AN ABSTRACT OF THE THESIS OF

<u>Roger Allen Jones</u> for the degree of <u>Master of Science</u>

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Title: <u>TRACE ELEMENT ABUNDANCES IN AUTOMOBILE EXHAUST PARTICULATE</u>

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The trace element abundances in automobile exhaust have been
measured using instrumental neutron activation analysis (INAA).
Gaseous and particulate emissions of three different types of auto-
mobiles (vehicles burning leaded fuel, vehicles burning unleaded fuel,
and vehicles burning unleaded fuel and employing a catalytic converter)
were sampled by inserting probes into the exhaust stream as the auto-
mobile (26 cars were tested) was being driven in one of six modes (idle,
25 mph, 40 mph, 55 mph, acceleration, and deceleration) on a chassis
dynamometer. Non-dispersive infrared analysers were used to monitor
the gaseous emissions while the particulate matter was captured on
either Nuclepore or Whatman-1 filtering media used in conjunction with
a high volume air sampler. The gaseous emissions mirrored previous
works. Particulate analysis revealed only five elements found with
any degree of reliability, namely, Br ($\sim$ 4000 $\mu g/m^3$, leaded fuel;
$\sim$ 10 $\mu g/m^3$, unleaded fuel); Cl ($\sim$ 1000 $\mu g/m^3$, leaded fuel); V ($\sim$ 0.02
$\mu g/m^3$, unleaded fuel); A ($\sim$ 45 $\mu g/m^3$, both fuels); and Mn ($\sim$ 2 $\mu g/m^3$,
both fuels). No correlation was found between gaseous and particulate
emissions. The trace elements Br and Cl are present in leaded fuel

with a molar ratio of ~ 3 Br/2Cl which suggests their presence as a mixture of PbClBr and PbO·PbBr$_2$. The Br in unleaded fuels, the V, and the Mn appear to be contaminants introduced into the gasoline either by handling in the refining or delivery service or by having used different brands of gasoline in the vehicle prior to its being tested for this work. The Al appears to come from engine component wear. Some Ba was detected, but at a level of $\sim 1/1000$ of the Br and Cl concentrations which suggests that trace elements due to lubricating oils are present at this level.

Trace Element Abundances in Automobile Exhaust Particulate

by

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I. INTRODUCTION

To Americans, automobiles have become a nearly indispensible mode of transportation, status symbols and perhaps things of beauty. Yet, these wonderful machines are an important source of polluted air. For example, the automobile is the main source of four atmospheric pollutants--CO, organic compounds, NO_x and Pb compounds.[1] In most areas, it is the dominant contributor to photochemical smog.

Although a great many studies have been made of the gaseous emissions from the automobile, the problems associated with the emission of particulate matter by automobiles have not been extensively studied. While the gaseous emissions are larger than the particulate, gasoline engines still introduce one million tons of particulate material into the United States' atmosphere annually.[13] Particulate matter, such as this, can serve to introduce certain trace elements such as Be, Cd, As, Se, Pb, Sb, Hg, Tl and V into our environment.[2,3] Most of these trace elements are mobilized on particulate matter derived from high temperature combustion sources such as fossil-fueled power plants, municipal incinerators, blast furnaces and internal combustion automobile engines.[4,5] These trace elements are important for a variety of reasons. First of all, many of them are known to be toxic. Pb, for example, can cause liver and kidney damage, gastrointestinal damage, mental health

effects in children, and abnormalities in fertility and pregnancy. Furthermore, the majority of these atmospheric trace elements are associated with small (<1μ) diameter particulate matter[6-10] allowing them to be readily assimilated into the human respiratory system.[11,12] Nonetheless, it should be noted that American Conference of Governmental Industrial Hygienists Threshold Limit Values for the maximum permissible concentration of these metals in the air are generally >100μg/m³, a concentration rarely reached in real atmospheres. Further, it has not been demonstrated unambiguously that any human health damage results from these trace metals in the atmosphere. Research continues on the possible importance to human health from the presence of these metals in urban environments.

Atmospheric trace elements from automotive emissions are also important as tracers of "fingerprints" of the automotive contribution to urban CO, NO_x, and other pollutant levels. In addition, the emitted particulate along with the associated trace elements can influence the meteorology of a given area by furnishing condensation nuclei for cloud formation or can increase light scattering, thereby reducing visibility. This particulate matter also poses problems for the catalytic convertor system used in modern automobiles to convert CO and hydrocarbons (HC) to CO_2 and H_2O. Herein one refers to the poisoning of the convertor by trace metal deposits.

A number of studies have been made on the composition of particulate matter collected outside the automobile exhaust system.[10,14] Table I, taken from Gordon,[10] shows the typical trace elements

Table I

Comparison of Emission Ratios for Elements on
Aerosols from Motor Vehicles

Element	Gordon[10]	Cahill and Feeney[15]
Pb	≡1	≡1
Br	0.38±0.03	0.37
Cl	0.10±0.03	0.17
Ca	0.054±0.044	0.12
Fe	0.050±0.031	0.20
Zn	0.014±0.003	0.03
Ba	0.013±0.004	NR*
Cu	0.0050±0.0034	<0.01
Cd	0.0024±0.0010	NR
Sb	0.0008±0.0006	NR
Ni	0.00061±0.00046	NR
Se	0.00049±0.0041	NR
Mg	<0.11	NR
Al	<0.054	0.12
Ti	<0.042	NR
Mn	<0.0071	NR
Cr	<0.0035	NR
V	<0.0015	NR
Co	<0.00045	NR
Ce	<0.00011	NR
Hf	<0.000088	NR
La	<0.00006	NR
Th	<0.000055	NR
Sm	<0.00004	NR
Ta	<0.000014	NR

*NR indicates not reported.

that were found to be associated with particulate collected in a tunnel in which there was heavy traffic. While such studies are useful, they fail to allow one to separate various sources of automotive emissions such as upswept tire dust, exhaust, etc., nor do they allow detailed conclusions about the emissions from specific engine types, or emissions as a function of fuel, engine and exhaust system parameters.

A much smaller number of studies has involved direct sampling of the automobile exhaust to determine the nature of the emitted particulate.[7,9,16] These studies have been concerned with the total particulate matter or the Pb content of the particulate. Among the conclusions of these studies were:

1. The higher the engine speed or load or fuel element content, the greater the lead or particulate emissions.

2. Some of the lead burned is retained in the engine, oil and exhaust system and re-emitted during high speed, high load conditions.

3. After an initial buildup in the exhaust system, lead emission rates do not change greatly with increased car mileage although the particle sizes do apparently increase.

4. Some of the emitted lead is associated with particles whose diameter is $>9\mu$, probably representing exhaust pipe material and $PbClBr$. The other portion of the emitted Pb is associated with particles whose diameter is $<1\mu$, probably in the form of $2PbBrCl \cdot NH_4Cl$.

5. Cars with well-conditioned exhaust systems burning unleaded fuel emit less total particulate than cars burning leaded fuel. The particulate from burning unleaded fuel appears to have a high (70%) C content and have a higher volume/mass ratio than the matter collected from leaded fuel operation.

While this information is valuable, additional detailed information concerning the trace element content of automobile exhaust is needed. For example, we know that in 1971, the automobile industry started mass-producing engines designed to be operated with low-lead and lead-free gasoline. Most of the 1975 model cars must be run on lead-free gasoline. As the number of vehicles burning unleaded fuel increases, it will no longer be possible to trace automobile exhaust by tracing Pb in urban atmospheres. Other indicators of the auto exhaust from these "lead-free" vehicles must be found. Furthermore, the preliminary data cited above shows some differences in the combustion of leaded and unleaded fuel, leading one to believe that the dependence of the behavior of the new "tracer" for auto exhaust upon engine operating conditions, etc. must be explored for cars burning unleaded fuel. The problem is further complicated by the increasing use of catalytic convertors. The effect of these converters upon particulate emissions is not known. The availability of specific trace element emission factors for automobiles burning leaded, or unleaded fuel or unleaded fuel plus a catalytic converter under various engine conditions will be very important to urban planners, environmental engineers, etc. in their predictions of the effect of

changes in traffic patterns, fuel, etc. upon air quality. This type of prediction is not possible with current data on "gross automobile contributions to air pollution" taken mostly at one engine speed, with leaded fuel and unknown mixtures of different vehicle types.

With these arguments in mind, we proposed a study in which we sampled directly the exhaust from a series of well-maintained fleet vehicles being run under different engine conditions on a chassis dynamometer. The cars tested were to include vehicles burning leaded or unleaded fuel or unleaded fuel with a catalytic converter. From this study we hoped to:

1. Determine the actual particulate trace element concentrations in the exhaust from the aforementioned three vehicle fuel-convertor systems.

2. To use the data of (1) to determine the effect of unleaded fuel and catalytic converters upon exhaust trace element concentrations.

3. To attempt to find a tracer(s) for auto exhaust for cars burning unleaded fuel and also those using catalytic converters.

4. To correlate trace element emissions with gaseous emissions, such as CO, HC, etc. if possible.

5. To correlate particulate emissions with the three fuel-converter types with different engine parameters, such as air-to-fuel ratio and load (e.g., high, low and medium cruise, acceleration and deceleration).

II. EXPERIMENTAL METHODS

To obtain an adequate characterization of the particular emissions of automobile engines, we chose to use a fleet of well-maintained automobiles for testing and to develop a sampling system capable of giving representative samples of automobile exhaust along with an analytical procedure capable of analyzing samples with superior sensitivity.

A. Description of Vehicles Tested

To remove the state of engine tune as a variable in our testing program, we chose to conduct our tests on fleet vehicles from the State of Oregon Motor Pool which have been well-maintained. These vehicles receive periodic service (oil, filter change, etc.) at 5,000 mile intervals and major tuneups at 15,000 mile intervals. Whenever any complaint is received about the operation of any vehicle it is attended to immediately. Automobiles burning leaded gasoline were borrowed from the Oregon State Motor Pool in Corvallis, Oregon, while those burning unleaded fuel were obtained from the State Motor Pool in Salem, Oregon. The leaded gasoline used was Mobil regular leaded (89 road octane no., 3.2 gPb/gallon[32]), while the unleaded fuel was Mobil unleaded (87 road octane no.[32]). A total of 26 cars was tested and a listing of these cars and their characteristics appears in Table II. As one can see from examining Table II, the cars burning leaded fuel were generally well-conditioned vehicles having mileages over 15,000 miles while the vehicles burning unleaded fuel generally

Table II. LISTING OF VEHICLES TESTED AND THEIR CHARACTERISTICS

Mfr.	Model	Year	Number of Cylinders	Engine Displacement (cubic in.)	Fuel Type	Catalytic Converter	Mileage	Ident. Number	Source	Date Tested
Dodge	Dart	1974	6	225	leaded	no	13,487	74-279	OSU	5/17/75
Dodge	Dart	1974	6	225	unleaded	no	10,854	74-330	OSU	8/5/75
Dodge	Dart	1974	6	225	leaded	no	19,000	74-283	OSU	9/19/75
Dodge	Dart	1974	6	225	leaded	no	19,516	74-292	OSU	9/22/75
Dodge	Coronet	1972	8	318	leaded	no	63,108	72-150	OSU	7/27/75
Dodge	Coronet	1972	8	318	unleaded	no	63,200	72-150	OSU	8/1/75
Dodge	Coronet	1973	8	318	leaded	no	51,701	73-215	OSU	9/26/75
Dodge	Coronet	1973	8	318	leaded	no	43,400	73-492	OSU	9/24/75
Dodge	Coronet	1973	8	318	leaded	no	50,388	73-496	OSU	9/25/75
Plymouth	Valiant	1975	6	225	unleaded	yes	9,136	124-304	STATE	9/25/75
Plymouth	Valiant	1975	6	225	unleaded	yes	11,711	124-312	STATE	10/2/75
Plymouth	Valiant	1975	6	225	unleaded	yes	9,936	124-323	STATE	8/13/75
Plymouth	Valiant	1975	6	225	unleaded	yes	16,640	124-316	STATE	10/2/75
Plymouth	Fury	1975	8	318	unleaded	yes	1,663	124-343	STATE	8/18/75
Plymouth	Fury	1975	8	318	unleaded	yes	4,614	124-343	STATE	10/3/75
Plymouth	Fury	1975	8	318	unleaded	yes	1,138	124-346	STATE	10/4/75
Plymouth	Fury	1975	8	318	unleaded	yes	4,040	124-347	STATE	10/6/75

Mfr.	Model	Year	Number of Cylinders	Engine Displacement (cubic in.)	Fuel Type	Catalytic Converter	Mileage	Ident. Number	Source	Date Tested
AMC	Hornet	1975	6	232	unleaded	no	4,687	123-349	STATE	10/4/75
AMC	Hornet	1975	6	232	unleaded	no	5,090	124-349	STATE	10/8/75
AMC	Hornet	1975	6	232	unleaded	no	6,028	124-351	STATE	10/19/75
AMC	Hornet	1975	6	232	unleaded	no	2,055	124-393	STATE	10/12/75
AMC	Hornet	1975	6	232	unleaded	no	8,120	124-404	STATE	10/19/75
AMC	Hornet	1975	6	232	unleaded	no	4,007	124-409	STATE	10/4/75
AMC	Hornet	1975	6	232	unleaded	no	4,882	124-412	STATE	10/8/75
AMC	Hornet	1975	6	232	unleaded	no	10,627	124-415	STATE	10/20/75
AMC	Hornet	1975	6	232	unleaded	no	2,932	124-417	STATE	10/12/75

had traveled less than 5,000 miles. The vehicles were primarily compact or intermediate-sized vehicles with 6 cylinder, 225 CID or 8 cylinder, 318 CID engines. The catalytic convertors used had the monolith (honeycomb) structure with a mixed Pt/Pd catalyst ($\sim$1.5-3g metal) and were manufactured by Universal Oil Products.

B. Sample Collection

Filtration was chosen as the method of particulate collection. The choice of a suitable filtering system was based upon:

1. The high temperature of the exhaust gases (150-600°F).

2. The high flow rate of the exhaust (20-200 cfm).

3. The small mass median equivalent diameter (MMED) of the particulate (45% of the particulate matter is associated with MMED < 5μ[8]).

4. The necessity for isokinetic sampling.

5. The desire to sample non-equilibrium modes of engine operation, i.e., acceleration and deceleration.

6. The desire to correlate trace element emissions with gaseous emissions.

7. The presence of time and monetary limitations.

All sample collection and automotive testing was done in the automotive lab of the Mechanical Engineering Department of Oregon State University. This lab is a modern automotive lab capable of testing automobiles according to the latest Environmental Protection Agency schedule.[17] Vehicles are run at various speeds and engine

conditions using the chassis dynamometer shown in Figure 1. The dynamometer instrumentation allows one to operate the vehicle at the right speed and road-load horsepower to simulate any given driving condition. The exhaust from the tailpipe is sampled for particulate and gaseous emissions under given operating conditions. The exhaust flow rate and volume are continuously monitored. The seven driving modes chosen for study in this work were: idle, 25 mph cruise, 40 mph cruise, 55 mph cruise, acceleration (15-55 mph at constant manifold vacuum) and deceleration (55-25 mph).

Figure 2 shows a photograph of a vehicle on the chassis dynamometer with the exhaust sampling system connected to it. Exhaust from the car's tail pipe entered a three foot long, three inch diameter stainless steel exhaust pipe extension. An expanded view of this section is shown in Figure 3. Probes were mounted in this section to sample a portion of the exhaust gas for particulate and gaseous emissions. Probe sampling for particulates was chosen rather than running all the exhaust gas through a filter because preliminary experiments showed that typical particulate filtration media [with small (0.2μ) pore size] could not withstand the flow rates encountered in the system. The speed of the pump drawing air into the probe was varied electrically to allow isokinetic sampling by the probe. The use of a probe sampler could cause problems if a non-uniform particulate concentration profile existed in the exhaust pipe. Although one study[8] reported severe underestimation of the particulate concentrations by <u>nonisokinetic</u> probe sampling, there appears to be no reason
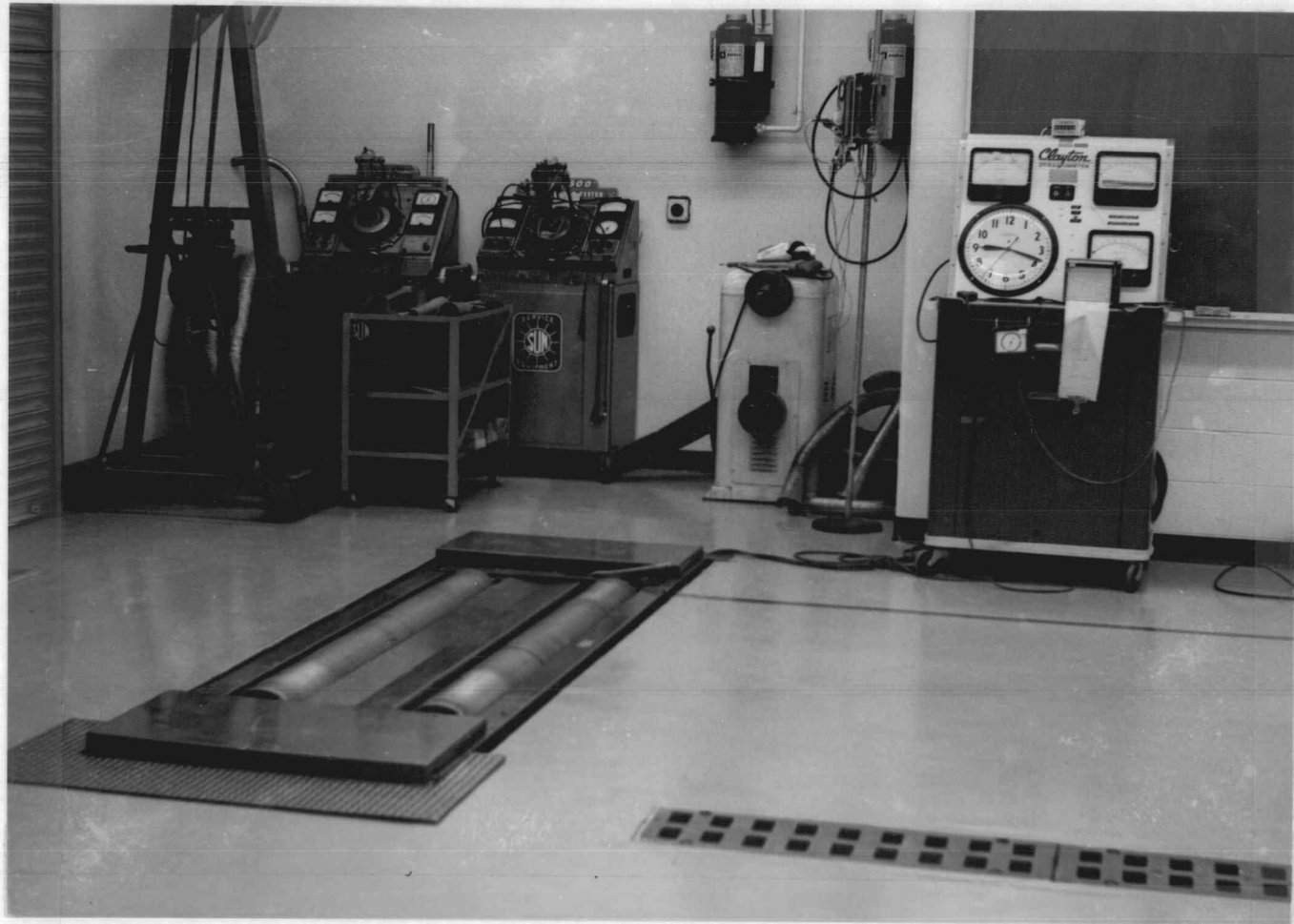
Figure 1.   Chassis dynamometer in automotive lab used in this study.

Figure 2. Photograph of vehicle on chassis dynamometer and connected to
exhaust sampling system. Particulate sampling equipment is in
the foreground.
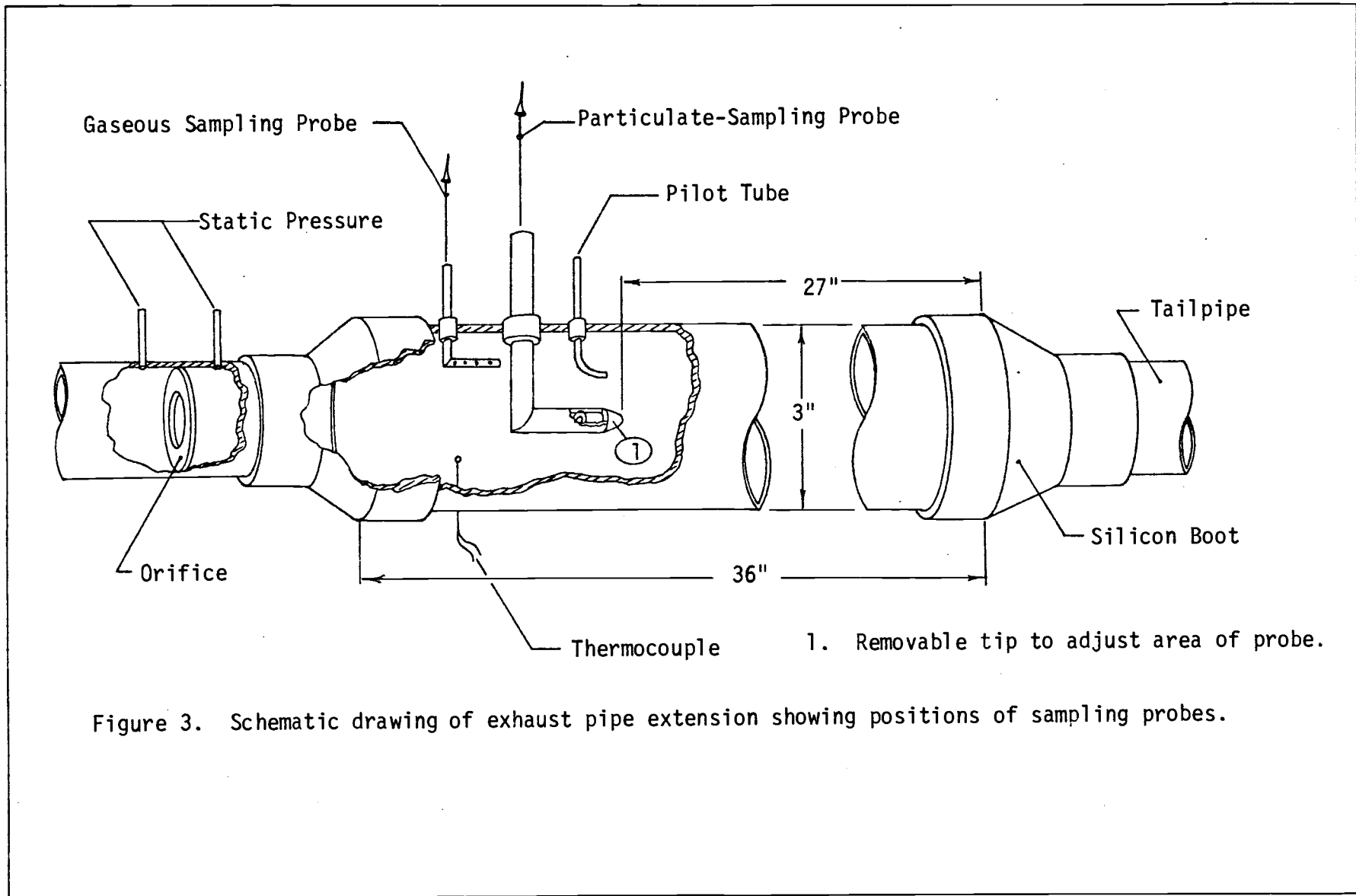
Figure 3. Schematic drawing of exhaust pipe extension showing positions of sampling probes.

to suspect a nonuniform concentration profile in the hot turbulent automobile exhaust gas.[16]

As shown in Figure 3, the particulate sampling probe was a 7/8 inch diameter stainless steel pipe that was inserted in the exhaust pipe extension. Different sized nozzles were attached to the probe to allow reasonable flow rates through the sampler over the wide range of exhaust system flow rates as the vehicle is operated between idle and 55 mph. A thermocouple monitored the temperature of the gases just before sampling. A gas collection probe was also inserted in the exhaust pipe extension to collect exhaust gas samples for analysis of gaseous pollutants.

Figure 4 shows a schematic diagram of the particulate exhaust sampling system. After the exhaust gas entered the particulate sampling probe, it passed through an orifice. The pressure drop in passing through this orfice was monitored using a Magnehelic direct reading pressure meter. Knowledge of this pressure drop as the gas of known temperature T passed through an orfice of known size allowed one to calculate the gas flow velocity in the sampling pipe (see Appendix I). Combining this information with the pipe diameter and the length of the sampling period allowed one to calculate the volume of exhaust sampled. [The flow rate in the particulate sampler was varied so as to be the same as that in the main exhaust pipe as measured by the pressure drop through an orifice(not shown) at the end of the three foot exhaust pipe extension. This insured isokinetic sampling.]

Following their passage through the pressure measuring section
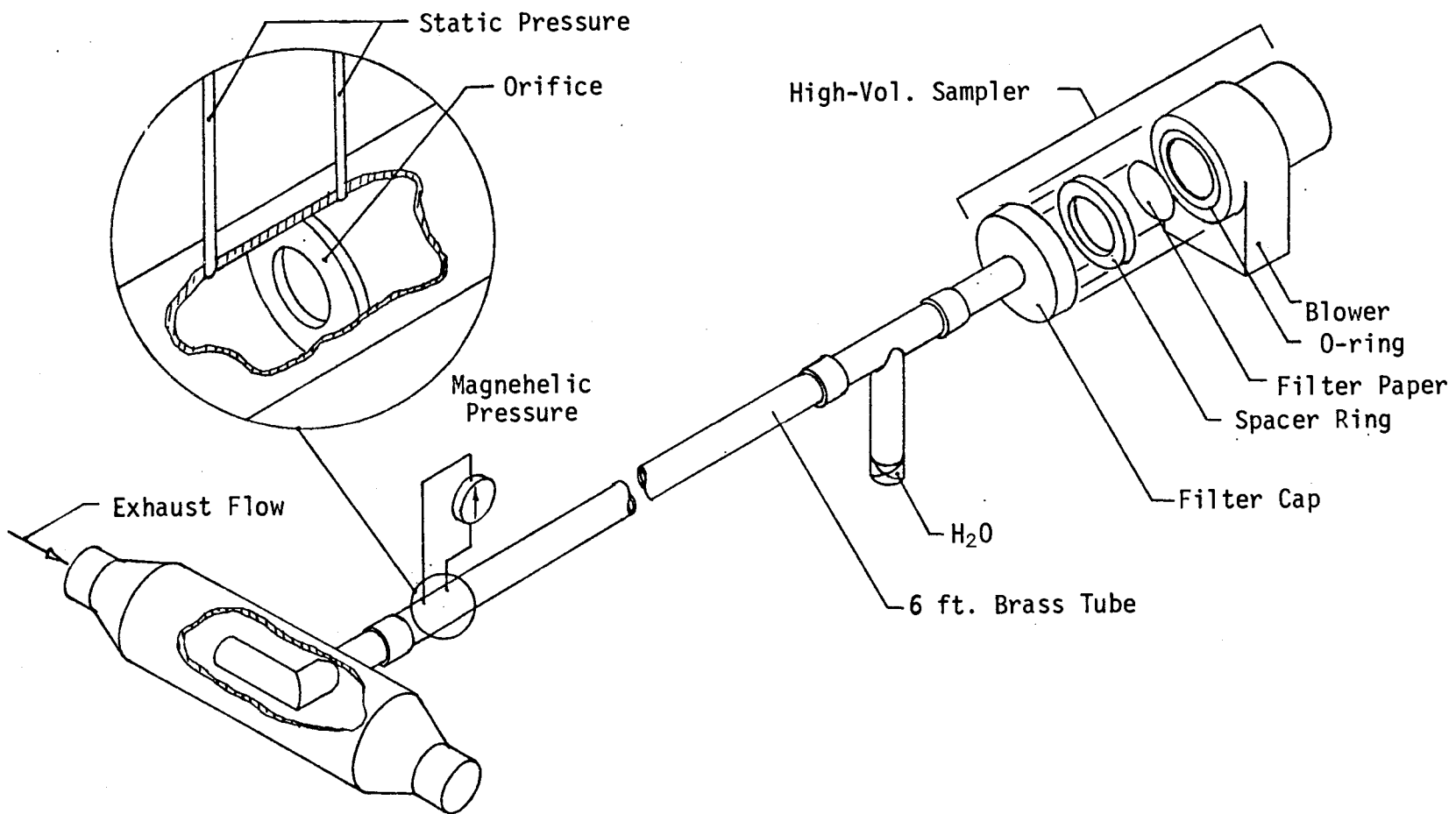
Figure 4. Schematic view of particulate sampling system.

of the particulate sampling train, the hot exhaust gases were cooled by their passage down a six foot length of brass pipe. (In preliminary work, this pipe was constructed of aluminum. A brass pipe was substituted for the aluminum pipe when it appeared that the aluminum pipe was being corroded by the exhaust gases.) A water drain at the end of this section of pipe allowed condensed moisture to be removed from the pipe. An auxiliary thermocouple monitored the gas temperature just prior to it passing through the filter paper to insure that the gas would not melt the Nuclepore filter paper (Nuclepore m.p. ∿ 140°C).

A Shepherd model 8000 high volume sampler was used to draw the exhaust sample through the probe, sampling system and filter paper. Figure 5 shows a photograph of this sampler as it was modified for this study. The sampler inlet was modified to be 0.5 inch in diameter so as to mate with the sampling train. A 1/4 inch thick spacer ring was then inserted between the entry pipe face plate and the filter paper to allow room for the sample gases to spread out over the entire filter area and to hold the filter paper in place. A variac was used to vary the motor speed to achieve isokinetic sampling.

The Shepherd air sampler inlet was washed with successive washes of 2N nitric acid, distilled-demineralized water, 95% alcohol and acetone prior to each sampling session to prevent contamination of the filter paper by contact with the sampler. The sampler was given an acetone wash between each sampling mode.

The filter paper used to collect the particulate material was

Figure 5. Shepherd Model 8000 high volume sampler with spacer ring and new entry orifice.
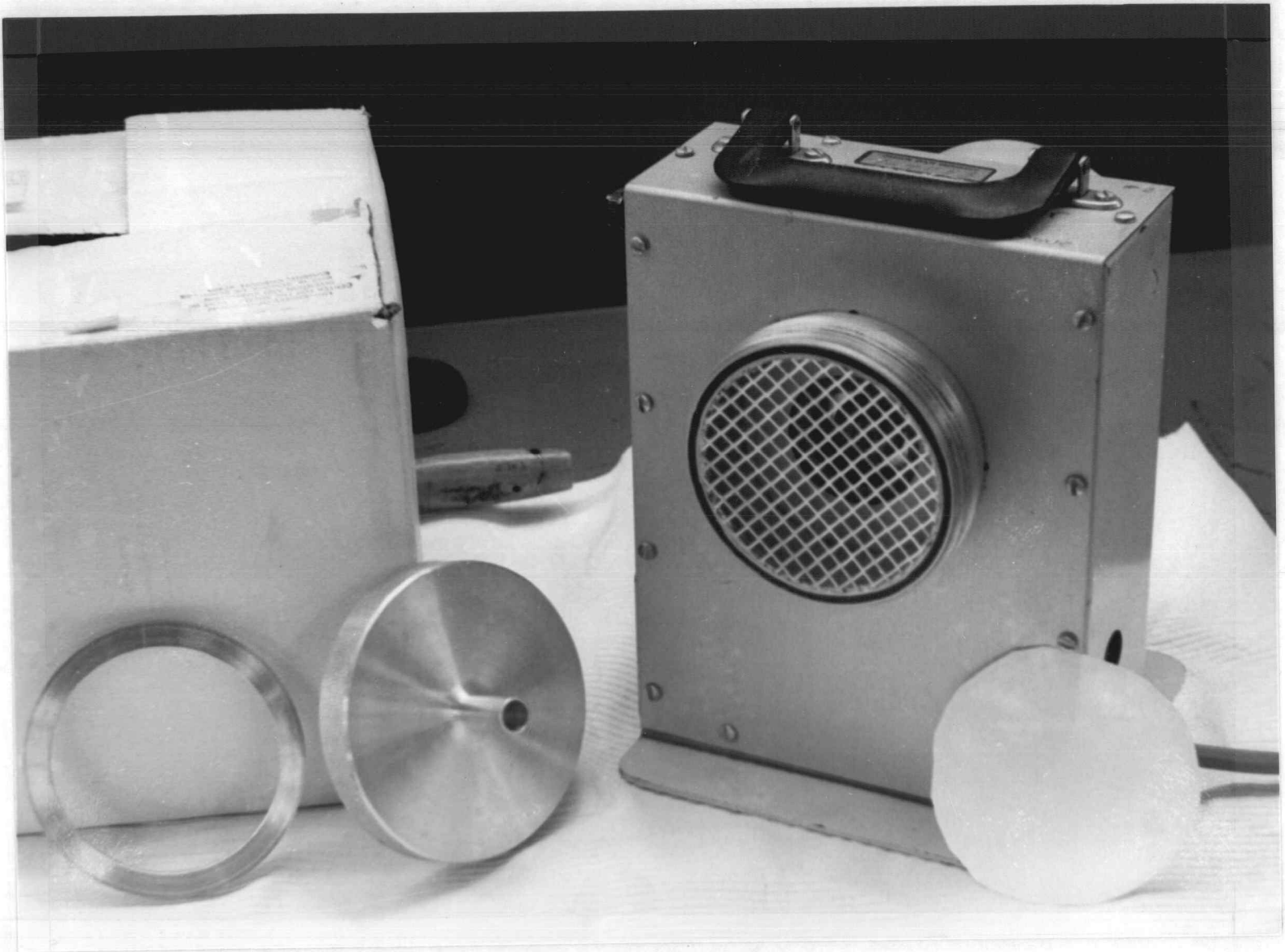
142 mm in diameter, Nuclepore N20 membrane filter with a pore size
of 0.2μ, or in cases where high flow rates were important, Whatman #1
filter paper. The Nuclepore paper was chosen because of its small,
uniform pore size and its low trace element content.[18] The 142 mm
diameter paper was cut to the 92 mm diameter size needed to fit the
sampler with a clean pair of scissors used exclusively for cutting
the Nuclepore filters. To insure maximum cleanliness, a 90 mm Whatman
#1 filter paper was placed between the Nuclepore filter and the air
sampler screen. In cases where the trace element abundances were very
low and high flow rates were needed for adequate sample volumes,
Whatman #1 filter paper was used. This paper allows six to ten times
the flow rate achieved with a Nuclepore filter, and as shown in
Table III, with a modest increase in the content of most trace elements,
with the notable exceptions to this being Na and Cl. The efficiency
of Whatman #1 filter paper for trapping particulate matter with
diameters $\geq 0.3\mu$ has been measured to be greater than 95%.[28]

In order to prevent contamination of the filters,[18] neither
the filters nor the air sampler inlet were ever touched by human
hands. While sampling or preparing the sampler for sampling, plastic
gloves were always worn and the filters were handled only with Teflon
tweezers. The data of Table III comparing the trace element content
of the Nuclepore filter paper after all pre-analysis handling with
other analyses of the "unhandled" paper shows the the efficacy of
the precautions used in handling the sample.

TABLE III. TRACE ELEMENT CONTENT OF FILTER PAPER (ng/cm^2)

A. NUCLEPORE MEMBRANE FILTERS			
Element	This Work*	Ricci et al.[19]	Shum & Loveland[18]	Manufacturers Specification for Max. Trace Element Content of Paper
Na	31	34	47 ± 2	35
Al	5.1	42	2.7 ± 0.3	58
Cl	49	39	80 ± 4	--
Br	2.8	0.92	1.7 ± 0.1	--
Mn	0.31	0.10	0.23 ± 0.05	3
Cu	0.82	--	--	3
V	0.015	0.33	--	--
Ti	--	--	2.1 ± 0.8	12
Sm	0.0021	--	< 0.0017	--
Eu	--	--	< 0.00016	00

*As measured after installation on sampler and removal

B. WHATMAN NO. 1 FILTER PAPER			
Element	This Work*	Shum & Loveland[18]	Keane & Fisher[27]
Na	1900	930 ± 20	1440
Al	41	9.5 ± 3.6	18
Cl	920	510 ± 20	900
Br	5.3	5 ± 2	--
Mn	2.3	1.0 ± 0.4	2.7
Cu	3.4	--	--
V	0.032	--	--

*As measured after installation on sampler and removal

The entire sample collection procedure may be summarized in a step-by-step manner as follows:

Cruise Speeds (25, 40, 55 mph)

1. Position the car on the chassis dynamometer and prepare it for testing using the EPA guidelines[17] (adjust tire pressure, etc.).

2. Operate the car at a cruise condition for a few minutes to warm up the engine and the tires.

3. Adjust the auto's speed to the desired speed using the dynamometer's speedometer.

4. Based upon the engine size and auto weight, set the dynamometer road-load horsepower in accordance with EPA regulations.[17]

5. Determine the exhaust gas flow rate in the main 3 foot exhaust pipe extension from the gas temperature and the pressure drop through the orifice at the end of the 3 foot extension.

6. Clean sampler, attach filter paper and connect to particulate sampling train. Using variac on sampler motor, adjust motor speek until pressure drop across orifice in particulate probe corresponds to that necessary to have the same flow rates in the exhaust pipe extension and the particulate sampling probe.

7. Monitor sampling time during sample. Shut off and remove sampler at end of sample period.

8. Remonitor temperature and sample gaseous emissions.

9. Advance to next sampling mode (driving condition).

Idle

The same procedure as above, except steps 3 and 4 were omitted.

Deceleration

Deceleration was assumed to have the same engine characteristics as the idle mode, an assumption which was substantiated by the gaseous emission data (see Chapter III). The procedure followed involved adjusting the equipment for "idle" mode sampling, accelerating the car to 55 mph, cruising momentarily at 55 mph and closing the throttle. Air sampling for a period of 30 seconds began with the closing of the throttle. During this 30 second period, the car would decelerate from 55 mph to ~25 mph. Four such 30 second "decel" samples were taken for each car.

Acceleration

Acceleration proved to be the most challenging sampling mode because both the temperature and exhaust gas flow rate constantly change during a normal acceleration. Therefore, it was decided to do a constant manifold vacuum acceleration (with the manifold pressure being ~10" of H_2O). Such accelerations were fairly representative of urban traffic conditions in that most of the test vehicles required ~30 sec to accelerate from 15 to 55 mph. To estimate the average exhaust temperature and flow rate during such an acceleration, exhaust flow rates and temperatures were measured as a function of speed and load horsepower at constant manifold vacuum with actual vehicles. These measured flow rates and temperatures were then

averaged over the conditions encountered during acceleration to give a single average "acceleration temperature" and "acceleration flow-rate."

It was found that the vehicle acceleration times were greatly affected by the engine's exhaust gas recirculation system (EGR). The EGR system is designed to reduce NO_x emissions by recirculating exhaust gas into the combustion chamber, thus diluting the air-fuel mixture, leading to a lowering of peak flame temperatures in the combustion chamber. The EGR system incorporates a vacuum switch located on the intake manifold that opens a valve in the tube connecting the exhaust pipe with the intake manifold. During acceleration, the manifold vacuum was lowered sufficiently to activate the EGR system. This caused a loss of engine power which led, for the Hornets, to a time of one minute to accelerate from 15 to 55 mph.

C. Sample Analysis

The gaseous pollutants in the exhaust were analyzed using commercially available gas analysis equipment. The oxygen content of the exhaust gas was measured using a Scott 150 paramagnetic resonance oxygen determination device. The hydrocarbon content of the exhaust was measured with a Beckman non-dispersive infrared analyzer with a 13 inch cell. The same IR analyzer was used at different wavelengths and with different gas cells to measure the CO and CO_2 content of the exhaust gas. The NO_x content of the exhaust was determined using a Scott 325 chemiluminescence detector. An AESI-SCM-7900 sample

conditioning module was used in all analyses to filter and compress the exhaust gas and to pump it through the appropriate gas analysis equipment. Figure 6 shows a photograph of the gas analysis equipment.

Instrumental neutron activation analysis (INAA) was chosen as the method for trace element analysis of the collected particulate matter. INAA was chosen because of its superior elemental detection sensitivity and its non-destructive character.

After collection of the particulate sample, the "dirty" filters were transferred to a small plastic bag, transported to the OSU Radiation Center, and prepared for irradiation. To assure reproducible irradiation and counting geometries, the filters were pelletized prior to irradiation. The pelletization was done using a Beckman KBr die with a Carver Laboratory press. After pelletization, the samples were sealed in clean polyvials and irradiated in the OSU TRIGA reactor.

The activation analysis procedure used to measure the trace element content of the particulate material was patterned after that of Shum and Loveland[18] and is summarized in Table IV. The samples or standards containing known amounts of the various trace elements were irradiated for two or three minutes in the pneumatic terminal of the OSU TRIGA reactor in a neutron flux of 6×10^{12} or 9×10^{12} n/cm^2-sec. (The reactor flux for a given power decreased by a factor of 0.7 during the period of this work due to rearrangements of the reactor core). The leaded fuel samples were irradiated for two minutes due to their lower trace element content. After irradiation, the sample was transferred into a new polyvial and counted immediately
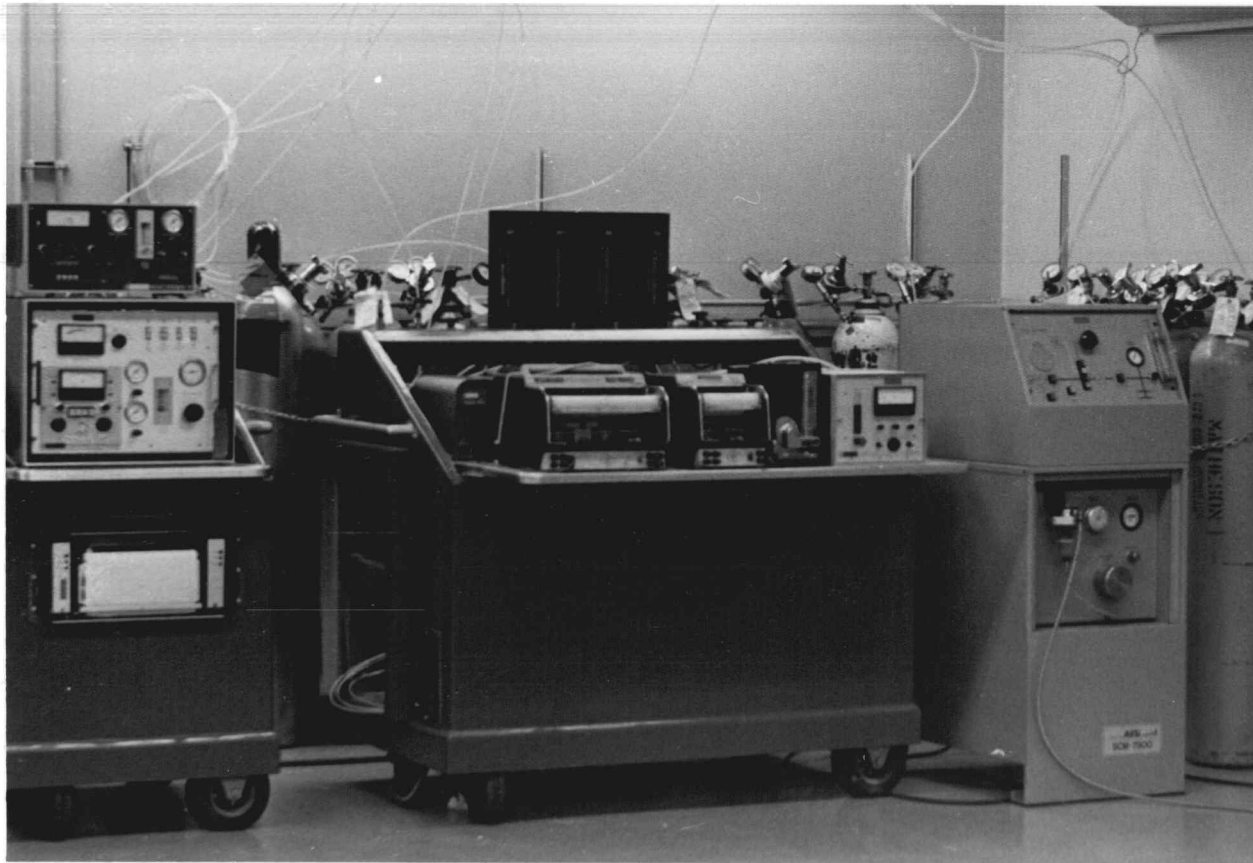
Figure 6. Gas analysis equipment used in this study.

Table IV. SUMMARY OF ACTIVATION ANALYSIS PROCEDURE*

Element	Radionuclide Detected	Half-life*	Length of Irradiation	Decay Time	Count Duration	Energy of Gamma-Ray Measured* (keV)
Al	^{28}Al	2.31 min.	2 or 3 min.	4 min.	420 sec.	1778.9
Ti	^{51}Ti	5.79 min.				320
V	^{52}V	3.75 min.				1434.4
Cl	^{38}Cl	37.3 min.				1642
Cu	^{66}Cu	5.1 min.				1039
Na	^{24}Na	14.96 hr.	2 or 3 min.	200-500 min.	1800 sec.	1368.5
Mn	^{56}Mn	2.58 hr.				846.9; 1810
Br	^{80}Br	17.6 min.				617
Ba	^{139}Ba	82.9 min.				165.8
Sm	^{153}Sm	47 hr.	6 hr.	12 hr.	2000-10000 sec.	103.2
Eu	^{152m}Eu	9.3 hr.				121.8
Zn	^{69m}Zn	13.8 hr.				438.7
Br	^{82}Br	35.9 hr.				776.6
As	^{76}As	26.5 hr.				657; 1215.8; 559
Sb	^{122}Sb	2.80 day				564; 686
K	^{42}K	12.36 hr.				1524.7
La	^{140}La	40.22 hr.				486.7; 1596
Sc	^{46}Sc	83.9 day	6 hr.	15-30 d	100k sec.	889.4; 1120
Cr	^{51}Cr	27.8 day				320
Fe	^{59}Fe	45.6 day				1292
Co	^{60}Co	5.26 yr.				1173.1
Hg	^{203}Hg	46.9 day				279.1
Ce	^{141}Ce	33 day				145.4
Yb	^{169}Yb	32 day				177; 197.8
Lu	^{177}Lu	6.7 day				208.3
Hf	^{181}Hf	42.5 day				136.5

*Taken from Lederer, et al.[20]

for 420 seconds with a 30 or 40 cm^3 Ge(Li) detector incorporated with a multichannel analyzer.

After the first counting was done, this measurement was immediately followed by a 1200-1800 second count. Table IV shows the elements whose concentrations are determined by the first two counts. The sample radioactivity was then allowed to decay for a week, and the sample was irradiated again in the rotating rack of the reactor at a flux of 3 x 10^{12} n/cm^2-sec. for six hours. After cooling for 12 hours, the sample was counted for 2,000-10,000 seconds. The sample was recounted for five hours after an additional cooling period of one month. The elements whose concentrations were determined in this second irradiation are also tabulated in Table IV.

Half lives measured for all radionuclides agreed with ±10 percent of the accepted values.[20] The energies of the gamma-rays used in the analysis of the various trace elements are listed in Table IV. Standards containing known amounts of the pure elements were irradiated along with the samples and counted under identical conditions. From the photopeak areas for samples and standards, elemental abundances were calculated for each sample.

The accuracy of the standards and procedure used was checked for each irradiation by irradiating NBS standard reference materials (orchard leaves, fly ash and coal) along with each sample and checking to see that the measured trace element content of the NBS standards agreed with the NBS certified values.

III. RESULTS AND DISCUSSION

A. Accuracy and Precision of Analyses

Table V shows the results of several analyses of the NBS Standard Reference Materials, 1571--Orchard Leaves, 1632--Coal, and 1633--Coal Fly Ash. Also shown in this table are the NBS certified values for elemental concentrations in these materials along with the reported elemental concentration values of other investigators.

For the NBS standard coal, all values reported agree within experimental error ($\leq$ 5%) with the NBS certified values or the work of other investigators, with the exception of Cu where only an upper limit was measured in this work. For the NBS biological standard orchard leaves, the values reported from this work for Mn and Na agree within experimental error with the NBS certified values. For the Cu abundance, a "virtual" upper limit was obtained again which agreed with the NBS certified value. For the other trace element abundances, the agreement amongst different investigators is modestly good ($\leq$ 20%) perhaps reflecting an intrinsic inhomogeneity in this standard reference material which has not permitted the NBS to certify elemental concentrations. The lesson to be drawn from this, perhaps, is that the better characterized newer standard reference material, (SRM-1632-coal) should replace the older orchard leaves standard for environmental trace element research.

The situation with respect to the analysis of NBS standard coal fly ash (SRM 1633) is akin to the orchard leaves situation although

TABLE V. TRACE ELEMENT CONCENTRATIONS IN NBS
STANDARD REFERENCE MATERIALS (µg/g)

A. NBS Standard Coal (SRM 1632)

Element	This Work*	NBS[22]	Ondov, et al.[21]
V	37 ± 1	35 ± 3	36 ± 3
Br	17 ± 2	----	19.3 ± 1.9
Cl	984 ± 34	----	890 ± 125
Mn	42 ± 1	40 ± 3	43 ± 4
Al	1.88 ± 0.01(%)	----	1.85 ± 0.13(%)
Na	426 ± 4	----	414 ± 20
Cu	< 30	18 ± 2	----
Ba	346 ± 26	----	352 ± 30

B. NBS Standard Orchard Leaves (SRM 1571)

Element	This Work[+]	NBS[22]	Shum[25]	Renter, et al.[23]	Morrison & Potter[24]
V	0.69 ± 0.15	----	----	----	< 0.7
Br	13 ± 2	(10)	----	8.9 ± 0.9	8.3 ± 0.5
Cl	795 ± 14	(700)	----	----	790 ± 44
Mn	94 ± 0.4	91 ± 4	99 ± 1	101 ± 10	86 ± 5
Al	364 ± 3	----	----	----	440 ± 25
Na	81 ± 3	82 ± 6	98 ± 10	----	77 ± 4
Cu	25 ± 21	12 ± 1	----	14 ± 1	10 ± 6
Ba	81 ± 29	----	----	----	51

C. NBS Standard Coal Fly Ash (SRM 1633)

Element	This Work[‡]	NBS[22]	Ondov, et al.[21]
V	230 ± 4	214 ± 8	235 ± 13
Br	< 15.9	----	12 ± 4
Cl	175 ± 57	----	42 ± 10
Mn	520 ± 2	493 ± 7	496 ± 19
Al	13.1 ± 0.1(%)	----	12.7 ± 0.5(%)
Na	3700 ± 14	----	3200 ± 400
Cu	290 ± 150	128 ± 5	----
Ba	2600 ± 200	----	2700 ± 200

* The weighted average of ∿6 determinations.
+ The weighted average of ∿7 determinations.
‡ The weighted average of ∿3 determinations.

perhaps somewhat better. The analysis reported by Ondov, et al.[21] represents the work of four highly respected laboratories employing instrumental neutron activation analysis to analyze NBS standard reference materials. The reported analyses for V, Mn, and Al agreed within experimental error with the work of Ondov, et al. The Na analysis appears slightly high ($\sim$ 10%) when compared to the "four-laboratory mean" reported by Ondov, et al. However, it does agree exactly with the analysis of the Na content of coal fly ash by the Battelle-Northwest member of the "four-laboratory consortium." Thus, the "error" in our data is akin to that made by other high-quality analytical laboratories in analyzing the Na content of fly ash. The copper analysis was once again quite uncertain and apparently not accurate. After obtaining these results for Cu abundances, I decided not to report any Cu concentrations determined in the exhaust particulate samples. The Cl content of NBS coal fly ash differs markedly ($\sim$ 400%) from the single value reported only by the University of Maryland members of the "four laboratory consortium." Since the Cl content of other samples appears to be correctly measured by the techniques employed in this work, there appears to be no reason for this discrepancy.

The data in Table V also give some indication of the relative precision of the trace element analyses. With the exception of the Cu analysis, where only upper limits could be reported with the standard reference materials, most analyses showed a precision or reproducibility of analyses of < 5%. This seems quite adequate for

analyses of concentrations which are themselves probably log-normally distributed. The methods used for trace element analysis in this work would appear to be both accurate and reasonably precise.

B. Gaseous Pollutant Concentrations

The concentrations of various gaseous materials [hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO_2), and oxides of nitrogen (NO_x)] in the exhaust of the twenty-six cars tested is shown in Tables VI, VII, VIII, IX, and X. (See Table II for a description of the vehicles, fuel, and convertor systems employed.) Since there appears to be wide variability in exhaust gas concentrations for a group of similar cars run under similar conditions with similar fuels, etc., a statistical treatment of the data seems to be necessary to extract meaningful information from it. Such a treatment of the data was carried out using standard statistical procedures as coded in the OSU CDC 3300 program "*SIPS".[26] For purposes of statistical analysis, the data were grouped into five groups, representing the five types of cars tested:

1. Hornets burning unleaded gas with no convertor (232 CID, 6 cylinder engines).

2. Furies burning unleaded gas with convertors (318 CID, 8 cylinder engines).

3. Valiants burning unleaded gas with convertors (225 CID, 6 cylinder engines)

4. Coronets burning leaded gas with no convertor (318 CID, 8 cylinder engines).

5. Darts burning leaded gas with no convertor (225 CID, 6 cylinder engines).

Table VI. HYDROCARBON (HC) CONCENTRATIONS (ppm) IN
AUTOMOBILE EXHAUST

Vehicle Number*	Fuel Type	Operating Mode					
		Idle	25	40	55	Accel	Decel
72-150	leaded	140	77	66	57	140	2000
72-150	unleaded	120	48	36	48	160	500
74-279	leaded	160	200	180	130	120	2400
74-330	unleaded	150	190	130	110	120	500
74-292	leaded	160	160	110	80	80	450
74-283	leaded	150	240	120	94	100	2200
73-215	leaded	60	530	240	220	190	580
73-492	leaded	230	130	120	100	110	2200
73-496	leaded	55	80	100	100	92	1600
124-343	unleaded	55	32	23	20	20	55
124-343	unleaded	20	18	15	10	---	---
124-347	unleaded	70	42	20	18	20	290
124-346	unleaded	170	100	15	18	25	1000
124-323	unleaded	240	130	24	16	---	---
124-312	unleaded	190	140	40	30	55	2500
124-304	unleaded	170	150	33	29	42	2500
124-316	unleaded	320	200	60	40	70	2500
124-417	unleaded	38	53	48	25	25	730
124-393	unleaded	26	42	38	18	22	950
124-404	unleaded	41	70	64	48	50	520
124-351	unleaded	30	58	45	17	20	440
124-349	unleaded	70	75	90	40	33	2500
124-349	unleaded	110	100	97	41	60	2200
124-409	unleaded	40	53	48	20	20	290
124-412	unleaded	160	110	65	32	38	1200
124-415	unleaded	23	43	40	17	23	540

* See Table II for vehicle description.

Table VII. CARBON MONOXIDE (CO) CONCENTRATIONS IN AUTOMOBILE EXHAUST.
ALL CONCENTRATIONS ARE % UNLESS OTHERWISE STATED.

Vehicle Number*	Fuel Type	Operating Mode					
		Idle	25	40	55	Accel	Decel
72-150	leaded	3.0	0.25	0.32	0.43	0.47	2.3
72-150	unleaded	1.7	0.28	0.30	0.36	---	---
74-279	leaded	5.3	1.3	0.50	0.50	0.75	4.6
74-330	unleaded	6.3	2.0	0.53	0.40	0.58	5.1
74-292	leaded	3.2	1.2	0.29	0.30	0.38	4.5
74-283	leaded	3.3	3.2	1.4	2.0	2.1	3.5
73-215	leaded	0.53	1.4	1.1	2.0	1.8	4.3
73-492	leaded	5.7	0.82	0.31	0.46	0.62	5.3
73-496	leaded	0.85	0.27	0.27	0.58	1.7	3.2
124-343	unleaded	470 ppm	430 ppm	390 ppm	370 ppm	380 ppm	460 ppm
124-343	unleaded	380 ppm	280 ppm	320 ppm	330 ppm	---	---
124-347	unleaded	2.9	260 ppm	460 ppm	450 ppm	0.24	3.2
124-346	unleaded	6.0	1.0	360 ppm	400 ppm	410 ppm	7.0
124-323	unleaded	8.5	0.17	0.040	0.035	---	---
124-312	unleaded	5.2	1.6	0.18	0.15	0.15	4.7
124-304	unleaded	5.3	1.9	0.14	0.13	0.15	7.1
124-316	unleaded	8.2	2.5	0.15	0.11	0.13	7.8
124-417	unleaded	0.27	0.27	0.27	0.24	0.27	2.0
124-393	unleaded	0.22	0.22	0.22	0.26	0.34	1.44
124-404	unleaded	0.35	0.36	0.44	0.36	0.35	2.4
124-351	unleaded	0.26	0.35	0.33	0.22	0.27	1.8
124-349	unleaded	0.80	0.30	1.4	0.27	0.29	6.0
124-349	unleaded	2.0	0.53	1.2	0.35	0.27	6.8
124-409	unleaded	0.27	0.20	0.20	0.21	0.22	1.6
124-412	unleaded	7.6	1.7	0.47	0.41	0.40	6.8
124-415	unleaded	2.0	0.53	1.2	0.35	0.27	6.8

* See Table II for vehicle description.

Table VIII. CARBON DIOXIDE (CO_2) CONCENTRATIONS (%)
IN AUTOMOBILE EXHAUST

Vehicle Number*	Fuel Type	Operating Mode					
		Idle	25	40	55	Accel	Decel
72-150	leaded	12	13	13	13	14	10
72-150	unleaded	12	13	13	14	13	--
74-279	leaded	10	11	12	11	12	6.9
74-330	unleaded	11	14	14	14	14	8.8
74-292	leaded	10	12	12	13	13	8.0
74-283	leaded	12	13	13	14	14	12
73-215	leaded	13	13	14	13	13	11
73-492	leaded	9.8	--	12	13	14	8.5
73-496	leaded	14	14	13	14	14	7.0
124-343	unleaded	14	15	14	14	14	14
124-343	unleaded	13	14	13	13	--	--
124-347	unleaded	13	14	13	13	13	12
124-346	unleaded	11	13	14	14	14	11
124-323	unleaded	8.6	13	13	14	--	--
124-312	unleaded	10	13	13	13	13	11
124-304	unleaded	7.0	13	14	14	14	9.1
124-316	unleaded	8.5	13	14	14	13	8.0
124-417	unleaded	12	14	14	14	13	12
124-393	unleaded	12	13	14	14	13	11
124-404	unleaded	13	13	13	13	13	12
124-351	unleaded	12	13	14	13	13	13
124-349	unleaded	13	13	13	13	13	7.3
124-349	unleaded	13	15	15	15	14	8.8
124-409	unleaded	12	12	13	12	13	12
124-412	unleaded	9.2	14	14	14	13	11
124-415	unleaded	12	13	14	14	13	13

* See Table II for vehicle description.

Table IX. OXYGEN (O_2) CONCENTRATIONS (%) IN AUTOMOBILE EXHAUST

Vehicle Number*	Fuel Type	Operating Mode					
		Idle	25	40	55	Accel	Decel
72-150	leaded	0.10	2.0	1.3	1.4	1.0	2.5
72-150	unleaded	1.7	1.2	2.3	1.4	---	---
74-279	leaded	0.50	1.0	1.2	1.3	1.0	2.5
74-330	unleaded	0.80	0.50	1.2	1.1	1.0	2.0
74-292	leaded	1.1	4.0	4.2	1.8	3.0	5.0
74-283	leaded	1.1	0.60	2.4	1.3	1.3	4.5
73-215	leaded	1.6	1.5	0.40	0.30	---	---
73-492	leaded	2.1	4.0	1.7	1.5	---	1.2
73-496	leaded	1.2	1.6	2.0	1.0	1.0	5.0
124-343	unleaded	2.0	0.90	1.9	2.0	2.0	1.0
124-343	unleaded	3.3	2.4	2.2	2.1	---	---
124-347	unleaded	0.50	0.50	2.0	2.0	2.0	0.020
124-346	unleaded	0.65	0.50	1.4	1.3	2.0	0.20
124-323	unleaded	1.5	0.35	2.0	1.5	---	---
124-312	unleaded	1.5	0.50	1.8	2.5	1.5	3.0
124-304	unleaded	2.3	1.0	1.8	2.0	1.7	2.1
124-316	unleaded	1.7	0.30	1.3	1.7	1.5	2.5
124-417	unleaded	4.9	2.5	1.5	2.6	1.7	2.0
124-393	unleaded	5.3	2.7	2.1	2.6	1.8	4.0
124-404	unleaded	1.8	1.0	1.2	1.7	1.4	2.5
124-351	unleaded	5.2	2.4	1.8	2.4	2.7	2.5
124-349	unleaded	1.3	1.0	1.3	0.95	1.5	3.5
124-349	unleaded	1.7	0.75	0.50	1.2	1.7	3.5
124-409	unleaded	1.6	2.6	2.1	2.7	2.5	2.8
124-412	unleaded	1.9	0.60	1.3	2.5	2.5	3.9
124-415	unleaded	4.7	3.1	2.3	2.8	2.4	2.0

* See Table II for vehicle description.

Table X. OXIDES OF NITROGEN (NO_x) CONCENTRATIONS (ppm) IN AUTOMOBILE EXHAUST

Vehicle Number*	Fuel Type	Operating Mode					
		Idle	25	40	55	Accel	Decel
72-150	leaded	---	---	---	---	---	---
72-150	unleaded	140	400	750	1500	---	---
74-279	leaded	100	170	1600	1500	2500	110
74-330	unleaded	50	630	1000	1300	2100	50
74-292	leaded	58	300	1000	800	900	60
74-283	leaded	110	600	900	1300	2000	100
73-215	leaded	75	750	2000	1700	---	---
73-492	leaded	---	---	1200	1800	1700	210
73-496	leaded	84	450	2000	2300	1800	50
124-343	unleaded	44	300	300	780	400	45
124-343	unleaded	68	1000	230	760	---	---
124-347	unleaded	52	250	300	770	500	15
124-346	unleaded	68	310	550	900	700	50
124-323	unleaded	40	260	620	1500	1500	---
124-312	unleaded	45	560	800	1300	800	45
124-304	unleaded	35	400	900	1300	1100	57
124-316	unleaded	37	350	900	1000	1100	50
124-417	unleaded	87	580	1300	330	550	87
124-393	unleaded	97	550	1200	320	500	65
124-404	unleaded	145	1200	2300	1300	1800	140
124-351	unleaded	65	650	1500	370	550	55
124-349	unleaded	130	1000	1500	900	1300	100
124-349	unleaded	105	700	1400	830	600	100
124-409	unleaded	120	850	1800	540	1000	115
124-412	unleaded	67	600	1500	470	500	75
124-415	unleaded	95	720	1600	530	850	80

* See Table II for vehicle description.

Tables XI, XII, XIII, XIV, and XV contain the geometric means of the exhaust gas concentrations for each of the above five vehicle types. Along with the computation of these averages, we compared the linear correlation coefficients between various engine operating parameters such as air to fuel ratio and exhaust gas concentrations for a specific engine operating condition such as idle, acceleration, etc. We considered a correlation coefficient to be statistically significant when there was less than a 5% chance of randomly getting a correlation coefficient as large as the experimental coefficient. The results of this correlation analysis of the data is shown in Table XVI. To facilitate comparisons of the gaseous emissions of the five vehicle classes tested, a way was sought to provide a single number that represented the emission of a particular gaseous pollutant, such as CO, averaged over the various driving modes encountered in "real life." A crude representation of the vehicle emissions expected during the Federal automotive testing program[17] could be obtained using the following equation:

$$\begin{pmatrix} \text{"Average"} \\ \text{concentration} \\ \text{of pollutant X} \\ \text{in automobile} \\ \text{exhaust} \end{pmatrix} = \frac{1}{4}\begin{pmatrix} \text{"Idle" mode} \\ \text{concentration} \end{pmatrix} + \frac{1}{4}\begin{pmatrix} \text{"acceleration"} \\ \text{mode concentration} \end{pmatrix}$$

$$+ \frac{1}{4}\begin{pmatrix} \text{"deceleration"} \\ \text{mode} \\ \text{concentration} \end{pmatrix} + \frac{1}{4}\begin{pmatrix} \text{"25 MPH cruise"} \\ \text{mode} \\ \text{concentration} \end{pmatrix} \quad (1)$$

Values of these "average" emissions for each vehicle class are tabulated in Table XVII.

TABLE XI. GEOMETRIC MEAN HYDROCARBON (HC) CONCENTRATIONS (ppm)
IN AUTOMOBILE EXHAUST

Vehicle Type	Operating Mode					
	Idle	25	40	55	ACC	DEC
Hornet	48 +45 -23	64 +26 -19	56 +23 -16	27 +14 -9	30 +15 -10	820 +880 -425
Fury	60 +85 -35	39 +41 -20	18 +4.3 -3.5	16 +5.9 -4.4	22 +3.0 -2.6	250 +830 -190
Valiant	220 +72 -54	150 +32 -26	37 +17 -12	27 +13 -9	55 +16 -12	2500 +0 -0
Coronet	100 +87 -47	120 +180 -69	93 +95 -47	90 +74 -40	130 +45 -34	1200 +1200 -580
Dart	160 +6 -5	200 +36 -30	130 +31 -26	100 +23 -19	100 +22 -19	1000 +1600 -600

TABLE XII.   GEOMETRIC MEAN CARBON MONOXIDE (CO) CONCENTRATIONS (%) IN AUTOMOBILE EXHAUST

Vehicle Type	Operating Mode					
	Idle	25	40	55	ACC	DEC
Hornet	0.69 +1.7 -0.49	0.39 +0.36 -0.19	0.49 +0.56 -0.27	0.29 +0.08 -0.06	0.29 +0.06 -0.04	3.2 +3.2 -1.6
Fury	0.42 +5.67 -0.39	0.070 +0.36 -0.06	0.040 +0.004 -0.007	0.039 +0.005 -0.005	0.072 +0.13 -0.047	1.0 +14 -0.94
Valiant	6.6 +2.0 -1.6	2.0 +0.49 -0.40	0.16 +0.02 -0.02	0.13 +0.02 -0.02	0.14 +0.02 -0.01	7.4 +0.51 -0.48
Coronet	1.7 +4.4 -1.2	0.46 +0.56 -0.25	0.39 +0.31 -0.17	0.61 +0.60 -0.30	0.97 0.96 -0.48	3.6 +1.6 -1.1
Dart	4.3 +1.8 -1.3	1.8 +1.1 -0.65	0.57 0.53 -0.27	0.59 +0.80 -0.32	0.55 +0.22 -0.16	4.4 +0.76 -0.64

TABLE XIII. GEOMETRIC MEAN CARBON DIOXIDE (CO_2) CONCENTRATIONS (%)
IN AUTOMOBILE EXHAUST

Vehicle Type	Operating Mode					
	Idle	25	40	55	ACC	DEC
Hornet	12 +1.3 -1.2	13 +0.8 -0.8	14 +0.6 -0.7	14 +1.0 -0.8	13 +0.3 -0.3	11 +2.3 -2.0
Fury	13 +1.4 -1.2	14 +0.8 -0.8	14 +0.6 -0.6	14 +0.6 -0.6	14 +0.6 -0.6	12 +1.6 -1.4
Valiant	9.0 +1.3 -1.2	13 +0.0 -0.0	14 +0.6 -0.6	14 +0.6 -0.5	13 +0.6 -0.5	9.0 +1.6 -1.4
Coronet	12 +1.7 -1.5	13 +0.5 -0.4	13 +0.7 -0.7	13 +0.6 -0.5	14 +0.6 -0.5	9.0 +2.0 -1.6
Dart	11 +1.0 -0.9	13 +1.3 -1.3	13 +1.0 -0.9	13 +1.6 -1.3	12 +1.0 -0.9	9.0 +2.3 -1.8

TABLE XIV.   GEOMETRIC MEAN OXYGEN (O_2) CONCENTRATIONS (%)
IN AUTOMOBILE EXHAUST

Vehicle	Operating Mode					
Type	Idle	25	40	55	ACC	DEC
Hornet	2.7 +2.2 -1.2	1.6 +1.4 -0.7	1.5 +0.9 -0.5	2.0 +1.0 -0.7	2.0 +0.6 -0.4	2.9 +0.9 -0.7
Fury	1.2 +1.8 -0.7	0.9 +0.94 -0.45	1.9 +0.4 -0.3	1.8 +0.5 -0.4	2.0 +0.0 -0.0	0.2 +1.0 -0.1
Valiant	1.7 +0.4 -0.3	0.5 +0.3 -0.2	1.7 +0.4 -0.3	1.9 +0.5 -0.4	1.6 +0.1 -0.1	2.5 +0.5 -0.4
Coronet	0.9 +2.3 -0.7	1.9 +1.1 -0.7	1.3 +1.4 -0.7	1.0 +0.9 -0.5	1.0 +0.0 -0.0	2.5 +2.6 -1.3
Dart	0.8 +0.4 -0.3	1.0 +1.6 -0.6	2.0 +1.6 -0.9	1.4 +0.3 -0.3	1.4 +1.0 -0.6	3.3 +1.8 -1.2

TABLE XV. GEOMETRIC MEAN OXIDES OF NITROGEN (NO_x) CONCENTRATIONS (ppm)
IN AUTOMOBILE EXHAUST

Vehcile Type	Operating Mode					
	Idle	25	40	55	ACC	DEC
Hornet	98 +31 -23	740 +220 -170	1500 +320 -270	560 +350 -210	770 +460 -280	87 +30 -21
Fury	57 +14 -11	390 +350 -180	330 +150 -100	800 +65 -61	520 +170 -130	32 +31 -15
Valiant	39 +5 -4	380 +140 -100	800 +150 -130	1300 +230 -190	1100 +320 -250	50 +7 -10
Coronet	96 +38 -27	510 +200 -150	1400 +820 -520	1800 +360 -290	1800 +70 -70	100 +180 -65
Dart	75 +36 -24	370 +320 -170	1100 +330 -250	1200 +620 -280	1800 +1000 -640	76 +35 -24

TABLE XVI. RESULTS OF CORRELATION ANALYSIS OF
EXHAUST GAS CONCENTRATIONS

Variables Being Tested	Vehicle Type	Is there a statistically significant linear correlation between variables being tested?
HC - CO concentration	Hornet	Yes
	Fury	No
	Valiant	Yes
	Coronet	Yes
	Dart	Yes
NO_x - HC concentrations	Hornet	No
	Fury	No
	Valiant	No
	Coronet	No
	Dart	No
Air/Fuel Ratio - HC concentration	Hornet	Yes, Anticorrelation
	Fury	Yes, Anticorrelation
	Valiant	Yes, Anticorrelation
	Coronet	Yes, Anticorrelation
	Dart	Yes, Anticorrelation
Air/Fuel Radio - NO_x concentration	Hornet	No
	Fury	No
	Valiant	No
	Coronet	Yes, Anticorrelation
	Dart	Yes, Anticorrelation
Air/Fuel Ratio - CO concentration	Hornet	Yes, Anticorrelation
	Fury	Yes, Anticorrelation
	Valiant	Yes, Anticorrelation
	Coronet	Yes, Anticorrelation
	Dart	Yes, Anticorrelation

TABLE XVII. "AVERAGE" EXHAUST GAS CONCENTRATIONS

Vehicle Type	Fuel	Convertor	Mean Air-to-Fuel Ratio	CO (%)	HC (ppm)	CO_2 (%)	O_2 (%)	NO_x (ppm)
Hornet	unleaded	no	15.6	1.20	240	12.3	2.3	420
Fury	unleaded	yes	14.7	1.39	93	13.3	1.1	250
Valiant	unleaded	yes	14.3	4.0	730	11.0	1.6	390
Coronet	leaded	no	15.3	1.7	390	12.0	1.6	630
Dart	leaded	no	15.5	2.8	370	11.2	1.6	580

What does this large mass of numbers mean? First of all, let us examine those factors which apparently influence gaseous emissions. Consider the air-to-fuel ratio of the material entering the combustion chamber. The correlation coefficient data of Table XVI substantiates that which would be expected from simple chemistry. As the air-to-fuel ratio increases, the concentrations of unburnt hydrocarbons and CO in the exhaust gas decreases. Graphically this is shown in Figures 7 and 8 which show the hydrocarbon and CO exhaust gas concentrations for Hornets operating in an "idle" mode versus the equivalence ratio. The actual decrease in CO concentration with increasing air to fuel ratio agrees well with theoretical predictions[29] of the $CO \rightarrow CO_2$ conversion at a temperature between the peak combustion temperature and the exhaust gas temperature. The increase in HC concentration with decreasing air-to-fuel ratio appears to be due to an increase in the thickness of the "quench layer" near the cold combustion chamber walls with decreasing air-to-fuel ratio. In this layer, heat loss from the fuel-air mixture to the cylinder walls is so great that ignition cannot occur.

As indicated by the correlation coefficient data of Table XVI and the graphical data of Figure 9, the situation with respect to NO_x is more complicated. The NO_x production rate increases as the oxygen concentration in the fuel-air mixture increases until the point is reached where further increases in air only drop the combustion temperature which quickly tends to reduce the thermodynamically unstable (at low temperature) NO_x concentration. One also sees considerable fluctuations in the NO_x concentration around this general trend.

Figure 7. Relative Hydrocarbon Concentration vs. Equivalence Ratio
(The equivalence ratio (ϕ) is the stoichiometric air-fuel
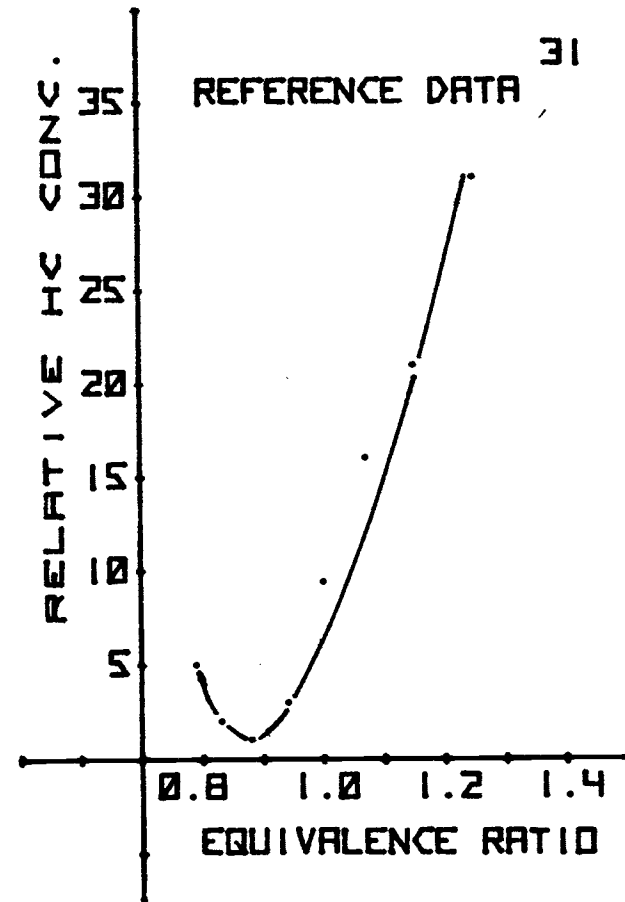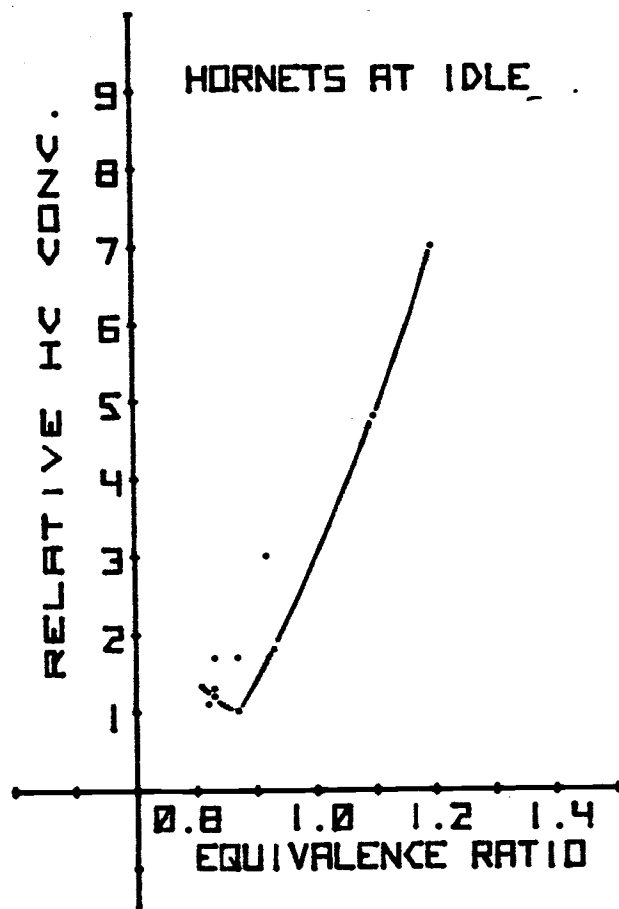ratio divided by the sample air-fuel ratio.)

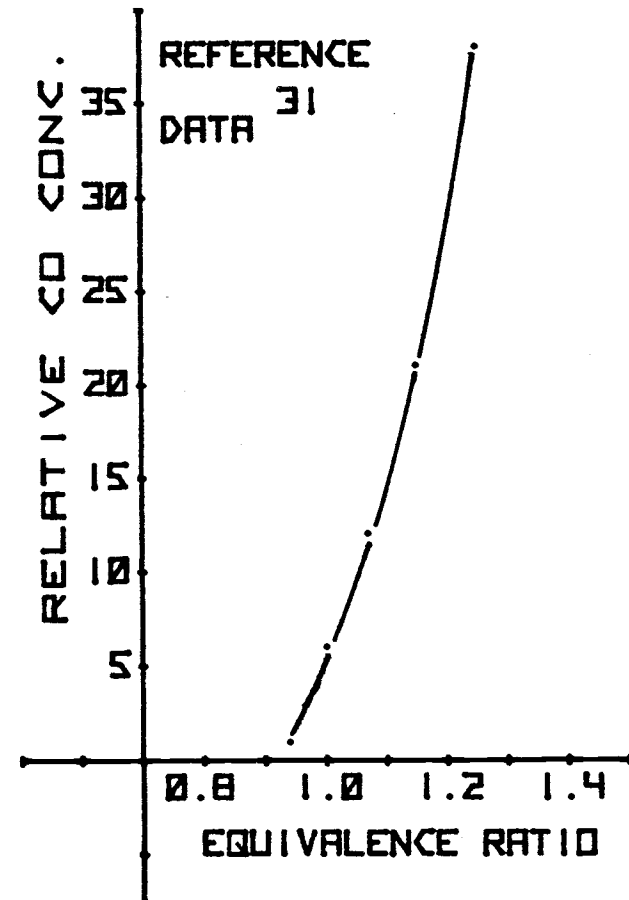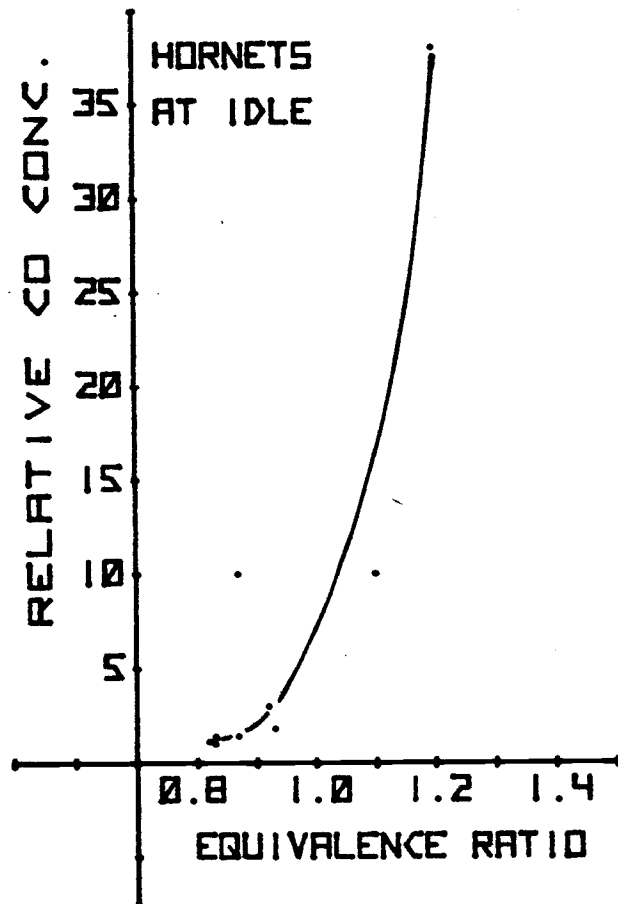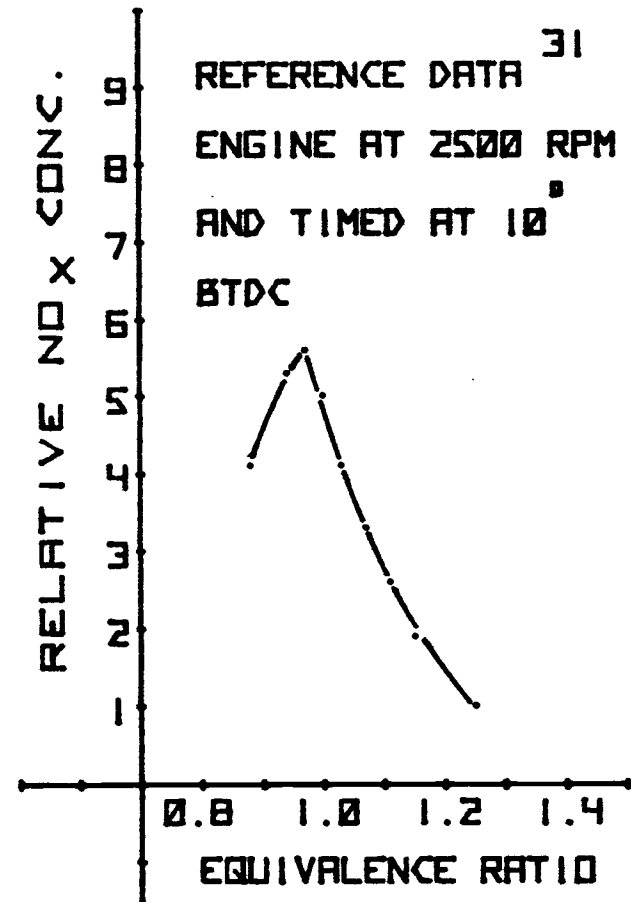Figure 8. Relative Carbon Monoxide Concentration vs. Equivalence Ratio

Figure 9. Relative Oxides of Nitrogen Concentration vs. Equivalence Ratio
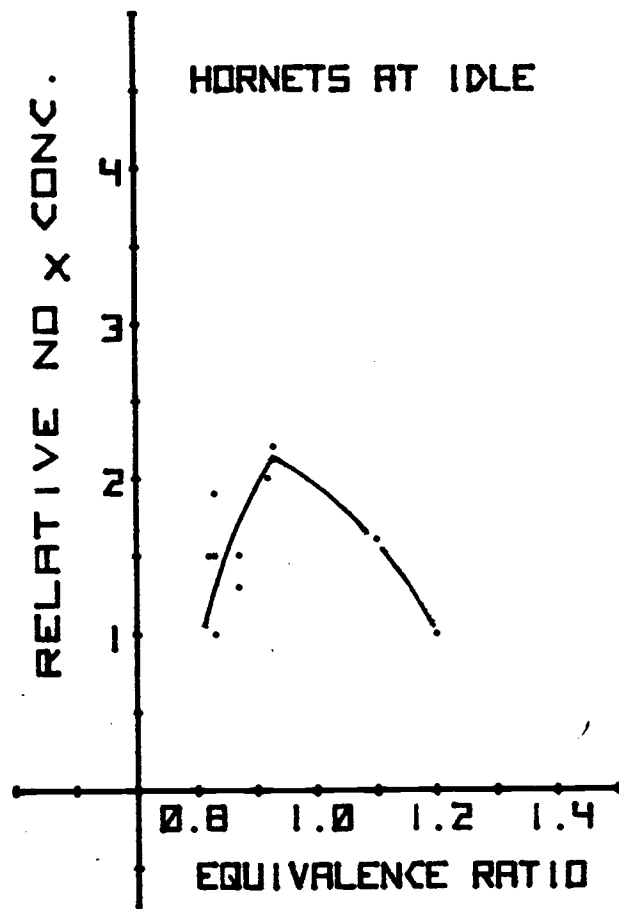
The next question to be discussed is how the gaseous emissions depend upon engine operating condition (idle, acceleration, deceleration, etc.). Each engine operating condition will have a different air-to-fuel ratio and a different "load" on the engine, leading to different pressures in the combustion chamber. If one examines the data in Tables XI to XV, normalizing each gas concentration for each vehicle type to the "deceleration mode" concentration for that vehicle type, one will conclude that within experimental error all cars tested show a similar dependence of gaseous emissions on driving mode. Therefore, weighted averages of all the gaseous emission data (relative to the "deceleration mode" concentrations) from all vehicles were computed and are shown in Table XVIII with the results being plotted in Figures 10 and 11. The results obtained in this study agree with those observed by other workers.[30,31] The dependences of HC and CO concentrations as a function of driving mode seem to simply reflect the dependence of the air-fuel ratio upon driving mode whereby the low air-to-fuel ratio during deceleration results in maximum HC and CO release. Similarly, the NO_x exhaust gas concentrations peak in those driving modes with the maximum air-to-fuel ratio and the maximum engine load. (The engine "load" at 55 MPH is $\sim$ 6 x the load at 25 MPH.) Increasing engine load leads to increasing pressure in combustion chamber leading to increased nitric oxide production rates.

How do the emissions from vehicles burning leaded fuel compare with those burning unleaded fuel or using convertors? As one can tell from our previous discussion, a straightforward answer to this

TABLE XVIII. DEPENDENCE OF EXHAUST GAS CONCENTRATIONS UPON
ENGINE OPERATING MODE

Exhaust Gas	Engine Operating Mode					
	Idle	25 MPH	40 MPH	55 MPH	Accel.	Decel.
HC (ppm)	0.10 ± 0.10	0.10 ± 0.09	0.06 ± 0.06	0.05 ± 0.05	0.06 ± 0.06	1.0 ± 1.02
CO (%)	0.72 ± 0.81	0.24 ± 0.27	0.08 ± 0.08	0.08 ± 0.08	0.10 ± 0.11	1.0 ± 0.83
NO_x (ppm)	1.1 ± 0.6	7.0 ± 3.7	14.5 ± 9.1	15.9 ± 9.5	17.4 ± 11.0	1.0 ± 0.57
CO_2 (%)	1.1 ± 0.22	1.3 ± 0.19	1.4 ± 0.20	1.4 ± 0.2	1.3 ± 0.2	1.0 ± 0.16
O_2 (%)	0.64 ± 0.48	0.52 ± 0.37	0.74 ± 0.41	0.71 ± 0.42	0.70 ± 0.42	1.00 ± 0.75
Air-to-Fuel Ratio	15.1 ± 0.7	15.5 ± 0.5	15.9 ± 0.4	15.9 ± 0.3	15.9 ± 0.4	12.3 ± 0.3

Figure 10. Gaseous Emissions vs. Engine Operating Mode
(This work)
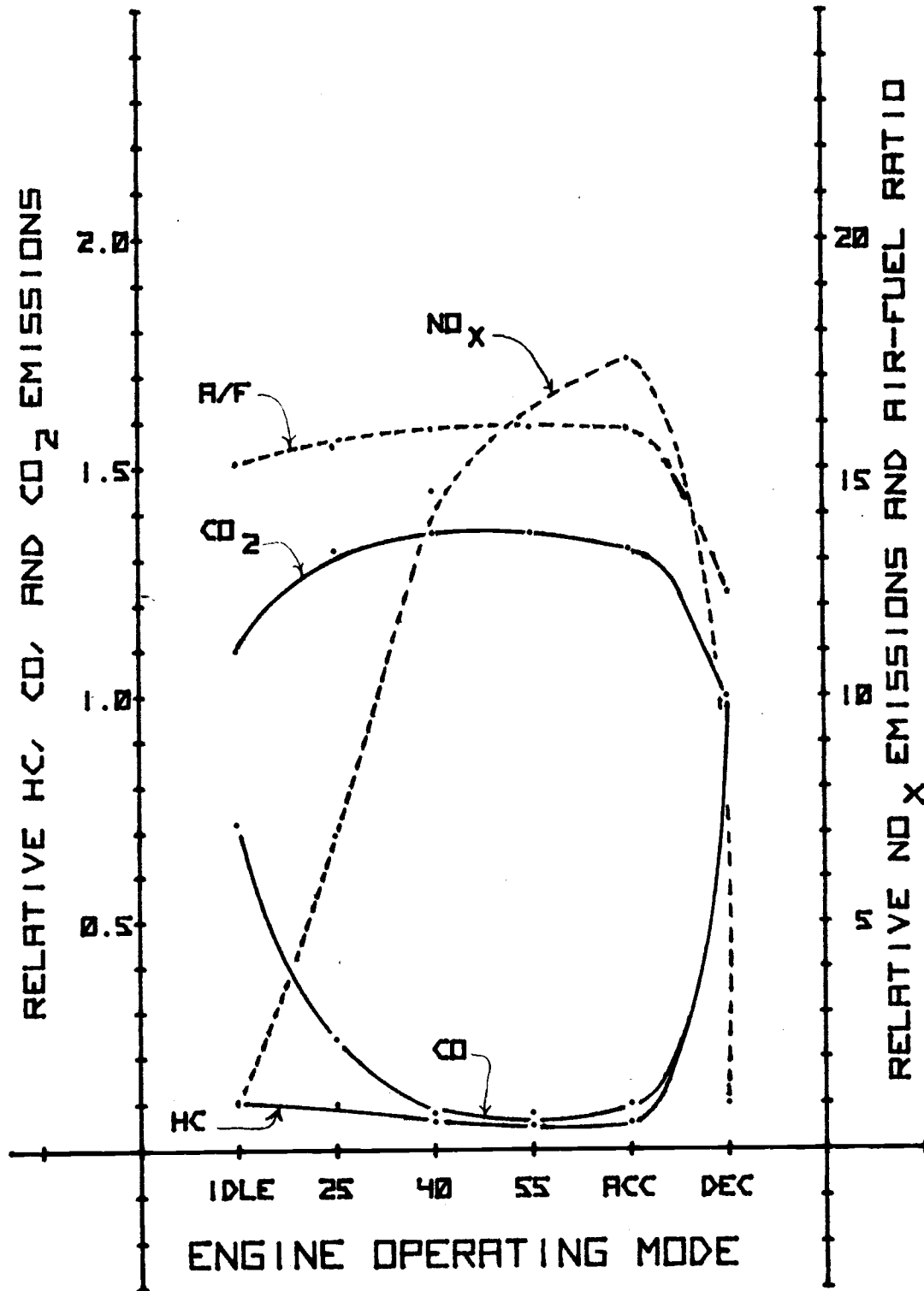
Figure 11. Reference Gaseous Emissions vs. Engine Operating Mode
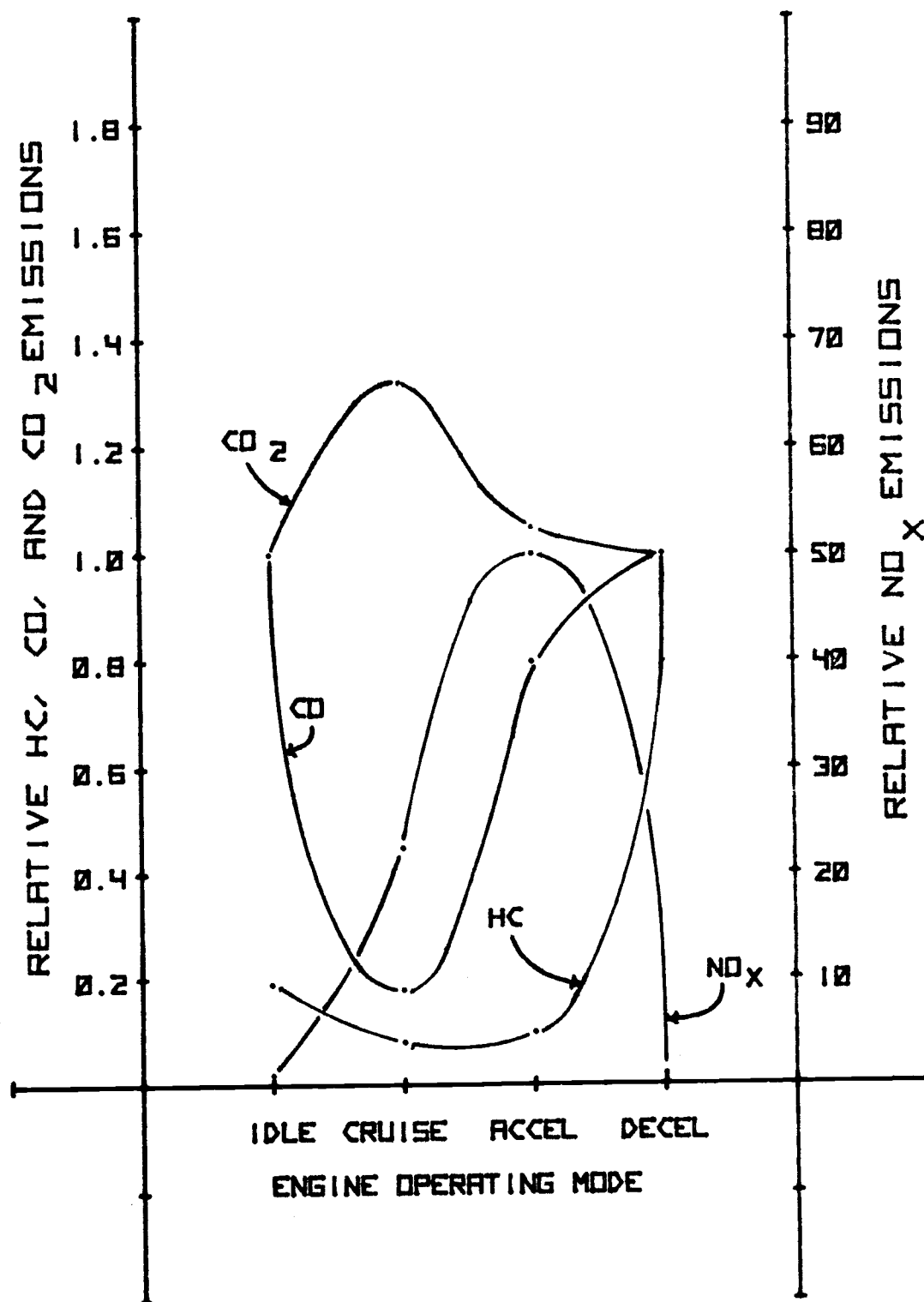
question may not be possible since the emissions from a vehicle are
a function of the air-to-fuel ratio, engine load and timing which
all varied between the "leaded fuel cars" versus the "unleaded fuel
cars." In general, however, if one examines the data of Table XVII
and compares the emissions from the "unleaded Hornets and Furies"
(mean air-to-fuel ratio of 15.2) with the "leaded Coronets and Darts"
(mean air-to-fuel ratio of 15.4), one sees a factor of 1.6 to 2.3
times less HC, CO, and NO_x emitted from the "unleaded fuel cars.
(The "unleaded Valiants" were eliminated from this comparison because
their engines had a mean air-to-fuel ratio of 14.3, which while they
had convertors and burned unleaded fuel, they also had the highest CO and
HC emissions of all vehicles tested.) The low emissions from the
unleaded fuel cars may simply be a reflection of their newer vintage,
lower mileage, etc. or that the engines themselves were designed
for lower emissions.

C. Trace Element Concentrations in Exhaust Particulate

There appear to be four possible contributors to trace element
concentrations in automobile exhaust. They are: (a) the fuel itself,
(b) any additives placed in the fuel by the manufacturer, (c) con-
taminants placed in the fuel by handling or burning, such as rust from
iron pipes, lubricating oil in the cylinders, engine or exhaust system
component wear, or (d) trace elements present in the oxidizing agent,
i.e., the air used to burn the fuel.

As indicated in Table IV, an extensive search was made to detect the presence of 28 different chemical elements in exhaust particulate. Only five elements were found with any degree of reliability, namely, Al, Mn, V, Cl, and Br. (The measured concentrations of these trace elements in the exhaust particulate of the 26 cars tested are shown in Tables XIX, XX, XXI, XXII, and XXIII. (See Table II for the description of the vehicles, fuel, and convertor systems employed.) Why so "little data"? Consider the potential sources of these elements. Gasoline itself is prepared by fractional distillation, and therefore, is relatively free of trace impurities at any reasonable concentration level. Leaded fuels contain additives of ethylene dibromide and ethylene dichloride, accounting for the presence of Br and Cl and nothing else. Oregon air is relatively free of trace element impurities.[18] Furthermore, the air volumes sampled were of the order of ~ 0.05 m^3 (due to irradiated sample activity limits) with the trace element impurities in the filters being of the order of ~ 100 μg/m^3. In Corvallis, Oregon air, Shum and Loveland[18] found only three chemical elements (Al, Fe, and Na) had abundances > 2000 μg/m^3. Thus, because of the small volumes of air sampled, only Al, Fe,* and Na* from the air could be expected to be detected.

When one considers possible "contaminants" as trace element sources, one might think first of lubricating oil which might be burnt in the cylinders. Lubricating oils are known[32] to contain

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*Unfortunately, high Fe and Na contents in the filter media used in this work precluded their measurement in exhaust particulate.

Table XXIX. BROMINE (Br) CONCENTRATIONS ($\mu g/m^3$) IN AUTOMOBILE EXHAUST

Vehicle Number*	Fuel Type	Operating Mode					
		Idle	25	40	55	Accel	Decel
72-150	leaded	920 ± 70	1400 ± 60	1200 ± 60	15000 ± 600	6200 ± 300	980 ± 50
72-150	unleaded	13 ± 4	46 ± 5	130 ± 9	4900 ± 200	5700 ± 200	---
74-279	leaded	1900 ± 100	1100 ± 40	920 ± 30	1900 ± 70	4300 ± 100	1600 ± 60
74-330	unleaded	45 ± 4	22 ± 3	84 ± 7	850 ± 50	230 ± 10	2300 ± 100
74-292	leaded	2400 ± 40	2100 ± 40	1600 ± 30	2300 ± 40	3200 ± 50	3300 ± 50
74-283	leaded	2800 ± 50	2100 ± 40	1000 ± 20	12000 ± 200	2800 ± 40	1400 ± 30
73-215	leaded	2500 ± 40	3000 ± 50	2900 ± 50	4700 ± 70	12000 ± 200	4400 ± 70
73-492	leaded	4100 ± 70	3600 ± 70	3100 ± 60	14000 ± 200	10000 ± 100	4700 ± 70
73-496	leaded	1500 ± 30	1400 ± 20	1300 ± 20	3500 ± 50	7100 ± 100	17000 ± 200
124-343	unleaded	<26	11 ± 8	<9.7	7.7 ± 4	24 ± 5	110 ± 8
124-343	unleaded	<5	11 ± 2	4.4 ± 2	19 ± 2	4.1 ± 1	130 ± 4
124-347	unleaded	<24	<17	<9.5	<15	6.0 ± 6.0	29 ± 7
124-346	unleaded	<30	<16	85 ± 20	18 ± 7	8.0 ± 7	27 ± 8
124-323	unleaded	<4.6	5.3 ± 3	<6.2	47 ± 5	11 ± 2	62 ± 5
124-312	unleaded	<4.3	<4.8	<5.7	<7.0	2.1 ± 1.7	<3.6
124-304	unleaded	<23	<15	12 ± 11	16 ± 8	9.6 ± 7	<14
124-316	unleaded	<27	8.2 ± 7	<12	12 ± 8	31 ± 7	27 ± 8
124-417	unleaded	<9.6	<23	<14	8.0 ± 7	12 ± 2	75 ± 5
124-393	unleaded	<9.0	<20	<14	<15	32 ± 3	230 ± 10
124-404	unleaded	---	---	---	---	---	---
124-351	unleaded	<10	18 ± 13	<46	320 ± 10	52 ± 4	81 ± 9
124-349	unleaded	---	---	---	---	---	---
124-349	unleaded	<9.8	<14	<44	7.9 ± 7	16 ± 9	220 ± 8
124-409	unleaded	14 ± 13	<15	<40	11 ± 7	27 ± 6	280 ± 9
124-412	unleaded	<27	<14	<43	<15	18 ± 10	20 ± 7
124-415	unleaded	<32	19 ± 10	<41	190 ± 10	22 ± 6	89 ± 9

* See Table II for vehicle description.

Table XX. CHLORINE (Cl) CONCENTRATIONS ($\mu g/m^3$) IN AUTOMOBILE EXHAUST

Vehicle Number*	Fuel Type	Operating Mode					
		Idle	25	40	55	Accel	Decel
72-150	leaded	470 ± 40	630 ± 40	610 ± 40	9400 ± 40	2600 ± 200	510 ± 50
72-150	unleaded	N	N	160 ± 30	1900 ± 90	2200 ± 100	---
74-279	leaded	750 ± 100	280 ± 30	260 ± 30	640 ± 50	1500 ± 100	430 ± 50
74-330	unleaded	N	N	88 ± 10	230 ± 20	84 ± 10	650 ± 40
74-292	leaded	730 ± 40	570 ± 40	630 ± 40	840 ± 60	1100 ± 50	1400 ± 60
74-283	leaded	690 ± 40	660 ± 40	330 ± 30	2500 ± 100	200 ± 90	580 ± 40
73-215	leaded	530 ± 30	1000 ± 50	770 ± 50	1400 ± 60	3800 ± 100	1400 ± 50
73-492	leaded	940 ± 40	830 ± 60	1100 ± 50	3600 ± 100	2900 ± 100	1600 ± 50
73-496	leaded	370 ± 30	440 ± 30	330 ± 30	990 ± 50	1400 ± 70	4400 ± 100
124-343	unleaded	<160	W	W	W	W	W
124-343	unleaded	N	N	N	110 ± 25	N	91 ± 10
124-347	unleaded	W	W	W	W	W	W
124-346	unleaded	W	W	W	W	W	W
124-323	unleaded	N	N	N	N	N	N
124-312	unleaded	N	N	N	N	N	N
124-304	unleaded	W	W	W	W	W	W
124-316	unleaded	W	W	W	W	W	W
124-417	unleaded	W	W	W	W	W	W
124-393	unleaded	W	W	W	W	190 ± 26	W
124-404	unleaded	---	---	---	---	---	---
124-351	unleaded	W	<170	W	W	W	W
124-349	unleaded	---	---	---	---	---	---
124-349	unleaded	W	W	W	W	W	W
124-409	unleaded	W	W	W	W	W	W
124-412	unleaded	W	W	W	W	W	W
123-415	unleaded	W	W	W	W	W	W

* See Table II for vehicle description.

N ($\leq$ 77 $\mu g/m^3$) is the upper-limit concentration for a Nuclepore blank.

W ($\leq$ 1500 $\mu g/m^3$) is the upper-limit concentration for a Whatman-1 blank.

Table XXI. VANADIUM (V) CONCENTRATIONS (μg/m^3) IN AUTOMOBILE EXHAUST

Vehicle Number*	Fuel Type	Operating Mode					
		Idle	25	40	55	Accel	Decel
72-150	unleaded	--	--	--	--	--	--
72-150	unleaded	--	--	--	--	--	--
74-279	leaded	--	--	--	--	--	--
74-330	unleaded	--	--	--	--	--	--
74-292	leaded	--	--	--	--	--	--
74-283	leaded	--	--	--	--	--	--
73-215	leaded	--	--	--	--	--	--
73-492	leaded	--	--	--	--	--	--
73-496	leaded	--	--	--	--	--	--
124-343	unleaded	< 0.38	0.045 ± 0.04	< 0.17	< 0.051	< 0.20	< 0.29
124-343	unleaded	0.91 ± 0.3	0.26 ± 0.09	0.18 ± 0.03	0.11 ± 0.07	0.18 ± 0.08	0.09 ± 0.02
124-347	unleaded	< 0.11	< 0.060	< 0.33	0.040 ± 0.03	< 0.028	0.14 ± 0.05
124-346	unleaded	0.12 ± 0.1	< 0.087	0.18 ± 0.1	< 0.26	0.16 ± 0.09	< 0.25
124-323	unleaded	--	--	--	--	--	--
124-312	unleaded	0.13 ± 0.04	< 0.097	0.085 ± 0.06	0.59 ± 0.09	0.21 ± 0.05	0.056 ± 0.05
124-304	unleaded	0.12 ± 0.08	< 0.20	< 0.052	0.031 ± 0.03	< 0.032	< 0.052
124-316	unleaded	0.13 ± 0.09	0.068 ± 0.05	< 0.13	< 0.089	0.072 ± 0.04	< 0.22
124-417	unleaded	0.094 ± 0.08	0.29 ± 0.09	< 0.16	< 0.073	< 0.071	< 0.057
124-393	unleaded	< 0.18	< 0.25	< 0.26	< 0.22	< 0.11	< 0.27
124-404	unleaded	--	--	--	--	--	--
124-351	unleaded	0.062 ± 0.06	< 0.088	< 0.79	0.068 ± 0.06	0.12 ± 0.07	< 0.086
124-349	unleaded	--	--	--	--	--	--
124-349	unleaded	0.093 ± 0.06	< 0.086	< 0.76	0.036 ± 0.03	< 0.34	0.089 ± 0.05
124-409	unleaded	0.21 ± 0.1	< 0.058	< 0.71	< 0.23	0.058 ± 0.04	0.071 ± 0.05
124-412	unleaded	< 0.58	< 0.084	0.16 ± 0.1	< 0.055	0.22 ± 0.1	< 0.055
124-415	unleaded	< 0.55	< 0.31	< 0.71	0.072 ± 0.05	< 0.063	< 0.27

* See Table II for vehicle description.

Table XXII. ALUMINUM (Al) CONCENTRATIONS ($\mu g/m^3$) IN AUTOMOBILE EXHAUST

Vehicle Number*	Fuel Type	Operating Mode					
		Idle	25	40	55	Accel	Decel
72-150	leaded	92 ± 5	74 ± 2	57 ± 2	--	160 ± 7	82 ± 3
72-150	unleaded	N	N	220 ± 4	< 570	1100 ± 800	--
74-279	leaded	--	17 ± 2	11 ± 2	54 ± 5	--	19 ± 3
74-330	unleaded	8.5 ± 0.9	--	19 ± 1	19 ± 1	23 ± 1	13 ± 2
74-292	leaded	43 ± 3	342 ± 8	34 ± 2	650 ± 12	70 ± 3	34 ± 3
74-283	leaded	7 ± 2	18 ± 2	31 ± 2	--	--	12 ± 2
73-215	leaded	150 ± 5	58 ± 3	70 ± 4	100 ± 5	120 ± 10	55 ± 3
73-492	leaded	17 ± 4	--	83 ± 4	--	--	53 ± 3
73-496	leaded	12 ± 2	58 ± 3	56 ± 4	140 ± 8	54 ± 5	--
124-343	unleaded	65 ± 6	65 ± 4	45 ± 6	46 ± 4	110 ± 4	300 ± 6
124-343	unleaded	9.0 ± 0.7	1300 ± 10	87 ± 2	630 ± 6	1000 ± 8	36 ± 1
124-347	unleaded	15 ± 5	20 ± 4	10 ± 5	5.2 ± 3	31 ± 3	21 ± 4
124-346	unleaded	12 ± 5	18 ± 3	86 ± 6	93 ± 4	112 ± 4	24 ± 4
124-323	unleaded	N	11 ± 1	N	18 ± 1	21 ± 1	8.4 ± 0.9
124-312	unleaded	16 ± 2	16 ± 2	N	N	20 ± 2	21 ± 2
124-304	unleaded	64 ± 18	9 ± 3	< 10	37 ± 4	16 ± 3	21 ± 3
124-316	unleaded	29 ± 6	56 ± 4	42 ± 7	77 ± 4	29 ± 4	33 ± 4
124-417	unleaded	34 ± 5	9 ± 5	29 ± 7	25 ± 4	140 ± 3	100 ± 5
124-393	unleaded	< 8.8	19 ± 7	14 ± 6	80 ± 5	163 ± 4	5 ± 0.8
124-404	unleaded	--	--	--	--	--	--
124-351	unleaded	< 11	58 ± 6	55 ± 8	35 ± 4	240 ± 5	100 ± 5
124-349	unleaded	--	--	--	--	--	--
124-349	unleaded	14 ± 5	37 ± 5	20 ± 8	48 ± 4	63 ± 4	44 ± 3
124-409	unleaded	6 ± 5	57 ± 4	13 ± 7	19 ± 3	100 ± 4	100 ± 4
124-412	unleaded	38 ± 6	16 ± 6	< 20	11 ± 4	52 ± 4	64 ± 4
124-415	unleaded	39 ± 6	6 ± 4	51 ± 7	11 ± 4	120 ± 4	14 ± 4

* See Table II for vehicle description.

N ($\leq$ 8.3 $\mu g/m^3$) is the upper-limit concentration for a Nuclepore blank.

Table XXIII. MANGANESE (Mn) CONCENTRATIONS ($\mu g/m^3$) IN AUTOMOBILE EXHAUST

Vehicle Number*	Fuel Type	Operating Mode					
		Idle	25	40	55	Accel	Decel
72-150	leaded	< 1.8	< 1.5	< 1.7	< 7.6	< 8.4	< 2.0
72-150	unleaded	N	< 0.30	< 0.59	< 6.4	< 8.2	--
74-279	leaded	--	--	--	--	--	--
74-330	unleaded	N	N	N	N	N	N
74-292	leaded	N	N	N	3.2 ± 1	0.85 ± 0.6	0.98 ± 0.5
74-283	leaded	N	1.1 ± 0.8	N	2.6 ± 1	N	0.80 ± 0.4
73-215	leaded	4.9 ± 0.09	0.71 ± 0.3	5.1 ± 0.4	2.4 ± 0.7	5.8 ± 1	2.9 ± 0.6
73-492	leaded	N	2.8 ± 0.2	0.94 ± 0.09	0.81 ± 0.2	5.6 ± 0.2	1.2 ± 0.09
73-496	leaded	0.60 ± 0.05	0.35 ± 0.06	0.69 ± 0.06	1.9 ± 0.1	3.4 ± 0.2	6.6 ± 0.3
124-343	unleaded	3.3 ± 0.4	1.0 ± 0.3	N	1.5 ± 0.2	0.78 ± 0.3	N
124-343	unleaded	0.83 ± 0.05	1.6 ± 0.06	0.75 ± 0.09	1.0 ± 0.1	0.47 ± 0.1	0.50 ± 0.1
124-347	unleaded	W	W	3.1 ± 0.9	W	W	W
124-346	unleaded	W	W	1.1 ± 0.4	W	0.65 ± 0.2	2.6 ± 0.3
124-323	unleaded	N	9.0 ± 0.3	N	5.1 ± 0.2	1.0 ± 0.08	N
124-312	unleaded	3.2 ± 0.09	4.1 ± 0.1	3.0 ± 0.1	22 ± 0.4	3.0 ± 0.1	2.4 ± 0.1
124-304	unleaded	W	1.6 ± 0.2	2.4 ± 0.3	W	1.3 ± 0.2	W
124-316	unleaded	5.3 ± 0.2	W	3.8 ± 0.3	4.4 ± 0.2	W	1.6 ± 0.2
124-417	unleaded	1.9 ± 0.4	2.3 ± 0.4	W	W	0.33 ± 0.08	28 ± 0.3
124-393	unleaded	24 ± 0.5	21 ± 0.6	10 ± 0.6	30 ± 0.7	7.5 ± 0.2	15 ± 0.6
124-404	unleaded	--	--	--	--	--	--
124-351	unleaded	W	W	W	W	W	W
124-349	unleaded	--	--	--	--	--	--
124-349	unleaded	W	W	3.3 ± 0.2	1.3 ± 0.7	W	W
124-409	unleaded	W	2.3 ± 0.8	W	1.0 ± 0.8	W	W
124-412	unleaded	W	W	W	1.1 ± 0.6	W	W
124-415	unleaded	W	W	W	W	W	W

* See Table II for vehicle description.

N ($\leq$ 0.52 $\mu g/m^3$) is the upper-limit concentration for a Nuclepore blank.

W ($\leq$ 3.8 $\mu g/m^3$) is the upper-limit concentration for a Whatman-1 blank.

Ca, Zn, and Ba in the form of additives. Perhaps we whould expect to see Ba as a typical representative of this group of elements as did Gordon and co-workers[10] (see Table I). But unfortunately even the ultrapure Nuclepore filters used in this work contain $\sim$ 180 µg Ba/filter. With a sample volume of $\sim$ 0.05 m^3, this "blank" Ba value corresponds to an exhaust gas abundance of 3600 µg/m^3. "Real" Ba concentrations were found to be $< \sim$ 1 µg/m^3 (using a technique that correctly measured Ba abundances in NBS standard reference materials --see Table IV). Since the Br and Cl concentrations in the exhaust of vehicles burning leaded fuel were $\sim$ 1000 µg/m^3, we are saying that the "real" Ba concentrations in the exhaust of these vehicles is $< \sim$ 1/1000 the Br or Cl concentrations. Yet Gordon, et al.[10] measured the Ba abundance to be $\sim$ 1/25 the Br or Cl concentrations. Are these data consistent? The answer seems to be "yes" if one remembers that Gordon, et al. and others measured the total elemental abundances in air near a freeway or in a tunnel, not the abundances in auto exhaust. Gordon, et al.'s data includes contributions from buses, trucks, and other vehicles that are diesel-powered in addition to automobiles. Presumably, these diesel-powered vehicles contributed the bulk of the Ba, Ca, and Zn in Gordon, et al.'s "typical automotive component" of urban air.* This discussion illustrates a point made earlier, i.e., that gross outdoor studies like that of Gordon, et al. must be carefully evaluated before the results are applied to deduce the "automotive" component of urban air throughout the United States.

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*This assumes that these trace elements do come from diesel oil and there may be some question of their presence in diesel oil.

The data for the five trace elements studied were grouped by vehicle type as done with the gaseous pollutant data and geometric mean concentrations* calculated for each vehicle type tested. These data are summarized in Tables XXIV, XXV, XXVI, XXVII, and XXVIII. Once again, Equation (1) was used to calculate average trace element emissions by each vehicle type averaged over engine operating modes encountered in "real life." The results of this calculation are tabulated in Table XXIX.

What can we learn from these data, about the generation of trace element-associated and its actual trace element content exhaust particulate? Consider first of all the vehicles (Coronets and Darts) burning leaded fuel. As expected, the emissions show large amounts of Cl and Br resulting from the use of the gasoline additives of ethylene dichloride and ethylene dibromide. The "Average" emission data contained in Table XXIX would indicate a Br/Cl molar ratio of $\sim$ 1.5 in the exhaust particulate. This is to be contrasted with the Br/Cl molar ratios of 1.7 found by Gordon, et al.[10] and 1.0 found by Cahill and Feeney.[15] X-ray crystallographic studies of exhaust gas particulate[9] have shown that major constituents are $PbClBr$ and $NH_4Cl \cdot 2PbClBr$. However, neither of these compounds have the correct molar ratio of Br/Cl of $\sim$ 1.5 to 1.7. This would tend to indicate the presence of excess Br perhaps in the form of $PbO \cdot PbBr_2$ in the particulate. In fact the molar data would be well accounted for by a particulate of $\sim$ 3/4 $PbClBr$ and $\sim$ 1/4 $PbO \cdot PbBr_2$. The dependence of

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*Davies test calculations showed the trace element concentrations to be log normally distributed.

TABLE XXIV. GEOMETRIC MEAN BROMINE (Br) CONCENTRATIONS ($\mu g/m^3$)
IN AUTOMOBILE EXHAUST

Vehicle Type	Operating Mode					
	Idle	25	40	55	ACC	DEC
Hornet	14 +0.0 -0.0	19 +0.7 -0.7	----	34 +180 -28	23 +14 -8.9	110 +160 -64
Fury	----	11 +0.0 -0.0	19 +140 -17	14 +9.1 -5.5	8.3 +9.4 -4.4	58 +76 -33
Valiant	----	6.6 +2.4 -1.8	12 +0.0 -0.0	21 +22 -11	9.1 +19 -6.1	41 +33 -18
Coronet	1900 +800 -920	2100 +1400 - 840	1900 +1300 -770	7700 +8500 -4000	8500 +3000 -2200	4300 +9500 -3000
Dart	2300 +500 -410	1700 +770 -530	1100 +400 -290	3700 +6600 -2400	3400 +830 -670	1900 +1100 -720

TABLE XXV. GEOMETRIC MEAN CHLORINE (Cl) CONCENTRATIONS ($\mu g/m^3$)
IN AUTOMOBILE EXHAUST

Vehicle Type	Operating Mode					
	Idle	25	40	55	ACC	DEC
Hornet	----	----	----	----	----	----
Fury	----	----	----	----	----	----
Valiant	----	----	----	----	----	----
Coronet	540 +260 -180	690 +300 -210	640 +420 -260	2600 +4600 -1700	2500 +1300 -870	1500 +2100 -880
Dart	723 +31 -30	470 +270 -170	380 +220 -140	1100 +1200 -570	690 +1400 -230	700 +600 -320

TABLE XXVI. GEOMETRIC MEAN VANADIUM (V) CONCENTRATIONS ($\mu g/m^3$)
IN AUTOMOBILE EXHAUST

Vehicle Type	Operating Mode					
	Idle	25	40	55	ACC	DEC
Hornet	0.10 +0.07 -0.04	0.29 +0.0 -0.0	0.16 +0.0 -0.0	0.06 +0.03 -0.02	0.12 +0.11 -0.06	0.08 +0.01 -0.01
Fury	0.33 +1.1 -0.25	0.19 +0.43 -0.13	0.18 +0.0 -0.0	0.07 +0.07 -0.03	0.17 +0.01 -0.01	0.11 +0.04 -0.03
Valiant	0.13 +0.01 -0.01	0.07 +0.0 -0.0	0.09 +0.0 -0.0	0.14 +0.95 -0.12	0.12 +0.14 -0.07	0.06 +0.0 -0.0
Coronet	----	---	---	---	---	---
Dart	----	---	---	---	---	---

TABLE XXVII. GEOMETRIC MEAN ALUMINUM (Al) CONCENTRATIONS ($\mu g/m^3$) IN AUTOMOBILE EXHAUST

Vehicle Type	Operating Mode					
	Idle	25	40	55	ACC	DEC
Hornet	21 +27 −12	21 +30 −13	26 +22 −12	26 +28 −14	110 +76 −46	41 +91 −28
Fury	18 +25 −11	74 +470 −64	43 +76 −27	61 +380 −53	140 +450 −110	48 +120 −34
Valiant	31 +31 −16	17 +22 −10	42 +0.0 −0.0	37 +40 −19	21 +6 −5	19 +15 −8
Coronet	41 +100 −29	63 +10 −8	66 +13 −11	120 +32 −25	100 +76 −44	62 +17 −13
Dart	17 +45 −13	47 +210 −39	23 +20 −11	87 +450 −73	40 +48 −22	20 +14 −8

TABLE XXVIII. GEOMETRIC MEAN MANGANESE (Mn) CONCENTRATIONS ($\mu g/m^3$) IN AUTOMOBILE EXHAUST

Vehicle Type	Operating Mode					
	Idle	25	40	55	ACC	DEC
Hornet	6.8 +34 −5.6	4.8 +12 −3.5	5.7 +6.8 −3.1	2.6 +11 −2.1	1.6 +13 −1.4	20 +11 −7.3
Fury	1.7 +3.7 −1.0	1.3 +0.5 −0.4	1.4 +1.5 −0.7	1.2 +0.4 −0.3	0.6 +0.2 −0.1	1.1 +2.5 −0.8
Valiant	4.1 +1.8 −1.2	3.9 +5.4 −2.3	3.0 +0.8 −0.6	7.9 +11 −4.7	1.6 +1.2 −0.7	2.0 +0.7 −0.5
Coronet	1.7 +5.9 −1.3	0.9 +1.7 −0.6	1.5 +2.9 −1.0	1.5 +1.2 −0.7	4.8 +1.7 −1.2	2.8 +3.8 −1.6
Dart	---	1.1 +0.0 −0.0	---	2.9 +0.5 −0.4	0.9 +0.0 −0.0	0.9 +0.1 0.1

TABLE XXIX. "AVERAGE" EXHAUST PARTICULATE TRACE ELEMENT ABUNDANCES ($\mu g/m^3$)

Vehicle Type	Fuel	Convertor	Mean Air-to-Fuel Ratio	Br	Cl	V	Al	Mn
Hornet	unleaded	no	15.6	42	----	0.15	48	8.3
Fury	unleaded	yes	14.7	19	----	0.20	70	1.2
Valiant	unleaded	yes	14.3	14	55	0.10	22	2.9
Coronet	leaded	no	15.3	4200	1300	----	67	2.6
Dart	leaded	no	15.5	2300	650	----	31	0.7

Br and Cl emissions upon driving mode is shown in Figure 12. As one can see from examining Figure 12, it appears most of the particulate associated with Br and Cl is released during high speed, high load conditions. Since it had previously been established that the Pb is emitted under the same conditions, one tends to think of the Pb, Br, and Cl coming from the same source. A deposit of $PbBr \cdot Cl$ (plus $PbO \cdot PbBr_2$) which was probably deposited on the cylinder walls or, most probably, on the exhaust system walls is broken loose by the high pressure and temperature (55 MPH) as well as the thermal shock (acceleration) due to the sudden change in pressure and temperature and swept out the exhaust pipe. This idea is further supported by the existence of a statistically significant linear correlation between the Br and Cl concentrations.

For the vehicles burning unleaded fuel (Hornets, Furys and Valiants) the situation is quite different. No statistically significant amounts of Cl could be found in the exhaust although traces of Br were found. Figure 13 shows the Br concentrations plotted vs. engine operating conditions for the vehicle types burning unleaded fuel. One is immediately struck by the similarity between (Br release vs. operating mode) and HC release vs. operating mode). Both HC and Br show maximum emissions during deceleration. However, detailed tests reveal no linear correlation between Br and HC emissions. What the data seem to be telling one is that the Br-associated particles are not the large cylinder-wall and exhaust-system "clinkers" knocked loose by high speed or accelerating conditions, but perhaps a finer

Figure 12.   Bromine and Chlorine Particulate Concentrations vs.
            Engine Operating Mode for Automobiles Burning
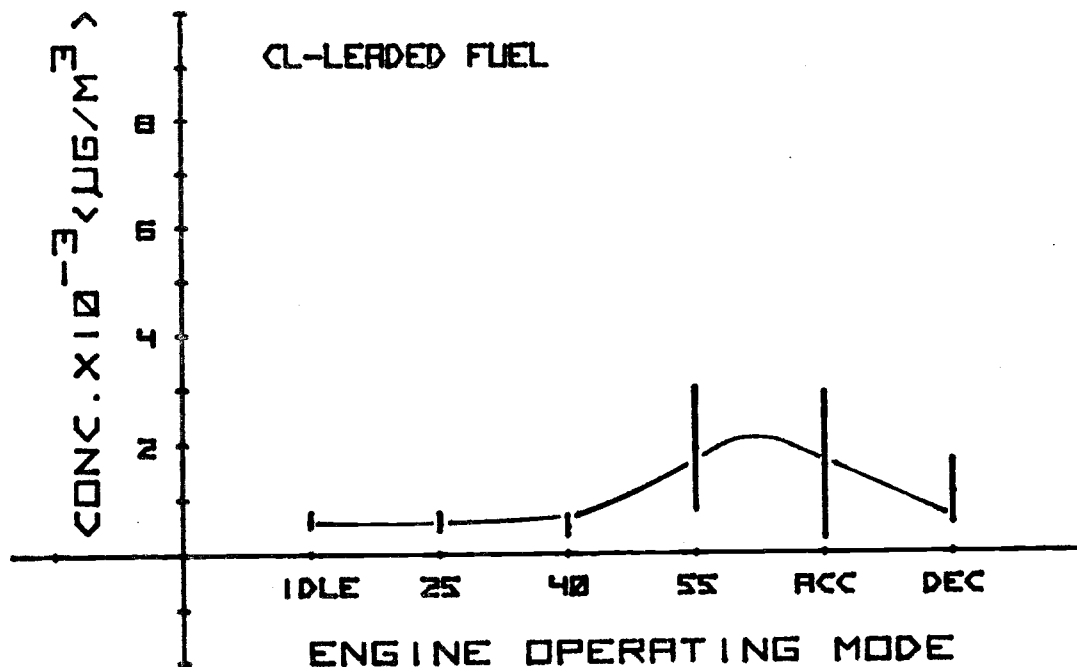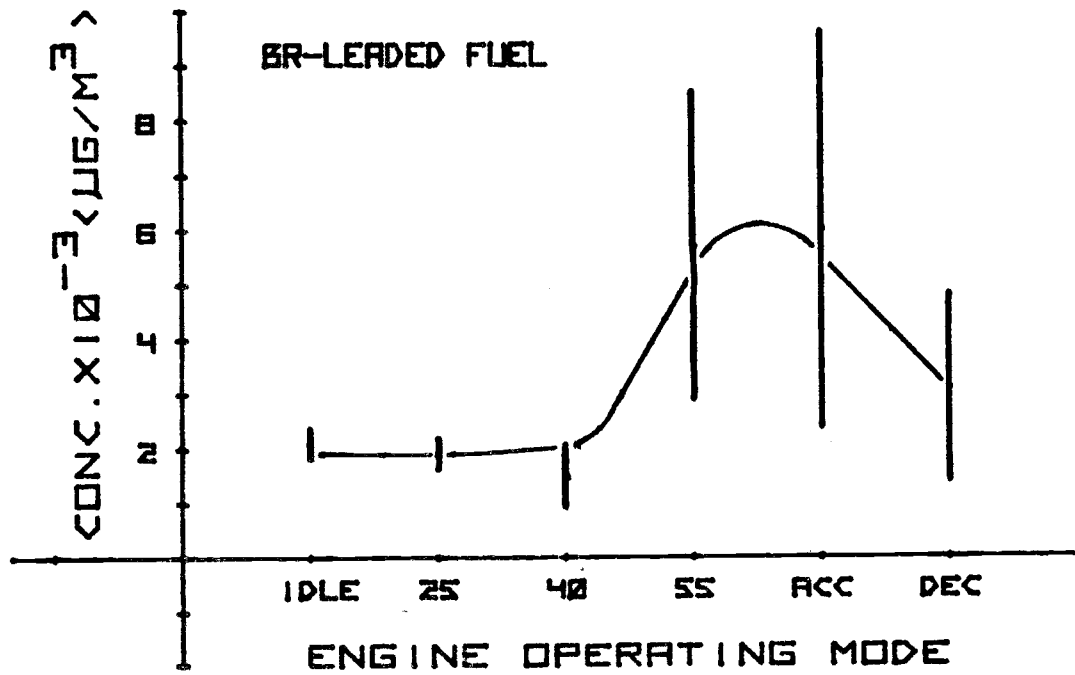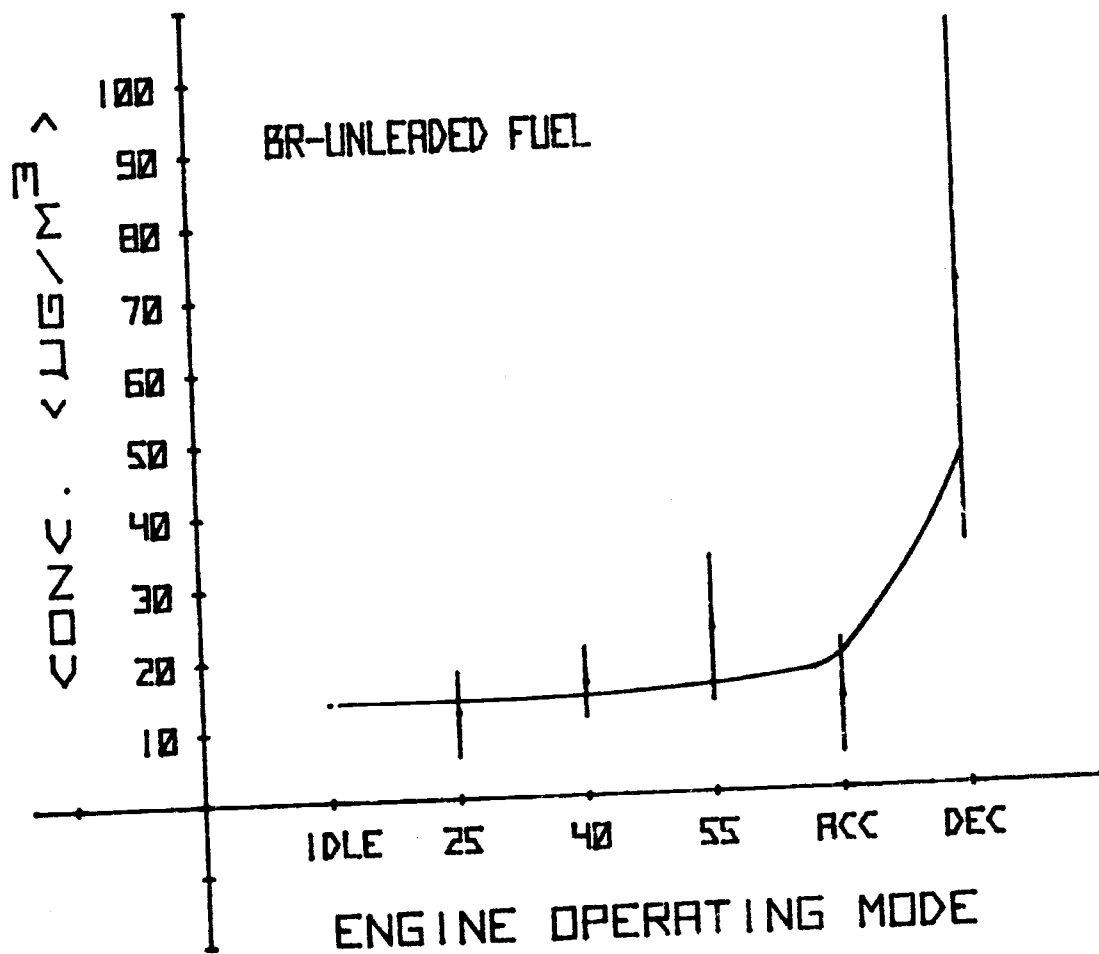   Leaded Gasoline

Figure 13. Bromine Particulate Concentrations vs. Engine Operating Mode for Automobiles Burning Unleaded Gasoline

particle formed and grown in the combustion chamber and released directly. Comparison of the Br data from this work with previous studies of particulate emissions from the burning of unleaded fuel[7] shows the Br-associated particulate to be quite different than most of the particulate in that the emission of Br particulate does not increase as rapidly as total particulate emission does with engine speed.

The origin of the Br in the exhaust particulate of vehicles burning unleaded fuels is open to speculation. One suggestion is that the Br results from the manufacturer handling unleaded gasoline in the same drums, piping, etc. used to handle leaded gasoline. If this were the origin of the Br, why doesn't it behave like the Br in leaded gasoline? Perhaps the Pb present in leaded gasoline exhaust acts as a site for the condensation of particulate matter, thus resulting in the particulate condensing in the exhaust system and then being re-entrained during high engine speed or high load. This view is given further support by the work of Sampson and Springer[16] who showed that leaded-fuel particulates deposit on exhaust system walls at a much more rapid rate than unleaded-fuel particulates.

Can Br act as a tracer for emissions of cars burning unleaded fuel? In a very limited, qualitative manner we have shown that Br is released in a manner similar to the hydrocarbons and vaguely similar to CO. However, there is no quantitative connection between Br concentration and either HC or CO concentration. Thus, Br levels might qualitatively (but not quantitatively) mirror the HC and CO

emissions from vehicles burning unleaded fuels. However, a further complication arises in that if the automotive contribution to Br levels in urban areas were reduced by a factor of $\sim$ 1/100 by the use of unleaded as opposed to leaded fuels (as indicated by the data of Table XXIX), then other sources of Br in urban atmospheres might contribute equally significant amounts to the total Br concentration. For example, if we use the data of Gordon, et al.[10] for trace element abundances in the Washington, D. C. atmosphere, and our factor of $\sim$ 1/100 for the reduction in Br contributed by vehicles in a "no-lead regime," we would expect $\sim$ 11 $\mu g/m^3$ of Br in Washington air from autos and about 8 $\mu g/m^3$ Br from refuse burners. While it would be simple to correct for the "refuse contribution" to the Br levels (by the use of Zn/Br ratios), the necessity of such a correction would perhaps detract from the utility of Br as an automotive tracer in urban atmospheres.

What about the behavior of the other three trace elements (Al, V, Mn) found in auto exhaust? Figures 14, 15, and 16 show the emissions of these elements vs. engine operating mode for the vehicles tested. The dependence of Al emissions upon engine operating mode generally indicates maximum release of Al during high speed, high load driving conditions. This is consistent with the idea that Al originates in the wearing down of engine components and the particles thus formed quickly deposit out on the exhaust system walls to be released during high speed, high load conditions. Mn and V show different release patterns than Al and presumably have a different origin. Manganese

Figure 14. Vanadium Particulate Concentrations vs. Engine
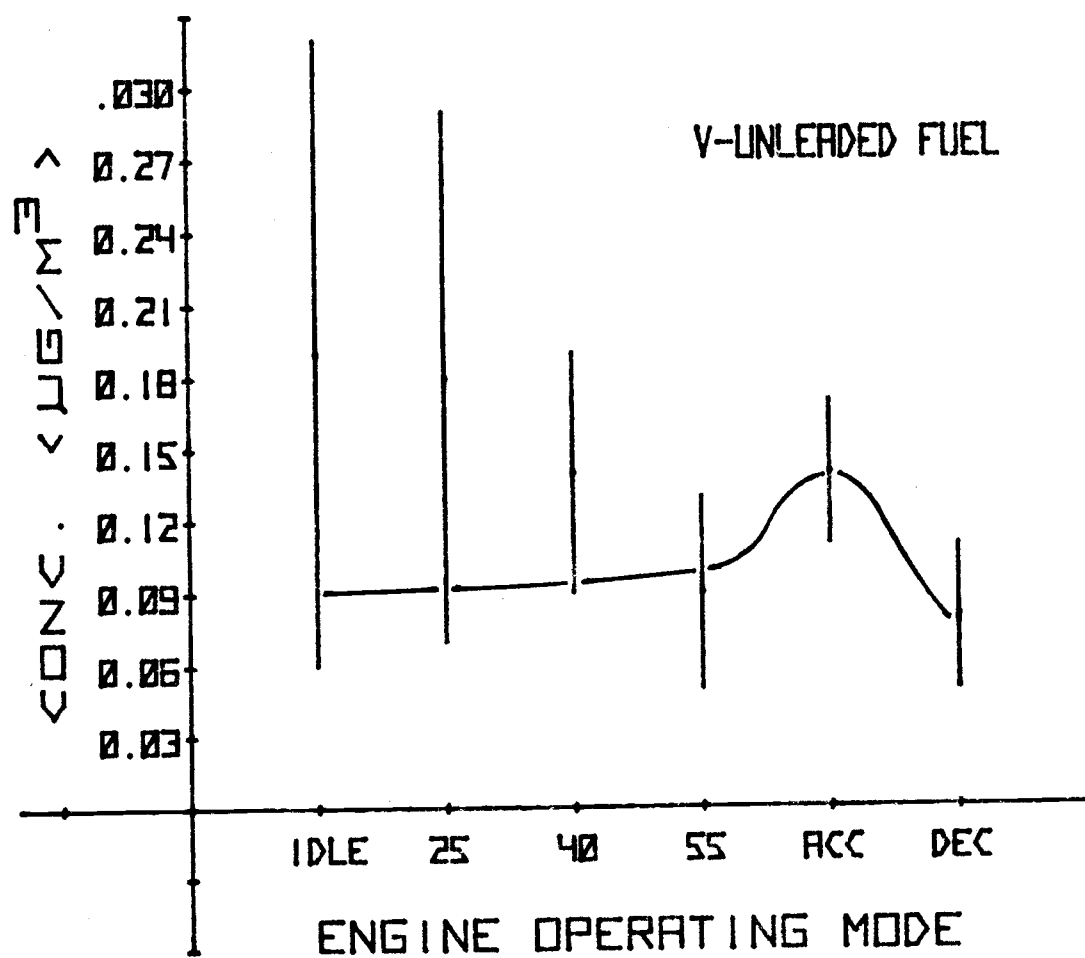Operating Mode.

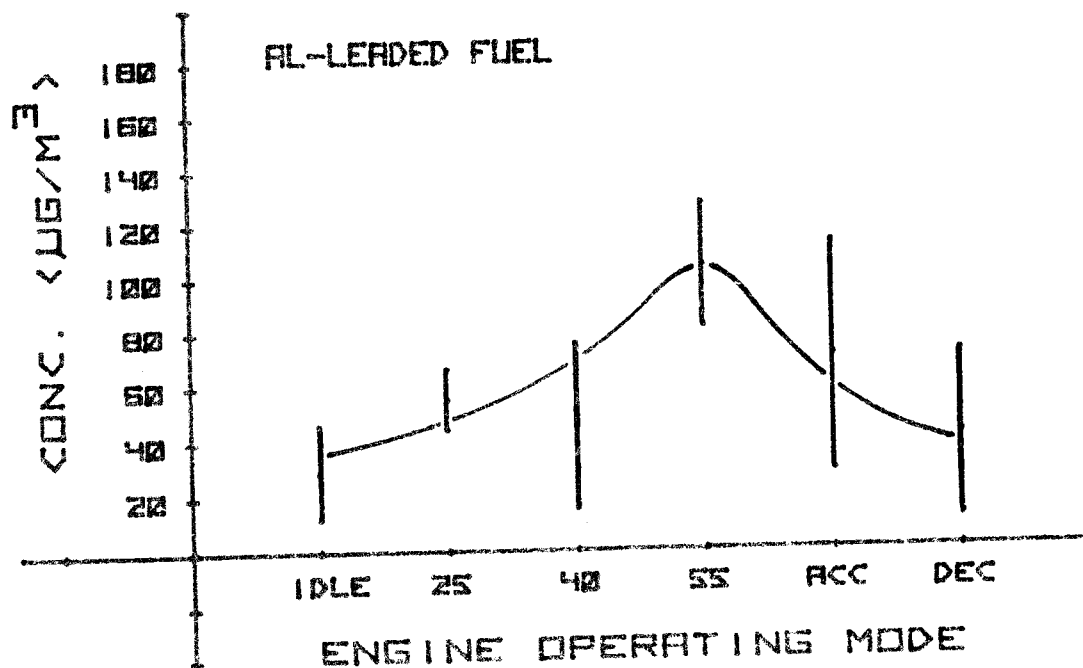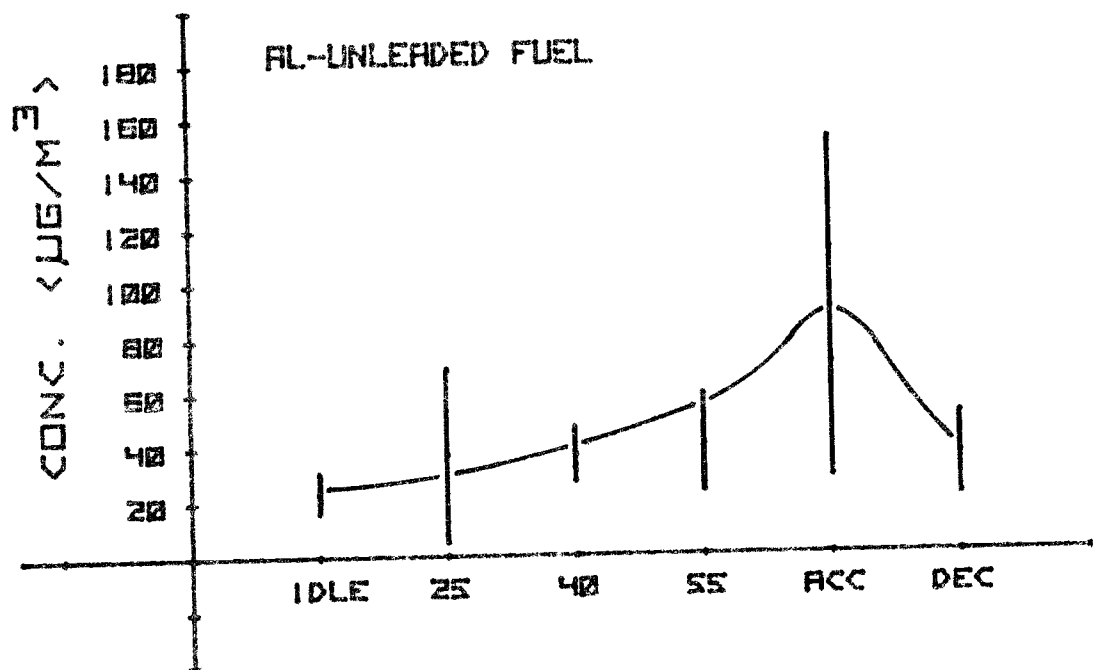Figure 15.   Aluminum Particulate Concentrations vs. Engine
Operating Mode

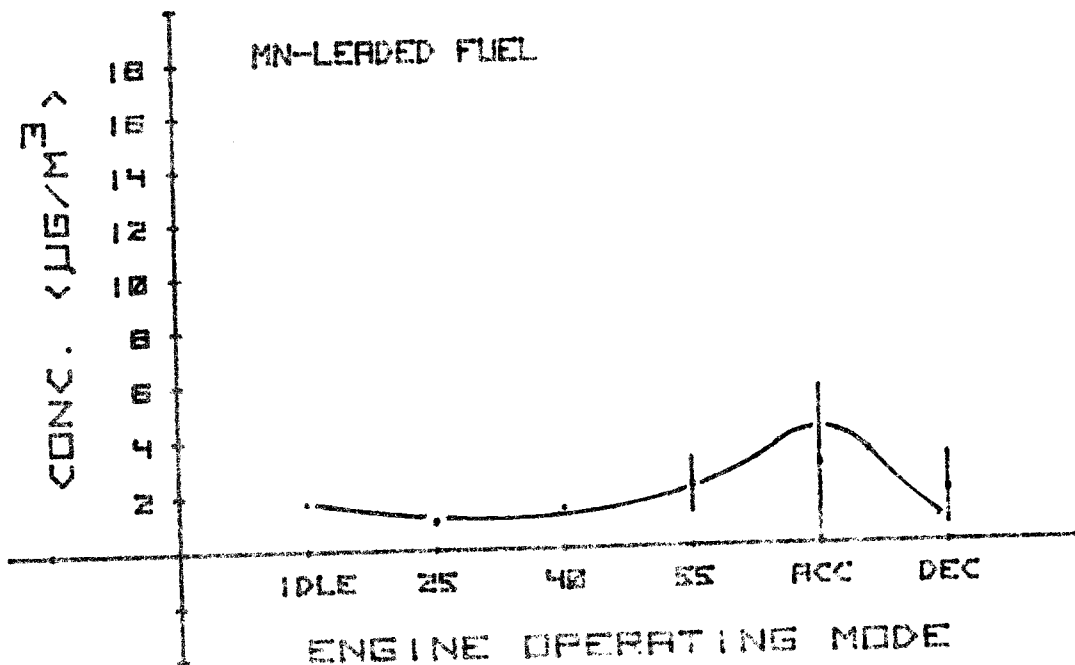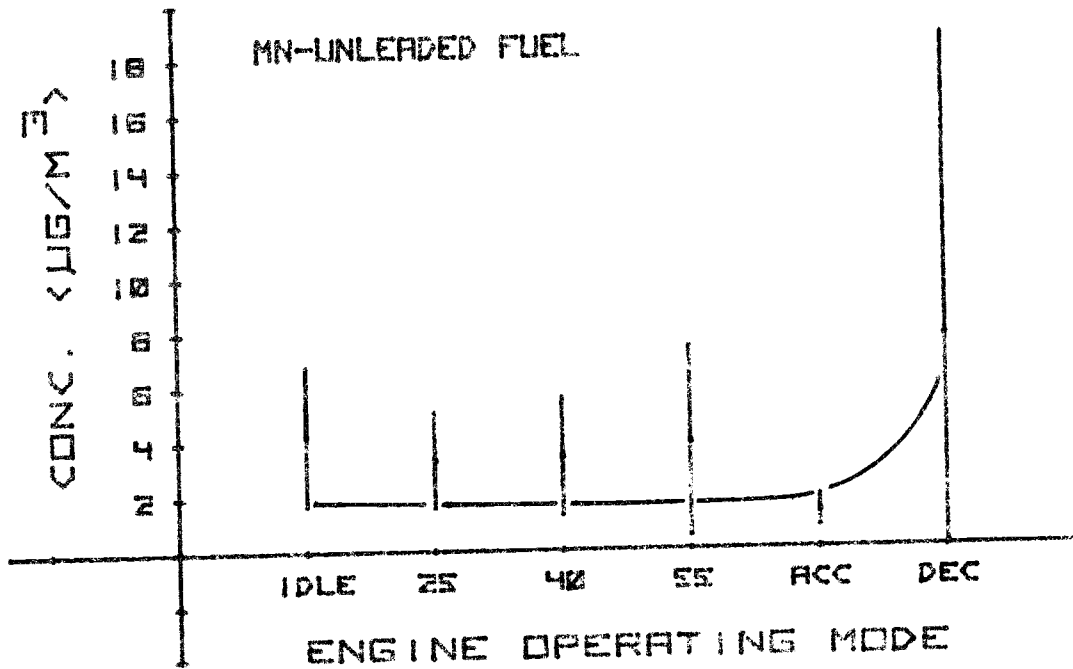Figure 16. Manganese Particulate Concentrations vs. Engine Operating Mode

MN-UNLEADED FUEL

MN-LEADED FUEL

compounds are sometimes used in both leaded and unleaded fuels as anti-knock compounds. However, according to the manufacturer,[32] the Mobil fuels used in these studies do not contain this additive. Nevertheless, one must remember that the vehicles used in these tests probably had used other types of gasoline prior to our experiments. Thus, it is quite possible that the Mn was due to contamination of the fuel tanks by the use of non-Mobil gasoline. This conjecture about the origin of the Mn component of the exhaust is consistent with the very high variability in Mn emissions amongst similar vehicles. V is traditionally associated with residual oil. However, as we have previously argued for the case of Ba, Ca, and Zn, it is dubious that our experiment was sensitive enough to detect any lubricating oil contaminants. A further clue as to the origin of the V might be found in the fact that the exhaust from vehicles burning leaded fuels did not contain any detectable amount of V. If V were due to lubricating oil contaminants, why should it be absent in the exhaust of leaded fuel vehicles? The origin of the V is not clear. One can say, however, that both Mn and V particulates appear to be formed in the combustion chamber and directly emitted into the exhaust without preliminary entrainment on the exhaust system walls.

A back-calculation on the Mn and V data, using ideal gas laws and air-fuel ratios, shows that they are present in the gasoline at 0.025 ppm Mn and 0.0014 ppm V. These levels, and their relative order, (an analysis of six crude oils revealed Mn concentrations of $\sim$ 0.2 to 3 ppm and V concentrations of $\sim$ 5 to 120 ppm)[34] suggests that Mn and V are contaminants introduced through handling the gasoline.

IV. CONCLUSIONS

What have we learned in this study? A simplified qualitative analytical chemist's picture of emissions from automotive engines emerges from this study. Consider first the gaseous emissions, CO, HC and NO_x, which have been well studied prior to this work. CO concentrations in the exhaust of the vehicles studied were of the order of 1-2% with the CO being the result of incomplete combustion of the fuel hydrocarbons. As such, the CO emissions decreased with increased air-to-fuel ratio in air-fuel mix and maximum CO emissions were observed during deceleration, a condition of minimum air to fuel ratio. CO emissions were reduced by roughly a factor of two by the use of unleaded fuel in vehicles with catalytic convertors. A similar description could be made for the hydrocarbon emissions which were typically of the order of 200-800 ppm. The NO_x emissions (typically 200-700 ppm) resulted from the high temperature, high pressure oxidation of the N_2 present in the air component of the air-fuel mixture. As such, the NO_x emissions show a maximum at an air to fuel ratio slightly on the lean side of the stoichiometric ratio and NO_x emissions maximize for high speed, high load driving. NO_x emissions appeared to be lower ($\sim$ 2x) in vehicles burning unleaded fuel compared to vehicles burning leaded fuel. This part of the story was known or suggested before this work and has been verified by this work.

The particulate emissions from these vehicles are primarily mixtures of Pb salts (where lead is present in the fuel) or carbonaceous particles

formed from dehydrogenation of fuel molecules followed by condensation and polymerization reactions. The principal chemical elements present in these particles are probably Pb, Br, Cl, C, Fe, and S with detectable traces of Al, Mn and V. Our data argue that lubricating oil components such as Ba, Ca, and Zn appear to be 1/1000 of the Br or Cl concentration thus directly contradicting the work of Gordon, et al.[10] who asserted that these elements were present at levels of $\sim$ 1/25 the Br or Cl concentrations in automobile exhaust. While we do not doubt the existence of lubricating oil derived trace elements in urban atomospheres, we do consider it important to point out that they do not originate in automobile exhaust.

The trace elements Br and Cl are present at levels of 500 - 10,000 $\mu g/m^3$ in the exhaust of vehicles burning leaded fuel. These elements are present in a molar ratio of $\sim$ 3Br/2Cl which is consistent with their presence as a mixture of PbBrCl and PbO$\cdot$PbBr$_2$. These Pb salts originate in oxidations of the gasoline additives tetraethyl lead, ethylene dichloride, and ethylene dibromide. These Pb salts deposit on the exhaust system walls and are primarily released during high speed, high load, or transient vehicle operation. A trace of Br ($\sim$ 10 $\mu g/m^3$) is present in the exhaust of vehicles burning unleaded fuel. Br-associated particulate apparently is released directly from the combustion chamber into the exhaust and shows a release pattern qualitatively similar to hydrocarbon. A possible origin of this Br is contamination of the gasoline by handling in facilities used previously to handle leaded gasoline. It appears as a trace impurity ($\sim$ 10-100 $\mu g/m^3$) in

automotive exhaust. Al is probably due to engine component wear and its mode of release resembles that of the Pb salts. V and Mn appear to be released directly from combustion chamber processes and there is some suspicion that Mn results from contamination of the vehicle gas tanks with fuels containing Mn anti-knock additives. Mean V concentrations are $\sim$ 0.2 $\mu g/m^3$ with mean Mn concentrations being $\sim$ 2 $\mu g/m^3$.

For vehicles burning leaded fuel, Pb or Br serve as excellent tracers of automotive exhaust. Leaded fuel vehicles can account[10] for the Pb, Br and Cl contents of many urban atmospheres. In the event of a "no lead regime" it is dubious that any trace element will be found that will "mark" automotive exhausts. The most likely candidates (Br, Al) are either due to contamination of "no-lead" fuel by handling in facilities used for leaded fuel or are present in such low levels relative to other sources of these elements as to make it difficult to use these elements as tracers of auto exhaust. Probably the HC or CO will continue to be the best indicator of automotive exhaust in urban atmospheres.

What improvements might one make in future studies of exhaust gas particulate? One would like to improve the sensitivity of the measurements by use of increased air volumes and "cleaner" filter media. In unraveling the details of how the particulate is formed, one would be greatly aided by a sorting of the particulate by aerodynamic size and a much better knowledge of the chemical composition of the particulate. One would like to know the Pb, C, S, Fe contents of particulate, the chemical state of these and other elements and the spatial distribution

of the elements within the particulate. In terms of data for urban planners, studies of the emissions from truck, bus and diesel-powered vehicles would be valuable.

There is much to be done. This work represents, hopefully, a step towards a better understanding of the composition of particulate matter from automotive combustion sources, how the particulate matter is formed and the structure of the "automotive component" of urban atmospheres.

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APPENDIX I

Calculation of Flow Rates in Particulate Sampling Probe

The steps followed in measuring the volume of exhaust passing through the particulate sampling probe were as follows:

1. The temperature (T) and pressure drom (ΔP) across the end orfice in the 3' long exhaust pipe extension were measured.

2. The calibration curve shown in Figure A-1 was used in conjunction with T and ΔP to estimate the flow rate in the exhaust pipe extension, F.

3. To get the exhaust flow rate, F', in the particulate sampling probe, the following relation was used:

$$F' = F \left(\frac{\text{cross sectional area of probe}}{\text{cross sectional area of the exhaust pipe extension}} \right)$$

Figure 17.   Calibration Curve for Exhaust Flow vs. Pressure Drop Across
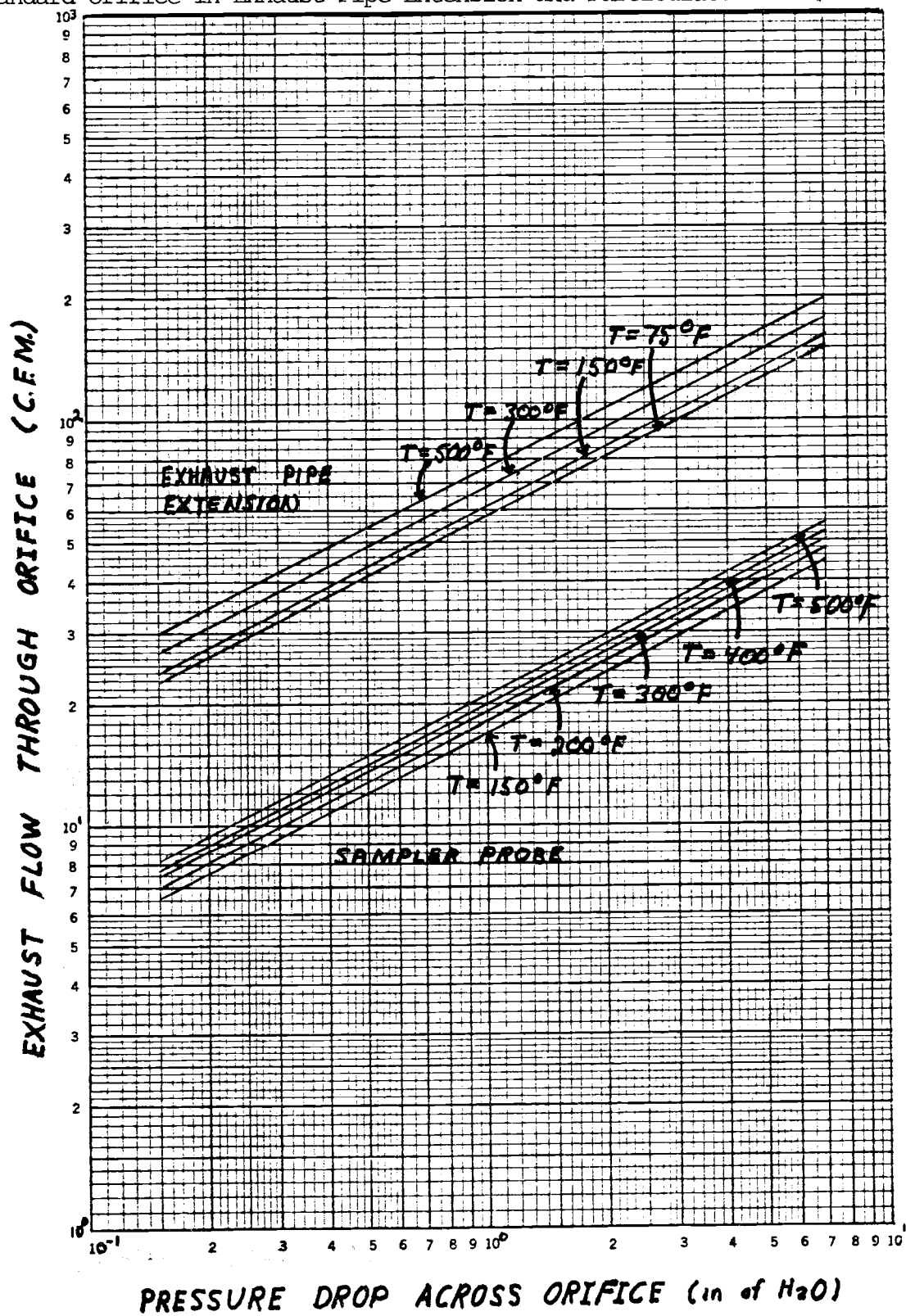Standard Orifice in Exhaust Pipe Extension and Particulate Probe.

Table XXX. AUTOMOBILE EXHAUST TEMPERATURES (°C)

Vehicle Number	Fuel Type	Operating Mode					
		Idle	25	40	55	Accel	Decel
72-150	leaded	110	160	230	300	320	110
72-150	unleaded	68	120	230	320	340	---
74-279	leaded	66	99	150	220	260	66
74-330	unleaded	120	170	180	220	250	120
74-292	leaded	66	79	120	180	200	66
74-283	leaded	66	93	160	260	170	66
73-215	leaded	85	99	120	190	180	85
73-492	leaded	85	110	130	200	200	82
73-496	leaded	80	140	150	220	200	80
124-343	unleaded	93	170	170	240	260	93
124-343	unleaded	93	150	200	200	200	93
124-347	unleaded	66	200	200	230	200	66
124-346	unleaded	120	150	250	250	230	120
124-323	unleaded	120	170	180	220	250	120
124-312	unleaded	52	66	93	180	160	52
124-304	unleaded	93	74	150	200	180	93
124-316	unleaded	120	91	150	160	150	120
124-417	unleaded	110	130	160	230	200	110
124-393	unleaded	68	120	160	260	230	68
124-404	unleaded	140	180	220	260	240	140
124-351	unleaded	150	170	210	310	260	150
124-349	unleaded	71	160	170	230	260	71
124-349	unleaded	140	150	200	270	230	140
124-409	unleaded	66	170	160	240	200	66
124-412	unleaded	85	140	200	220	200	85
124-415	unleaded	150	150	210	310	260	150

Table XXXI. VOLUME OF AIR (S.C.M.) SAMPLED

Vehicle Number*	Fuel Type	Operating Mode					
		Idle	25	40	55	Accel	Decel
72-150	leaded	0.044	0.088	0.068	0.074	0.018	0.044
72-150	unleaded	0.044	0.071	0.088	0.044	0.036	---
74-279	leaded	0.26	0.23	0.23	0.13	0.062	0.095
74-330	unleaded	0.044	0.050	0.042	0.041	0.061	0.026
74-292	leaded	0.049	0.042	0.047	0.037	0.044	0.049
74-283	leaded	0.049	0.048	0.049	0.036	0.042	0.049
73-215	leaded	0.048	0.041	0.035	0.033	0.024	0.048
73-492	leaded	0.048	0.020	0.035	0.035	0.024	0.048
73-496	leaded	0.048	0.039	0.034	0.031	0.027	0.048
124-343	unleaded	0.045	0.043	0.045	0.032	0.042	0.045
124-343	unleaded	0.045	0.043	0.043	0.049	0.097	0.045
124-347	unleaded	0.046	0.042	0.044	0.048	0.088	0.046
124-346	unleaded	0.043	0.044	0.042	0.046	0.084	0.043
124-323	unleaded	0.049	0.041	0.036	0.043	0.054	0.049
124-312	unleaded	0.052	0.047	0.039	0.032	0.947	0.050
124-304	unleaded	0.048	0.046	0.049	0.043	0.079	0.048
124-316	unleaded	0.045	0.045	0.036	0.044	0.073	0.045
124-417	unleaded	0.044	0.030	0.030	0.054	0.15	0.044
124-393	unleaded	0.046	0.030	0.030	0.043	0.13	0.046
124-404	unleaded	0.042	0.028	0.028	0.043	0.080	0.042
124-351	unleaded	0.042	0.029	0.029	0.042	0.12	0.042
124-349	unleaded	0.046	0.034	0.028	0.043	0.090	0.046
124-349	unleaded	0.043	0.029	0.029	0.043	0.067	0.047
124-409	unleaded	0.046	0.043	0.030	0.048	0.10	0.046
124-416	unleaded	0.045	0.030	0.029	0.046	0.061	0.046
124-415	unleaded	0.042	0.037	0.031	0.042	0.099	0.042

* See Table II for vehicle description.