, and xylenes were present in the exhaust of the Taurus in the ratio 1:1.5:1.8, respectively; and for the Camry the ratio was 1:2:3, respectively. This indicates an enrichment of benzene to toluene and to xylenes in exhaust as compared to the fuel which contains benzene, toluene, and xylenes, in a 1:4:4 ratio, respectively.

- Styrene emissions were quite variable (<0.1 to 0.95 mg/mi), possibly due to the higher reactivity of styrene relative to benzene, toluene, or xylenes. A more repeatable method for sampling styrene may be needed to measure styrene in exhaust.

- 1,3-Butadiene constituted an average of 0.26 percent of total hydrocarbons from the FTP test on the Taurus and 0.49 percent on the Camry. 1,3-Butadiene was found at measurable levels only in the first 505 seconds (bag 1) of the cold-start portion of the FTP, prior to the catalysts achieving the desired operating temperature.

- In the FTP tests, butane was measured from the FTP, HFET, and NYCC tests of both vehicles at higher concentrations than any of the other C_4 compounds measured. In the HFET and NYCC tests, isobutane and butane made up from 80 to 100 percent of C_4 compounds produced by the Taurus and the Camry.

- Chloroform and methylene chloride were measured above the minimum detection limits in the exhaust of the Taurus. Chloroform, methyl bromide, methyl chloroform, and methylene chloride were found above the minimum detection limits in the exhaust of the Camry.

- Methyl chloroform and methylene chloride were measured in background samples at concentrations (within ± one standard deviation) that overlapped several sample concentrations. The variable levels of these compounds indicate that their presence is

not firmly established. Additional experimentation is recommended.

- Fuel analyses of drum samples and fuel tank samples of fuel indicated no chloride above 1.0 ppm.

- Chlorine was detected in oil samples from both vehicles, however, oil consumption rates to produce the level of methylene chloride measured in exhaust would have to be much higher than the observed rates.

- From contacting both Ford Motor Company and Toyota, it could not be determined that chlorinated hydrocarbons were present in plastic parts in the fuel-handling systems.

- Halogenated hydrocarbons measured in the exhaust of the Taurus and Toyota were well below the Permissible Exposure Limits established by OSHA. Permissible Exposure Limits are time-weighted volume concentrations over an eight-hour work day. However, these limits do no consider the carcinogenic effects of a compound.

- Formaldehyde and acetaldehyde constituted from 69 to 100 percent of total aldehydes and ketones measured for both vehicles, with the highest percentages observed during HFET and NYCC cycles.

- Acrolein was found in the FTP and NYCC tests of the Taurus and in the FTP test of the Camry.

- Most of the phenols that were found were measured in the HFET and NYCC tests of the Taurus and the Camry. Phenol was not detected in the exhaust of either vehicle on any of the test cycles. Cresols were only found at measurable levels during the NYCC test on the Taurus.

- Aluminum, silicon, sulfur, and calcium were the trace elements present in the greatest quantities in particulate samples from both vehicles tested over multiple FTP tests. Iron was also found at measurable levels in Camry samples, possibly due to rust in the exhaust system and/or engine wear. The sources of sulfur are probably the oil and the fuel. Calcium is likely due to calcium in the oil. Aluminum could be derived from wear of engine parts or from the alumina wash coat on the catalyst. The source of silicon could be traces of dust in the intake air of the vehicle. Silicon is also present in silicon-based engine gaskets as a sealant component.

- Aluminum, sulfur, calcium, and iron were found in the highest concentrations in the HFET and NYCC tests of the Taurus. The Camry emitted primarily calcium and iron of the metals measured, in the HFET and NYCC tests.

I. INTRODUCTION

Gasoline-powered passenger cars are the largest source of motor vehicle emissions. There is growing concern, particularly in California, about the emission of toxic substances into the atmosphere. California has prepared toxic air contaminant and candidate toxic air contaminant lists of substances of greatest concern. This program has attempted to detect and quantify these compounds in the exhaust of two gasoline-powered passenger vehicles.

A. Project Objective

The objective of this study has been to screen, measure, and quantify a selected list of these toxic substances. This objective was accomplished in several steps, first by searching the literature for previous research efforts in this area, and then by performing screening tests for some of the listed substances. After narrowing the list of compounds to those found in the literature search and in the screening tests, final emissions tests were performed.

B. Test Vehicles and Fuels

The two test vehicles evaluated in this program were a 1987 Ford Taurus and a 1986 Toyota Camry. The California-certified Taurus was equipped with a three-way plus oxidation catalyst. The 50-state certified Camry was equipped with a three-way catalyst only. Both vehicles had electronic fuel injection and closed-loop feedback control. The test fuel was Chevron regular unleaded gasoline without ethanol or methanol.

C. Test Procedures

The test vehicles were operated on a chassis dynamometer over the Federal Test Procedure (FTP), the Highway Fuel Economy Test (HFET), and the New York City Cycle (NYCC). Multiple segments of the cycles were driven to provide sufficient samples for the various toxic substances. Screening tests were performed initially in the program using the FTP cycle. Final emissions testing was conducted with the FTP, HFET, and NYCC driving cycles.

D. Emissions Measurement Procedures

The compounds or groups of compounds evaluated, along with sampling methods used, are described below.

Sampling Methods	Substance Evaluated
Tedlar Bag	Hydrocarbons, carbon monoxide, carbon dioxide, oxides of nitrogen, 1,3-butadiene
Carbosieve/Tenax Trap	Volatile organic compounds
Polyurethane Foam Trap	Semi-volatile organic compounds
Thermosorb/N Trap	Nitrosamines
Liquid Impinger	Aldehydes and ketones
Liquid Impinger	Phenols
Filter	Trace metals and other elements, radionuclides, organic solubles

II. GENERAL EQUIPMENT, INSTRUMENTS, PREPARATIONS, AND PROCEDURES

This section describes the vehicles, fuel, and oils used in emissions tests. In addition, the sampling system, test procedures, and calculations employed to process the data are reviewed.

A. Test Vehicles

Two vehicles were selected for testing in this program. The vehicles had to meet several criteria established by CARB. The criteria are listed below.

- 1981 or newer
- Electronic fuel injection
- Closed-loop feedback control
- Representative of vehicles currently in use in California, i.e., certified for sale in California
- Mileage greater than 25,000 but less than 50,000 miles

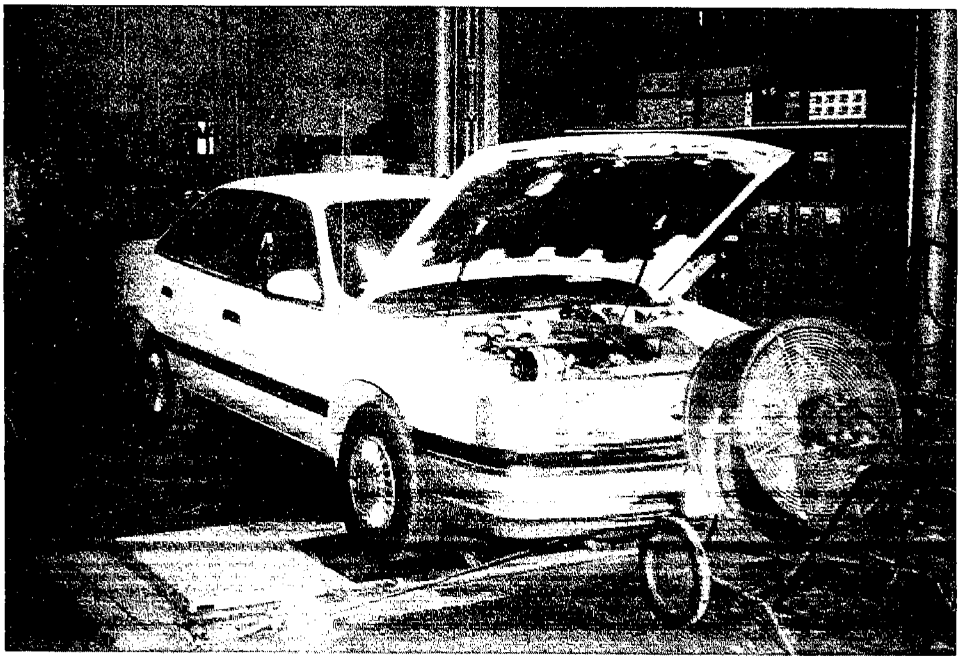
In addition,

- One vehicle should be from a foreign manufacturer and the other from a domestic manufacturer
- One vehicle had to be equipped with a three-way catalyst and the other with a three-way plus oxidation catalyst.

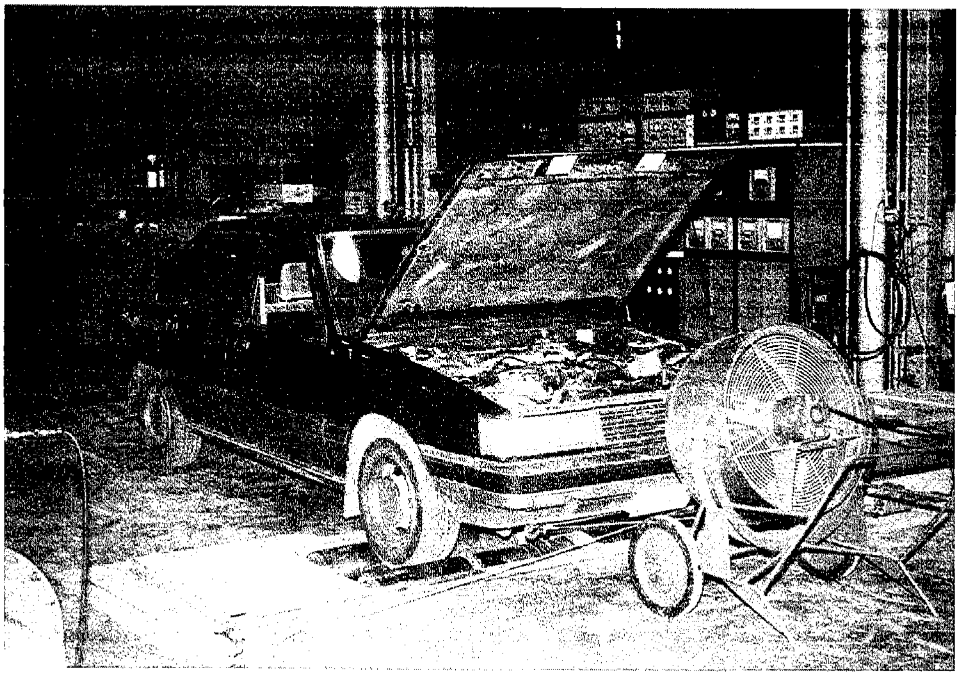
A 1986 Toyota Camry equipped with a three-way catalyst only and with 50-state certification was easily located. However, a 50-state or California-certified vehicle with a three-way plus oxidation catalyst was more difficult to find. A four-month effort was expended in locating the second vehicle that met the desired criteria. The vehicle located was a 1987 Ford Taurus. Both vehicles had electronic fuel injection and closed-loop feedback control. Descriptions of the vehicles are given in Table 1. The vehicles are shown in Figure 1. The Toyota Camry had accumulated mileage less than the desired 25,000 miles, however, CARB approved use of the Camry with over 20,000 miles on the odometer.

TABLE 1. VEHICLES EVALUATED

	Ford Taurus	Toyota Camry
Model Year	1987	1986
Body Type	4-Door	4-Door
Transmission Type	A-3	A-4
Cylinders	I4	I4
Displacement, L	2.5	2.0
Odometer Miles	28,500	20,600
Engine Family	HFM2.5V5HCH9	GTY2.0V5FBB3
ID Number	1FABT52D5HA157262	JT25V16E3G0486387
Chassis Dynamometer		
Inertia Setting, lbs	3000	2875
Road Load, hp @ 50 mph	7.4	8.1



1987 FORD TAURUS



1986 TOYOTA CAMRY

FIGURE 1. TEST VEHICLES

Before acceptance as test vehicles, the Taurus and Camry were adjusted to the manufacturer's operating specifications and subjected to the California Inspection and Maintenance (I/M) Program.(1)* A Test Analyzer System (TAS) was used to measure hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO_2), and oxygen (O_2) during a high rpm and an idle test. When initially received, the Ford Taurus produced carbon monoxide at levels exceeding the California standard. The spark plugs appeared fouled and were replaced, however, no effect on the emissions was observed. The single fuel injector was then replaced and the vehicle was retested. Emissions from the Taurus were then within California emissions standards for the High RPM and Idle RPM tests, and for the FTP test. No problem was experienced with injector malfunction throughout the remainder of the test program.

The results of the TAS tests along with the appropriate California standards are given in Table 2 for both vehicles. The Camry was tested three times (for repeatability) and the Taurus once. Both vehicles passed the High RPM and Idle Test plus the Emission Control System Inspection and the Functional Test of the I/M Program.

TABLE 2. RESULTS OF HIGH RPM AND IDLE RPM TESTS ON A FORD TAURUS AND A TOYOTA CAMRY

Ford Taurus

	High rpm Test		Idle Test	
Emission	Standard	Test	Standard	Test
HC (ppm)	220 (max)	1	100 (max)	17
CO (%)	1.2 (max)	0.01	1.0 (max)	0.02
CO_2 (%)	7.0 (min)	12.4	7.0 (min)	12.7
O_2 (%)	--	3.8	--	3.3

Toyota Camry

	High rpm Test				Idle Test			
Emission	Standard	Test 1	Test 2	Test 3	Standard	Test 1	Test 2	Test 3
HC (ppm)	220 (max)	2	3	3	100 (max)	0	1	0
CO (%)	1.2 (max)	0.00	0.00	0.00	1.0 (max)	0.00	0.00	0.00
CO_2 (%)	7.0 (min)	15.4	15.4	15.4	7.0 (min)	15.5	15.6	15.6
O_2 (%)	--	1.0	1.0	1.0	--	0.5	0.4	0.4

The vehicles were also tested over a three-bag FTP before acceptance into the program. The FTP emissions results are given in Table 3 for the Taurus and the Camry. California emissions standards are also provided. Regulated emissions from both vehicles were within California emission standards. After consultation with the Contract Manager, the vehicles were accepted as test vehicles.

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

TABLE 3. FTP EMISSIONS RESULTS FOR INITIAL TESTING OF A FORD TAURUS AND TOYOTA CAMRY

Emissions	Taurus Emissions Rate, g/mile	Toyota Emission Rate, g/mile	California Emission Standard, g/mile
HC	0.25	0.14	0.41 (0.39)[a]
CO	3.35	2.35	7.0
NO_x	0.45	0.32	0.7

---

[a] Non-methane value.

B. Test Fuel and Oil

Specifications for the test fuel required that the fuel be a regular unleaded gasoline, that it contain no ethanol or methanol, and that it be obtained from the refiner with the largest sales volume in California. At the time of the fuel selection, Chevron was the refiner having the largest sales volume of fuel in California. For this reason, five 55-gallon drums of unleaded gasoline were obtained from Chevron Research Company. The fuel was analyzed and the results were typical of unleaded fuels used by SwRI in other programs. Fuel analysis results are given in Table 4. Two subsequent analyses were performed on the fuel to monitor the integrity of the fuel during the course of the program. The results of all three analyses plus an analysis for benzene, toluene, and xylenes are provided in Table 5. The results of an analysis of the fuel by Chevron Research Company is also provided in Appendix A.

Samples of engine oil from the Ford Taurus and the Toyota Camry were analyzed by X-ray fluorescence for metals and other elements. A total of 21 elements were analyzed. Of these elements, those present in the highest concentrations were magnesium, zinc, phosphorus, and calcium from the Taurus, and zinc, phosphorus, and calcium from the Camry. Results of analyses for trace metal and other elements are given in Table 6.

C. Dynamometer, CVS, and Exhaust Sampling System

A Clayton Model ECE-50 passenger car dynamometer with a direct drive variable inertia system was utilized for all testing. This inertia system simulates equivalent weights of vehicles from 1,000 lb to 8,875 lbs in 125 lb increments. A nominal 18-inch diameter by 16-foot length dilution tunnel was used in conjunction with a constant volume sampler (CVS). The CVS used for these evaluations was SwRI CVS Number 2. This unit has a nominal capacity of 315 SCFM. A cooling fan of 5,000 CFM capacity was used in front of the test vehicles during all tests. Vehicle hoods were maintained fully open during testing and were closed during soak periods. Both the dynamometer and the CVS were calibrated, maintained, and operated in accordance with the manufacturer's instructions and the appropriate sections of the code of Federal Regulations applicable to light-duty vehicles.(2) Two views of the dynamometer and CVS are shown in Figure 2.

A diagram of the sampling system is shown in Figure 3. Sampling positions for regulated and unregulated emissions are indicated. Gaseous emissions samples were taken in Tedlar bags, on solid sorbent traps, and in impingers. Particulate was sampled on fluorocarbon filters and on Teflon-coated glass fiber filters. Several views of the sampling system are shown in Figure 4.

D. Instrumentation for Regulated Emissions

Bag samples of dilute exhaust were evaluated for hydrocarbons, carbon monoxide, carbon dioxide, and oxides of nitrogen using SwRI Bag Carts No. 1 and No. 2. These carts were designed,

TABLE 4. FUEL ANALYSIS OF CHEVRON UNLEADED GASOLINE[a]

Measurement	Results
Distillation, D-86	
IBP, °F	95
5	118
10	132
20	158
30	184
40	208
50	231
60	255
70	280
80	300
90	332
95	352
End Point, °F	399
Recovery, %	98.3
Residue, %	0.9
Loss, %	0.8
Hydrocarbon Types	
Aromatics, L.V. %[b]	37.0
Olefins, L.V. %	7.9
Saturates,. L.V. %	55.1
Manganese Content, g/gal	<0.001
Motor Octane Number, Clear	83.2
Research Octane Number, Clear	93.0
R+M/2 88.1	
Oxygenates, L.V. %	
Methanol	<0.1
Tertiary Butyl Alcohol	<0.1
Methyl Tertiary Butyl Ether (MTBE)	<0.1
Ethanol	<0.1
Lead Content, D-3237, g/gal	<0.002
Phosphorus Content, D-3231, g/gal	0.0006
Reid Vapor Pressure, D-323, psi @ 100°F	8.4
Total Sulfur, D-3246, Wt. %	0.002
API Gravity @ 60°F	53.6[c]
Density, g/mL @ 81°F	0.756[c]

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[a] Fuel analysis was performed by Core Laboratories of Houston, Texas.
[b] L.V.% = liquid volume percent.
[c] API gravity and density measured by Southwest Research Institute.

TABLE 5. PERIODIC FUEL ANALYSIS OF CHEVRON UNLEADED GASOLINE[a]

Measurement	First Analysis February '88	Second Analysis May '88	Third Analysis September '88	Fourth Analysis January '89
Distillation, D-86				
IBP °F	95	97	92	--[c]
5	118	121	117	--
10	132	136	132	--
20	158	162	160	--
30	184	186	184	--
40	208	210	210	--
50	231	234	234	--
60	255	258	258	--
70	280	281	281	--
80	300	298	300	--
90	332	334	334	--
95	352	356	358	--
End Point, °F	399	404	403	--
Recovery, %	98.3	98.2	97.3	--
Residue, %	0.9	0.9	1.3	--
Loss, %	0.8	0.9	1.4	--
Reid Vapor Pressure, D-323, psi @ 100°F	8.4	8.5	8.7	--
API Gravity @ 60°F	53.6[b]	53.8[b]	53.7[b]	--
Butane, g/gal	--	72.7[b]	72.1[b]	--
Total Chloride by microcoulometry, ppm wt.[d]	--	--	<0.1	--
Benzene, volume %	--	--	--	2.44[b]
Toluene, volume %	--	--	--	9.74[b]
Xylenes, volume %	--	--	--	9.41[b]

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[a] Fuel analysis was performed by Core Laboratories of Houston, Texas.
[b] Analysis performed by Southwest Research Institute.
[c] Not measured.
[d] Total chloride includes bromide and chloride.

TABLE 6. METAL AND TRACE ELEMENT COMPOSITION OF ENGINE OIL FROM THE FORD TAURUS AND THE TOYOTA CAMRY

	Concentration, ppm		Minimum Detection Limit, ppm
Element	Ford Taurus	Toyota Camry	
Bromine	<50	<50	50
Chlorine	140	30	10
Manganese	3	<1	1
Magnesium	1109	19	100[a], 1[b]
Iron	82	27	1
Chromium	4	1	1
Copper	59	67	1
Boron	17	<1	1
Barium	<1	<1	1
Silver	<1	<1	1
Aluminum	16	5	1
Zinc	1294	1008	100
Tin	<15	15	15
Silicon	43	24	1
Antimony	<1	<1	1
Phosphorus	1116	978	100
Lead	48	9	1
Nickel	<1	<1	1
Molybdenum	10	1	1
Calcium	336	1688	1[a], 100[b]
Sodium	204	17	0.1

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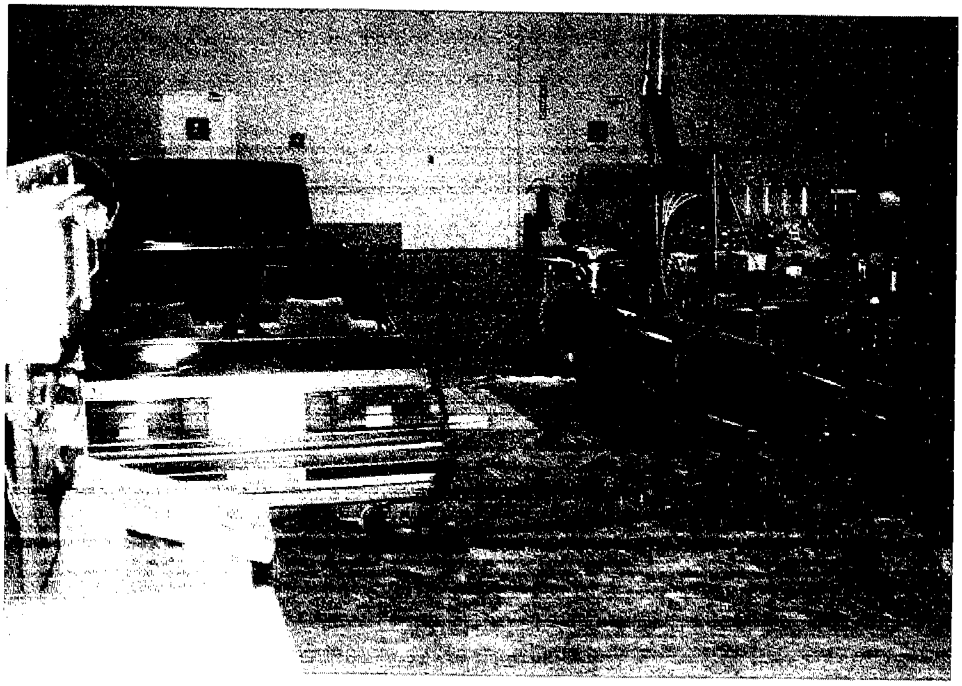
[a] Minimum detection limit for Ford Taurus
[b] Minimum detection limit for Toyota Camry



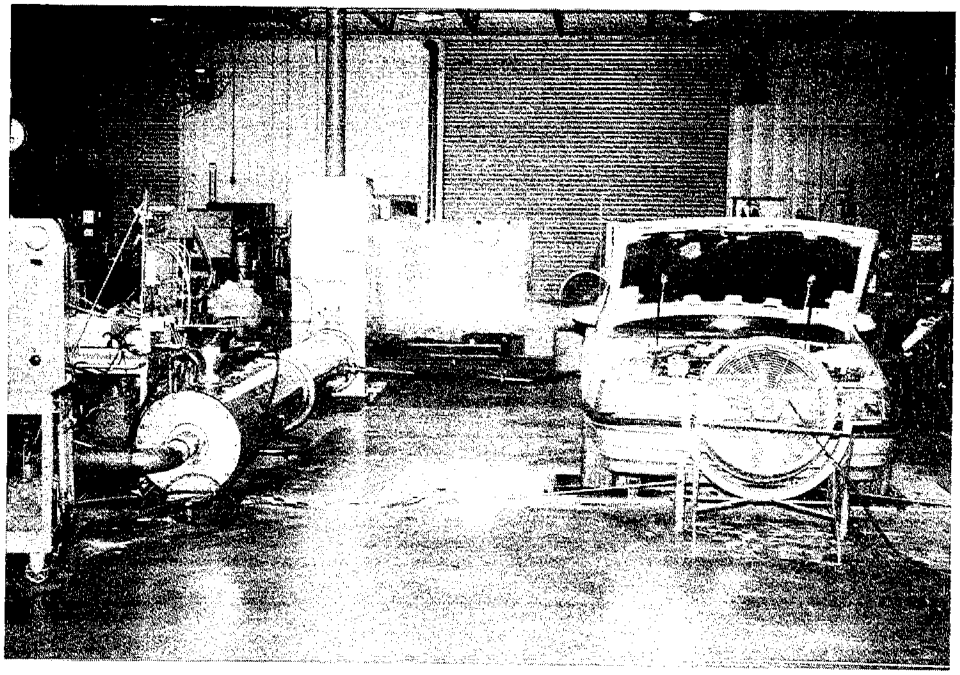


FIGURE 2. VIEWS OF THE DYNAMOMETER, DILUTION TUNNEL, AND INTAKE TO THE CVS

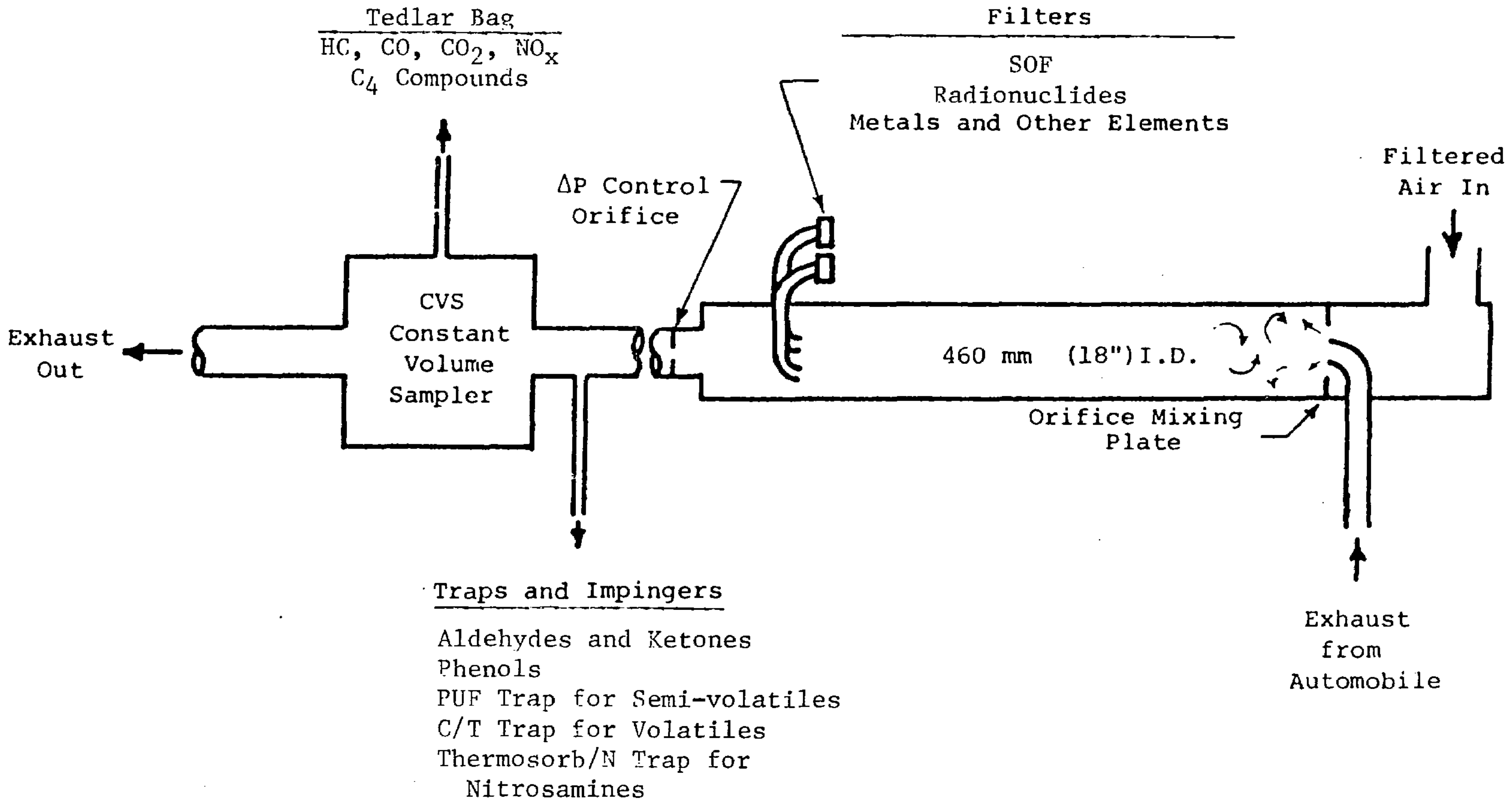
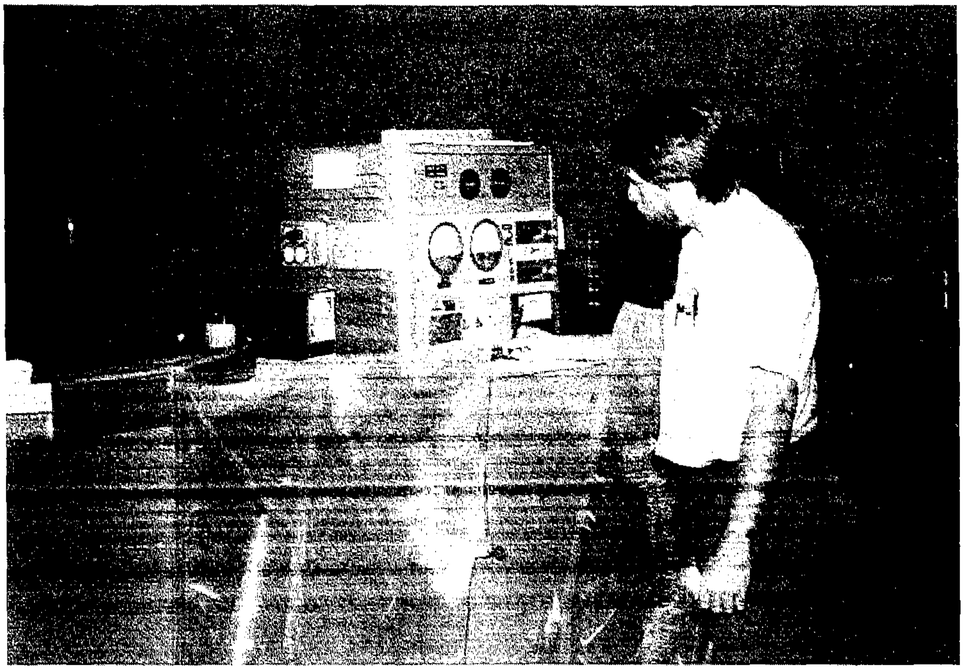
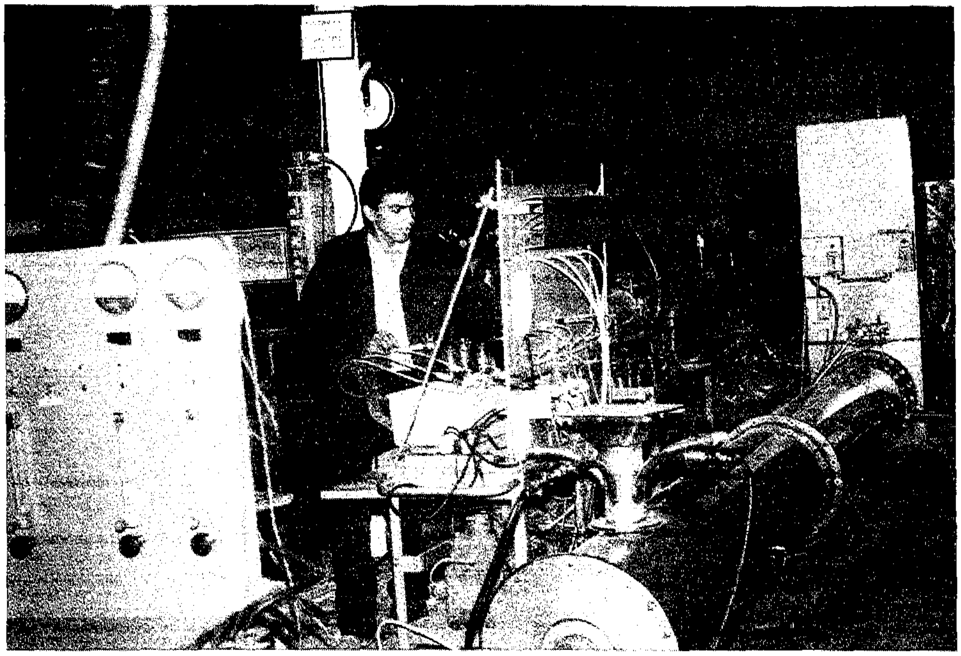


FIGURE 3. EMISSIONS SAMPLING SYSTEM

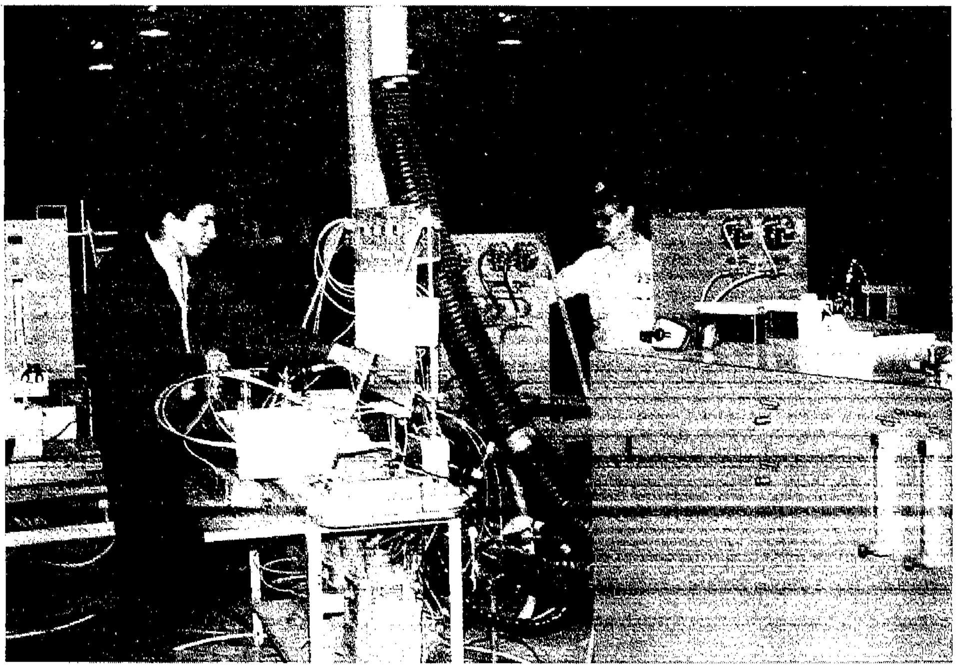


BAG SAMPLING

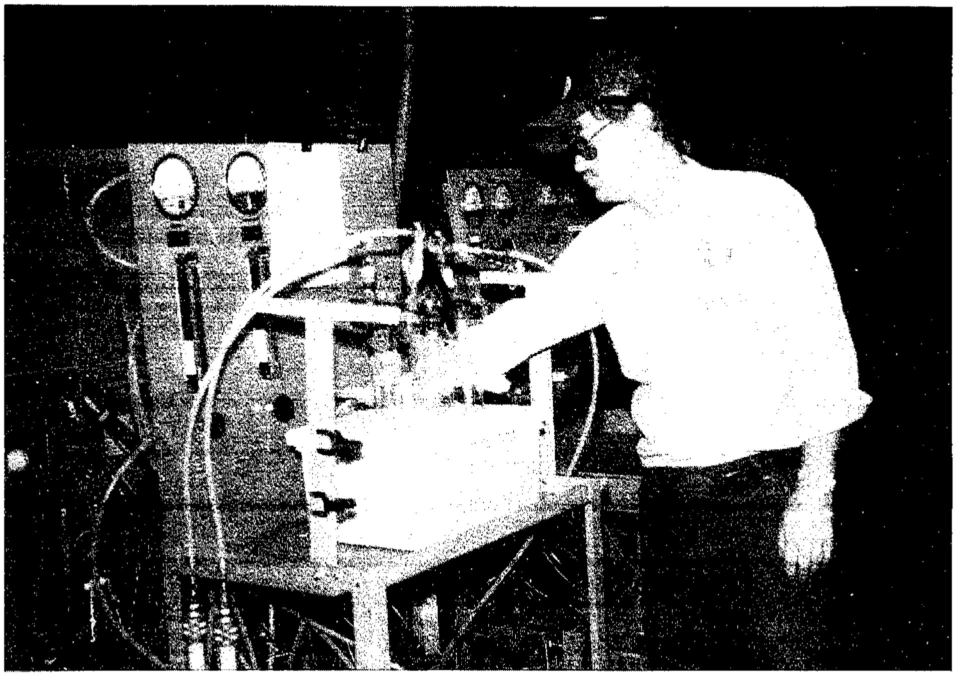


FILTER SAMPLING

FIGURE 4. VIEWS OF THE EMISSIONS SAMPLING SYSTEM



IMPINGER SAMPLING (ALDEHYDES AND KETONES)



IMPINGER SAMPLING (PHENOLS)

FIGURE 4 (CONT'D). VIEWS OF THE EMISSIONS SAMPLING SYSTEM

calibrated and operated in accordance with the appropriate sections of the Code of Federal Regulations applicable to light-duty vehicles. Fuel consumption was calculated based on the carbon balance method.

E. Emissions Test Procedures

Three emissions test procedures were used in this program. They are listed below:

FTP -	Federal Test Procedure(2) (uses the Urban Dynamometer Driving Schedule).
HFET -	Highway Fuel Economy Driving Schedule.(3)
NYCC -	New York City Cycle.(4)

The FTP uses the Urban Dynamometer Driving Schedule (UDDS) which is 1,372 seconds in duration. The UDDS, in turn, is divided into two segments; the first consisting of 505 seconds and the second consisting of 867 seconds. The FTP is composed of a cold-start 505 and a stabilized 867 followed by a ten-minute soak and then a hot-start 505. For unregulated emissions, sampling was continued through an additional 867 second segment. The HFET and NYCC are hot-start, single-segment driving cycles. Sampling schedules for screening tests and final emissions tests are provided in Tables 7 and 8. As indicated in Tables 7 and 8, the vehicles were sometimes operated over multiple cycles of the driving cycles for sampling unregulated emissions. In the third screening tests and final emissions tests, testing was conducted over five UDDS cycles. This included a cold-start UDDS, three hot-start UDDS's, and a forced-cooled-start UDDS. The purpose of the forced-cooled-start test was to approach the weighting factors used in FTP data calculations. The weighting factors for the FTP are 43 percent for the cold-start and 57 percent for the hot-start. With the five UDDS cycles, the weighting factor was 40 percent cold-start and 60 percent hot-start. The vehicle was prepared for the forced-cooled-start by directing fans on the engine with the hood open until the engine oil temperature decreased to 80-84°F. Multiple testing over the HFET and NYCC was also performed, however, since these are "hot-start" tests, no additional cooling between tests was required. Cycle duration, distance driven, and average speed of the FTP, HFET, and NYCC are given in Table 9. Diagrams of speed versus time of the cycles are shown in Figure 5.

F. Calculations

A composite value in mass per distance for the three-bag, three-sample FTP (1,3-butadiene and regulated emissions) is calculated using the following formula:

$$\frac{\text{MASS}}{\text{DISTANCE}} = \frac{0.43 \text{ x } (\text{MASS 1} + \text{MASS 2})}{(\text{DIST. 1} + \text{DIST. 2})} + \frac{0.57 \text{ x } (\text{MASS 3} + \text{MASS 2})}{(\text{DIST. 3} + \text{DIST. 2})}$$

Assuming distance 3 is equal to distance 1, this equation can be reduced to:

$$\text{3-Bag FTP M/D} = \frac{0.43 \text{ x } (\text{M1} + \text{M2}) + 0.57 \text{ x } (\text{M3} + \text{M2})}{\text{D1} + \text{D2}}$$

For the four-bag, two-sample FTP (C/T traps for volatile organics and Thermosorb/N for nitrosamines), composite values were determined in this project using the following formula:

$$\frac{\text{MASS}}{\text{DISTANCE}} = \frac{0.43 \text{ x } (\text{M1} + \text{M2})}{(\text{D1} + \text{D2})} + \frac{0.57 \text{ x } (\text{M3} + \text{M4})}{(\text{D3} + \text{D4})}$$

TABLE 7. SAMPLING SCHEDULE FOR SCREENING TESTS ON A FORD TAURUS AND A TOYOTA CAMRY

Screening Test	Sampling Media	Cold-Start		Hot-Start		Hot-Start 2		Hot-Start 3		Forced-Cooled-Start[a]	
		Bag 1 505	Bag 2 867	Bag 1 505	Bag 2 867	Bag 1 505	Bag 2 867	Bag 1 505	Bag 2 867	Bag 1 505	Bag 2 867
1	Bag	√[b]	√	√	√	—[c]	—	—	—	—	—
	C/T Trap	√	→	√	→	—	—	—	—	—	—
	PUF Trap	√	→	√	→	—	—	—	—	—	—
	T/N Trap	—	—	—	—	—	—	—	—	—	—
	47 mm Filter	√	→	√	→	—	—	—	—	—	—
2	Bag	√	√	√	√	√	√	√	√	√	√
	C/T Trap	√	→	√	→	—	—	—	—	—	—
	PUF Trap	√	→	→	→	→	→	→	→	→	→
	T/N Trap	—	—	—	—	—	—	—	—	—	—
	47 mm Filter	√	→	→	→	→	→	→	→	→	→
3	Bag	√	√	√	√	—	—	—	—	—	—
	C/T Trap	√	→	√	→	—	—	—	—	—	—
	PUF Trap	—	—	—	—	—	—	—	—	—	—
	T/N Trap	√	→	√	→	—	—	—	—	—	—
	8 x 10" Filter	√	→	→	→	→	→	→	→	→	→
Raw Exhaust	C/T Trap	√	→	√	→	—	—	—	—	—	—
	PUF Trap	√	→	√	→	—	—	—	—	—	—

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[a] Engine cooled to an engine oil temperature of 80-84°F. This was accomplished by directing fans at the engine with the hood open.

[b] √ - Sample taken.

[c] Not sampled.

TABLE 8. SAMPLING SCHEDULE FOR FINAL EMISSIONS TESTS ON A FORD TAURUS AND A TOYOTA CAMRY

	Cold-Start		Hot-Start		Hot-Start 2		Hot-Start 3		Forced-Cooled-Start[a]	
Sampling Media	Bag 1 505	Bag 2 867	Bag 1 505	Bag 2 867	Bag 1 505	Bag 2 867	Bag 1 505	Bag 2 867	Bag 1 505	Bag 2 867
Bag	√[b,c]	√[c]	√[c]	√[c]	√	√	√	√	√[c]	√[c]
Bubbler/DNPH	√ →	→	√ →	→	→	→	→	→	Continue →	
Bubbler/1N KOH	√ →	→	√ →	→	→	→	→	→	Cold-Start →	
C/T Trap	√ →	→	√ →	→	–[d]	–	–	–	–	–
PUF Trap	√ →	→	→	→	→	→	→	→	→	→
T/N Trap	√ →	→	√ →	→	–	–	–	–	–	–
47 mm Filter	√ →	→	→	→	→	→	→	→	→	→

Sampling Media	HFET 1	HFET 2	HFET 3	HFET 4	NYCC 1	NYCC 2	NYCC 3	NYCC 4
Bag	√[c]	√[c]	√	√	√[c]	√[c]	√	√
Bubbler/DNPH	√ →	→	→	→	√ →	→	→	→
Bubbler/1N KOH	√ →	→	→	→	√ →	→	→	→
C/T Trap	√ →	→	–	–	√ →	→	–	–
PUF Trap	√ →	→	→	→	√ →	→	→	→
T/N Trap	√ →	→	–	–	√ →	→	–	–
47 mm Filter	√ →	→	→	→	√ →	→	→	→

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[a] Engine cooled to an engine oil temperature of 80-84°F. This was accomplished by directing fans at the engine with the hood open.

[b] √ - Sample taken.

[c] 1,3-butadiene measured on these bags only.

[d] Not sampled.

TABLE 9. SUMMARY OF DRIVING SCHEDULE PARAMETERS

	Duration, Seconds	Distance, Miles	Average Speed, mph
FTP:			
505	505	3.60	25.7
867	867	3.85	16.2
UDDS	1372	7.45	19.5
HFET	765	10.25	48.2
NYCC	599	1.19	7.1

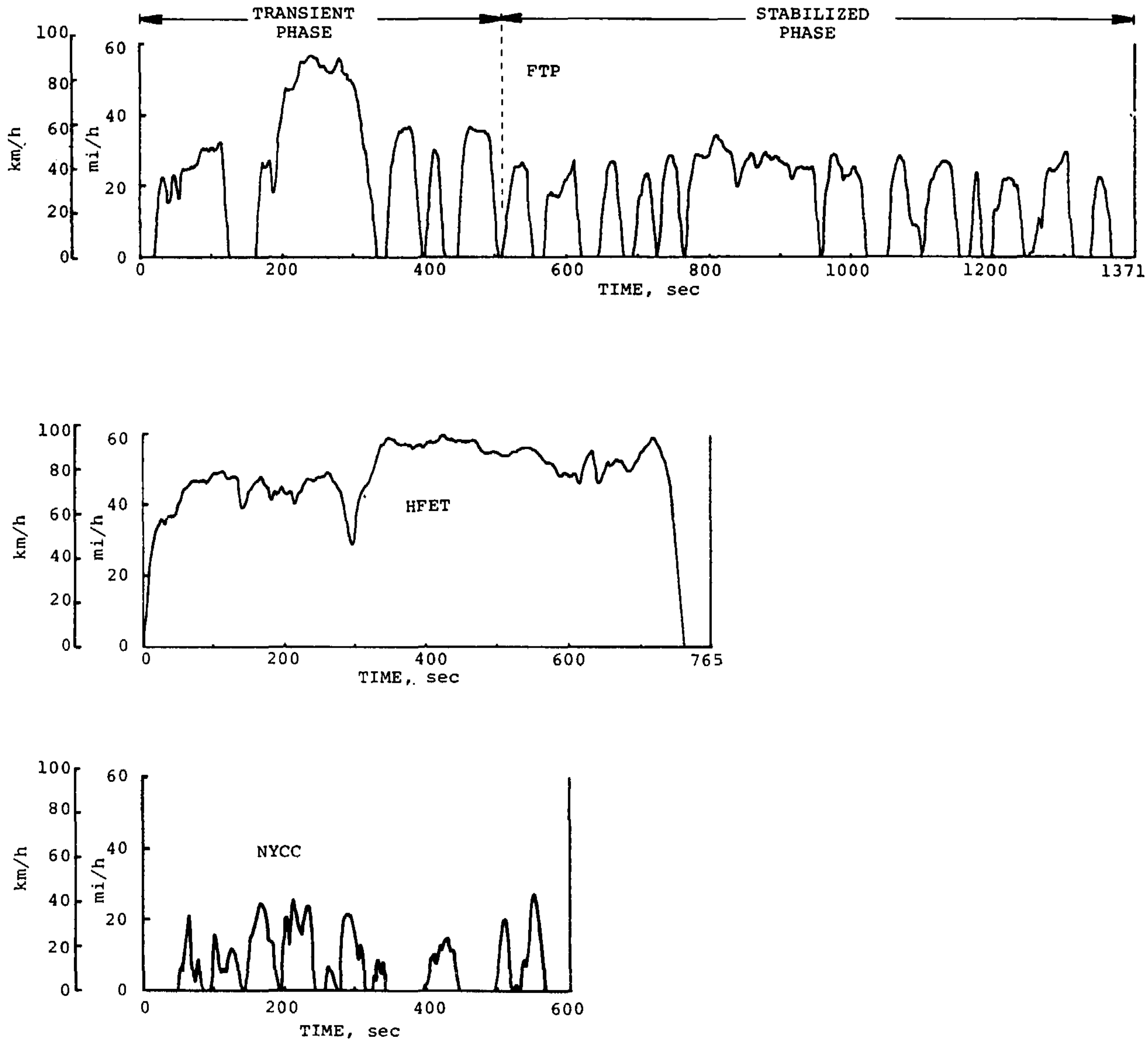

FIGURE 5. FTP, HFET, AND NYCC DRIVING CYCLES, SPEED VS TIME

Assuming Distance 3 is equal to Distance 1 and Distance 4 is equal to Distance 2, then this equation can be reduced to:

$$\text{4-Bag FTP M/D} = \frac{0.43 \times (M1 + M2) + 0.57 \times (M3 + M4)}{D1 + D2}$$

Therefore, with the assumption that the changes in distance traveled are negligible, the composite results with the four-cycle FTP relative to results with the three cycle FTP will differ only as the mass emissions emitted during Cycle 4 differ from those emitted during Cycle 2.

For a single sample 10-Bag FTP (PUF trap for semi-volatiles, 47 mm filters for trace metals and other elements and radionuclides, and 8 x 10 in. filters for soluble organic fraction) obtained in this study, a composite value (not weighted) was obtained using the following formula:

$$\text{10-Bag FTP Composite} = \frac{\text{Total Mass}}{\text{Total Distance Driven}}$$

A 10-bag FTP was composed of one cold-start UDDS, three hot-start UDDS cycles, and one forced-cooled-start UDDS. In the first screening test only, PUF traps and 47 mm filters were sampled in four-bag, two sample FTP segments as described previously.

Impinger samples for aldehydes and ketones and for phenols were taken over the first two bags (cold-start UDDS) and last two bags (forced-cooled-start UDDS) of a 10-bag FTP (five UDDS cycles). These samples were designated "cold-start" samples. Another set of impinger samples was taken over bags three through eight (three hot-start UDDS cycles) of the 10-bag FTP and were designated "hot-start" samples. A composite value was obtained as follows:

$$\text{10-Bag FTP M/D} = \frac{0.43 \times \text{MASS Cold-Start}}{(D1 + D2 + D9 + D10)} + \frac{0.57 \times \text{MASS Hot-Start}}{(D3 + D4 + D5 + D6 + D7 + D8)}$$

Minimum detection limits were calculated by first determining the lowest mass or concentration of each substance measurable on the respective detector. These values were then converted to a mg/mi basis depending on test cycle. For example, the detection limit of benzene on a Carbosieve/Tenax (C/T) trap is 20 ng. The C/T trap was sampled over one UDDS portion of the FTP cycle. The minimum detection limit was determined as follows:

$$\text{MDL, mg/mi} = \text{MDL, ng} \times \frac{\text{CVS, vol., scf}}{\text{Sample vol., scf}} \times \frac{10^{-6}\ \text{mg/ng}}{\text{Cycle distance, mi}}$$

MDL = 20 ng
CVS vol. = 7381 scf

Sample vol. = 0.164 scf
Cycle distance = 7.4 mi

$$\text{MDL, mg/mi} = \frac{20 \times 7381 \times 10^{-6}}{0.164 \times 7.4}$$

MDL, mg/mi = 0.1 mg/mi

III. ANALYTICAL PROCEDURES

Several methods were employed for measuring unregulated emissions from the exhaust of the Ford Taurus and the Toyota Camry. A list of the target compounds and sampling media is provided in Table 10. As shown, exhaust was sampled in Tedlar bags, on solid sorbent materials (Carbosieve/Tenax, polyurethane foam, and Thermosorb/N), in impingers, and on filters. This section provides brief descriptions of the procedures used for evaluating unregulated emissions collected by various sampling media. Detailed descriptions of the procedures for measuring phenols and 1,3-butadiene, along with discussions of their development, validation, and qualification, are available in the following EPA reports: "Analytical Procedures for Characterizing Unregulated Emissions from Vehicles Using Middle-Distillate Fuels," EPA Report EPA-600/2-80-068(5) and "Butadiene Measurement Methodology," EPA Report EPA 460/3-88-005.(6)

1,3-Butadiene - The analysis of 1,3-butadiene was accomplished by collecting dilute exhaust in Tedlar bags and analyzing the samples with a gas chromatograph equipped with a flame ionization detector (FID). The gas chromatograph system utilizes a Perkin-Elmer Model 3920B gas chromatograph with an FID, two pneumatically-operated and electrically-controlled Seiscor valves, and an analytical column. The analytical column is a 9 ft x 1/8-inch stainless steel column containing 80/100 Carbopack C with 0.19% picric acid. The carrier gas is helium, which flows through the column at a rate of 27 mL/min. The column temperature is maintained at 40°C for analysis. To quantify the results, the sample peak areas are compared to the peak areas of a certified low concentration standard. The standard was run before and after each set of sample bags. The analytical column, sampling loop, and Seiscor valves are all housed in a GC oven and are operated with the aid of a specially fabricated control system. Once the 1,3-butadiene peak has eluted, a backflush valve is activated and the C_5 and heavier molecular weight hydrocarbons are backflushed from the analytical column. Under normal conditions, it is not necessary to backflush the calibration standards since they are free of contaminants that would interfere with the analytical column.

In addition to 1,3-butadiene, the procedure provided separation and relative exhaust concentrations for six other C_4 hydrocarbons including: isobutane, butane, 1-butene, isobutylene, cis-2-butene, and trans-2-butene. An external 1,3-butadiene standard in zero air was used to quantify the results. The standard was obtained from Scott Specialty Gases and was certified to ± 2 percent. Detection limits for the procedure are on the order of 0.03 ppmC 1,3-butadiene in dilute exhaust.

Volatile Organics - Volatile organic compounds were sampled from dilute and raw exhaust onto Carbosieve/Tenax (C/T) traps (8 inches long × 1/4-inch diameter) at a nominal flowrate of 200 mL/min. This flowrate allowed approximately 5 liters of dilute exhaust to pass through a trap during a 23-minute UDDS test. This volume is well within the safe sampling volumes recommended in the literature search to minimize trap break-through. Analysis of volatile organics in the screening tests was by GC/MS. A clean representative trap was spiked with a standard solution containing compounds of interest. This solution was used as a one-point standard for quantitation. Each trap (sample, blank or standard) was spiked immediately before analysis with 250 ng of an internal standard and surrogate mixture. Standards were prepared from neat compounds obtained from the EPA repository or from various chemical suppliers. After spiking, the sample trap was then inserted into a Tekmar 4000 and desorbed at 220°C directly onto the GC/MS analytical column. The analysis was conducted at the following conditions:

GC Conditions:

Column: packed glass column with 1% SP1000 on Carbopack B (60/80 mesh)
Carrier Gas and Column Flow: Helium at 30 mL per min
Injector Temperature: 200°C
GC Temperature Profile: Ambient for 3 minutes then increased to 45°C, followed by ramp to 230°C at 8°C/min.

TABLE 10. TARGET COMPOUNDS AND SAMPLING MEDIA FOR EMISSIONS SCREENING TESTS ON A FORD TAURUS AND A TOYOTA CAMRY

Compound	Sampling Media
Acrolein[a]	Bubbler
Halogenated Hdyrocarbons	
Allyl chloride	C/T[b]
Benzyl chloride	PUF[c]
Carbon tetrachloride	C/T
Chlorobenzene	C/T
1,3-Dichlorobenzene	PUF
1,2-Dichlorobenzene	PUF
Chloroform[d]	C/T
Chlorophenols	PUF
Dichlorophenols	PUF
Trichlorophenols	PUF
Tetrachlorophenols	PUF
Pentachlorophenols	PUF
Chloroprene	C/T
P-Dichlorobenzene	C/T
Ethylene dibromide[a]	C/T
Ethylene dichloride	C/T
Hexachlorobenzene	PUF
Methyl bromide[d]	C/T
Methyl chloroform	C/T
Methylene chloride	C/T
Perchloroethylene	C/T
Polychlorinated biphenyls	PUF
Monochlorobiphenyls	
Dichlorobiphenyls	
Trichlorobiphenyls	
Tetrachlorobiphenyls	
Pentachlorobiphenyls	
Hexachlorobiphenyls	
Octachlorobiphenyls	
Nonachlorobiphenyls	
Decachlorobiphenyls	
Trichloroethylene	C/T
Vinyl chloride	C/T
Vinylidene chloride	C/T
Nitrogen Compounds	
Acrylonitrile	C/T
Nitrobenzene	PUF
Nitrosamines	Thermosorb/N
N-Nitrosodimethylamine[f]	
N-Nitrosodiethylamine	
N-Nitrosodipropylamine	
N-Nitrosodibutylamine	
N-Nitrosopiperidine	
N-Nitrosopyrrolidine	
N-Nitrosomorpholine	
Oxygenates	
1,4-Dioxane	C/T
di-(2-Ethylhexyl)phthalate	PUF
Ethylene oxide	C/T
Maleic anhydride	PUF
Propylene oxide[d]	C/T
Phenol[a]	Bubbler
Cresols[a]	Bubbler
Radionuclides	
alpha	Filter
beta	Filter
gamma	Filter
Hydrocarbons	
Benzene	C/T
1,3-Butadiene[e]	Bag
Styrene	C/T
Toluene	C/T
Xylenes	C/T
Trace metals and Other Elements	Filter

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[a] Not sampled in screening tests.

[b] C/T = Carbosieve/Tenax trap.

[c] PUF = Polyurethane foam trap.

[d] Compounds previously measured in exhaust but included in screening tests with other volatile organic compounds trapped on Carbosieve/Tenax.

[e] 1,3-Butadiene sampled in first and second set of screening tests.

[f] Compound previously measured in exhaust but included in screening tests with N-Nitrosomorpholine.

Mass Spectrometer Conditions: (Finnigan 3300 with Incos data system):

Mass Range: 38 to 300 amu
Scan Rate: 2 seconds per scan
Electron Energy: 70 eV
Emission Current: 0.60 mA
Analyzer Temperature: 100°C

The C/T traps were prepared for sampling by packing a 1/4-inch diameter tube with 0.3 g (± 0.05 g) of Carbosieve and 1.2 g (± 0.3 g) of Tenax (GC grade.) The traps were purged for 15 to 30 minutes with nitrogen at approximately 30 mL/min. By directing flow from Carbosieve to Tenax, impurities are driven from the Tenax without permanently depositing them on the Carbosieve. While maintaining a constant flow, the oven temperature was adjusted to 200 to 225°C and the traps were allowed to purge for 18 hours before use.

In the final emissions tests, halogenated volatile organics were analyzed by the more sensitive and selective method of GC with an electrolytic conductivity detector (ELCD). The C/T sample traps were placed on the Tekmar 4000 and thermally desorbed with preset flow rates and temperatures. A heated transfer line carried the compounds of interest to a cryofocussing loop installed in-line with the GC column. The cryofocussing loop is an 1/8-inch stainless steel tube packed with 60/80 mesh silanized glass beads. The loop was cooled with liquid nitrogen, thermally desorbed, then flash-heated with a wrapped heater for GC injection.

Compounds of interest were separated using a Vocol capillary column. Detection was performed using a Hall detector (ELCD) which is highly specific to chlorinated compounds.

Quantitation standards were prepared as follows:

1. A methanol solution was prepared containing the standard compounds at known concentrations.
2. A six liter SUMMA® passivated canister (which has a non-reactive nickel-chrome oxide surface) was evacuated.
3. A known amount of the standard solution was added to the evacuated canister through a septum port.
4. The canister was pressurized and the pressure recorded for determination of volume and standard concentration.
5. A known volume of this gaseous standard was transferred through a preconditioned Carbosieve/Tenax trap. The volume was determined by using a Tylan FC-280 mass flow controller which enabled a fixed flow rate for a prescribed period.

The volatile organic hydrocarbons benzene, toluene, xylenes, and styrene were analyzed by GC/MS in the final emissions tests. The analysis was performed according to the procedure described previously.

<u>Semi-Volatile Organics</u> - Semi-volatile organic compounds were sampled on polyurethane foam (PUF) traps from dilute and raw exhaust at a flowrate of 4 L/min. The PUF traps had been previously cleaned by Soxhlet extraction with methylene chloride for 25 hours. Upon completion of extraction, residual solvent was removed by purging with an inert gas. Cleanliness was verified by re-extraction followed by GC/MS analysis using the same analytical conditions as for samples. After sampling, PUF traps were Soxhlet extracted for 16 hours with 300 mL DCM. Extracts were dried with sodium sulfate and reduced to a final volume of 0.5 mL by using a combination of Kuderna-Danish concentration and

"inert gas blow-down" techniques. All target compounds were quantitated versus authentic materials (when available), using an internal standard technique. Internal standards were added to extracts just prior to GC/MS analysis.

GC Conditions:

Column: J & W Scientific DB-5 0.25 µm film thickness; 0.25 mm I.D. x 30 m fused silica capillary column
Carrier Gas and Column Flow: Helium at 1 mL/min.
Injector Temperature: 275°C
GC Temperature Profile: 40°C for 2 min then 10°C/min to final 295°C
Injection Type: Splitless injection with 40 second inject time
Injection Volume: 1 µL

Mass Spectrometer Conditions:

Mass Range: 35 to 525 amu
Scan Rate: 1 second per scan
Electron Energy: 70 eV
Emission Current: 50 mA
Analyzer Temperature: 110°C

In the raw exhaust screening tests, water condensate was collected before the PUF trap. These water samples were analyzed for semi-volatile organics by GC/MS.

Nitrosamines - Gas-phase nitrosamines were sampled from dilute exhaust on Thermosorb/N cartridges obtained from Thermedics, Inc. The sampling flowrate was 2 L/min. After sampling, the cartridges were sealed and mailed to Thermedics Inc. for analysis. At Thermedics, the sorbate was eluted with 1.5 to 1.8 mL of a mixture of 25 percent methanol and 75 percent methylene chloride. The samples were subsequently analyzed by gas-liquid chromatography (GLC) with a thermal energy analyzer (TEA) and quantitated by comparison to external standards.

GLC Conditions:

Inlet Temperature: 150°C
Column Temperature: 140°C to 200°C at 4°C per min
Column: 10' long × 1/8" O.D. stainless steel
Packing: 10% Carbowax 20M + 2% KOH on Chromosorb W-AW, 80/100 mesh
Carrier: Helium @ 30 cc/min

TEA Analyzer Conditions:

Pyrolyzer: 475°C
Oxygen: 5 cc/min
Pressure: 1.0 torr
Attenuation: x4

Aldehydes and Ketones - The aldehydes and ketones that were included in this analysis are: formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, isobutyraldehyde/methylethylketone (not resolved from each other under normal operating conditions and so reported together), benzaldehyde, and hexanaldehyde. The measurement of the aldehydes and ketones in exhaust is accomplished by bubbling the dilute exhaust at 4 L/min through chilled glass impingers containing an acetonitrile solution of 2,4-dinitrophenylhydrazine (DNPH) and perchloric acid. The exhaust sample is collected continuously during the test cycle. For analysis, a portion of the acetonitrile solution is injected into a liquid chromatograph equipped with a UV detector. External standards of the aldehyde and ketone DNPH derivatives are used to quantify the results. These standards were prepared by making hydrazone derivatives of the various aldehydes and ketones. Sample sets were bracketed with standards analyzed before and after. Standard areas had to repeat within ± 10 percent for the sample analyses to be accepted. Detection limits for this procedure are on the order of 0.005 ppm aldehyde or ketone in dilute exhaust.

Sampling System - Two glass impingers in series, each containing 25 mL of an acetonitrile absorbing solution (0.625 g/L DNPH and five drops 1N perchloric acid), were used to collect exhaust samples for the analysis of aldehydes and ketones. These compounds are converted to their 2,4-dinitrophenylhydrazone derivatives in an acidic DNPH solution. The two glass impingers trap approximately 99+ percent of the carbonyl compounds. The temperature of the impingers was maintained at 0-5°C by an ice water bath, and the flow rate through the impinger was maintained at 4 L/minute by the sample pump. A dry gas meter was used to determine the total flow through the impinger during a given sampling period. A dryer was included in the system to prevent condensation in the pump, flowmeter, dry gas meter, etc. Upon completion of each driving cycle, the impingers were removed from the sampling cart and the contents transferred to a 25 mL volumetric flask. When sampling intervals allowed, additional acetonitrile was added to the impingers to adjust for evaporation losses. The addition of acetonitrile was generally required when sampling periods exceeded 20 minutes. The samples were refrigerated until analyzed to preserve the acrolein derivative.

Analytical Procedure - A Perkin Elmer Series 2/2 liquid chromatograph with a Perkin Elmer LC-15B fixed wavelength UV detector operating at a wavelength of 350 nm was used to analyze the sample. A 10 µL portion of the sample was injected into the liquid chromatograph system with the use of a model 7105 septumless injector. The analytical column is a 25 cm x 4.6 mm Zorbaz ODS column and is preceded in the system by a 5 cm x 4.6 mm Permaphase ODS guard column. The mobile phase is acetonitrile-water (72:28) with a gradient to 100 percent acetonitrile at a rate of 1 percent per minute. The solvent flow was maintained at 0.3 mL per minute for the analysis. Analysis time was on the order of 40 minutes. To quantify the results, the sample peak areas were compared to the peak areas of standard solutions. Detection limits for this procedure are on the order of 0.005 ppm aldehyde or ketone in exhaust.

Phenols - Phenols were sampled from dilute exhaust into chilled impingers containing an aqueous solution of 1 N potassium hydroxide. The sample flowrate was 9 L/min. After sampling, the contents of each impinger were acidified, extracted with ether, and concentrated. The ether extract was analyzed by GC/FID on a Perkin-Elmer gas chromatograph. This procedure analyzes for the following phenols: phenol, salicylaldehyde, m- and p-cresol, p-ethylphenol/2-isopropylphenol/2,3-xylenol/3,5-xylenol/2,4,6-trimethylphenol (not resolved from each other under normal operating conditions and so reported together), 2-n-propylphenol, 2,3,5-trimethylphenol, and 2,3,5,6-tetramethylphenol.

The column used to separate phenols was a 6-foot × 1/8-inch Teflon column packed with 10 percent OS-138/H_3PO_4/SP-1200 on 100/120 mesh Chromosorb W-AW. The carrier gas, nitrogen, flowed through the column at 50 mL/min. The column temperature was programmed from 70 to 170°C at a rate of 4°C per minute with an initial eight minute hold at 70°C. External standards in methylene chloride were used for quantitation. Sample sets were bracketed with standards analyzed before and after. For sample analyses to be accepted, standards had to repeat within ± 10 percent. Standards were obtained from commercial suppliers. An o-chlorophenol internal standard was used to spike each sample for peak identification.

Metals and Other Trace Elements - Metals and other trace elements were collected as particulate on a 47 mm Fluoropore filter, which was then sent to the EPA Research Triangle Park (RTP) laboratory for analysis by X-ray fluorescence spectroscopy. The diluted exhaust sample was taken from within the dilution tunnel. Weight gain on the filter was determined by weighing the filter on a microbalance before and after sampling. Emission rates for a total of 31 metals and other elements were determined with the analysis.

The instrument used for x-ray analysis was a Siemens MRS-3 wavelength dispersive x-ray spectrometer. It is a combination of fixed-angle monochromators for the analysis of Na, Mg, A1, Si, P, S, Cl, K, Br, Sr, Mo, Cd, and Pb plus a scanning monochromator for the analysis of Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sn, Sb, Cs, Ba, Pt, and Hg. After analysis, sample filter responses were compared to glass fusion and standard reference material (SRM) quality control standard responses for quantification purposes. Blank filters (unsampled) were also analyzed to correct for background levels of the elements. Membrane filters (including Fluoropore filters) are preferred for x-ray filter analysis because the deposit resides entirely on the filter surface without any penetration into the volume of the filter. No correction for depth penetration is therefore necessary when analyzing membrane filters. Membrane filters also exhibit fewer interfering peaks relative to glass fiber filters.

Radionuclides - Particulate was sampled on fluorocarbon filters (Millipore) for radionuclide measurement. Particulate samples were analyzed for determination of the gross alpha, beta, and gamma activity trapped on the filter. Separate counting systems were set up for each type of radiation. The counting systems, manufactured by Ludlum Instrument Company, are described below:

	Item	Model Number	Serial Number
Alpha System	Counter	1000	46091
	Detector	43-2	PR-034170
	Sample Holder	180-1	PR-036731
Beta System	Counter	1000	52501
	Detector	44-21	PR-034344
	Sample Holder	180-1	PR-045583
Gamma System	Counter	2200	36755
	Detector	44-2	PR-022876
	Sample Holder	180-1	PR-034567

Each counting system was calibrated with the appropriate NIST (formerly NBS) traceable standard. For the alpha system, Americium 241 was used. For the beta system, Technetium 99 was used; and for the gamma system, Cobalt 60 was used. Counting of the background radiation and the standard source was done periodically between counting of the samples to assure that the efficiency of the counting systems did not change. The filters were placed on individual planchettes without covers to keep the sample holders from becoming contaminated. The sample holder assured that the counting geometry was maintained for all counting. When counting alpha and beta particles, the uncovered samples were placed as close to the detector as possible without touching it to minimize attenuation of the particles before reaching the detector. The results of all counting were recorded on a standardized counting record sheet. Calculations were performed on the counting results to convert them to the amount of activity in curies, and the minimum detectable activity (given in Appendix G) was calculated from the efficiency of the system as determined by counting the standard source.

Soluble Organic Fraction - Particulate samples were collected on 8 × 10-inch Teflon®-coated glass fiber filters (Pallflex) for the determination of soluble organic fraction during the screening tests. The filters were Soxhlet-extracted with methylene chloride and the organic solubles were concentrated under dry nitrogen and then weighed. Soluble organic fraction was determined by comparison with particulate mass. The organic solubles were then analyzed by GC/MS for semi-volatile organic compounds according to the procedure described previously.

IV. LITERATURE REVIEWS

Two computer-assisted literature reviews were conducted to determine if the compounds listed in Tables 11 and 12 had been detected in automobile exhaust. The first review covered all of the compounds in Table 11 and all except the last three in Table 12 (styrene, hexachlorobenzene, and di-2-ethylhexylphthalate). In addition, epichlorohydrin, hexachlorocyclopentadiene, and phosgene were included in the initial literature search. At the request of ARB, these compounds were deleted and replaced with styrene, hexachlorobenzene, and di-2-ethylhexylphthalate. The second literature search investigated the latter three compounds.

Procedures for sampling and analyzing for all of these compounds were also reviewed. Databases were searched using the name of each compound or groups of compounds in combination with a second descriptor, gasoline, and with a third descriptor from the following list: vehicle, automobile, engine, exhaust, or emission. The literature search was conducted from 1970 to the present using Dialog Information Service, Inc. (DIS) and Orbit IV System Development Corporation (OSD). The databases selected for computer searching from DIS were Chemical Abstracts, National Technical Information Service, Compendex, and EI Engineering Meeting. The file that was searched from OSD was Society of Automotive Engineers.

A. Vehicle Emissions

The results of the literature search indicated that several compounds listed in Tables 11 and 12 have been investigated as potential components of vehicle emissions. These compounds have included phenol, cresols, dimethylnitrosamine, acrolein, methyl bromide, ethylene dibromide, chloroform, propylene oxide, ethylene oxide, and styrene.

Phenols and Cresols - Seizinger, et al., detected phenol and cresols, which are partially oxidized combustion products, in raw exhaust. A 1970 Ford Maverick was tested under simulated city driving conditions with several aromatic and non aromatic hydrocarbon fuels.(7) Levels of phenol and cresols ranging from 0.1 to 6.7 ppm were found in the exhaust. Samples were collected in Teflon bags and analyzed with a gas liquid chromatograph (GLC) coupled to a mass spectrometer. Mulawa and Cadle measured phenol and cresol emissions from several diesel and gasoline (catalyzed and non-catalyzed) vehicles over the 1975 Federal Test Procedure Driving Cycle (FTP).(8) Raw and dilute exhaust gases were sampled using an aqueous alkaline solution. Phenol was measured at 0.4 to 9.1 mg/km and cresols at 0.01 to 1.1 mg/km. Stenberg, et al., found somewhat higher emissions of phenol, 3.2 to 4.0 mg/km, while testing a 1976 2.1 liter Volvo 245 and a 1976 2.0 liter Saab over the 1972 FTP driving cycle with leaded gasoline.(9) These results were obtained by cryogenic trapping of dilute exhaust. Hinkamp, et al., measured several phenols emissions as a function of fuel type.(10) Hinkamp tested three vehicles, a 1970 5.7 liter Chevrolet, a 1968 5.0 liter Ford, and a 1970 5.2 liter Plymouth, over the FTP driving cycle. Leaded regular, leaded premium, and unleaded premium gasolines were used as test fuels. Phenols, sampled in an aqueous alkaline solution, were measured in the range of 0.20 to 0.48 g per gallon of fuel burned. Gross studied the effect of fuel on various phenols emissions using three vehicles, a 1966 V8 5.2 liter, 1968 V8 5.0 liter, and a 1970 V8 5.7 liter tested over the 7-mode cycle test.(11) Both leaded and unleaded fuels were used for testing the non catalyst equipped vehicles. Phenols were measured at levels between 0.08 and 0.78 g/gal of fuel used, with the higher levels corresponding to fuels with higher aromatic content.

Dimethylnitrosamine - Vehicle exhaust has also been analyzed for dimethylnitrosamine (DMNA), a potent carcinogen produced by the reaction of NO_x and dimethylamine. Urban investigated the presence of DMNA in the exhaust of vehicles tested under modified and malfunction conditions.(12,13) No DMNA was measured from a 1979 catalyst-equipped Mercury Marquis driven over the FTP, the Congested Freeway Cycle (SET), and the Highway Fuel Economy Test (HFET) driving schedules. In a second malfunction study, from 0.00 to 0.15 mg/km of DMNA was measured

TABLE 11. CARB TOXIC AIR CONTAMINANTS AND CANDIDATE TOXIC AIR CONTAMINANTS

(1) 1,3-butadiene
(2) acrolein
(3) chloroform
(4) carbon tetrachloride
(5) ethylene bromide
(6) ethylene dichloride
(7) methylene chloride
(8) perchloroethylene
(9) trichloroethylene
(10) vinyl chloride
(11) ethylene oxide
(12) phenol
(13) cresols
(14) nitrobenzene
(15) dialkylnitrosamines

Note: Substances listed in order of priority, where lowest number denotes the highest priority.

TABLE 12. ADDITIONAL CARB CANDIDATE TOXIC AIR CONTAMINANTS

chloroprene
allyl chloride
chlorophenols
polychlorinated byphenyls
acrylonitrile
1,4-dioxane
n-nitrosomorpholine
radionuclides
methyl chloroform
vinylidene chloride
maleic anhydride
p-dichlorobenzene
benzyl chloride
chlorobenzene
methyl bromide
propylene oxide
styrene
hexachlorobenzene
di-(2-ethylhexyl) phthalate

Note: List is not in priority order.

in the exhaust of four catalyst-equipped 1978 vehicles and one non-catalyst-equipped 1977 vehicle. The vehicles were tested over the FTP, SET and HFET driving cycles using unleaded gasoline. Vehicle exhaust was sampled using Tenax traps.

In a third program by Urban,(14) trace levels of DMNA (~0.0001 mg/km) were measured from a catalyst-equipped 1978 Pontiac Sunbird and a catalyst-equipped 1978 Saab 99 tested over the FTP, SET, and HFET driving schedules. Vehicle exhaust was sampled for DMNA using Tenax traps.

In a study by Smith and Urban, no DMNA was detected from two catalyst-equipped 1981 Ford Escorts or two catalyst-equipped 1981 VW Rabbits operating on methanol and methanol-gasoline fuel.(15) The trapping media for DMNA were Thermosorb/N traps. These traps were analyzed using a gas chromatograph coupled to a TEA analyzer.

Acrolein - Acrolein emissions were measured in raw exhaust by Seizinger and Dimitriades from a 1970 Ford Maverick operating over the 7-mode California cycle.(7) Several aromatic and non aromatic hydrocarbon test fuels were used, producing 0.2 to 5.3 ppm of acrolein in exhaust. In another program by Seizinger and Dimitriades using several hydrocarbon fuels, 0.05 ppm acrolein was emitted by a catalyst-equipped 1971 medium-sized sedan.(16) The vehicle was tested over the 7-mode cycle of the 1968 Federal Emissions Test Procedure. In both programs, dilute exhaust was sampled in Teflon bags and then adsorbed onto a Chromosorb trap.

Smith measured acrolein in the exhaust of a 1983 1.6 liter Ford Escort equipped with a methanol-fueled engine.(17) The vehicle was operated with an alcohol blend composed of 90 percent methanol and 10 percent gasoline over the FTP driving cycle and at steady-state conditions. Acrolein emissions ranged from 0.1 to 0.9 mg/km for FTP tests and from "none detected" to 0.4 mg/km for steady-state tests. With the catalyst removed, acrolein emissions were higher, ranging from below the detection limit to 2.2 mg/km for FTP tests, and from below the detection limit to 1.4 mg/km for steady state tests. Acrolein was sampled in acidic dinitrophenylhydrazine solutions and analyzed by high pressure liquid chromatography (HPLC).

Methyl Bromide, Ethylene Dibromide, and Chloroform - Halogenated hydrocarbons in the exhaust of vehicles fueled with leaded gasoline can often be traced to compounds added to scavenge lead, such as ethylene dibromide and ethylene dichloride. Methyl bromide, which was measured by Harsch and Rasmussen in raw exhaust from a 1972 Rambler and a 1975 Ford Pinto(18), is probably a combustion product of ethylene dibromide. The Rambler emitted 71 to 217 μg/m^3 (18.0 to 55 ppb) of methyl bromide, and the Pinto produced from less than 4 μg/m^3 to 5 μg/m^3 (<1 to 1.3 ppb) of methyl bromide.

Leinster, et al., measured ethylene dibromide in the exhaust of a 1.6 liter Ford Cortina using leaded fuel and operated over the European ECE driving cycle.(19) The compound was measured in raw exhaust in concentrations ranging from 80 to 154 μg/m^3 (10.2 to 20 ppb). Ethylene dibromide was sampled on Chromosorb 102 and analyzed by GC with an electron capture detector (ECD). Chloroform was measured by Harsch, et al(20) in the exhaust of a 1972 Rambler (non-catalyst-equipped) and a catalyst-equipped 1975 Ford Pinto. Samples were collected in stainless steel canisters and analyzed by GC-ECD. Tests on the Rambler with leaded gasoline yielded 5.6 to 6.8 ppb chloroform, and tests on the Pinto with unleaded gasoline produced 0.1 ppb chloroform.

Propylene Oxide and Ethylene Oxide - Seizinger and Dimitriades investigated the presence of propylene oxide in the raw exhaust of a catalyst-equipped 1971 medium sedan operating over the 7-mode cycle of the 1968 Federal Emissions Test Procedure.(16) The compound, sampled on Chromosorb 102, was measured at levels ranging from the detection limit to 0.37 ppm. Ethylene oxide was measured in the exhaust of a 1970 Ford Maverick operating on a number of hydrocarbon fuels over the 7-mode California cycle.(21) No ethylene oxide was detected in the samples. Sampling was conducted in Tedlar bags on raw exhaust with subsequent GC analysis.

Styrene - Seizinger and Dimitriades identified styrene as one of the components in exhaust organics from a 1970 Ford Maverick.(51) The vehicle was operated under simulated city driving conditions with several aromatic and non-aromatic hydrocarbon fuels. Raw exhaust samples were collected in Teflon bags, concentrated onto Chromosorb 102, and analyzed by GLC/FID, MS. Quantitative values for styrene were not given.

Styrene was also measured in the exhaust of a Labeco single cylinder CLR engine by Ninomiya and Golovoy.(52) Between 0.0001 and 0.0006 moles of styrene per mole of toluene in the fuel were emitted by the engine at varying air/fuel ratios. Two fuels were used in the study, toluene and a toluene/heptane blend. The exhaust sample, which was introduced directly to the analytical system by heated stainless steel tubing, was analyzed by GC/FID.

In summary, several hydrocarbon compounds have been investigated as possible components of exhaust from gasoline-fueled vehicles. The literature review indicated that the following compounds have been searched for in automotive exhaust:

Phenol
Cresols
Dimethylnitrosamine
Acrolein
Methyl bromide
Ethylene dibromide
Chloroform
Propylene oxide
Ethylene oxide
Styrene

All compounds except ethylene oxide were found at measurable levels in exhaust, with catalyst-equipped and non-catalyst-equipped vehicles operated on leaded and unleaded gasoline and alcohol fuels. The remaining compounds listed in Tables 11 and 12 were not mentioned in the literature in relation to vehicle emissions.

B. Methods for Sampling and Analysis

Various methods for sampling and analyzing the compounds in Tables 11 and 12 were investigated. Many of the procedures which were developed for ambient air sampling are adaptable to measurements of automotive exhaust.

The sampling media for trace gaseous components include solid sorbents such as Tenax, carbon molecular sieve, polyurethane foam, charcoal, Thermosorb/N, etc.; liquid sorbents such as organic solvents, caustic solutions, or dinitrophenylhydrazine; and cryogenic traps. Analysis methods include gas chromatography with flame ionization, electron capture, mass spectrometry, flame photometric, or thermal energy detectors, or high pressure liquid chromatography with ultraviolet or fluorescence detectors.

For the three added compounds, several types of sampling and analysis methods were used by researchers for di-2-ethylhexylphthalate, styrene, and hexachlorobenzene. Sampling media included filters (Teflon, glass fiber, Millipore), filters combined with solid sorbents (Florisil, polyurethane foam, Tenax, charcoal), liquid sorbents, and cold traps. Analysis of exhaust samples was by gas chromatography (GC) with mass spectrometry (MS), selected ion monitoring (SIM), flame ionization (FID), flame photometric (FPD), nitrogen-phosphorus (NPD), or electron capture (ECD) detectors or by liquid chromatography (LC) with ultraviolet (UV) detection.

A summary of sampling methods and analytical procedures for each compound or item listed in Tables 11 and 12 is given in Tables 13 and 14. The goal of the procedure review was to determine those methods which are most applicable to sampling and analyzing trace halogenated and oxygenated hydrocarbons, organic nitrogen compounds, radionuclides and styrene in automotive exhaust. The methods must be sufficiently sensitive and encompass all the compounds listed in Table 11 and as many in Table 12 as economically feasible.

Sampling with Tenax GC and Carbosieve III - When possible, U.S. EPA suggested methods were implemented for sampling and analysis. These methods, which are reviewed in a CARB and an EPA methods report,(25,28) have been used for ambient air monitoring at ppb and sub-ppb contaminant levels.

Two solid sorbents, Tenax GC and Carbosieve III (carbon molecular sieve), were used as described in EPA procedures T01 and T02 for sampling a majority of the compounds listed in Tables 11 and 12. Tenax GC is used for sampling volatile organic and volatile halogenated organic non-polar compounds with boiling points between 80 and 200°C. Carbon molecular sieve is applicable to the trapping of highly volatile organic and non-polar halogenated organic compounds that boil between -15 and 120°C. A stainless steel trap containing both Tenax GC and Carbosieve III was utilized in the sampling system to trap the following compounds.

Table 1 Compounds
Chloroform
Carbon tetrachloride
Ethylene dibromide
Ethylene dichloride
Methylene chloride
Perchloroethylene
Trichloroethylene
Vinyl chloride
Phenol
Cresols
Nitrobenzene

Table 2 Compounds
Chloroprene
Allyl chloride
Chlorophenol
Epichlorohydrin
Acrylonitrile
Dioxane
Hexachlorocyclopentadiene
Methyl Chloroform
Vinylidene chloride
p-dichlorobenzene
Benzyl chloride
Chlorobenzene
Methyl bromide
Propylene oxide
Phosgene

Breakthrough volumes or retention volumes have been measured for these and other compounds on Tenax.(23,28,29) Safe sampling volumes have ranged from about 4 liters per gram of Tenax for volatile chloroform (b.p. 62°C) to 240 liters per gram of Tenax for tetrachloroethylene (b.p. 121°C) at 20 to 38°C. The volume capacities include a safety factor, which is a reduction of actual breakthrough volume by 33 percent to account for variations in atmospheric conditions.(28) More volatile compounds are not as effectively retained on Tenax, and will pass through a Tenax trap if actual sampling volumes exceed the safe sampling volume compounds. For this reason, Carbosieve III was used to sample the more volatile hydrocarbons. The safe sampling volume of volatile organics on Carbosieve III is about 67 liters per 0.4 g of carbon molecular sieve(28) at 37°C. When sampling for vinyl chloride, the safe sampling volume is about 20 liters.

Breakthrough volumes of pollutants on Tenax GC or Carbosieve III are not adversely affected by the presence of water in automotive exhaust as are breakthrough volumes on charcoal. Tenax GC and Carbosieve III do not adsorb water; while charcoal does, thus reducing the available sites for adsorbing volatile hydrocarbons. Water vapor can also cause problems with other trapping methods

TABLE 13. METHODS FOR SAMPLING AND ANALYSIS

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
1,3-Butadiene	-4.4	Tedlar bag sample, GC/FID		22
Acrolein	52.5-53.5	Tenax	Breakthrough volume measured, 2.4 L/g	23
		DNPH in impinger, extraction, HPLC		24
		1% sodium bisulfite impinger, mercuric chloride hexylresorcinol, GC/FID	10-30 ppb, negative interference from phenols, ethylene, propylene	24
		Impinger DNPH, HPLC	Method needs validation, free from interference	25
		4-hexylresorcinol	Good sensitivity, specificity	25
		DNPH coated cartridge		25
		Tenax GC, 13X molecular sieve, GC/MS		25
		DNPH impinger, extraction, HPLC/UV		28
		DNPH impinger or 4-hexylresorcinol, or Florisil		25
		Teflon bag, GLC/FID	Vehicle exhaust	7
		Chromosorb 102 column chromatography clean-up, GLC/MS	Vehicle exhaust, cryogenic concentration of exhaust organics not feasible	16
		Acidic DNPH impinger, HPLC/UV	Vehicle exhaust	17
Chloroform	61.7	Tenax, Carbopack BHT, GC/MS		26
		Tenax	Breakthrough volume measured, 31 L/g	23
		Cold Pyrex bead packed trap, GC/FID	Trapping temp. given -60 to -95°C.	27

TABLE 13 (CONT'D). METHODS FOR SAMPLING AND ANALYSIS

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
Chloroform (Cont'd)	61.7	Tenax, GC/MS	EPA Method T01. Retention volume 8 L/g @ 38°C.	28
		Carbon molecular sieve, GC/MS	EPA Method T02. Method used in one laboratory.	28
		Cryogenic trapping, GC/FID or GC/ECD	EPA Method T03. For compounds with boiling points of -10 to 200°C.	28
		Sample into a canister, cryogenic concentration, GC/FID or GC/MS	For compounds with boiling points of -100 to 175°C.	24
		Tenax, GC/MS	For compounds with boiling points of 60-200°C. Possible artifacts from reactive compounds, O_3, NO_x	24
		Tenax, thermal desorption into canisters, GC/FID or GC/MS	Possible artifact formation. For compounds with boiling points of 60-200°C.	24
		Stainless steel canister, GC/ECD	Vehicle exhaust	20
Carbon tetrachloride	76.5	Tenax, GC/MS		26
		Tenax	Breakthrough volume measured, 31 L/g	23
		Cold Pyrex bead packed trap, GC/FID	Trapping temp. given -125°C.	27
		Tenax, GC/MS	EPA Method T01. Retention volume 8 L/g @ 38°C.	28
		Carbon molecular sieve, GC/MS	EPA Method T02. Method used in one laboratory.	28

TABLE 13 (CONT'D). METHODS FOR SAMPLING AND ANALYSIS

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
Carbon tetrachloride (Cont'd)	76.5	Sample into a canister, cryogenic concentration, GC/FID or GC/MS	For compounds with boiling points of -100 to 175°C.	24
		Tenax, GC/MS	For compounds with boiling points of 60-200°C. Possible artifacts.	24
		Tenax, thermal desorption into canisters, GC/FID or GC/MS	Poor recovery	24
Ethylene dibromide	131-132	Tenax, GC/MS	Breakthrough volume measured, 10 L	29
		Cold Pyrex bead packed trap, GC/FID	Trapping temp. -75°C.	27
		Tenax, GC/MS	EPA Method T01. Retention volume, 60L/g @ 38°C.	28
		Chromosorb 102, thermal desorption, GC/ECD	Vehicle exhaust	19
Ethylene dichloride	83.5	Tenax	Breakthrough volume measured, 27 L/g	23
		Cold Pyrex bead packed trap, GC/FID	Trapping temp. given -50 to -90°C.	27
		Tenax, GC/MS	EPA Method T01. Retention volume, 10 L/g @ 38°C.	28
		Carbon molecular sieve, GC/MS	EPA Method T02. Method used in one laboratory	28
		Cryogenic trapping, GC/FID or GC/ECD	EPA Method T03. For compounds with boiling points of -10 to 200°C.	28

TABLE 13 (CONT'D). METHODS FOR SAMPLING AND ANALYSIS

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
Ethylene dichloride (Cont'd)	83.5	Sample into a canister, cryogenic concentration, GC/FID or GC/MS	For compounds with boiling points of -100 to 175°C.	24
		Tenax, GC/MS	For compounds with boiling points of 60 to 200°C. Possible artifacts.	24
		Tenax, thermal desorption into canisters, GC/FID or GC/MS	For compounds with boiling points of 60 to 200°C. Possible artifacts.	24
Methylene Chloride	40	Tenax, GC/MS		26
		Tenax	Breakthrough volume measured, 1.5 L/g	23
		Carbon molecular sieve, GC/MS	EPA Method T02. Method used in one laboratory.	28
		Sample into a canister, cryogenic concentration, GC/FID or GC/MS	For compounds with boiling points of -100 to 175°C.	24
		Carbon molecular sieve, thermal adsorption into canister, GC/FID or GC/MS	For compounds with boiling points of 0 to 100°C. High desorption temp. (350°C) may decompose labile compounds.	24
Perchloroethylene	130-146	Carbopack B, GC/MS		26
		Charcoal, GC/MS	NIOSH method	30
		Tenax	Breakthrough volume measured, 240 L/g	23
		Cold Pyrex bead packed trap, GC/FID	Trapping temp. given -50 to -90°C.	
		Tenax, GC/MS	EPA Method T01. Retention volume, 80 L/G @ 38°C.	28

TABLE 13 (CONT'D). METHODS FOR SAMPLING AND ANALYSIS

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
Perchloro-ethylene (Cont'd)	130-146	Cryogenic trapping, GC/FID or GC/ECD	EPA Method T03. For compounds with boiling points of -10 to 200°C.	28
		Sample into a canister, cryogenic concentration, GC/FID or GC/MS	For compounds with boiling points of -100 to 175°C.	24
		Tenax, thermal desorption into canisters, GC/FID or GC/MS	For compounds with boiling points of 60 to 200°C. Possible artifacts.	24
		Tenax, GC/MS	For compounds with boiling points of 60 to 200°C. Possible artifacts.	24
Trichloro-ethylene	113-114	Carbopack B, GC/MS		26
		Charcoal, GC/MS	NIOSH method	30
		Tenax	Breakthrough volume measured, 28 L/g	23
		Cold Pyrex bead packed trap, GC/FID	Trapping temp. -50 to -90°C.	27
		Tenax, GC/MS	EPA Method T01. Retention volume, 20 L/g @ 38°C.	28
		Cryogenic trapping, GC/FID or GC/ECD	EPA Method T03. For compounds with boiling points of -10 to 200°C.	28
		Sample into a canister, cryogenic concentration, GC/FID or GC/MS	For compounds with boiling points of -10 to 175°C.	24
		Tenax, GC/MS	For compounds with boiling points of 60 to 200°C. Possible artifacts.	24

TABLE 13 (CONT'D). METHODS FOR SAMPLING AND ANALYSIS

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
Trichloroethylene (Cont'd)	113-114	Tenax, thermal desorption into canisters, GC/FID or GC/MS	For compounds with boiling points of 60 to 200°C. Possible artifacts.	24
Vinyl chloride	37	Carbosieve B, GC/MS	Requires high desorption temp., may cause reactions. Breakthrough volume, 4 L.	29
		Cold Pyrex bead packed trap, GC/FID	Trapping temp, given -115 to -125°C.	27
		Carbon molecular sieve, GC/MS	EPA Method T02. Method used in one laboratory.	28
Ethylene oxide	10.7	Columbia JXC charcoal, solvent desorption, GC/FID	Recovery poor with humidity >60% and sample volume >10 L. No interferences.	31
		Tedlar Bag, GC/FID	Vehicle exhaust	21
		Cold Pyrex bead packed trap, GC/FID	Trapping temp. -75°C.	27
		Sample into a canister, cryogenic concentration, GC/FID or GC/MS	For compounds with boiling points of -100 to 175°C.	24
		Charcoal, solvent desorption, GC/FID	NIOSH[a], much poorer sensitivity than thermal desorption. Charcoal better than Tenax for highly volatile compounds.	24
		Direct gas, GC/FID or GC/MS	Detection limit, 0.01 ppm	24
Phenol	182	Tenax, GC/MS	Breakthrough volume >10 L	29
		Tenax, GC/MS	For compounds with boiling points of 60 to 200°C. Possible artifacts.	24

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[a] NIOSH - National Institute for Occupational Safety and Health.

TABLE 13 (CONT'D). METHODS FOR SAMPLING AND ANALYSIS

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
Phenol (Cont'd)	182	Teflon bag, GLC/MS and GLC/FID	Raw automotive exhaust	7
		Aqueous alkaline solution in impinger, GC/FID	Raw and dilute automotive exhaust	8
		NaOH impinger, steam distillation, GC/FID or GC/MS		24
		Cryogenic trapping, capillary column, GC/FID or ECD or MS	Dilute automotive exhaust	9
		Aqueous alkaline solution impinger, 4-aminoantipyrene, spectrophotometer, visible	Vehicle exhaust	10
		Water condensate, extraction, UV spectrophotometer	Vehicle exhaust	11
Cresols	191-202	Tenax, GC/MS	For compounds with boiling points of 60 to 200°C. Possible artifacts.	24
		PUF, XAD-2, Chromosorb 102, solvent desorption, GC/ECD or GC/MS		24
		NaOH impinger, steam distillation, GC/FID or GC/MS		24
Nitrobenzene	210-211	Tenax	Breakthrough volume, 69,000 L/g	23
		Sample into a canister, cryogenic concentration, GC/FID or GC/MS		24
		Tenax, GC/MS	Possible artifacts	24
		Tenax, thermal desorption into canisters, GC/FID or GC/MS	Possible artifacts	24
Dialkyl-nitrosamines	151-153 175-177	(dimethyl) GC high resolution/MS, parent ion monitoring, peak matching		32

TABLE 13 (CONT'D). METHODS FOR SAMPLING AND ANALYSIS

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
Dialkyl-nitrosamines (Cont'd)	151-153 175-177	(dimethyl) Tenax, GC/MS peak matching		33
		Thermosorb/N, GC/chemiluminescence	Also evaluated activated charcoal, activated alumina, silica gel, Florisil, Tenax. Minimum artifact formation.	34
		Impinger with caustic, GC/MS		35
		(dimethyl) Thermosorb/N, desorption with solvent, GC/thermal energy analyzer (TEA) or GC/MS or GC/NPD	TEA expensive	24
		Thermosorb/N sorbent, GC/MS		25
		Tenax trap, GLC/MS	Vehicle exhaust	12,13,14
		Thermosorb/N trap, solvent desorption, GC/TEA	Vehicle exhaust	15
loroprene	59.4	Sample into a canister, cryogenic concentration, GC/FID or GC/MS		24
		Tenax, GC/MS	Possible artifacts	24
		Tenax, thermal desorption into canisters, GC/FID or GC/MS	Possible artifacts	24
Allyl chloride	45	Tenax	Breakthrough volume, 5 L/g	23
		Carbon molecular sieve, GC/MS	EPA Method T02. Method used in one laboratory.	28
		Sampling into a canister, cryogenic concentration, GC/FID or GC/MS		24

TABLE 13 (CONT'D). METHODS FOR SAMPLING AND ANALYSIS

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
Allylchloride (Cont'd)		Charcoal, solvent desorption, GC/FID	NIOSH, much poorer sensitivity than thermal desorption. Charcoal better than Tenax for highly volatile compounds.	24
		Carbon molecular sieve, thermal adsorption into canister, GC/FID or GC/MS	High desorption temp. (350°C) may decompose labile compounds	24
Chlorophenols	2-175 2,4-210 2,6-219	Tenax, GC/MS	Breakthrough volume, p-chloro >10 L pentachloro >10 L 2,4,6-trichloro >10 L	29
PCB		PUF + XAD-2 or PUF + Florisil PR. Hivol sampler 200-250 L/min, 300 m^3, solvent extraction, GC/ECD or GC/FID	Also tested PUF alone, PUF + Chromosorb 102, PUF + Porapak R, PUF + Tenax GC. Cartridge reusable.	36
		PUF, solvent extraction, cleanup on alumina. Hivol sampler 100-250 L/min, 360 m^3, GC/ECD or GC/FPD	At 225 L/min for 24 hr, recovery is 70-85%. Preferable sampling period <24 hr.	37
4,4'-Dichlorobiphenyl 2,4,5-Trichlorobiphenyl 2,4',5-Trichlorobiphenyl 2,2',5,5'-Tetrachlorobiphenyl 2,2',4,5,5'-Pentachlorobiphenyl 2,2',4,4',5,5'-Hexachlorobiphenyl		PUF, GC/ECD, hivol sampler 200-280 L/min, solvent extraction, column chromatography cleanup	EPA Method T04	28
		PUF, XAD-2, or Chromosorb 102, solvent desorption, GC/ECD or GC/MS, 1500 m^3	3 ng/m^3, can use lower volume for higher conc., 1-10 $\mu g/m^3$	24
		PUF, solvent extraction, GC/FID or GC/MS or HPLC fluorescence	EPA Method T04. Interference from contaminants.	25

TABLE 13 (CONT'D). METHODS FOR SAMPLING AND ANALYSIS

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
Epichlorohydrin	116.5	Tenax	Breakthrough volume, 69 L/g	23
		Impinger with alcoholic KOH, reflux to saponify, potentiometric titration or GLC		38
		PUF and charcoal, solvent desorption GC/FID. 10-200 mL/min, 30 L	NIOSH 2 mg/m^3	39
		Sample into canister, cryogenic concentration, GC/FID or GC/MS		24
		Tenax, thermal desorption, GC/MS 20 L	1-200 ppt, artifacts from reactive compounds	24
		Tenax, thermal desorption into canisters, GC/FID or GC/MS	0.01-1 ppb, artifact problem	24
Acrylonitrile	78	Porapak N, GC/MS 25°C, 100 mL/min	Breakthrough volume, 3.5 L	29
		Tenax, 5 to 600 mL/min, 20°C	Breakthrough volume, 3.5 L/g, <100 ppm, humidity to 95%	23
		Charcoal 50-200 mL/min, 100 min. solvent desorption, GC/NPD	73% desorption. NPD more sensitive, specific than FID.	40
		Cold Pyrex bead packed trap, GC/FID	Trapping temp., -40 to 75°C	27
		Carbon molecular sieve, GC/MS 10-500 mL/min, 30-100 L/cartridge	EPA Method T02.	28
		Sample into canister, cryogenic concentration, GC/FID or GC/MS		24
		Carbon molecular sieve, thermal desorption into canister GC/FID or GC/MS, 20 L	0.01-1 ppb. High desorption temp. (350°C) may decompose labile compounds.	24
		Carbon molecular sieve, desorb to cryogenic trap, GC/MS or /ECD or /FID	EPA Method T02. Contamination at ppb levels.	25

TABLE 13 (CONT'D). METHODS FOR SAMPLING AND ANALYSIS

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
1,4-Dioxane	101	Charcoal, thermal desorption, GC/MS, 1 L/min, 240 L	NIOSH	30
		Charcoal, solvent extraction, GC/ECD or GC/FID	NIOSH. Small amounts of water reduce breakthrough volume significantly	25
n-Nitrosomorpholine	139-140	Thermosorb/N, solvent desorb GC thermal energy analyzer (TEA) or GC/MS, GC/NPD	TEA expensive, 25 ng/m^3	24
		KOH trap, GC/TEA	Artifact formation	25
Radionuclides		Filter paper, count alpha, beta, or gamma particles		50
Hexachlorocyclopentadiene	239 @ 753 mm Hg	Benzene or hexane impinger, GC/ECD	>97% extraction efficiency @ 20°C	41
		Chromosorb 102, GC/FPD	FPD not as sensitive as ECD; longer sampling time	41
		Tenax, thermal desorption, GC/MS, 20 L	1-200 ppt, artifacts from reactive compounds	24
		Tenax, thermal desorption into canisters, GC/FID or GC/MS, 20 L	0.01-1 ppb, artifact problem	24
		PUF, XAD-2, or Chromosorb 102, solvent desorption, GC/ECD or GC/MS, 1500 m^3	ng/m^3, can use lower volume for higher conc., 1-10 µg/m^3	24
		Charcoal, solvent extraction, GC/ECD or GC/FID	NIOSH, small amounts of water reduce breakthrough volume significantly	25
Methyl chloroform	74	Carbopack B, 25 L, GC/MS		26
		Charcoal, thermal desorption, GC/MS, 1 L/min, 240 L	NIOSH	30
		Cold Pyrex bead packed trap, GC/FID, 1.5 L, 40 L/min	Trapping temp., -50 to -100°C	27

TABLE 13 (CONT'D). METHODS FOR SAMPLING AND ANALYSIS

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
Methyl chloroform (Cont'd)	74	Tenax, thermal desorption, GC/MS	EPA Method T01. Retention volume, 6 L/g @ 38°C	28
		Carbon molecular sieve, GC/MS, thermal desorption, 10-500 mL/min, 30-100 L/cartridge		28
		Sample into canister, cryogenic concentration, GC/FID	Detection limit, 1 ppb	24
		Tenax, thermal desorption, GC/MS, 20 L	1-200 ppt, artifacts from reactive compounds	24
		Tenax, thermal desorption into canisters, GC/FID or GC/MS, 20 L	0.01 to 1 ppb, artifact problem	24
Vinylidene chloride	37	Carbosieve B, GC/MS	Requires high temp. may cause reactions	29
		Charcoal thermal desorption, GC/MS, 1 L/min, 240 L	NIOSH	30
		Cold Pyrex bead packed trap, GC/FID	Trapping temp. -80 to -125°C	27
		Carbon molecular sieve, thermal desorption GC/MS, 10-500 mL/min 30-100 L/cartridge	EPA Method T02	28
		Cryogenic trapping, GC/FID or GC/ECD	EPA Method T03	28
		Sample into canister, cryogenic concentration, GC/FID or GC/MS	1 ppb	24
		Tenax, thermal desorption, GC/MS, 20 L	1-200 ppt, artifacts from reactive compounds	24
		Tenax, thermal desorption into canisters, GC/FID or GC/MS, 20 L	0.01 to 1 ppb, artifact problem	24

TABLE 13 (CONT'D). METHODS FOR SAMPLING AND ANALYSIS

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
Maleic anhydride	202	Tenax, 5-600 mL/min to 20°C	Breakthrough volume, 440 L/g <100 ppm humidity to 95%	23
		No routine validated analysis. Tenax GC, GC/FID or water impinger, HPLC/UV		25
p-Dichlorobenzene	174-181	No method found		--
Benzylchloride	179	Cold Pyrex bead packed trap, GC/FID	Trapping temp. -15°C	27
		Sample into canister, cryogenic concentration, GC/FID or GC/MS	Detection limit, 1 ppb	24
		Tenax, thermal desorption, GC/MS, 20 L	1-200 ppt, artifacts from reactive compounds	24
		Tenax, thermal desorption into canisters, GC/FID or GC/MS, 20 L	0.01 to 1 ppb, artifact problem	24
Chlorobenzene	132	Tenax, GC/MS, 1 L 100 mL/min. 25°C	<100 ppm, Breakthrough volume, >10 L	29
		Tenax, 5-600 mL/min, to 20°C	Breakthrough volume, 130 L/g, <100 ppm, humidity to 95%	23
		Cold Pyrex bead packed trap, 1.5 L, 40 mL/min, GC/FID	Trapping temperature 0 to -75°C	27
		Tenax, thermal desorption, GC/MS	EPA Method T01. Retention volume, 150 L/g @ 38°C	28
		Cryogenic trapping, GC/FID or GC/ECD	EPA Method T03	28
		Sample into canister, cryogenic concentration, GC/FID or GC/MS	Detection limit, 1 ppb	24

TABLE 13 (CONT'D). METHODS FOR SAMPLING AND ANALYSIS

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
Chlorobenzene (Cont'd)	132	Tenax, thermal desorption, GC/MS, 20 L	1-200 ppt. Artifacts from reactive compounds	24
		Tenax, thermal desorption into canisters, GC/FID or GC/MS, 20 L	0.01-1 ppb, Artifact problem	24
Methyl bromide	4	Stainless steel can, GC/ECD	10 ppt detection limit	18
Propylene oxide	34	Porapak N, GC/MS, 1L, 100 mL/min, 25^oC	<100 ppm, Breakthrough volume, 1.5 L	29
		Sample into canister, cryogenic concentration, GC/FID or GC/MS	Detection limit, 1 ppb	24
		Tenax, thermal desorption, GC/MS, 20 L	1-200 ppt, Artifacts from reactive compounds	24
		Tenax, thermal desorption into canisters, GC/FID or GC/MS, 20 L	0.01-1 ppb, Artifact problem	24
		Charcoal, solvent extraction, GC/ECD or GC/FID	NIOSH, small amounts of water reduce breakthrough volumes	25
		Chromosorb 102, column chromatography cleanup, GLC/MS	Vehicle exhaust	16
Phosgene	8	GLC/ECD	0.02 ppm, rapidly hydrolyzes in H_2O	42
		Piezoelectricquartz crystal	µg/L, experimental	43
		GC/ECD or GC/IR	1 ppb-1 ppm, no interference from NH_3, H_2O, CO_2. Trichloroethylene, dioxane, ethylene oxide, acetone, ethanol, interfere with IR	44
		GC/ECD, alcoholysis into 2-propanol	0.001 ppm	45
		GC/ECD	1 ppb to 2 ppm, HCl, CCl_4, do not interfere	46
		GC/pulsed flow coulometry		47

TABLE 14. METHODS FOR SAMPLING AND ANALYSIS OF DI-2-ETHYLHEXYLPHTHALATE, STYRENE, AND HEXACHLOROBENZENE

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
di-2-Ethylhexylphthalate	384	Teflon filter, thermal desorption, GC/MS, packed column, ng/m^3 detection	Compared well with toluene extraction of filter	53
		Cyclohexane extraction of particulate, high speed LC/UV		54
		Teflon filter, methanol extraction, GC/MS, SIM, 0.1-20 ng/m^3	Significant background contamination glassware, solvents	55
		Teflon filters, solvent desorption, HPLC/UV, 0.05 mg/m^3	Tried mixed cellulose ester filters, too	56
		Glass fiber filter, benzene extraction, GC/MS, FID	Background level 8 μg filter	57
		Impinger/ethylene glycol, 1.7 cfm, hexane extraction, Florisil cleanup, GC/ECD/MS. Recovery >90%, ng/m^3	Solvents apparatus precleaned	58
		Florisil, solvent elution, LC separation, GC/ECD, 1 ng/m^3 94-104% recovery	Background contamination glassware, Florisil, solvent	59
		Florisil, solvent elution, GC/ECD, 2-4 L/min	Solvent distilled to prevent contamination	60
		PUF/Glass fiber filter, petroleum ether extraction, Florisil cleanup, GC/ECD packed column, ng/m^3	PUF better recovery in moist air than Amberlite XAD-2 or Florisil	61
		Two PUF plugs/glass fiber filter, benzene extraction, GC/MS, SIM 0.35 m^3/min, pg/m^3 to ng/m^3	Blank <5 pg/m^3	62
Styrene	145.2	Tenax GC, thermal desorption, GC, capillary column, minimum 4 μg/trap		64
		Tenax thermal desorption, GC/FID, MS	Four methods compared	65
		Tenax thermal desorption (EPA SW846 Method 5030), GC/MS (EPA Method 8240)		66

TABLE 14 (CONT'D). METHODS FOR SAMPLING AND ANALYSIS OF DI-2-ETHYLHEXYLPHTHALATE, STYRENE, AND HEXACHLOROBENZENE

Compound	Boiling Point, °C	Sampling and Analysis Method	Comments	Reference
Styrene (Cont'd)	145.2	Charcoal, 200 mL/min, solvent desorption, GC/FID 5-1500 ppm, >90% recovery	Greatest error is measuring flowrate	67
		NIOSH method, charcoal, solvent desorption, 100-400 ppm, GC/FID		68
		Charcoal NIOSH Method S127	No styrene detected even though physical symptoms in humans were present	69
		3M diffusive samplers, GC/FID, capillary column, 0.1-2.4 ppm	Compared with charcoal sampler	70
		Impinger/acetic acid, GC/FID, 88-107% recovery, 0.1 to 120 ppm, 200 mL/min	To avoid polymerization at thermal desorption temperatures	71
		Cold trap, extract with hexane, derivative to dibromide, GC/ECD, capillary column	Halogenate for greater detection sensitivity. Interference butadiene, ketones, phenols	72
		Pyrolysis GC two step program 600°C then 725°C, packed column, GC/MS, 200 ppm detection limit	Major factor affecting precision-reproducible positioning of sample in pyrolysis coil	73
Hexachlorobenzene	322 (sublimes)	Chromosorb 101, 2 L/min, solvent extraction, ~95% trapping efficiency, 0.4-6 $\mu g/m^3$, GC/ECD	Storage to 6 days room temperature	74
		Millipore filter, Tenax trap, solvent extraction, GC/ECD, packed column, 0.4-3.5 L/min, ~0.4 to 24 $\mu g/m^3$		75
		Tenax, solvent extraction, derivatization, GC/ECD, packed column, 2.4 to 1200 ppb	No hexachlorobenzene found	76
		PUF, solvent extraction, GC/MS		

✓

which might otherwise be acceptable for sampling volatile organic compounds. In particular, moisture can condense on the surfaces of glass sampling bulbs or stainless steel canisters. In addition, water vapor will freeze at the sub-zero temperatures in cryogenic traps, potentially blocking sample flow.(24)

A study was performed by Pellizzari, et al., evaluating six sampling methods for trace pollutants in ambient air samples.(48) Several of the compounds of interest in the current program were included in the study. The sampling methods that were investigated included three types of bags (Teflon, Tedlar, and polyethylene-aluminized), glass bulbs, stainless steel canisters, Tenax GC, charcoal, and cryogenic traps. For general use, Tenax GC and stainless steel canisters provided the highest recovery of doped samples. Tenax GC worked best when sampling volumes were less than the breakthrough volumes. Stainless steel canisters gave the highest recoveries of the volatile compounds.

A major disadvantage associated with the use of Tenax for sampling ambient air is the possibility of artifact formation from the presence of ozone or contaminants.(24) Ozone is not usually produced by combustion engines so is not a great concern. Contamination can be minimized by proper cleaning and handling of the Tenax and the trap.

No sampling methods were found for methyl bromide or phosgene. However, the low boiling points of the compounds, 4 and 8°C, respectively, make them candidates for sampling on carbon molecular sieve. Two compounds from the above list, dioxane and phosgene, were sampled in diesel exhaust using Tenax. This work was being performed in another program with the California Air Resources Board.(49)

Analysis of the compounds trapped on Tenax and Carbosieve III is by gas chromatography with detection by mass spectrometry. A VOCOL capillary column from Supleco is used for separation of the above compounds. Capillary columns provide better resolution and more sensitivity than packed columns.

1,3-Butadiene - Southwest Research Institute has developed a method for sampling and analyzing 1,3-butadiene in automotive exhaust for the U.S. EPA.(22) Tedlar bag samples of dilute exhaust were analyzed by GC with a flame ionization detector using a stainless steel column packed with picric acid on Graphpac GC. This method was used for the subject program.

Acrolein - Acrolein was measured by a method currently in use at Southwest Research Institute.(17) This method is similar to EPA method T05. Dilute exhaust is drawn through a chilled impinger containing a solution of acidified dinitrophenylhydrazine in acetonitrile. An extraction is not performed as in method T05. The sample is analyzed directly by high pressure liquid chromatography (HPLC) with an ultraviolet detector (UV) set at 350 nm.

Ethylene Oxide - Ethylene oxide is a volatile, lightweight compound (b.p. 11°C, m.w. 44) which is not easily sampled or analyzed. Charcoal is the NIOSH-recommended sampling sorbent. However, water vapor in exhaust will tend to deactivate the charcoal. Therefore, the Tenax GC/Carbosieve III trap used to sample many of the volatile hydrocarbons was also analyzed for ethylene oxide.

Dialkylnitrosamines and N-Nitrosomorpholine - Vehicle exhaust was sampled for dialkylnitrosamines and n-nitrosomorpholine on Thermosorb/N cartridges. Thermosorb/N has been found to produce lower background levels of nitrosamines than Tenax.(24) The dialkylnitrosamines that were sampled and analyzed included the following compounds:

n-nitrosodimethylamine
n-nitrosodiethylamine
n-nitrosodipropylamine
n-nitrosodibutylamine

n-nitrosopiperidine
n-nitrosopyrrolidine

After sample collection, the Thermosorb/N traps were sent to Thermedics Inc. in Massachusetts for analysis. At Thermedics, the traps are backflushed with a 25 percent solution of methanol in dichloromethane. The first 1.5 to 1.8 mL of this eluate is analyzed by GC with a thermal energy analyzer, a detector specific to nitrosamines.

Polychlorinated Biphenyls, Maleic Anhydride, Hexachlorocyclopentadiene - Dilute vehicle exhaust was sampled and analyzed for polychlorinated biphenyls, maleic anhydride, and hexachlorocyclopentadiene using a method similar to EPA method T04. Polyurethane foam (PUF) was used as the sampling medium. The PUF cartridge was subsequently Soxhlet extracted with 60 percent ether in hexane for 24 hours. The extract was concentrated and then analyzed by GC/MS using a glass capillary column.

A Teflon-coated glass fiber filter (Pallflex) was used before the PUF cartridge for sampling particulate. The particulate was Soxhlet extracted with methylene chloride. The organic solubles were scanned for particulate associated organics.

Radionuclides - Exhaust samples were collected on a fluorocarbon filter medium, for subsequent analysis of radionuclides. The particulate on the filters was analyzed for alpha, beta, and gamma activity using Ludlum detectors and counters.

Di-2-ethylhexylphthalate (DEHP) - Di-2-ethylhexylphthalate (DEHP) is one of the primary phthalate esters produced for the manufacture of plastics. Several researchers sampled DEHP on Teflon or glass fiber filters and solvent or thermally desorbed DEHP from the trap.(53-57) Analysis by GC/MS or GC/MS and GC/SIM provided detection in the ng/m^3 range and analyses by HPLC/UV provided detection in the mg/m^3 range.

A second method for sampling DEHP was an impinger method with ethylene glycol as the trapping medium.(58) The sample was solvent-extracted, cleaned on Florisil, and analyzed by GC/ECD and GC/MS. Recovery was reported to be better than 90 percent at the ng/m^3 level.

DEHP was also sampled on Florisil, solvent eluted, and analyzed by GC/ECD for levels of DEHP in the ng/m^3 range.(59,60) Recovery was 94-104 percent of added DEHP.(95) Polyurethane foam (PUF) combined with glass fiber filters was the sampling medium used by two laboratories.(61,62) The sampling process was followed by solvent extraction and analysis by GC/ECD or GC/MS and GC/SIM. Detection of DEHP by these methods was in the pg/m^3 to ng/m^3 range. Southwest Research Institute also employs PUF as the sampling medium for DEHP followed by solvent extraction and analysis by GC/MS. This analytical method was used in the screening tests for DEHP since PUF was used for sampling several other compounds and it was not be difficult to incorporate DEHP into the analysis.

A prevalent problem noted by several authors in the sampling and analysis of DEHP was background contamination of glassware, solvents, Florisil, filters, and hardware with DEHP. Singmaster and Crosby also noted DEHP contamination of air conditioner filters, solvents, and syringes in µg and ng quantities.(63) Background levels of DEHP were monitored and careful cleaning procedures were implemented to minimize DEHP contamination.

Styrene - Styrene, used primarily as a raw material in the production of plastics, has been sampled by several solid sorbent methods. Atmospheric styrene was sampled on Tenax, thermally desorbed and analyzed by GC/FID and GC/MS.(64-66) Southwest Research Institute currently employs this procedure for styrene measurement, which is an EPA method. With a boiling point of 145°C, styrene is a good candidate for sampling on Tenax. The boiling point range over which Tenax is an acceptable absorbent is 80 to 200°C.

Charcoal has also been used as a trapping medium for styrene, particularly in personal samplers worn by workers.(67,69) The charcoal is solvent desorbed and then analyzed by GC/FID. Detection limits for styrene for similar methods vary considerably, from about 5 to 400 ppm. In one of the studies,(69) no styrene was detected even though physical symptoms in humans were present.

A 3M diffusive sampler was also used for sampling styrene.(70) The trap was desorbed and analyzed by GC/FID. Styrene was measurable in the range 0.1 to 2.4 ppm.

A liquid sorbent method was developed to avoid polymerization of styrene at thermal desorption temperatures.(71) Styrene was trapped in an impinger containing acetic acid an then analyzed by GC/FID. Between 0.1 and 120 ppm of styrene was measured.

To improve sensitivity for detecting styrene, a procedure was used in which atmospheric styrene was cold trapped, extracted with hexane, and derivatized to the dibromide.(72) Analysis was conducted using GC/ECD, the ECD being sensitive to halogenated compounds. Butadiene, ketones, and phenols interfered with this procedure. Since it is likely that these compounds would be present in exhaust, this method would not be feasible for measuring styrene in exhaust.

Pyrolysis GC/MS has also been employed to measure styrene.(73) The detection limit for this method was 200 ppm, higher than desirable for this program. Styrene was sampled on Carbosieve/Tenax, thermally desorbed, and analyzed by GC/MS. The boiling point of styrene falls within the range that Tenax is capable of trapping. Also, thermal desorption provides higher detection sensitivity than solvent desorption since the entire sample is analyzed. At the concentration levels of styrene that were likely to be present in exhaust and at a thermal desorption temperatures of 180°C, it was unlikely that polymerization of styrene would occur. Carbosieve/Tenax was also used to sample several other volatile organic and volatile halogenated organic compounds, so that incorporating styrene into the analysis would not be difficult.

Hexachlorobenzene - Hexachlorobenzene is a compound used in the production of pesticides. It has been sampled on Chromosorb 101, solvent-extracted, and analyzed by GC/ECD.(74) Tenax has also been used in combination with a filter as a sorbent for hexachlorobenzene, followed by solvent extraction, and analysis by GC/ECD.(75) In another method utilizing Tenax as a sorbent, the sampled Tenax was solvent-extracted, derivatized, and analyzed by GC/ECD.(76)

A procedure for the measurement of hexachlorobenzene in air was developed at Southwest Research Institute.(77) Sampling is on polyurethane foam, which is subsequently solvent extracted and analyzed by GC/MS. This procedure (similar to EPA method T04) was utilized in the screening test for sampling and analyzing for hexachlorobenzene.

V. SCREENING TESTS

The purpose of the screening tests was to determine which of the targeted compounds (see Table 10) were present in exhaust and to focus on those compounds in the final emissions tests. Only those compounds that had not previously been measured in exhaust as determined by the literature search were evaluated in the screening tests.

The literature searches revealed that several of the compounds listed on Tables 11 and 12 had been measured in the exhaust of gasoline-powered (leaded and unleaded) or alcohol-powered vehicles. The vehicles included both catalyzed and non-catalyzed versions. The literature review indicated that the following compounds had been found at measurable levels in automotive exhaust:

- phenol
- cresols
- dimethylnitrosamine
- acrolein
- methyl bromide
- ethylene dibromide
- chloroform
- propylene oxide
- styrene

It was not necessary to include these compounds in the screening test portion of the program since they had already been measured in exhaust. Some of these compounds were sampled and analyzed anyway because the sampling media and methods of analyses were common for other compounds included in the screening tests. These analyses included sampling dimethylnitrosamine on Thermosorb/N along with n-nitrosomorpholine, and sampling methyl bromide, ethylene dibromide, chloroform, propylene oxide, and styrene on Carbosieve/Tenax traps with other volatile organic compounds.

The compounds and radionuclides that were analyzed in the screening tests are given in Table 10. The test vehicles were operated over the Urban Dynamometer Driving Schedule (UDDS) in combinations of cold-start, hot-start, and forced-cooled-start tests. Three sets of screening tests were performed on each vehicle, sampling dilute exhaust. The test sequences are shown below:

	Test Date		
Screening Test	Ford Taurus	Toyota Camry	Test Sequence
1	2/29/89	2/29/89	4-Bag FTP (2 UDDS)
2	4/5/88	3/31/88	4-Bag FTP plus 2 hot-start UDDS plus forced-cooled-start UDDS (5 UDDS)
3	6/22/88	6/21/88	4-Bag FTP (2 UDDS)

Regulated gaseous emissions were measured on each screening test from the Ford Taurus and the Toyota Camry. A summary of FTP emissions results and fuel economy from screening tests is given in Table 15. Hydrocarbons, carbon monoxide, and oxides of nitrogen emissions were within California emissions standards. Regulated emissions repeated reasonably well, indicating that the cars operated repeatably for the various tests. Computer printouts of the regulated emissions tests on the Taurus and Toyota are given in Appendices B and C, respectively.

The screening tests also included measurement of unregulated emissions on several solid sorbent materials. Carbosieve/Tenax (C/T) was used for trapping volatile organic compounds, polyurethane foam (PUF) for semi-volatile organics, and Thermosorb/N (T/N) for n-nitroso compounds. Dilute exhaust gas was sampled in Tedlar bags for regulated gaseous emissions and for 1,3-butadiene. Aldehydes (and ketones) and phenols were sampled in impingers. Particulate emissions were sampled on fluorocarbon filters and Teflon-coated glass fiber filters for the measurement of trace metals and

TABLE 15. FTP REGULATED VEHICLE EMISSIONS RESULTS

Emission	1987 Ford Taurus Emission Rate, g/mi Initial Test	Screening Test #1	Screening Test #2	Screening Test #3	California Emissions Standard, g/mile
Hydrocarbons	0.25	0.25	0.30	0.22	0.41(0.39)[a]
Carbon Monoxide	3.35	3.64	3.97	3.10	7.0
Oxides of Nitrogen	0.45	0.45	0.48	0.43	0.7
Fuel Economy, mpg	23.68	22.15	22.58	21.84	

Emission	1986 Toyota Camry Emission Rate, g/mi Initial Test	Screening Test #1	Screening Test #2	Screening Test #3	California Emissions Standard, g/mile
Hydrocarbons	0.14	0.17	0.18	0.17	0.41(0.39)[a]
Carbon Monoxide	2.35	2.24	2.09	2.52	7.0
Oxides of Nitrogen	0.32	0.27	0.27	0.25	0.7
Fuel Economy, mpg	29.09	29.35	30.49	29.42	

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[a] Non-methane

other elements, radionuclides (alpha, beta, and gamma activity), and organic solubles. A list of the compounds and the respective sampling media is given in Table 10.

The first screening tests involved sampling on C/T and PUF solid sorbent materials and on filters throughout a cold-start UDDS cycle. A second set of samples was taken during a hot-start UDDS cycle. Dilute exhaust was sampled in a Tedlar bag on each bag segment of the UDDS, for a total of four bags. The sampling schedule for each of the screening tests is shown in Table 7.

In the second set of screening tests, sampling times for the PUF traps and the filters were extended to improve the detection limits of the compounds and radionuclides being analyzed. In the third set of screening tests, background dilution air was drawn through the C/T, PUF, and T/N traps for a period of time equivalent to actual sampling conditions. None of the semi-volatile target compounds listed in Table 10 were detected above the minimum detection limit for the PUF or T/N traps. The C/T background levels of volatile organics were subtracted from sample concentrations to provide background-corrected values. In addition, 8 × 10-inch Teflon-coated glass fiber filters were used to collect particulate for subsequent determination of semi-volatiles content of the organic solubles.

The final screening test performed involved sampling raw exhaust through C/T and PUF trap materials. The purpose of raw exhaust testing was to determine if some of the targeted volatile and semi-volatile compounds, thus far not detected, would be measurable in non-diluted raw exhaust. Ice water baths were installed upstream of the C/T and PUF traps to cool the raw exhaust and to condense water from the exhaust.

A C/T and a PUF trap were sampled for each UDDS for each vehicle. A condensate sample was also collected with each PUF trap. No water condensed in the water trap upstream of the C/T due to the lower flowrate through the C/T trap. Raw exhaust was sampled directly from the vehicles at constant flowrates for the C/T and PUF traps. During transient operation, the volume of exhaust produced by the vehicle varies with engine speed. Emission rates can not be calculated for a direct comparison to the dilute exhaust emissions.

A summary of the screening test results for the Ford Taurus and the Toyota Camry are given in Tables 16 and 17. More detailed data are given in Appendices D and E. Trace metal and other elemental emissions from the first and second screening tests are given in Tables 18 and 19. Detailed metals data and minimum detection limits are listed in Appendices F and G. Minimum detection limits for other compounds are given in Appendix H.

The detection limits, as described in this report, for 1,3-butadiene, aldehydes and ketones, and phenols are defined as the measured value that can vary within ± 1 detection limit. For example, a value measured at the detection limit of 0.02 mg/mi could vary ± 0.02 mg/mi, or from 0.0 to 0.04 mg/mi. The detection limits for halogenated hydrocarbons and other unregulated hydrocarbons (except for 1,3-butadiene) are defined as values that exceed a signal to noise ratio of 5 to 1. Detection limits for nitrosamines correspond to values that are greater than a signal to noise ratio of 3 to 1 and the detection limits for trace metals and other elements must be exceeded by a factor of three or more for a sample value to be reported as measureable. When "not detected" is mentioned, this means the substance was not detected at any level. When the word "Trace" is used, this refers to the fact that a response was produced for a substance but at levels below the detection limit and was therefore not quantifiable.

Of the target compounds sampled in the screening tests, selected hydrocarbons that were measured from both vehicles included benzene, 1,3-butadiene, styrene, toluene, and xylenes. Tables 16 and 17 list amounts from each test from the Ford Taurus and Toyota Camry, respectively. Benzene, toluene, and xylenes were measured at levels well above their minimum detection limits (see Appendix H) for both vehicles. Styrene concentrations were variable, and 1,3-butadiene was measured above the detection limit from both vehicles.

TABLE 16. TEST RESULTS FOR UNREGULATED EMISSIONS FROM SCREENING TESTS ON A FORD TAURUS

		Emission Rate, mg/mi			
Compound	Sampling Media	First Screening Test	Second Screening Test	Third Screening Test[a]	Raw Exhaust Test
Total Hydrocrabons	Bag	250	300	220	b
Individual Hydrocarbons					
Benzene	C/T[c]	12	13	8	b
1,3-Butadiene	Bag	0.7	0.8	b	b
Styrene	C/T	ND[d]	1.0	0.3	0.5
Toluene	C/T	19	22	13	b
Xylenes	C/T	18	22	47	b
Halogenated Hydrocarbons					
Methyl chloroform	C/T	Trace[e]	0.6	Trace	Trace
Methylene chloride	C/T	1.0	0.4	0.4	ND

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[a] Background corrected.
[b] Not measured.
[c] C/T - Carbosieve/Tenax trap.
[d] ND - None detected. Less than the detection limit.
[e] Trace - Detected but not quantifiable above the detection limit.

TABLE 17. TEST RESULTS FOR UNREGULATED EMISSIONS FROM SCREENING TESTS ON A TOYOTA CAMRY

		Emission Rate, mg/mi			
Compound	Sampling Media	First Screening Test	Second Screening Test	Third Screening Test[a]	Raw Exhaust Test
Total Hydrocarbons	Bag	170	180	170	b
Individual Hydrocarbons					
Benzene	C/T[c]	12	5	5	b
1,3-Butadiene	Bag	0.8	0.9	b	b
Styrene	C/T	ND[d]	0.7	0.3	0.03
Toluene	C/T	30	12	14	b
Xylenes	C/T	31	14	36	b
Halogenated Hydrocarbons					
Chlorobenzene	C/T	ND	ND	ND	Trace
Chloroform	C/T	ND	ND	ND	Trace
Methyl chloroform	C/T	e	Trace[f]	ND	0.01
Methylene chloride	C/T	e	Trace	Trace	0.01
Pentachlorophenol	PUF[c]	ND	Trace	b	ND

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[a] Background corrected.
[b] Not measured.
[c] C/T - Carbosieve/Tenax trap, PUF - polyurethane foam trap.
[d] ND - None detected. Less than the detection limit.
[e] High levels of methylene chloride and methyl chloroform-possible artifact.
These measurements repeated on second set of screening tests.
[f] Trace - Detected but not quantifiable above the detection limit.

TABLE 18. TRACE METALS AND OTHER ELEMENTS FROM THE FIRST SET OF SCREENING TESTS OF A FORD TAURUS AND A TOYOTA CAMRY OPERATED OVER A COLD-START UDDS AND A HOT-START UDDS

	FTP Emissions, µg/mi[a]		
	1987 Ford Taurus	1986 Toyota Camry	Detection Limit, µg/mi
Magnesium	43	5	3
Aluminum	84	18	4
Silicon	28	14	8
Phosphorus	97	8	2
Sulfur	180	49	4
Chlorine	97	6	5
Potassium	8	ND[b]	4
Calcium	94	60	5
Chromium	250[c]	240[c]	68
Iron	1900	990	49
Nickel	78	ND	46
Copper	200	130	54
Zinc	100	ND	56
Strontium	ND	300	209
Tin	30	ND	30

---

[a] Total particulate emissions were not determined during initial screening tests. Refer to Table 21 for total particulate emissions measured during later screening tests.

[b] ND - None detected. Less than the detection limit.

[c] Chromium emissions relatively high compared to second screening tests and final emission tests.

TABLE 19. TRACE METALS AND OTHER ELEMENTS FROM THE SECOND SET OF SCREENING TESTS OF A FORD TAURUS AND A TOYOTA CAMRY OPERATED OVER A COLD-START UDDS, THREE HOT-START UDDS, AND A FORCED-COOLED-START UDDS

	FTP Emissions, μg/mi[a]		
	1987 Ford Taurus	1986 Toyota Camry	Detection Limit, μg/mi
Sodium[b]	--	--	21
Magnesium	15	2	0.5
Aluminum	61	36	0.8
Silicon	15	17	1.4
Phosphorus	26	5	0.3
Sulfur	99	37	0.7
Chlorine	31	12	0.9
Potassium	6	3	0.7
Calcium	49	37	0.9
Titanium	ND[c]	2	1.2
Chromium	22	28	11
Manganese	13	14	8.5
Iron	1600	1100	8.8
Nickel	12	ND	8.1
Copper	39	35	9.4
Zinc	36	ND	9.9
Bromine	ND	19	19
Strontium	69	63	36
Lead	90	ND	69

---

[a] Total particulate emissions were not determined. Refer to Table 21 for total particulate emissions measured during later screening tests.

[b] Suspected occurrence of uncorrectable systematic biases.

[c] ND - None detected. Less than the detection limit.

Corrections for background levels of compounds sampled on C/T and PUF traps were applied to the third set of screening tests. In general, the third set of screening tests produced lower amounts of these hydrocarbon compounds than the first two screening tests.

The second group of compounds, the chlorinated hydrocarbons, were measured at low levels in the screening tests. Methyl chloroform and methylene chloride were detected at trace or higher levels in the exhaust of the Ford Taurus. The raw exhaust test did not indicate the presence of any additional target compounds. The Toyota Camry showed trace levels of methyl chloroform, methylene chloride, and pentachlorophenol in the three screening tests. The raw exhaust test also indicated trace levels of chlorobenzene and chloroform.

Trace metals and other elements were analyzed in particulate samples from the first and second screening tests. The results of these analyses are summarized in Tables 18 and 19, respectively. Total particulate emissions were not routinely measured in this program. However, as part of the screening tests, 8 × 10-inch filters were sampled for later extraction for soluble organic fraction. Particulate emission rates for these 8 × 10-inch filters were calculated and are reported in Table 21. In the first screening test, a filter was sampled for each UDDS of the FTP. To improve detection limits in the second screening test, the test length per filter was increased to five UDDS cycles (cold-start, 3 hot-starts, forced-cooled-start).

Typically, the same metals and other elements were measured in both screening tests on both vehicles. Two elements appeared in only one of the screening tests on the Taurus, lead in the first screening test and tin in the second screening test. Both metals were either at or near the detection limits. The metals and other trace elements present in the highest concentrations in the exhaust of the Taurus in the first screening test were sulfur, chromium, and copper. For the Camry, chromium, copper, and strontium were measured at the highest emission rates. Aluminum, sulfur, calcium, and strontium were the most prevalent elements from both vehicles in the second screening tests. Relatively high levels of iron were also found in both screening tests from both vehicles, possibly due to rust in the exhaust systems and/or engine wear. Chromium emissions were relatively high in the first screening tests as compared to later screening and final emission tests for both vehicles. The filters from the shorter 2-bag tests of the first screening tests had approximately twice the chromium levels as the 10-bag tests of the second screening tests. The source of the higher chromium emissions is unknown.

Dilution tunnel background levels of the metals and elements are given in Table 20. The background results (in µg/mi) are calculated as comparison values only using average FTP test parameters and weights of each element on the filter. The values have no meaning other than to present the background data in a form that can be compared to the vehicle data. For this background measurement, dilution air was sampled through the dilution tunnel onto fluorocarbon filters for a period of 116 minutes. No vehicle was operated at this time. Sulfur, potassium, calcium, iron, and copper were measured in the dilution tunnel background sample at levels above the minimum detection limits.

In addition to particulate analysis for trace metals and other elements, particulate was sampled on 8 × 10-inch Pallflex filters to determine organic solubles. Each vehicle was operated over a cold-start UDDS, three hot-start UDDS cycles, and a forced-cooled-start UDDS to collect particulate. Background filters were also sampled with room air for an equivalent test length of about 116 minutes.

The 8 × 10-inch filters were extracted with methylene chloride to determine soluble organic fraction. In addition, two clean, non-sampled 8 × 10-inch filters were extracted. These results are given in Table 21. As seen, blank and background extractable levels make up about one-fourth to three-fourths of the extractables from the sample filters. The organic solubles from these filters were analyzed for semi-volatile organic compounds and for chlorobenzene and styrene. The only compound of interest detected in the methylene chloride extracts was di(2-ethylhexyl)phthalate, which was found

TABLE 20. BACKGROUND TRACE METALS AND OTHER ELEMENTS FROM DILUTION TUNNEL ON MILES EQUIVALENT BASIS[a] FOR THE FIRST AND SECOND SCREENING TESTS

	Background Trace Metals and Other Elements, µg/mi[b]
Sodium	ND[c]
Magnesium	Trace[d]
Aluminum	Trace
Silicon	Trace
Phosphorus	ND
Sulfur	8
Chlorine	Trace
Potassium	3
Calcium	11
Titanium	ND
Vanadium	ND
Chromium	Trace
Manganese	ND
Iron	49
Cobalt	ND
Nickel	ND
Copper	32
Zinc	ND
Arsenic	Trace
Selenium	ND
Bromine	ND
Strontium	Trace
Molybdenum	ND
Cadmiun	ND
Tin	ND
Antimony	ND
Cesium	ND
Barium	ND
Platinum	ND
Mercury	ND
Lead	ND

---

[a] Background sampling period was approximately equivalent to five UDDS cycles. Mass of individual elements was divided by 37.4 miles (distance of five UDDS) to provide background levels of a miles basis.

[b] Total particulate emissions were not determined in this test.

[c] ND - None detected. Less than the detection limit.

[d] Trace - Detected, but not quantifiable above the detection limit.

TABLE 21. PARTICULATE EXTRACTION RESULTS FROM 8x10-INCH PARTICULATE FILTERS SAMPLED OVER FIVE UDDS CYCLES

		Sample		Background		
Vehicle	Part. Rate, g/mi	Part. Mass, mg	Extractable Mass, mg	Part. Mass, mg	Extractable Mass, mg	Soluble Organic Fraction[a]
Ford Taurus	0.008	29.1	3.1	2.6	2.3	10%
Toyota Camry	0.007	25.2	4.2	2.0	2.0	16%

	Blank
Filter	Extractable Mass, mg
1	1.1
2	1.0

---

[a] At the low levels of extractables material obtained (< 10 mg), soluble organic fraction can vary within a range of roughly ± 50 percent.

In the raw exhaust screening tests, C/T and PUF traps were sampled and analyzed for volatile and semi-volatile organic compounds, respectively. The results are given in Tables 16 and 17 for the Taurus and Camry, respectively. Styrene was measured in the exhaust of both vehicles. Trace amounts of methyl chloroform were found in the Ford Taurus exhaust. Trace levels of chlorobenzene and chloroform were detected in the exhaust of the Toyota Camry. In addition, methyl chloroform and methylene chloride were also found in the raw exhaust test on the Camry. The water condensate samples collected with each PUF trap were analyzed for semi-volatile organic compounds. None of these compounds were found in the PUF or water trap samples.

The screening tests indicated the presence of several of the targeted compounds in exhaust at trace levels or at concentrations above the minimum detection limits. They are listed below:

Benzene
1,3-Butadiene
Styrene
Toluene
Xylenes

Chlorobenzene
Chloroform
Methyl chloroform
Methylene chloride
Pentachlorophenol

Metals and other trace elements

In addition, the compounds listed below have been found in exhaust by other researchers (as determined in the literature search).

- phenol
- cresols
- dimethylnitrosamine
- acrolein
- methyl bromide
- propylene oxide

The final emissions tests included sampling and analyses for these two lists of unregulated compounds in the exhaust of the Ford Taurus and the Toyota Camry. Regulated emissions (HC, CO, and NO_X) and fuel economy were also measured.

VI. VEHICLE TESTING

Final emissions tests were conducted on the Ford Taurus and the Toyota Camry for the measurement of regulated and several unregulated emissions compounds. The compounds, which are listed in Table 22, had been measured in the exhaust of the Taurus and/or Camry in the screening tests or were determined (from the literature search) to have been previously found in exhaust. The literature search covered research programs that measured emissions from catalyst-equipped and non-catalyst-equipped vehicles operated on leaded and unleaded gasoline and alcohol fuels.

The list of aldehydes and ketones, hydrocarbons, phenols, and nitrosamines was expanded to include additional compounds that were not on the original list of target compounds. These compounds were added because it was possible to sample and analyze for these additional compounds with little additional effort by the same methods selected for measuring the original target compounds; acrolein, 1,3-butadiene, phenol, and cresols.

Sampling media and analysis methods are also listed in Table 22. The method for analyzing the volatile halogenated hydrocarbons (chlorobenzene, chloroform, ethylene dibromide, methyl bromide, methyl chloroform, and pentachlorophenol) in exhaust was changed for the final emission tests. An electrolytic conductivity detector was used because of its increased selectivity to halogenated hydrocarbons relative to that of the mass spectrometer. The sampling and analysis methods for pentachlorophenol, selected hydrocarbons, metals and other elements, and nitrosamines were not altered from those used in the screening tests. The methods for sampling and analyzing aldehydes (and ketones) and phenols were those recommended earlier in the program. In addition to the unregulated emissions listed in Table 22, regulated gaseous emissions and fuel economy were also measured in the final emissions tests.

The test cycles and sampling schedule for the measurement of the various unregulated emissions are listed in Table 8. Each vehicle was first operated over several UDDS segments; one cold-start UDDS, then three hot-start UDDS cycles, followed by a forced-cooled-start. Before the cooled-start test, each vehicle was cooled using fans directed at the engine with the hood open. The forced-cooled-start test was initiated once the engine oil reached a temperature of 80 to 84°F.

The vehicles were also operated over two additional driving cycles, the Highway Fuel Economy Test (HFET) and the New York City Cycle (NYCC). The HFET is characterized by a higher average speed than the UDDS, 48.2 mph versus 19.5 mph. The NYCC has a lower average speed of 7.1 mph, more typical of congested city driving. The vehicles were operated over four cycles each of the HFET and the NYCC to provide sufficient sampling time for unregulated emissions, since the durations of these two cycles are shorter than that of the FTP. The UDDS is approximately 23 minutes, the HFET is about 13 minutes, and the NYCC is 10 minutes in length.

TABLE 22. FINAL TARGET COMPOUN[illegible] SAMPLING MEDIA, AND ANALYTICAL METHODS

Compound	Sampling Media	Analytical Method
Aldehydes and Ketones	Bubbler/ DNPH[a]	HPLC/UV[b]
Formaldehyde		
Acetaldehyde		
Acrolein		
Propionaldehyde		
Acetone		
Crotonaldehyde		
Isobutyraldehyde/ methylethylketone[c]		
Benzaldehyde		
Hexanaldehyde		
Halogenated Hydrocarbons		
Chlorobenzene	C/T[d]	GC/ELCD[e]
Chloroform	C/T	GC/ELCD
Ethylene dibromide	C/T	GC/ELCD
Methyl bromide	C/T	GC/ELCD
Methyl chloroform	C/T	GC/ELCD
Methylene chloride	C/T	GC/ELCD
Pentachlorophenol	PUF[f]	GC/MS[g]
Hydrocarbons		
Benzene	C/T	GC/MS
1,3-Butadiene	Bag	GC/FID[h]
Propylene oxide	C/T	GC/MS
Styrene	C/T	GC/MS
Toluene	C/T	GC/MS
Xylenes	C/T	GC/MS
Metals and Other Trace Elements	Filter	X-ray

Compound	Sampling Media	Analytical Method
Nitrosamines	Thermosorb/N	GLC/TEA[i]
N-Nitrosodimethylamine		
N-Nitrosidiethylamine		
N-Nitrosidipropylamine		
N-Nitrosidibutylamine		
N-Nitrosopiperidine		
N-Nitrosopyrrolidine		
N-Nitrosomorpholine		
Phenols	Bubbler/1N KOH	GC/FID
Phenol		
Salicylaldehyde		
m- and p-Cresol		
p-Ethylphenol/ 2-Isopropylphenol/ 2,3-Xylenol/3,5-Xylenol/ and 2,4,6-Trimethylphenol[c]		
2-n-Propylphenol		
2,3,5-Trimethylphenol		
2,3,5,6-Tetramethylphenol		

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[a] DNPH = Dinitrophenylhydrazine.
[b] HPLC/UV = High pressure liquid chromatography/ultraviolet detector.
[c] Coelution.
[d] C/T - Carbosieve/Tenax trap.
[e] GC/ELCD = Gas chromatography/electrolytic conductivity detector.
[f] PUF = Polyurethane foam.
[g] MS = Mass spectrometer.
[h] FID = Flame ionization detector.
[i] TEA = Thermal energy analyzer.

VII. RESULTS

Final emissions tests were conducted on the Ford Taurus and Toyota Camry for regulated and several unregulated emissions as described in the previous section. Each car was operated over three test cycles, the FTP, HFET, and NYCC for emissions measurements. Regulated and unregulated emissions results from these tests are reported in this section.

A. Regulated Emissions

Computer printouts of regulated emissions data are listed in Appendices B and C for the Ford Taurus and the Toyota Camry, respectively. A summary of regulated emissions and fuel economy values is given in Table 23 for the FTP cycles from the screening tests and the final emissions tests. Hydrocarbon, carbon monoxide, and oxides of nitrogen emissions were within California Emissions Standards for both vehicles. Fuel economy repeated well for the FTP tests.

Regulated emissions and fuel economy from the HFET and NYCC tests are summarized in Table 24. Gaseous emissions were measured on each of the four HFET and NYCC tests conducted on each vehicle. For individual tests results, refer to Appendices B and C, for the Taurus and Camry.

B. Benzene, Toluene, Xylenes, and Styrene Emissions

Several aromatic hydrocarbons were measured in the final emissions tests. They included benzene, toluene, xylenes, and styrene. Emissions of these compounds from screening tests and from final emissions tests for the FTP cycle are listed in Table 25 for the Ford Taurus and the Toyota Camry. Minimum detection limits for unregulated emissions measured in the final emissions tests are given in Appendix I. Benzene, toluene, and xylenes were measured in all screening tests and final emissions tests at levels well above the minimum detection limits for both vehicles. The results from a second Carbosieve/Tenax trap that was sampled simultaneously during the final FTP emissions test are also included. Average values and standard deviations are given in the table. More detailed cold-start and hot-start UDDS data are provided in Appendix J. Xylenes were present in the highest amounts, followed by toluene, and then benzene for both vehicles.

In a separate study on the same Camry, in which benzene and toluene were measured using an alternate analysis procedure which included bag collection and GC/FID analysis, roughly equivalent amounts of benzene and toluene were measured. Benzene was measured at 8 mg/mi by GC/FID compared to an average of 9 mg/mi for benzene trapped on C/T and analyzed by GC/MS. Toluene was quantified at 17 mg/mi by GC/FID, and the average level of toluene measured in this program by GC/MS was 18 mg/mi.

Styrene emissions showed greater variability on a test-to-test basis than benzene, toluene, or xylenes. Levels of styrene were measured that ranged from below the detection limit to several times the detection limit. This result is possibly due to the higher reactivity of styrene relative to benzene, toluene, or xylenes, and to lower levels of styrene in exhaust (i.e., close to the detection limit). While exiting the engine at elevated temperatures or traversing the dilution tunnel, styrene may be subject to polymerization or oxidation due to its higher reactivity. A more sensitive and repeatable method of sampling and analyzing styrene may be needed to more accurately quantify it at the levels present in exhaust.

Backup C/T traps were sampled during two cold-start UDDS tests, one for the Taurus and one for the Camry. Negligible levels of benzene, toluene, and xylenes were measured in the backup traps. Over 70 percent of total benzene, toluene, and xylenes measured in the FTP were from the cold-start UDDS segment of the test.

TABLE 23. FTP REGULATED VEHICLE EMISSIONS RESULTS

Emission	1987 Ford Taurus Emission Rate, g/mi Initial Test	Average of Screening Tests	Before Final Test	Final Emissions Test	California Emissions Standard, g/mile
Hydrocarbons	0.25	0.26	0.31	0.31	0.41(0.39)[a]
Carbon Monoxide	3.35	3.57	4.65	4.54	7.0
Oxides of Nitrogen	0.45	0.45	0.52	0.53	0.7
Fuel Economy, mpg	23.68	22.19	21.77	22.19	

Emission	1986 Toyota Camry Emission Rate, g/mi Initial Test	Average of Screening Tests	Before Final Test	Final Emissions Test	California Emissions Standard, g/mile
Hydrocarbons	0.14	0.17	0.19	0.19	0.41(0.39)[a]
Carbon Monoxide	2.35	2.28	3.71	3.21	7.0
Oxides of Nitrogen	0.32	0.26	0.30	0.31	0.7
Fuel Economy, mpg	29.09	29.75	27.92	28.62	

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[a] Non-methane value.

TABLE 24. AVERAGE REGULATED GASEOUS EMISSIONS AND FUEL ECONOMY FROM A FORD TAURUS AND TOYOTA CAMRY OPERATED OVER THE HIGHWAY FUEL ECONOMY TEST (HFET) AND THE NEW YORK CITY CYCLE (NYCC)

	Ford Taurus Emissions, g/mi		Toyota Camry Emissions, g/mi	
	HFET	NYCC	HFET	NYCC
Hydrocarbons	0.06	1.00	0.02	0.31
Carbon Monoxide	1.15	10.63	0.12	5.17
Oxides of Nitrogen	0.31	0.84	0.06	0.51
Fuel Economy, mpg	33.5	12.4	43.1	16.3

TABLE 25. BENZENE, TOLUENE, XYLENES, AND STYRENE EMISSIONS FROM A FORD TAURUS AND A TOYOTA CAMRY OPERATED OVER THE FTP CYCLE

	Ford Taurus Emissions, mg/mi				
	First Screening Test	Second Screening Test	Third Screening Test	Final Emissions Test 1	Final Emissions Test 2
Total Hydrocarbons	250	300	220	310	310
Benzene Avg. - 15 SD - 6.3	12	13	8	24	19
Toluene Avg. - 23 SD - 7.8	19	22	13	34	25
Xylenes Avg. - 27 SD - 12.0	18	22	47	28	19
Styrene Avg. - 0.25 SD - 0.41	ND[a]	0.95	0.29	ND	ND

	Toyota Camry Emissions, mg/mi			
	First Screening Test	Second Screening Test	Third Screening Test	Final Emissions Test
Total Hydrocarbons	170	180	170	190
Benzene Avg. - 9 SD - 4.7	12	5	5	14
Toluene Avg. - 18 SD - 8.1	30	12	14	18
Xylenes Avg. - 26 SD - 9.9	31	14	36	21
Styrene Avg. - 0.53 SD - 0.48	ND	0.70	0.32	1.1

---

[a] ND - none detected. Less than the detection limit.

Benzene, toluene, xylenes, and styrene were also detected during HFET and NYCC tests. These results are shown in Table 26 for the Ford Taurus and the Toyota Camry. In the HFET test, the Taurus produced slightly higher levels of toluene than xylenes. Relative to the FTP results, the ratio of benzene to toluene and xylenes was much smaller. Styrene was not detected in the HFET sample from the Taurus. Roughly equivalent amounts of benzene, toluene, and xylenes were emitted by the Camry during the HFET. Styrene was also detected at levels near the detection limit from the Camry.

The emissions of benzene, toluene, and xylenes from the Taurus during the lower-speed, shorter-distance NYCC test were considerably higher on a per mile driven basis than from the higher-speed, longer distance highway test or from the FTP test. The three compounds were produced at roughly equivalent levels. No styrene was detected in the Taurus NYCC sample. The C/T trap that was used for sampling of aromatic hydrocarbons from the Camry during the NYCC test was incorrectly sampled and thus no data was obtained.

C. 1,3-Butadiene and Other C_4 Compounds

The Tedlar bag sample used for measuring regulated gaseous emissions was analyzed for 1,3-butadiene and other four-carbon compounds. Bag samples from the cold-start transient 505 second "bag 1" and stabilized 867 second "bag 2," and from the hot-start transient 505 second "bag 3" of the UDDS cycle of the FTP were analyzed. The last two bags of the forced-cooled-start were also analyzed. In addition, bags from the first two tests of the HFET and from the NYCC were analyzed for C_4 compounds. Time constraints did not permit analysis of all bags.

A summary of the analyses is given in Tables 27 and 28 along with total hydrocarbon emissions for the Ford Taurus and the Toyota Camry, respectively. Results from previous screening tests are also listed. As a fraction of total hydrocarbons, 1,3-butadiene constituted an average of 0.26 percent for FTP tests on the Taurus and 0.49 percent on the Camry. Trace amounts of 1,3-butadiene were detected in the HFET and NYCC tests on the Taurus. No 1,3-butadiene was measured above the detection limits in HFET or NYCC tests on the Camry.

Elapsed times between sampling and analysis of bag samples for 1,3-butadiene for final emissions tests are provided in Appendices K and L for the Taurus and Camry, respectively. Previous experimental tests have indicated that if the sample is analyzed within 30 minutes of sample collection, the resulting value will be within the repeatability of the procedure. If the sample is allowed to stand more than one hour before analysis, significant sample loss can occur. Because of the possibility of significant sample loss, sample bags were analyzed for 1,3-butadiene as soon after collection as possible. Emissions of 1,3-butadiene by individual bags or segments on the FTP of the final emissions tests are listed in Appendix M for the Taurus and Camry. As shown, 1,3-butadiene is found in measurable levels only in bag 1 from the cold-start portion of the FTP. During the bag 1 or first 505 seconds of the cold-start UDDS, the catalysts on the vehicles have not reached the desired operating temperature, and are therefore not operating as efficiently during the cold 505 as during the 867 second portion of the cycle or during the hot-start 505 second segment. The inefficiency of the catalysts during the cold-start 505 would explain the higher levels of 1,3-butadiene.

In addition to 1,3-butadiene, six other C_4 compounds were analyzed. They were butane, isobutane, 1-butene, isobutylene, cis-2-butene, and trans-2-butene. Emission rates of these compounds are summarized in Tables 29 and 30 for the Ford Taurus and Toyota Camry, respectively. Individual test results for C_4 compounds are given in Appendices N and O for the Taurus and Camry, respectively. Butane was measured from the FTP, HFET, and NYCC tests of both vehicles at higher concentrations than any of the other C_4 compounds, making up from 33 to 100 percent of C_4 compounds measured. In the FTP tests on both vehicles, all of the C_4 compounds were found. In the HFET and NYCC tests on the Taurus, isobutane was present at levels second only to butane. Together, isobutane and butane constituted 88 percent of C_4 compounds from the HFET tests and 80

TABLE 26. BENZENE, TOLUENE, XYLENES, AND STYRENE EMISSIONS FROM A FORD TAURUS AND TOYOTA CAMRY OPERATED OVER HFET AND NYCC DRIVING SCHEDULES

	Ford Taurus Emissions, mg/mi		Toyota Camry Emissions, mg/mi	
	HFET	NYCC	HFET	NYCC[a]
Total Hydrocarbons	60	1000	20	310
Benzene	0.5	60	0.7	NA
Toluene	3.4	63	0.6	NA
Xylenes	2.9	63	0.8	NA
Styrene	ND[b]	ND	0.1	NA

---

[a] NA - Data not available.
[b] ND - none detected. Less than the detection limit.

TABLE 27. 1,3-BUTADIENE EMISSION SUMMARY FOR FTP, HFET, AND NYCC TESTS ON A FORD TAURUS

	FTP Emissions, mg/mi, except as noted				
	Screening Test 1	Screening Test 2	Final Emissions Test 1	Final Emissions Test 2	Avg.
Total Hydrocarbons	250	300	310	310	293
1,3-Butadiene	0.68	0.82	0.78	0.79	0.77
1,3-Butadiene as a Percent of Total Hydrocarbons	0.27	0.27	0.25	0.26	0.26

	HFET and NYCC Emissions, mg/mi, except as noted					
	HFET			NYCC		
	Test 1	Test 2	Avg.	Test 1	Test 2	Avg.
Total Hydrocarbons	60	70	65	1050	1070	1065
1,3-Butadiene	Trace[a]	Trace	Trace	Trace	Trace	Trace
1,3-Butadiene as a Percent of Total Hydrocarbons	0	0	0	0	0	0

---

[a] Trace - Detected but not quantifiable above the detection limit.

TABLE 28. 1,3-BUTADIENE EMISSION SUMMARY FOR FTP, HFET, AND NYCC TESTS ON A TOYOTA CAMRY

	FTP Emissions, mg/mi, except as noted				
	Screening Test 1	Screening Test 2	Final Emissions Test 1	Final Emissions Test 2	Avg.
Total Hydrocarbons	170	180	190	190	183
1,3-Butadiene	0.81	0.87	0.98	0.87	0.88
1,3-Butadiene as a Percent of Total Hydrocarbons	0.48	0.48	0.52	0.46	0.49

	HFET and NYCC Emissions, mg/mi, except as noted					
	HFET			NYCC		
	Test 1	Test 2	Avg.	Test 1	Test 2	Avg.
Total Hydrocarbons	20	20	20	250	270	206
1,3-Butadiene	ND[a]	ND	ND	ND	ND	ND
1,3-Butadiene as a Percent of Total Hydrocarbons	0	0	0	0	0	0

---

[a] ND - None detected. Less than the detection limit.

✓

TABLE 29. AVERAGE FTP, HFET, AND NYCC C_4 COMPOUNDS AND TOTAL HYDROCARBON EMISSIONS FROM THE FINAL EMISSIONS TESTS OF A FORD TAURUS

	C_4 and Total Hydrocarbon Emissions, mg/mi		
	FTP	HFET	NYCC
Total Hydrocarbons	310	65	1065
1,3-Butadiene	0.78	Trace[a]	Trace
Butane	6.35	2.5	52.1
Isobutane	2.15	0.82	21.5
1-Butene	1.50	0.26	5.5
Isobutylene	1.40	0.20	5.2
cis-2-Butene	0.81	Trace	4.3
trans-2-Butene	0.80	Trace	3.0

---

[a] Trace - Detected but not quantifiable above the detection limit.

TABLE 30. AVERAGE FTP, HFET, AND NYCC C_4 COMPOUNDS AND TOTAL HYDROCARBON EMISSIONS FROM THE FINAL EMISSIONS TESTS OF A TOYOTA CAMRY

	C_4 and Total Hydrocarbon Emissions, mg/mi		
	FTP	HFET	NYCC
Total Hydrocarbons	190	20	260
1,3-Butadiene	0.93	ND[a]	ND
Butane	2.25	0.28	5.7
Isobutane	0.83	ND	3.4
1-Butene	1.06	ND	0.45
Isobutylene	0.84	ND	0.65
cis-2-Butene	0.51	ND	ND
trans-2-Butene	0.42	ND	ND

---

[a] ND - None detected. Less than the detection limit.

percent from the NYCC tests. For the Camry, butane was the only C_4 compound detected in the HFET tests. In the NYCC tests, butane and isobutane were the most abundant of the C_4 compounds, making up 89 percent of C_4 compounds.

D. Halogenated Hydrocarbons

Volatile halogenated hydrocarbons were sampled on Carbosieve/Tenax traps as in the screening tests, however, in the final emissions tests, analysis was by GC using an electrolytic conductivity detector (ELCD) instead of a mass spectrometer. GC/ELCD provided improved detection limits for these compounds. Halogenated hydrocarbon emissions are summarized in Table 31. FTP halogenated hydrocarbon emissions are subdivided into cold- and hot-start values in Appendix P.

Chloroform was measured in the exhaust of the Ford Taurus on the FTP and HFET tests. Methylene chloride was detected during the NYCC test of the Taurus. For the Toyota Camry, duplicate C/T traps were sampled on the FTP and on the HFET tests. Trace levels of methylene chloride were detected in the FTP test on both traps from the Camry. One of the FTP C/T traps also indicated the presence of methyl chloroform. In the HFET test, chloroform was measured in both C/T traps. Methyl bromide was also found at a trace level and just above the detection limit for the two traps. In the NYCC test on the Camry, chloroform was the only halogenated hydrocarbon detected.

Several possible sources of halogenated hydrocarbons were investigated to explain their presence in exhaust. Fuel and oil samples were analyzed for chlorine and bromine. In addition, the fuel-handling system was examined as possibly contributing to halogenated compounds in the exhaust.

A fuel analysis for chlorides and bromides in the gasoline test fuel showed no chloride or bromide present at a detection limit of 1.0 ppm. In the fuel system, the fuel has the most surface contact with the fuel tank. Any leaching of halogenated compounds from the fuel system would more likely occur in the fuel tank. A fuel sample was drawn from the fuel tank of each test vehicle and analyzed for chlorides. No chlorides or bromides were measured above the 1.0 ppm detection limit.

Samples of oil from each vehicle were analyzed for bromine and chlorine. No bromine was measured at a detection limit of 50 ppm. Chlorine was measured in both oil samples, 140 ppm for the Ford Taurus and 30 ppm for the Toyota Camry, at a detection limit of 10 ppm. Small amounts of chlorine are present in some lubricating oil additives, which could account for some of the chlorine in the oil. Possible contamination from the antifreeze in the engine coolant system was also considered as a source of chlorine. The oils were analyzed for the presence of ethylene glycol, the major constituent of antifreeze, to determine if the antifreeze was contaminating the oil. A Taurus oil sample was found to contain 90 ppm ethylene glycol while a Camry oil sample did not contain any ethylene glycol at a detection limit of 50 ppm. To determine if the chloride in the oil and exhaust originated from the antifreeze, antifreeze samples were analyzed and found to contain 50 ppm chlorine in the Taurus and 10 ppm chlorine in the Camry at a detection limit of 1 ppm. The chlorine measured in the oil sample of the Taurus might have the antifreeze as one source, however, the chlorine concentration in ethylene glycol was only about one third of the chlorine level measured in the oil of the Taurus.

An oil consumption rate was calculated to determine the amount of oil needed to produce the 1.4 mg/mi of methylene chloride (1.2 mg/mi of Cl) found in exhaust. Based on the chlorine concentration measured in an oil sample from the Taurus (140 ppm by wt), it was determined that a vehicle would have to consume about one quart of oil for every 100 miles of operation to produce this level of methylene chloride. This high oil consumption figure is inconsistent with the observed oil consumption rates and other related emissions.

Since the fuel and oil were determined not to be the only possible sources of chlorine and bromine in the exhaust, the fuel systems of the vehicles were also investigated. Ford Motor Company

TABLE 31. SUMMARY OF HALOGENATED HYDROCARBON EMISSIONS FROM A FORD TAURUS AND A TOYOTA CAMRY

Compound	Ford Taurus Emissions, mg/mi			Toyota Camry Emissions, mg/mi			Minimum Detection Limits, mg/mi		
	FTP	HFET	NYCC	FTP[a]	HFET[a]	NYCC	FTP	HFET	NYCC
Chloroform	0.09	0.02	ND[b]	ND	0.05	0.9	0.01	<0.01	0.02
Methyl bromide	ND	ND	ND	ND	0.15	ND	0.02	0.01	0.08
Methyl chloroform	ND	ND	ND	0.03	ND	ND	0.01	<0.01	0.02
Methylene chloride	ND	ND	1.4	Trace[c]	ND	ND	0.02	0.01	0.06

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[a] Average of two sets of C/T traps sampled in parallel.
[b] ND - None detected. Less than the detection limit.
[c] Trace - Compound was detected but was not quantifiable above the detection limit.

was contacted in an effort to identify nonmetallic parts in the fuel system that might contribute to chlorinated compounds in the exhaust. Fuel return and fuel supply lines are made of nylon tubing. The cover on the hose, which does not contact the fuel, is made from chlorinated polyethylene. The electric pump in the fuel tank contains plastic parts or plastic-coated parts that are composed of fluorocarbon elastomers. No other parts of the fuel system were identified as containing chlorinated plastic parts. Toyota was also contacted to determine possible sources of chlorine from the fuel system of the Camry. It could not be determined that chlorinated hydrocarbons were present in the fuel-handling system.

Methyl chloroform and methylene chloride are solvents that are used for various purposes in the Department of Emissions Research. An attempt was made to exclude these solvents from the laboratories, however, they were the only two halogenated hydrocarbon compounds that were found in the exhaust that also appeared in the background samples. Table 32 summarizes background and sample concentrations of methyl chloroform and methylene chloride measured on C/T traps. Standard deviations are also given for the background trap data.

For the Taurus, background concentrations of methyl chloroform exceeded or were equivalent to sample concentrations from the HFET and from the NYCC tests. Only methylene chloride from the NYCC test was measured above background level. For the Camry, background methyl chloroform exceeded or was equivalent to sample concentrations on one of the CFTP samples and on the HFET sample. In the second CFTP sample, the level of methyl chloroform present was within one standard deviation of the average background for methyl chloroform. Even though a value can be calculated for methyl chloroform for the second CFTP, the concentration is near background levels. Trace amounts of methylene chloride were measured in the two FTP tests on the Camry. As shown in Table 32, background methylene chloride concentrations (± one standard deviation) overlap the sample concentrations from one of the CFTP's and from the HFTP at the levels measured.

In an attempt to determine the relative importance of the levels of halogenated hydrocarbons in exhaust, the following comparisons were made. Emission rates of chloroform, methylene chloride, methyl bromide, and methyl chloroform from the vehicles were calculated on a raw exhaust basis for comparison to Permissible Exposure Limits (PEL). The Occupational Safety and Health Administration (OSHA) provides PEL data for hazardous compounds. Raw exhaust estimates and PEL's are shown below:

		Ford Taurus Emissions, mg/m^3		
	PEL,mg/m^3	FTP	HFET	NYCC
Chloroform	240	0.06	0.01	ND[a]
Methyl bromide	80	ND	ND	ND
Methyl chloroform	1900	ND	ND	ND
Methylene chloride	1738	ND	ND	0.04

		Toyota Camry Emissions, mg/m^3				
	PEL, mg/m^3	FTP Trap 1	FTP Trap 2	HFET Trap 1	HFET Trap 2	NYCC
Chloroform	240	ND	ND	0.06	0.06	0.36
Methyl bromide	80	ND	ND	Trace[b]	0.04	ND
Methyl chloroform	1900	ND	0.02	ND	ND	ND
Methylene chloride	1738	Trace	Trace	ND	ND	ND

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[a] ND - none detected. Less than the detection limit.
[b] Trace - detected but not quantifiable above the detection limit.

TABLE 32. BACKGROUND AND SAMPLE METHYL CHLOROFORM AND METHYLENE CHLORIDE ON CARBOSIEVE/TENAX TRAPS

	Average Background and Standard Deviation, ng/SCF		
	Sample 1	Sample 2	Sample 3
Methyl chloroform	380 ± 83	370 ± 120	370 ± 120
Methylene chloride	30 ± 24	43 ± 21	43 ± 20

	Methyl Chloroform and Methylene Chloride on Carbosieve/Tenax Traps from Ford Taurus and a Toyota Camry, ng/SCF					
	Cold-Start Trap 1	Cold-Start Trap 2	Hot-Start	HFET Trap 1	HFET Trap 2	NYCC
Ford Taurus						
Methyl chloroform	ND[a]	--[b]	ND	240	--	190
Methylene chloride	ND	--	ND	ND	--	520
Toyota Camry						
Methyl chloroform	42	450	240	ND	19	ND
Methylene chloride	48	63	55	ND	ND	ND

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[a] ND - None detected. Less than the detection limit.
[b] Repeat measurement not made on Taurus.

The raw exhaust emissions of halogenated hydrocarbons from the Taurus and the Camry are well under the Permissible Exposure Limits established by OSHA for an eight-hour work day. Dilution of raw exhaust into the surrounding atmosphere will lower the concentrations even further. However, OSHA limits do not typically allow for carcinogenic effects, which can occur with any finite amounts.

E. Aldehydes and Ketones

Ten aldehydes and ketones were measured in the final emissions tests on the Ford Taurus and Toyota Camry. The ten compounds are listed: formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, isobutyraldehyde and methylethyl ketone (not resolved from each other under normal operating conditions and so reported together), benzaldehyde, and hexanaldehyde.

Acrolein was the primary aldehyde targeted for this program. However, since sampling and analysis for a number of other aldehydes and ketones could also be done at the same time, they were included in the analysis. A summary of aldehyde and ketone emissions is given in Table 33 for the Taurus and the Camry. Detailed aldehyde and ketone emissions results are given in Appendix Q. The greatest number of aldehyde and ketone compounds was measured in the FTP tests for both vehicles. Formaldehyde and acetaldehyde constituted from 69 to 100 percent of total aldehydes and ketones for both vehicles, with the highest percentages from the HFET and NYCC cycles. From the Taurus, formaldehyde and acetaldehyde made up 75 percent, 96 percent, and 84 percent of total aldehydes and ketones from the FTP, HFET, and NYCC tests, respectively. Acrolein was measured in the FTP and NYCC tests of the Taurus. Formaldehyde and acetaldehyde from the Camry constituted 69 percent, 100 percent, and 100 percent of total aldehydes and ketones for the FTP, HFET, and NYCC tests, respectively. Acrolein was measured only during the FTP test.

Total aldehyde and ketone emissions on a mg/mi basis were highest for the FTP, followed by the NYCC, and then the HFET cycles. The FTP and NYCC cycles, which consist of more stop-and-go driving, apparently favor the production of aldehydes and ketones over highway driving on the HFET.

Formaldehyde and acetaldehyde emissions were compared with values measured from four 1978 and 1979 gasoline-powered, 3-way catalyst-equipped vehicles. The vehicles were tested under a program for the U.S. EPA.(78) Ranges of emissions for formaldehyde and acetaldehyde from the four vehicles on the EPA project are summarized below.

	Emission Rates, mg/mi		
	FTP	HFET	NYCC
Formaldehyde	0.3-5.5	0.1-5.5	1.4-5.8
Acetaldehyde	0.3-0.6	0.3-0.5	1.5-3.1

Formaldehyde and acetaldehyde emissions measured on the Taurus and Camry were of similar magnitude relative to these values.

F. Phenols

The following phenols were sampled and analyzed on the Ford Taurus and Toyota Camry: phenol, salicylaldehyde, m-cresol and p-cresol, p-ethylphenol/2-isopropylphenol/2,3-xylenol/3,5-xylenol/2,4,6-trimethylphenol (not resolved from each other under normal operating conditions and so reported together), 2-n-propylphenol, 2,3,5-trimethylphenol, and 2,3,5,6-tetramethylphenol. The phenols targeted for this program were phenol and the cresols. As was the case for the aldehydes and ketones,

TABLE 33. FINAL EMISSION TEST RESULTS OF ALDEHYDES AND KETONES FROM FTP, HFET, AND NYCC TESTS ON A FORD TAURUS AND A TOYOTA CAMRY

	Ford Taurus Emission Rate, mg/mi[a]		
	FTP	HFET	NYCC
Aldehydes and Ketones			
Formaldehyde	2.10	0.42	1.50
Acetaldehyde	1.08	0.27	1.84
Acrolein	0.40	ND[b]	0.11
Acetone	0.14	0.03	ND
Propionaldehyde	0.20	ND	ND
Crotonaldehyde	0.19	ND	ND
Isobutyraldehyde/ Methylethylketone	0.12	ND	ND
Benzaldehyde	ND	ND	0.55
Hexanaldehyde	ND	ND	ND
Total Aldehydes & Ketones	4.23	0.72	4.00
Total Hydrocarbons	310	60	1000

	Toyota Camry Emission Rate, mg/mi[a]		
	FTP	HFET	NYCC
Aldehydes and Ketones			
Formaldehyde	1.20	Trace[c]	0.44
Acetaldehyde	0.74	Trace	0.33
Acrolein	0.26	ND	ND
Acetone	0.17	ND	ND
Propionaldehyde	ND	ND	ND
Crotonaldehyde	0.07	ND	ND
Isobutyraldehyde/ Methylethylketone	0.07	ND	ND
Benzaldehyde	0.32	ND	ND
Hexanaldehyde	ND	ND	ND
Total Aldehydes and Ketones	2.83	Trace	0.77
Total Hydrocarbons	190	20	310

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[a] Minimum detection limits for aldehydes and ketones are 0.04 mg/mi for the FTP, 0.03 mg/mi for the HFET, and 0.1 mg/mi for the NYCC.

[b] ND - None detected. Less than the detection limit.

[c] Trace - Detected but not quantifiable above the detection limit.

additional phenols were included in the program because the sampling and analysis could be done along with phenol and the cresols.

Phenolic emissions results are summarized in Table 34 for the Ford Taurus and the Toyota Camry. Phenol was not found in the exhaust of either vehicle on any of the test cycles. Cresols (meta and para) were measured from the Ford Taurus during the NYCC cycle. The cold-start UDDS sample from the Taurus was inadvertently destroyed during analysis. The only phenol detected in the hot-start UDDS was 2,3,5,6-tetramethylphenol at 1.5 mg/mi. A variety of phenols were measured in the HFET and NYCC tests of the Taurus. Total phenol emissions from the HFET test were about 13 percent of total hydrocarbons and from the NYCC test about 14 percent of total hydrocarbons. The relative amounts of these phenols appear unusually high as compared to the total hydrocarbons. Additional work should be carried out to provide a more definite investigation of these compounds.

Fewer phenol compounds were measured from the Camry. No phenols were detected in the cold-start UDDS, contrary to what might be expected for cold-start operation. The reason for this occurance is not known. The five co-eluting phenols and 2,3,5,6-tetramethylphenol were measured in the HFET and NYCC tests. Total phenol emissions from the HFET test were about 4 percent of total hydrocarbons, and from the NYCC test about 3 percent of total hydrocarbons.

G. Trace Metals and Other Elements

Trace metals and other elements were analyzed on particulate samples by X-ray fluorescence. Duplicate filters were sampled for the Ford Taurus during the HFET and NYCC tests and for the Toyota Camry during the FTP, HFET, and NYCC tests. Metal and other elemental emissions are summarized in Table 35 for the FTP tests on the Taurus and Camry. A complete listing of FTP results is given in Appendix R. The FTP filters were each sampled over five UDDS cycles. This included one cold-start, three hot-starts, and one forced-cooled-start UDDS cycles. Aluminum, silicon, sulfur, and calcium were present in the greatest quantities in the exhaust of both vehicles. Iron was also found at measurable levels in the particulate samples from the Camry. The source of iron was possibly rust in the exhaust system and/or engine wear. Sulfur is present in the fuel and the oil and could contribute to sulfur measured in exhaust. One source of calcium is probably engine oil. Another possible source of calcium that would account for the disproportionate amount of calcium in exhaust (relative to magnesium from the Taurus and zinc from both cars) is calcium carbonate or calcium silicate from dust in the intake air. The source of silicon could also be traces of dust in the intake air of the vehicle. Another possibility is that silicon-based gaskets in the engine could have silicon in the sealant. Aluminum could be derived from wear of engine parts or from the alumina wash coat used on catalysts ($Al_2 O_3$).

Background levels of trace metals and other elements were measured on a filter sampling dilution air only (no vehicle) from the CVS tunnel over a sampling period equivalent to two UDDS cycles. These background quantities were calculated on a mile-equivalent basis, based on a 14.8 mile distance as comparison values only using average FTP test parameters and weights of each element on the filter. The values have no meaning other than to present the background data in a form that can be compared to the vehicle data. Background results are given in Table 36. Silicon, phosphorus, potassium, calcium, and chromium were measured. Trace amounts of arsenic and tin were also detected.

Trace metals and other elements were measured while the vehicles were operated over four HFET tests and four NYCC tests. Duplicate particulate samples were taken for each vehicle during the HFET and NYCC tests. The results of the analyses of the filters are listed in Appendices S and T for the Ford Taurus and the Toyota Camry, respectively. Summaries of the elemental data are given in Tables 37 and 38 for the two vehicles. In the exhaust from the Taurus on the HFET and NYCC tests, aluminum, sulfur, calcium, and iron were found in the highest concentrations. The Camry emitted primarily calcium and iron in the HFET and NYCC tests.

TABLE 34. FINAL EMISSIONS TEST RESULTS OF PHENOLS FROM FTP, HFET, AND NYCC TESTS ON A FORD TAURUS AND A TOYOTA CAMRY

	Ford Taurus Emissions, mg/mi		
	FTP[a]	HFET	NYCC
Total Hydrocarbons	310	60	1000
Phenol		ND[b]	ND
Salicylaldehyde		0.3	5.2
m- and p-Cresol		ND	3.9
3-Ethylphenol/ 2-Isopropylphenol/ 2,3-Xylenol/3,5-Xylenol/ 2,4,6-Trimethylphenol [c]		ND	46
2-n-Propylphenol		1.2	15
2,3,5-Trimethylphenol		3.9	20
2,3,5,6-Tetramethylphenol		2.2	46

	Toyota Camry Emissions, mg/mi		
	FTP	HFET	NYCC
Total Hydrocarbons	190	20	310
Phenol	ND	ND	ND
Salicylaldehyde	ND	ND	ND
m- and p-Cresol	ND	ND	ND
3-Ethylphenol/ 2-Isopropylphenol/ 2,3-Xylenol/3,5-Xylenol/ 2,4,6-Trimethylphenol [c]	ND	0.1	1.7
2-n-Propylphenol	ND	ND	ND
2,3,5-Trimethylphenol	ND	ND	ND
2,3,5,6-Tetramethylphenol	ND	0.7	8.2

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[a] Cold-start sample inadvertently destroyed.
[b] ND - None detected. Less than the detection limit.
[c] Coelution.

TABLE 35. FTP TRACE METAL AND OTHER ELEMENTAL EMISSIONS FROM THE FINAL EMISSIONS TEST OF A FORD TAURUS AND A TOYOTA CAMRY

	Ford Taurus Emissions, µg/mi[a]	Toyota Camry Emissions, µg/mi[a]		
	Final Emissions Test	Final Emissions Test, Filter No. 1	Final Emissions Test, Filter No. 2	Detection Limit, µg/mi
Magnesium	9	Trace[b]	3	0.7
Aluminum	37	16	19	0.9
Silicon	21	16	13	1.8
Phosphorus	13	3	3	0.7
Sulfur	49	13	13	1.7
Chlorine	14	4	5	0.7
Potassium	4	3	4	0.5
Calcium	49	25	32	1.0
Titanium	Trace	ND[c]	Trace	1.3
Chromium	Trace	38	Trace	13
Iron	9	270	300	8.7

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[a] Total particulate emissions were not determined. Refer to Table 21 for total particulate emissions determined during screening tests.

[b] Trace - Detected but not quantifiable above the detection limit.

[c] ND - None detected. Less than the detection limit.

TABLE 36. BACKGROUND TRACE METALS AND OTHER ELEMENTS FROM DILUTION TUNNEL ON MILE-EQUIVALENT BASIS[a] FOR THE FINAL EMISSIONS TESTS

	Background Trace Metals and Other Elements, µg/mi[b]
Sodium	ND[c]
Magnesium	ND
Aluminum	ND
Silicon	6
Phosphorus	1
Sulfur	ND
Chlorine	ND
Potassium	2
Calcium	20
Titanium	ND
Vanadium	ND
Chromium	60
Manganese	ND
Iron	ND
Cobalt	ND
Nickel	ND
Copper	ND
Zinc	ND
Arsenic	Trace[d]
Selenium	ND
Bromine	ND
Strontium	ND
Molybdenum	ND
Cadmium	ND
Tin	Trace
Antimony	ND
Cesium	ND
Barium	ND
Platinum	ND
Mercury	ND
Lead	ND

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[a] Background sampling period was approximately equivalent to two UDDS cycle. Mass of individual elements was divided by 14.68 miles (distance driven over a two UDDS) to provide background levels on a miles basis.

[b] Total particulate emissions were not determined in this test.

[c] None detected. Less than the detection limit.

[d] Trace - Detected but not quantificable above the detection limit.

TABLE 37. AVERAGE HFET AND NYCC TRACE METAL AND OTHER ELEMENTAL EMISSIONS FROM FINAL EMISSIONS TESTS OF A FORD TAURUS[a]

	HFET Emissions, µg/mi	HFET Detection Limit, µg/mi	NYCC Emissions, µg/mi	NYCC Detection Limit, µg/mi
Magnesium	10	0.6	Trace[b]	5.6
Aluminum	22	0.8	28	6.9
Silicon	10	1.7	Trace	15
Phosphorus	12	0.6	10	5.4
Sulfur	30	1.6	50	14
Chlorine	6	0.7	Trace	6.0
Potassium	2	0.5	Trace	4.1
Calcium	18	0.8	59	7.5
Titanium	Trace	1.1	Trace	10
Chromium	Trace	12	Trace	106
Manganese	ND[c]	8.4	Trace	76
Iron	400	8.0	310	71
Zinc	Trace	8.9	Trace	80
Barium	Trace	3.6	ND	32
Platinum	Trace	32	ND	292

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[a] Total particulate emissions were not determined. Refer to Table 21 for total particualte emissions measured during screening tests.
[b] Trace - Detected but not quantifiable above the detection limit.
[c] ND - None detected. Less than the detection limit.

TABLE 38. AVERAGE HFET AND NYCC TRACE METAL AND OTHER ELEMENTAL EMISSIONS FROM FINAL EMISSIONS TESTS OF A TOYOTA CAMRY[a]

	HFET Emissions, µg/mi	HFET Detection Limit, µg/mi	NYCC Emissions, µg/mi	NYCC Detection Limit, µg/mi
Magnesium	Trace[b]	0.6	ND[c]	5.6
Aluminum	9	0.8	Trace	6.9
Silicon	6	1.7	Trace	15
Phosphorus	3	0.6	ND	5.4
Sulfur	8	1.6	Trace	14
Chlorine	2	0.7	ND	6.0
Potassium	1	0.5	Trace	4.1
Calcium	17	0.8	61	7.5
Titanium	Trace	1.1	Trace	10
Chromium	Trace	12	Trace	106
Manganese	Trace	8.4	ND	76
Iron	130	8.0	180	71
Bromine	ND	24	Trace	208
Molybdenum	ND	212	Trace	1860
Tin	Trace	4.9	ND	45

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[a] Total particulate emissions were not determined. Refer to Table 21 for total particulate emissions measured during screenign tests.
[b] Trace - Detected but not quantifiable above the detection limit.
[c] ND - None detected. Less than the detection limit.