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PETROLEUM VERSUS ALTERNATE-SOURCE FUEL EFFECTS ON LIGHT-DUTY DIESEL EMISSIONS

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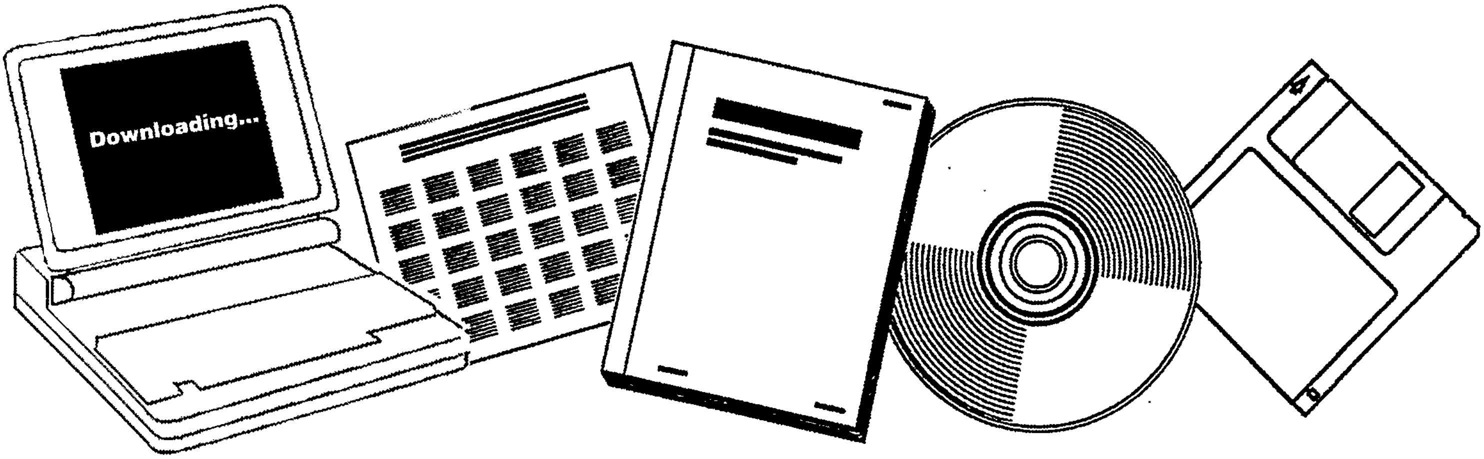

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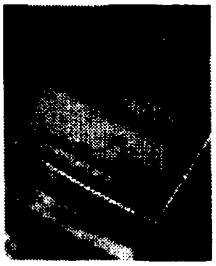

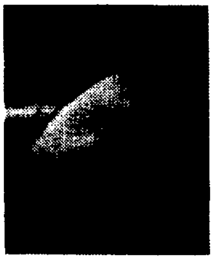

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EPA 460/3-83-007

Petroleum Versus Alternate-Source Fuel Effects on Light-Duty Diesel Emissions

by

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Contract No. 68-03-3073
Work Assignment 5

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This project was conducted for the U.S. Environmental Protection Agency by the Department of Emissions Research, Southwest Research Institute. The laboratory testing phase of the project began in June 1982, and was completed in January 1983. The work was performed under EPA Contract No. 68-03-3073, Work Assignment No. 5, and was identified within Southwest Research Institute as Project 05-6619-005. The scope of work defined by the EPA is located in Appendix A of this report. The EPA Project Officer was Mr. Robert J. Garbe, and the Branch Technical Representative was Mr. Thomas M. Baines, both of the Characterization and Technical Applications Branch, Emission Control Technology Division, Environmental Protection Agency, 2565 Plymouth Road, Ann Arbor, Michigan. The Southwest Research Institute Project Manager was Charles T. Hare, and the Project Leader and Principal Investigator was Bruce B. Bykowski.

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This report was furnished to the Environmental Protection Agency by Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas, in fulfillment of Work Assignment 5 of Contract 68-03-3073. The contents of this report are produced herein as received from Southwest Research Institute. The opinions, findings, and conclusions expressed are those of the author and not necessarily those of the Environmental Protection Agency. Mention of company or product names is not to be considered as an endorsement by the Environmental Protection Agency.

Publication No. EPA 460/3-83-007

FOREWORD

This project was conducted for the U.S. Environmental Protection Agency by the Department of Emissions Research, Southwest Research Institute. The laboratory testing phase of the project began in June 1982, and was completed in January 1983. The work was performed under EPA Contract No. 68-03-3073, Work Assignment No. 5, and was identified within Southwest Research Institute as Project 05-6619-005. The scope of work defined by the EPA is located in Appendix A of this report. The EPA Project Officer was Mr. Robert J. Garbe, and the Branch Technical Representative was Mr. Thomas M. Baines, both of the Characterization and Technical Applications Branch, Emission Control Technology Division, Environmental Protection Agency, 2565 Plymouth Road, Ann Arbor, Michigan. The Southwest Research Institute Project Manager was Charles T. Hare, and the Project Leader and Principal Investigator was Bruce B. Bykowski.

ABSTRACT

This report describes laboratory emissions evaluation of several alternate-source diesel fuels in a 1980 Volkswagen Rabbit. These evaluations are essentially a continuation of a previous study of several alternate-source fuels under EPA Contract 68-03-2884, Task Specification No. 3. The complete fuel matrix consisted of a No. 2 petroleum diesel fuel as base, mixtures of base fuel plus coal-derived liquids, shale oil diesel fuel, shale jet fuel, and a blend of petroleum stocks with coal and shale liquids. Two of the eleven fuels were evaluated during this latest project.

Vehicle operating procedures used for test purposes included those specified in Federal Regulations (FTP)(1)* and several steady-state modes. Both regulated and unregulated gaseous and particulate emissions were measured using a CVS-PDP and dilution tunnel operating on the entire exhaust stream of the engine. DOAS odor analysis was performed on raw exhaust samples during steady-state operation. Biological response evaluations, BaP measurement, and HPLC fractionation were conducted on the organic soluble portion of the particulate. The majority of the sampling and analytical procedures used were developed during earlier EPA Contracts 68-02-2494(2), 68-03-2707(3), 68-02-1230(4,5,), and 68-03-2440.(6)

After laboratory emission evaluations of the fuels were completed, the resulting data base, representing alternate-source fuels, was analyzed statistically along with data available in the literature representing petroleum-based fuels. Regression analysis was used to determine whether alternate-source materials affected exhaust emissions more strongly, less strongly, or to about the same extent as petroleum-based fuels.

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

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I. INTRODUCTION

The world's supply of crude oil is being depleted, creating incentives for discovery and utilization of alternate sources of fuels. Although interest has waned somewhat due to the current oil glut, it is considered important to continue research and development in preparation for the time when alternate-source fuels become a viable alternative. This study was designed to determine if alternate-source fuels, as currently available, will disproportionately affect exhaust emissions as compared to petroleum-based fuels. A light-duty diesel vehicle was used for test purposes. Diesel engines offer more sensitive evaluation of alternate fuel effects than gasoline cars do. No exhaust aftertreatment system has to be used on diesel automobiles to meet HC and CO standards for 1983, but a catalytic converter system is used on gasoline-fueled vehicles. Changes in diesel exhaust emissions due to alternate fuels thus affect the atmosphere and the recipient directly, but the catalyst on a gasoline vehicle tends to reduce the impact of changes in emissions seen in the raw exhaust.

This study continued the work performed under EPA Contract 68-03-2884, Task Specification No. 3. As discussed in that report(7), alternate fuel utilization and long-term research are basically still in their infancy due to the absence of large-volume production. Pilot plant yields are small, and the cost for pilot plant production of quantities suitable for testing in this program was prohibitive. Materials available in test quantities mostly represent first-generation alternate source materials. "First generation" refers to materials derived from alternate sources with little or no after-treatment, such as hydrogenation or catalytic cracking. In most cases, these currently available liquids did not have the specifications to run "as is." These liquids were blended with a petroleum base fuel to permit observation of any changes in emissions.

Selection of compounds used in both studies was made on the basis of availability, variety, and anticipation of second-generation compositions. Substances investigated include coal-derived liquids from the Solvent Refined Coal (SRC-II), Exxon Donor Solvent (EDS), and the Hydrocarbon Research (H-Coal) processes, shale oil products, a broadcut fuel containing n-butane among other stocks, and a mixture of coal, shale, and petroleum products.

A literature search was conducted to obtain published reports of technical papers presenting data on petroleum fuel effects on light-duty diesel emissions. The data from these studies and the data generated from the alternate source studies were normalized and statistically analyzed to present data in such a manner that a determination might be made as to the effects of alternate-source fuels on emissions as compared to petroleum fuels.

II. SUMMARY AND CONCLUSIONS

The major objective of this project was to determine if the effects of property variation in alternate-source fuels on exhaust emissions were the same, less pronounced, or more pronounced than the effects of property variation in petroleum fuels. This study generated exhaust emissions data using several alternate-source diesel fuels in a 1980 Volkswagen Rabbit. The same vehicle was used in an earlier study(7) to evaluate several other alternate-source fuels. Data from this study and the previous study(7) were combined to represent alternate-source fuel effects on light-duty diesel exhaust emissions. Data regarding petroleum fuel effects on light-duty diesel emissions were obtained by reviewing available studies found in a library literature search.

One of the major challenges in performing this work was to formulate a statistical analysis test plan which would strengthen the statistical arguments, while minimizing the number of assumptions and maximizing the applications of the conclusions. The data base available had some severe limitations which restricted the application of more advanced statistical concepts. These limitations were that experiments were performed at differing times, under differing test conditions, and with differing objectives. Due to these conditions, it was expected that only general trend information would be available at the conclusion of this project. Decisions on whether petroleum fuels and alternate-source fuels affected exhaust emissions similarly or differently were based on calculated chi-square values or goodness-of-fit statistics.

The most important observations and conclusions reached as a result of this project (not necessarily in order) are as follows:

1. SASOL middle distillate fuel was associated with exhaust emissions similar to those observed while evaluating a shale diesel marine fuel. In general, the SASOL fuel was associated with the same or slightly lower emission levels as compared to the base fuel.

2. The 25 percent H-Coal blend has properties and emission results similar to the 25 percent EDS blend (both coal-derived liquids). Both fuel blends were associated with increases in emissions.

3. It appears that further treatment of "first generation" coal liquids by hydrogenation or catalytic cracking would result in "second generation" materials which do not increase exhaust emissions. This conclusion is based on comparing results of "first generation" liquids (SRC-II, EDS, H-Coal) and "second generation" materials (shale diesel marine, Paraho JP-5, SASOL).

4. Review of various studies obtained by the library literature search indicated a wide variety of conclusions concerning fuel effects on exhaust emissions. In most cases, the primary conclusion appeared to be that the vehicle/engine type, followed by driving cycles, affected exhaust emissions on a g/km basis more than changes in fuel properties.

5. Bivariate correlation coefficients indicated that the various studies reviewed were associated with differing types of fuel property-exhaust emission relationships. For a particular fuel property-exhaust emission data pair, it was not uncommon for the correlation coefficients to range from -0.166 to 0.908. Some of these data having poor correlations yielded linear regression equations whose slope was opposite that observed with other studies.

6. For each fuel property-exhaust emission data pair, data from the petroleum-based fuel studies were used to generate prediction equations. The alternate-source fuel properties were inserted into the equations to yield predicted emissions. The observed and predicted emissions were used to determine goodness-of-fit of the models. Based on these calculations, the effects of alternate-source fuels on exhaust emissions are statistically indistinguishable from those associated with petroleum fuels.

7. It is not recommended to use detailed statistical analysis to evaluate the effects of alternate-source fuels versus petroleum fuels on exhaust emissions using the currently available data. Reasons include lack of good data bases, poor correlation within available bases, and the apparent stronger effects of engine displacement and driving cycle on exhaust emissions. Comparisons between alternate-source and petroleum fuels should be performed with the raw data, unless an adequate statistical experimental design was formulated prior to program initiation.

III. TEST VEHICLE AND FUELS

The test vehicle used was the identical vehicle previously employed to evaluate other alternate-source fuels in a previous study(7), continuity being the primary concern. Fuel selection was directed principally by availability of alternate-source (non-petroleum) materials not evaluated under the previous alternate-source study. Alternate-source materials were analyzed thoroughly to establish the properties of each fuel in detail.

A. Test Vehicle

The test vehicle was 1980 Volkswagen Rabbit diesel. A description of the vehicle is provided in Table 1, and it was supplied to the Contractor by EPA for test purposes.

TABLE 1. DESCRIPTION OF TEST VEHICLE

Vehicle Model	Volkswagen Rabbit
Engine Model	Family D
Model Year	1980
V.I.N.	17A0926720
Engine No.	CK591126
Body Type	2-Door Hatchback
Inertia equivalent, kg (lb_m)	1021 (2250)
Transmission	5-speed manual
Displacement ℓ(in^3)	1.47 (90)
Cylinders	4
Power, kW (hp) @ rpm	(48) @ 5000
Injection System	Bosch
Combustion Chamber	Swirl Chamber
Compression Ratio	23:1
Distance on Vehicle, km	2806[a], 4980[b]

[a] at project initiation
[b] at project completion

Initially, the vehicle was driven 220 km for conditioning using the base fuel. Emission tests were conducted to determine whether or not any shifts had occurred in the baseline emissions observed during the previous study.(7) The test results are summarized in Table 2. Complete test results can be found in Appendix B, pages B-2 and B-3. The variability was considered satisfactory for the purpose of continuing evaluation of alternate-source fuels.

TABLE 2. COMPARATIVE EMISSIONS DATA, TWO STUDIES

	Average FTP Emissions	
	Earlier Study	Current Study
HC, g/km	0.31	0.29
CO, g/km	0.96	0.99
NO_x, g/km	0.66	0.70
Particulate, g/km	0.25	0.27
Fuel, ℓ/100 km	6.37	6.40

B. Test Fuels

Most of the available alternate-source fuels were previously evaluated under another project.(7) Two additional fuels evaluated during this project were a SASOL coal-derived middle distillate, and a blend of 25 percent H-Coal in base fuel (DF-2). Due to the good ignition characteristics of the SASOL fuel (reflected in its cetane number), it was run "as-is." The H-Coal material required blending with the base fuel to permit reasonable vehicle operation. A 25 percent blend was chosen to be consistent with the other two coal-derived blends previously tested (SRC-II and EDS). Complete fuel characterization was a part of this sutdy. Properties of all the alternate-source fuels tested in both the current and previous projects are listed in Table 3.

TABLE 3. FUEL PROPERTIES AND COMPOSITION.

Description	Base DF-2	Shale Diesel Marine	Paraho JP-5	Coal Case 5A	35% SRC-II	Broadcut Mid-Continent	25% SRC-II	25% EDS	25% EDS Naphtha	25% H-Coal	SASOL Mid. Dist.
Fuel Code (EM-	329-F	453-F	473-F	474-F	475-F	476-F	478-F	482-F	485-F	526-F	527-F
Cetane No. (D613)	50	49	45	42	31	35	38	44	45	42	50
Cetane Index (D976)	50	52	42	41	32	49	38	42	45	46	52
Gravity, °API @ 60°F	37.5	37.9	43.6	31.1	28.2	44.1	31.7	33.8	38.3	32.8	44.5
Density, g/mℓ @ 60°F	0.837	0.835	0.808	0.870	0.886	0.806	0.867	0.856	0.833	0.861	0.804
Carbon. wt. %	85.8	86.3	85.9	86.5	86.2	86.1	86.4	86.5	86.3	86.8	85.7
Hydrogen, wt. %	13.0	13.4	13.7	12.4	11.8	13.2	12.3	12.7	13.3	12.5	14.0
Nitrogen, ppm (oxid. pyrolysis)	48	5	<1	1600	3400	1000	2000	267	142	980	<1
Sulfur (1 amp), %	0.24	<0.005	0.005	0.100	0.31	0.17	0.23	0.16	0.28	0.21	<0.01
Calculated H/C, numeric	1.81	1.85	1.90	1.71	1.52	1.83	1.70	1.75	1.84	1.72	1.96
Carbon No. range (.G.C.)	8-24	9-20	10-15	9-24	8-20	3-24	8-20	8-20	7-20	9-20	10-24
Aromatics, vol. %	21.3	28.5	22.	34.9	47.0	16.2	39.9	36.4	25.5	37.2	24.0
Olefins, vol. %	1.7	2.1	2.	1.4	0.6	0.0	1.2	0.0	0.5	1.2	0.0
Paraffins, vol. %	77.0	69.4	76.	63.7	52.4	83.8	58.9	63.6	74.0	61.6	76.0
Viscosity, cs @ 100°F (D445)	2.36	2.61	1.38	3.08	2.53	1.53	2.45	2.37	1.76	2.31	2.14
Gum, mg/100 mℓ (D481)	14.3	0.3	1.4	38.8	89.7[b]	23.8	30.1	60.0	13.1	54.6	24.4
Total solids, mg/ℓ	7.4	0.3	--	--	13.1	--	7.2	3.1	1.2	16.3	0.8
Metals in fuel, x-ray	0[a]	0[a]	0	0	0	0	9ppm Fe	0	0	--[c]	0
Boiling Range, °C (IBP-EP,D86)	191-340	207-317	179-248	192-366	171-328	21-354	178-327	179-353	108-334	182-331	190-404
10% point	219	236	189	234	207	53	209	207	157	212	200
20% point	231	246	192	244	215	121	220	218	182	223	206
30% point	242	252	196	253	225	151	231	227	203	231	210
40% point	251	259	198	259	234	178	240	239	223	239	217
50% point	260	266	202	267	243	216	250	251	238	247	223
60% point	269	272	206	276	252	239	259	263	254	256	233
70% point	278	278	211	277	263	255	270	276	267	267	249
80% point	290	286	218	292	274	270	281	293	281	279	278
90% point	307	295	228	330	292	303	303	316	302	299	339
95% point	323	302	237	353	309	327	319	336	319	316	392
Residue, wt. % (D86)	1.3	1.0	1.5	1.5	1.0	1.0	1.0	1.5	1.5	1.0	1.0

[a] <10 ppm of Cr, Fe, No, Cu, Zn, and Mg; <70 ppm Pb; <100 ppm Al and Si

[b] Sample not dry after 1 hr. in steam lit block

[c] 38 ppm Fe, 14 ppm Cu, 21 ppm Cr, <60 ppm Pb

TABLE 3 (CONT'D). FUEL PROPERTIES AND COMPOSITION.

Substance	Base DF-2	Shale Diesel Marine	Paraho JP-5	Coal Case 5A	35% SRC-II	Boradcut Mid-Continent	25% SRC-II	25% EDS	25% EDS Naphtha	25% H-Coal	SASOL Mid. Dist.
Fuel Code (EM-	329-F	453-F	473-F	474-F	475-F	476-F	478-F	482-F	485-F	526-F	527-F
Boiling Range, °C (IBP-EP,D2887)	104-387	118-341	157-286	140-416		24-399	129-508	128-419	72-455	122-382	161-487
10% point	197	216	175	217		68	193	192	139	196	188
20% point	220	237	187	238		123	214	210	174	214	198
30% point	239	254	195	254		155	232	228	197	230	208
40% point	256	265	201	264		196	248	243	225	241	216
50% point	268	274	210	271		233	259	257	249	254	228
60% point	280	285	216	284		251	271	273	264	266	241
70% point	292	297	224	299		262	285	289	279	278	261
80% point	307	307	234	315		280	302	305	298	294	292
90% point	330	319	244	344		314	321	332	314	316	358
95% point	347	325	254	367		342	345	356	336	335	410
Residue, wt. % (D2887)	0.0	0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0
Composition, Volume %											
Kerosene											
Petroleum	0.0	0.0	0.0	17.3	0.0	22.0	0.0	0.0	0.0	0.0	0.0
JP-5	0.0	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
JP-8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Diesel											
Petroleum	100.0	0.0	0.0	66.7	65.0	23.0	75.0	75.0	75.0	75.0	0.0
Shale DFM	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Coal	0.0	0.0	0.0	16.0	35.0	6.2	25.0	25.0	25.0	25.0	100.0
Light Cycle Oil	0.0	0.0	0.0	0.0	0.0	5.2	0.0	0.0	0.0	0.0	0.0
LSR Naphtha	0.0	0.0	0.0	0.0	0.0	7.4	0.0	0.0	0.0	0.0	0.0
HSR Petroleum	0.0	0.0	0.0	0.0	0.0	4.8	0.0	0.0	0.0	0.0	0.0
Shale	0.0	0.0	0.0	0.0	0.0	20.9	0.0	0.0	0.0	0.0	0.0
Coal (Simulated)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N-Butane	0.0	0.0	0.0	0.0	0.0	10.5	0.0	0.0	0.0	0.0	0.0

[a] <10 ppm of Cr, Fe, NI, Cu, Zn, and Mg; <70 ppm Pb; <100 ppm Al and Si

IV. INSTRUMENTATION AND ANALYTICAL PROCEDURES

Analytical procedures and equipment used to measure regulated and unregulated emissions are described briefly in this section. These procedures were used in earlier EPA Contracts(2,3,6,7), and are routinely used in present-day emission testing.

A. Vehicle Operation and Smoke Measurements

The VW Rabbit was operated to simulate road experience on a 2-roll Model ECE-50 Clayton light-duty chassis dynamometer, of the type qualified for Federal light-duty certificaiton.(8) Inertia and power absorption settings used for all test work on this dynamometer were set to simulate operations of an earlier model VW Rabbit tested in a previous study.(7)

Care was taken to insure that the vehicle's fuel system was purged properly before testing of each fuel. All test fuels were withdrawn from individual 19 liter cans. Prior to test, a 2 liter sample of test fuel was used to run the vehicle, with the return line routed to a container subsequently discarded. After this purge, the vehicle was operated for approximately 30 minutes, followed by FTP and HFET driving cycles, to remove any residuals from other fuels, and to insure that the vehicle fuel system contained only the fuel to be tested.

Exhaust smoke measurements were made using an optical light-extinction smokemeter, of the type specified in Federal regulations for heavy-duty diesel engine smoke certification.(9) The smokemeter was mounted on a 51 mm (2 in.) O.D. tailpipe extension when in use. The control/readout unit for the smokemeter was mounted remote from the vehicle under test, and continuous recordings of smoke opacity were made concurrently with vehicle speed traces. Smoke measurements were made over the first 505 seconds of the cold-start FTP cycle, while the vehicle was operated on the chassis dynamometer. This procedure was developed for research purposes on an earlier EPA Contract, No. 68-03-2417.(10)

B. Regulated and Unregulated Gaseous Emissions

Regulated gaseous emissions of hydrocarbons (HC), carbon monoxide (CO), and oxides of nitrogen (NO_x) were collected and analyzed using procedures and equipment described in the Federal Register.(8) The method of hydrocarbon analysis was an updated version of that proposed, and eventually adopted for, the 1980 Federal Register.(9)

The unregulated gaseous emissions measured were aldehydes, phenols, and odor. Aldehydes were measured using the 2,4-dinitrophenylhydrazine (DNPH) method.(2) The method consists of withdrawing a continuous sample of dilute exhaust at a rate of 0.24 m^3/hr, and bubbling the sample through glass impingers containing DNPH in hydrochloric acid. This process forms the aldehydes, phenylhydrazone derivatives, which are eventually injected into a gas chromatograph equipped with a flame ionization detector for separation and identification.

Phenols were measured using the ether extraction procedure.(2) The first step was to collect dilute exhaust in impingers containing aqueous potassium hydroxide, at a rate of 1.02 m^3/hr. The contents of the impingers are acidified and extracted with ethyl ether, and are eventually injected into a gas chromatograph equipped with a flame ionization detector.

Exhaust odor was evaluated using the A. D. Little "Diesel Odorant Analytical System" (DOAS). The procedure used in this study was the same as used in previous studies(5,10), and described in detail in the final report on another study.(11) The vehicle was operated at 3 steady-state modes; idle, 50 kph, and 85 kph. Raw exhaust samples were taken for a specified time so that the required amount of exhaust would pass through the Chromosorb 102 traps. TIA (total intensity of aroma) values are defined by either:

$$\text{TIA} = 1 + \log_{10} (\text{LCO}, \mu g/\ell)$$

or

$$\text{TIA} = 0.4 + 0.7 \log_{10} (\text{LCA}, \mu g/\ell),$$

whichever generates the highest value. "LCO" represents liquid column oxygenates, and "LCA" represents liquid column aromatics.

C. Particulate Collection, Mass Rate, and Aerodynamic Sizing

Particulate collection for this project was performed using a 457 mm (18 inch) diameter by 5 m (16 feet) long dilution tunnel operating on total vehicle exhaust. Other associated equipment includes probes, pumps, and filter holders to withdraw and collect the particulate on filters, and a balance to determine the mass of particulate collected.

The dilution tunnel is identical to that used in a previous study.(7) A 114 mm (4.5 inch) probe was located at the downstream end of the tunnel. This large probe was used to withdraw a dilute exhaust sample at a rate of 3.4 m^3/min (120 SCFM) through a 500 x 500 mm (20 x 20 inch) Pallflex filter (Pall Corporation). The dilution tunnel used is shown schematically in Figure 1. Some of the equipment necessary for collecting particulate and relating it to undiluted vehicle emissions is not shown in the schematic. It includes a constant volume sampler (CVS) operating at a nominal capacity of 12.6 m^3/min (450 CFM) to withdraw and measure unsampled air/exhaust mixture, and the positive-displacement pump (capacity 3.4 m^3/min) used for the 500 x 500 mm filter system.

Particle sizing was accomplished using a radial-slot impactor. The impactor system contained stainless steel stages on which particulate matter was supposedly fractionated by size, and a final Pallflex backup filter. The impactor was locatd at the downstream end of dilution tunnel. In operation, each stage was placed on a plate such that the slots in each stage decreased in width from sample entrance down to the filter. Each stage was rotated 45 degrees so the particulate matter passing through the slots impacted on a solid portion of the following plate. Particle retention characteristics were

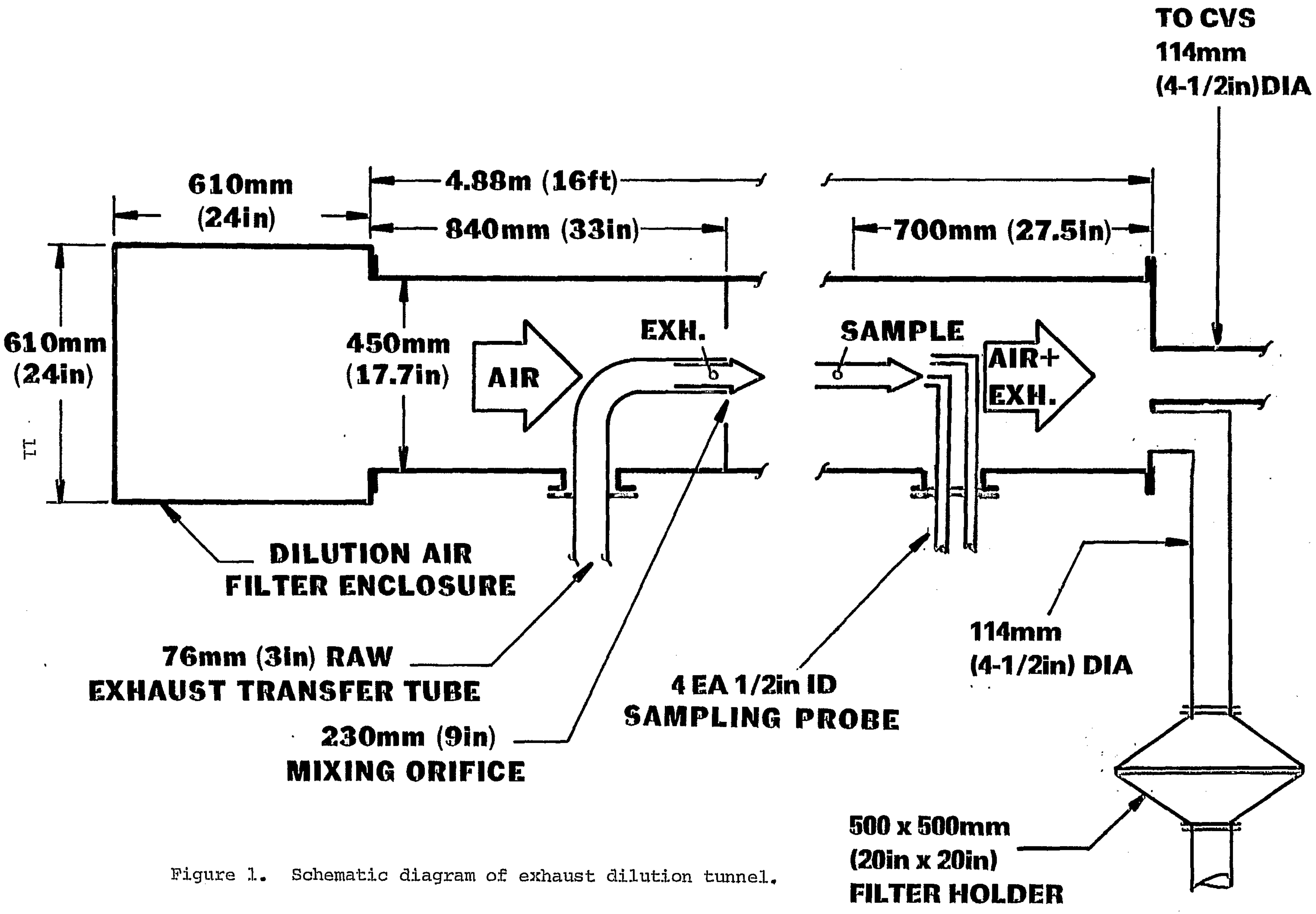

Figure 1. Schematic diagram of exhaust dilution tunnel.

related to the slot size and flowrate through the impactor. The flowrate was controlled using a metal bellows vacuum pump, pressure gauge, and flowmeter. The flowrate was maintained at 2.8 ℓ/min (0.1 CFM) to achieve particle sizing down to 0.1 micrometer.

The mass of particulate matter collected on sample filters and impactor discs was determined on a microbalance. This balance is enclosed in a vibration-resistant, temperature- and humidity-controlled chamber to minimize outside interferences. Filters and other materials for weighing were allowed to stabilize in the chamber for a minimum of 12 hours before they were weighed. The sensitivity of the balance is 1 μg. Air to the chamber flows at about 17 m^3/hr on a one-pass basis, and keeps the chamber pressure at about 2.5 kPa above atmospheric. The control system keeps chamber conditions at 22.2 ± 0.6°C and 63 ± 2 percent relative humidity, and air entering the chamber is filtered through a 99.99 percent DOP-efficient filter.

D. Analysis of Particulate Composition

Particulate samples were acquired by several methods for various analyses. After determining particulate matter weights, the samples were subjected to analysis for major elements and trace elements. Some particulate samples were collected in order to obtain the soluble fraction of particulate matter. Analysis of the soluble fraction is discussed in the next section.

1. Trace Elements

Analysis for trace elements (metals and sulfur) in the particulate matter was performed on 47 mm Fluoropore filter samples. As provided in the contract agreement, these determinations were made at EPA's Research Triangle Park laboratories as part of the EPA in-house measurement program. The instrumentation used for these analyses was a Siemens MRS-3 x-ray fluorescence spectrometer.

2. Major Elements

Samples collected on 47 mm glass fiber filters were sent to Galbraith Laboratories and analyzed for carbon and hydrogen content by combustion and subsequent gas analysis. The equipment used was a Perkin-Elmer Model 240B automated thermal conductivity CHN analyzer. Results of this analysis were reported in percent of submitted mass and calculated weight of element detected on the filter. These results make the filter weighing accuracy very important.

E. Analysis of the Soluble Fraction of Particulate Matter

The soluble fraction of particulate matter was obtained by extraction from the 500 x 500 mm (20x20 inch) Pallflex filters. This large filter enabled enough soluble material to be extracted so that the total amount could be divided into smaller aliquots, then analyzed for a variety of constituents.

1. Total Soluble Organics

The 500 x 500 mm filters were weighed before and after test to determine the weight of particulate matter. Each filter was extracted using methylene chloride in a Soxhlet apparatus. The solvent volume was reduced at low temperature and under vacuum. The remaining solvent/solubles were transferred to a preweighed container, and the solvent was evaporated by nitrogen purging. The total mass of solubles was determined gravimetrically, and the percent of solubles in the particulate matter calculated.

2. Major Elements

One aliquot of the dried, weighed soluble extract was submitted to Galbraith Laboratories and analyzed for carbon, hydrogen, oxygen, and sulfur by the technique and instrumentation described in Section IV, D.2 (Perkin-Elmer 240B). An additional aliquot of soluble extract was submitted to SwRI's U.S. Army Fuels and Lubricants Research Laboratory for nitrogen analysis by oxidative pyrolysis and chemiluminescence.

3. Solubles Boiling Range and Individual n-Paraffin Analysis

Another aliquot of soluble extract was submitted to SwRI's U.S. Army Fuels and Lubricants Research Laboratory for determination of the boiling range and reference to normal paraffins. The procedure is a high-temperature variation of ASTM D2887-73. Each aliquot was dissolved in carbon disulfide, and an internal standard (C_9 and C_{11} compounds) was added to quantitate results. The maximum temperature that this column reached was 450°C, eluting compounds boiling up to 650°C.

4. Benzo(a)pyrene (BaP) and Ames Bioassay

An additional 500 x 500 mm (20x20 inch) filter was extracted, and the extract was divided into eleven aliquots. One aliquot was used to determine the BaP content of the soluble extract. This analysis was performed by SwRI's Department of Emissions Research. The procedure, developed by others (12), is based on high-performance liquid chromatography to separate BaP from other organic solubles in particulate matter; and it incorporated fluorescence detection to measure BaP. The instrument used was Perkin-Elmer 3B liquid chromatograph equipped with a MPF-33 fluorescence spectrophotometer. Excitation was at a wavelength of 383 nm, and emission was read at 430 nm. The remaining ten aliquots were shipped on dry ice to EG&G for Ames bioassay testing. The Ames test refers to a bacterial mutagenesis plate assay with Salmonella typhimurium, according to the method of Ames.(13)

5. Fractionation by Relative Polarity

The composition of the organic soluble portion of the particulate matter is complex, and its separation into individual compounds is very difficult. Fractionation of the solubles by high performance liquid chromatography (HPLC) separates the sample into a series of fractions of increasing molecular polarity. This procedure is discussed in detail in a CRC report.(14)

Briefly, an organic solubles sample is initially carried in a solvent composed of 95 percent hexane and 5 percent methylene chloride, a relatively non-polar mixture. After a period of time, the ratio of methylene chloride to hexane, and therefore solvent polarity, is increased to a rate of 5 percent methylene chloride per minute. At 100 percent methylene chloride, the carrier solvent is moderately polar. A fluorescence detector is used at an excitation wavelength of 330 nm and an emission wavelength of 418 nm. A UV detector is used at wavelength of 254 nm. At these wavelengths fluorescence and UV responses of compounds are mapped as a function of column elution time, reflecting polarity.

V. TEST PLANS AND OPERATING SCHEDULE

The following section describes the vehicle operating schedules, exhaust analysis test plan, Quality Assurance Project Plan, and statistical analysis test plan. A summary of the exhaust constituents evaluated is given in Table 4. Discussion of the analytical techniques is presented in Section IV of this report.

A. Vehicle Test Plan

The vehicle followed two transient cycles, FTP and HFET, during most sample collection and measurement runs. These cycles are routinely used in emission testing and are well documented in other works.(1,3,6,10) Smoke evaluation was performed separately during the cold transient portion of the FTP (first 505 seconds). The cold transient portion incorporates all of the most interesting modes from a smoke standpoint, including cold engine start, first idle, first acceleration, second idle, and second acceleration. Steady-state modes at idle, 50 kph, and 85 kph were used to obtain raw exhaust samples for odor analysis. Vehicle running time on the steady-state modes was governed by the sample volume requirements of the odor measurement procedure (DOAS).

The test plan incorporating the cycles and evaluations for each test fuel is given in Table 5. Samples taken over each 2-bag FTP were defined as a "cold FTP" or a "hot FTP." Testing for each fuel required a minimum of three days. After the first day of testing, as many of the results as possible were reviewed to determine whether or not replicate analysis would be required on the second day of testing. It was important to determine the validity of the tests as early as possible, to avoid costly reruns and depletion of limited test fuel quantities by repurging the fuel system. Procedure for fuel system purging between test fuels is discussed in Section IV. Duplicate filter samples were collected on Day 2, and retained for possible replicate analyses. In some cases, samples were stored in their most stable form, then submitted for analysis as a group (rather than individually) to minimize the effects of day-to-day variability in an analytical procedure.

B. Quality Assurance Project Plan

A Quality Assurance Project Plan was prepared following EPA QAMS-005/80, entitled, "Guidelines and Specifications for Preparing Quality Assurance Project Plans," December, 1980. This project plan(15) was forwarded to the EPA in June 1982, prior to initiation of technical efforts.

A substantial portion of the program expenditures was made to prepare the Quality Assurance Project Plan. Costs for this effort were not originally included in the Work Plan. Therefore, some technical efforts originally planned were reduced to compensate for the Quality Assurance Project Plan efforts.

TABLE 4. OUTLINE OF CHEMICAL AND PHYSICAL EXHAUST EVALUATIONS

Exhaust Component under Study	Constituent(s) analyzed for	Collection Method	Analysis technique(s)
Smoke	smoke (visible	--	EPA smokemeter (continuous)
gases	HC, CO, CO_2, NO_x	sample bag	constant volume sampler
	aldehydes	wet impinger	DNPH
	odor	DOAS traps	DOAS sampler
	phenols	wet impinger	extraction, GC
particulate	total mass	Pallflex filters	gravimetric
	size distribution	impactor-filter	gravimetric
	sulfur & trace elements	filter, 47 mm Fluoropore	x-ray fluorescence
	carbon, hydrogen in particulate	filter, 47 mm glass fiber	combustion (commercial)
	organic extractable substances	"20x20" filter	soxhlet extraction
	BaP in organic solubles	--	LC, fluorescence detection
	molecular weight range of organic solubles	--	GC
	carbon, hydrogen in solubles	--	combustion (commercial)
	biological response of solubles	--	Ames bioassay
	polarity profile of solubles	--	HPLC

TABLE 5. TEST PLAN FOR EACH FUEL

Analysis or Sample	Day 1			Day 2[a]						Day 3 cold transient (505 seconds)
	Cold FTP	Hot FTP	HFET	Cold FTP	Hot FTP	HFET	Idle	50 kph	85 kph	
gaseous HC, CO, NO_x, CO_2	X	X	X	X	X	X	X	X	X	–
sulfur & trace elements	X	X	X	–	–	–	–	–	–	–
particle size distribution	X[b]		–	–	–	–	–	–	–	–
organic extractables[c]	X	X	X	–	–	–	–	–	–	–
total particulate mass	X	X	X	X	X	X	X	X	X	–
C & H in particulate	X	X	X	–	–	–	–	–	–	–
odor	–	–	–	–	–	–	X	X	X	–
aldehydes	–	–	–	X	X	X	–	–	–	–
phenols	–	–	–	X	X	X	–	–	–	–
BaP and Ames bioassay	–	–	–	X	X	–	–	–	–	–
smoke	–	–	–	–	–	–	–	–	–	X

[a] Repeat samples optional
[b] One sample collected for entire 4-bag FTP
[c] Organic extractables divided into aliquots for HPLC, carbon & hydrogen, and boiling range analysis

C. Statistical Anaylsis Test Plan

The principal objective of this study was to determine the degree to which alternate-source fuels affect exhaust emissions as compared to petroleum fuels. Several statistical approaches were available to meet this objective. Attempts were made to strengthen the statistical arguments while minimizing the number of assumptions and maximizing the applicability of the conclusions. It was not within the scope of the project to perform a detailed statistical analysis. However, the data were collected and treated in such a way that future efforts could continue with such analysis.

A literature search was conducted to obtain studies dealing with petroleum fuel property effects on exhaust emissions. Due to the wide variety of vehicles, fuels, test cycles, and measurement techniques used in previous studies, a method to relate all these studies in terms of general trends was developed. The data from all studies, on both petroleum and alternate-source fuels, were normalized to a selected fuel property level. Regression analysis was performed on each study's normalized data to yield linear equations for each selected (fuel property-exhaust emission) data pair. Analysis of the resulting line plots yielded general observations of trends for petroleum fuels versus alternate-source fuels. Bivariate correlation coefficients for each selected fuel property-exhaust emission data pair were also determined on each study. Goodness-of-fit was calculated by inserting the alternate-source fuel properties into the petroleum fuel exhaust emission prediction equations. These goodness-of-fit results were used to determine whether or not emission effects observed with property variation in petroleum fuels and alternate-source fuels differed statistically.

VI. GASEOUS AND PARTICULATE EMISSION RESULTS

This report section includes results and discussion on regulated gaseous emissions, aldehydes, phenols, exhaust odor, visible smoke, total particulate mass emissions, particle size distribution, and particulate matter elemental analysis. In addition, it includes information on organic solubles in particulate matter, elemental analysis of the solubles, BaP in solubles, boiling range of organic solubles by gas chromatograph analysis, polarity profile of the solubles, and bioassay analysis. Confidence limits could not be calculated due to an insufficient number of data points. Emission repeatability was good, with replicate results on the same fuel deviating five percent or less from the results of the first run. Exhaust emission results from the alternate-source fuels tested in the earlier study(7) are not reiterated in this section. Some of those results are presented with the data from petroleum fuel studies in Section VII.

A. Regulated Gaseous and Particulate Emission Results

Data on regulated gaseous emissions, including CO_2 and fuel consumption, were obtained by analysis of bag samples collected from the CVS-diluted exhaust. Particulate results were obtained concurrently by filtration of diluted exhaust. These results are summarized in Tables 6 and 7. They are reported for each individual bag, a calculated 3-bag FTP, and a calculated 4-bag FTP. The computer printouts for all the tests are located in Appendix C, pages C-2 through C-15.

TABLE 6. AVERAGE REGULATED GASEOUS EMISSIONS DATA

Fuel	Item	Emissions (g/km) and Fuel Usage (ℓ/100 km) by Driving Schedule									
		FTP Bag Number				(Calculated)	(Calculated)		Steady-State		
		1	2	3	4	3-bag FTP	4-bag FTP	HFET	Idle[a]	50 kph	85 kph
Base EM-329-F	HC	0.40	0.26	0.33	0.25	0.31	0.31	0.35	2.13	0.17	0.39
	CO	1.23	0.82	1.03	0.80	0.96	0.95	1.04	9.30	0.54	1.20
	CO_2	179.	164.	156.	163.	165.	165.	133.	1136.	124.	134.
	NO_x	0.67	0.67	0.64	0.66	0.66	0.66	0.61	5.78	0.53	0.67
	Fuel	6.94	6.33	5.95	6.32	6.37	6.36	5.17	0.44	4.77	5.22
SASOL EM-527-F	HC	0.51	0.21	0.39	0.18	0.32	0.31	0.23	1.56	0.14	0.24
	CO	1.43	0.88	1.21	0.82	1.08	1.07	1.25	7.95	0.54	1.38
	CO_2	174.	156.	150.	152.	158.	157.	132.	1125.	116.	129.
	NO_x	0.64	0.65	0.62	0.66	0.64	0.64	0.60	5.52	0.52	0.60
	Fuel	7.05	6.24	6.05	6.08	6.35	6.30	5.35	0.45	4.66	5.24
25% H-Coal EM-526-F	HC	0.50	0.31	0.35	0.22	0.36	0.33	0.39	10.74	0.38	0.35
	CO	1.33	0.97	0.97	1.06	1.12	1.15	1.28	24.69	0.79	1.12
	CO_2	184.	164.	158.	160.	166.	165.	143.	1067.	119.	143.
	NO_x	0.72	0.72	0.70	0.71	0.71	0.71	0.74	5.31	0.53	0.73
	Fuel	6.88	6.07	5.89	5.91	6.18	6.14	5.34	0.42	4.42	5.33

[a] Emission in g/h instead of g/km, fuel in ℓ/h instead of ℓ/100 km

The SASOL middle distillate fuel yielded gaseous and particulate emission results similar to the base fuel, EM-329-F, during the FTP. Fuel consumption was also unaffected. During the HFET, the SASOL fuel was

TABLE 7. AVERAGE PARTICULATE MASS EMISSIONS DATA

Fuel Code	Fuel Type	Grams Particulate per Kilometer				
		Calculated 1981 FTP	HFET	Steady-State		
				Idle[a]	50 kph	85 kph
EM-329-F	Base DF-2	0.25	0.25	0.71	0.17	0.28
EM-527-F	SASOL	0.23	0.25	0.42	0.14	0.27
EM-526-F	25% H-Coal	0.28	0.33	1.11	0.18	0.31

[a] Emissions in g/h instead of g/km

associated with a 34 percent reduction in HC, but a 20 percent increase in CO. A slight increase in fuel consumption was observed during the HFET. NO_x and particulate were essentially unaffected. The steady-state driving modes indicated that the SASOL fuel was generally associated with the same or slightly lower emission levels as compared to the base fuel. During the idle condition, particulate emissions with the SASOL fuel were about 41 percent lower.

Results with the H-Coal fuel blend, EM-526-F, indicated general increases in emissions and slight decreases in fuel consumption over both the transient cycles and all steady-states, as compared to the base fuel. The previous study(7) indicated similar results while testing a 25 percent EDS fuel blend. The EDS (Exxon Donor Solvent) material is a "first generation" coal-derived liquid produced by a process somewhat similar to the H-Coal process. Therefore, these results are not unexpected.

Of some interest is that data from the previous study(7) and this one have both shown that the "first generation" coal-derived materials tend to increase emissions. It was speculated in the earlier report that "second generation" materials would yield lower emissions than their "first generation" counterparts. The SASOL material, although not extracted from coal in the same way as the other coal liquids investigated, is an upgraded or "second generation" coal-derived fuel. This "second generation" material was associated with emissions similar to the base fuel. In the previous study, the upgraded shale oil liquids tested also yielded results similar to the base fuel. It is probable that further treatment of "first generation" coal-derived liquids by hydrogenation and catalytic cracking would result in "second generation" liquids which might not affect exhaust emissions adversely. This projection depends strongly on the degree of hydrotreatment used, and the desired quality of the end product.

B. Aldehyde and Phenol Results

Concentrations of several individual low-molecular weight aldehydes were determined in CVS-diluted exhaust. The results for each aldehyde species and their sums during the FTP are presented in Table 8. "Total" aldehydes refers to the sum of the individual aldehydes determined using the procedure discussed in Section IV. Table 9 represents the phenol results for the fuels tested. HFET results for both aldehydes and phenols are presented in Table 10. Aldehyde and phenol emissions for both alternate-source fuels were lower than those observed for the base fuel, regardless of driving cycle. These results were unexpected, and investigation into the analyses did not uncover any errors.

C. Results of Odor Analysis

This subsection contains results from instrumental odor evaluations (DOAS). The chromatographic procedure separates an oxygenate fraction (liquid column oxygenates, LCO) and an aromatic fraction (liquid column aromatics, LCA). Studies(11,16) have been made in an attempt to correlate instrumental analysis to a panel of trained human evaluators. One study(16) indicated that TIA (LCO-based) of less than 1.0 would be rated by a trained panel at less than "D"-1. A perceived odor intensity of "D"-1 by the Turk method is considered a light (barely perceptible) odor. It should be noted that since the TIA (total intensity of aroma) is calculated using a logarithmic equation, each increase of one unit in the TIA value relates to a concentration increase by a factor of ten.

Results of the odorant analysis are listed in Table 11. The TIA values (LCO-based) indicate that the SASOL fuel exhibited lower exhaust odorant levels than the base fuel. The 25 percent H-Coal blend, EM-526-F, was associated with higher exhaust odorant levels during the idle and 50 kph steady-state, but lower levels during the 85 kph steady-state condition. Similar results were reported in the earlier study(7) with the 25 percent EDS blend. In that study, the shale diesel marine resulted in lower odor levels than the base fuel.

D. Visible Smoke Emissions

Visible smoke was measured using an EPA-type smokemeter over the first 505 seconds (the "cold transient phase") of the FTP. Data taken on a 2-pen strip chart recorder consisted of vehicle speed and smoke opacity versus time. The traces, which were analyzed manually, are located in Appendix C, pages C-16 and C-17. The results, along with previously-run base fuel results, are summarized in Table 12.

These data show a marked increase of smoke during vehicle operation with the 25 percent H-Coal blend. Similar results were previously reported in the earlier study(7) with other coal-derived liquids. The SASOL fuel followed the trends reported with use of the Shale Diesel Marine fuel. During the cold-start and first acceleration, both fuels were associated with high smoke opacities as compared to the base fuel. During the second acceleration at 164 seconds, both fuels yielded lower smoke levels compared to the base fuel. Apparently, the Shale Diesel Marine and the SASOL combustion characteristics improve after vehicle warmup.

TABLE 8. FTP ALDEHYDE EMISSIONS DATA

Operating Schedule	Compound(s)	Concentration (mg/km) by Fuel Tested		
		Base EM-329-F	SASOL EM-527-F	25% H-Coal EM-526-F
Cold FTP	Formaldehyde	7.	0.0	0.0
	Acetaldehyde	2.	0.0	0.0
	Acetone[a]	2.	0.0	0.0
	Hexanaldehyde	0.0	0.0	0.0
	Benzaldehyde	0.0	0.0	0.0
	"Total"	11.	0.0	0.0
Hot FTP	Formaldehyde	10.	0.0	0.0
	Acetaldehyde	2.	0.0	0.0
	Acetone[a]	3.	0.0	0.0
	Hexanaldehyde	0.0	0.0	0.0
	Benzaldehyde	0.0	4.	0.0
	"Total"	15.	4.	0.0
Calculated 1981 FTP	Formaldehyde	9.	0.0	0.0
	Acetaldehyde	2.	0.0	0.0
	Acetone[a]	3.	0.0	0.0
	Hexanaldehyde	0.0	0.0	0.0
	Benzaldehyde	0.0	2.	0.0
	"Total"	14.	2.	0.0

[a] Includes acrolein and proponol

TABLE 9. FTP PHENOL EMISSIONS DATA

Operating Schedule	Compound(s)	Concentration (mg/km) by Fuel Tested		
		Base EM-329-F	SASOL EM-527-F	25% H-Coal EM-526-F
Cold FTP	Phenol	0.0	0.0	0.0
	Salicylaldehyde	0.0	0.0	0.0
	m-Cresol + p-Cresol	1.	0.0	0.0
	Group 5[a]	4.	0.0	0.0
	2,3,5-trimethylphenol	0.4	0.0	0.0
	2,3,5,6-tetramethylphenol	0.3	0.0	0.0
	2-n-propylphenol	7.	0.0	0.0
	"Total"	13.	0.0	0.0
Hot FTP	Phenol	0.0	0.0	0.0
	Salicylaldehyde	0.0	0.0	0.0
	m-Cresol + p-Cresol	0.1	0.0	0.0
	Group 5[a]	2.	0.0	0.0
	2,3,5-trimethylphenol	0.1	0.0	0.0
	2,3,5,6-tetramethylphenol	0.2	0.0	0.0
	2-n-propylphenol	8.	0.0	0.0
	"Total"	10.	0.0	0.0
Calculated 1981 FTP	Phenol	0.0	0.0	0.0
	Salicylaldehyde	0.0	0.0	0.0
	m-Cresol + p-Cresol	0.7	0.0	0.0
	Group 5[a]	3.	0.0	0.0
	2,3,5-trimethylphenol	0.3	0.0	0.0
	2,3,5,6-tetramethylphenol	0.3	0.0	0.0
	2-n-propylphenol	8.	0.0	0.0
	"Total"	12.	0.0	0.0

[a] Group 5 consists of p-ethylphenol, 2-isopropylphenol, 2,3-xylenol, 3,5-xylenol, 2,4,6-trimethylphenol

TABLE 10. HFET PHENOL AND ALDEHYDE EMISSIONS DATA

	Concentration (mg/km) by Fuel Tested		
Fuel Type	Base	SASOL	25% H-Coal
Fuel Code	EM-329-F	EM-527-F	EM-526-F
Phenols			
Phenol	0.0	0.0	0.0
Salicylaldehyde	0.0	0.0	0.0
m-Cresol + p-Cresol	1.	0.0	0.0
Group 5[a]	2.	0.0	0.0
2,3,5-trimethylphenol	0.03	0.0	0.0
2,3,5,6-tetramethylphenol	0.6	0.0	0.0
2-n-propylphenol	4.	0.0	0.0
"Total"	7.	0.0	0.0
Aldehydes			
Formaldehyde	9.	1.	0.0
Acetaldehyde	1.	0.0	0.0
Acetone[b]	5.	0.0	0.0
Hexanaldehyde	0.0	0.0	0.0
Benzaldehyde	0.0	0.4	0.0
"Total"	15.	1.	0.0

[a] Group 5 consists of p-ethylphenol, 2-isopropylphenol, 2,3-xylenol, 3,5-xylenol, 2,4,6-trimethyphenol

[b] Includes acrolein and propanol

TABLE 11. RESULTS OF ODOR ANALYSIS AT STEADY STATES

Date	Fuel Code	Fuel Type	Condition	LCA, µg/ℓ	LCO, µg/ℓ	TIA	
						LCA	LCO
12/12/80	EM-329-F	Base DF-2	Idle	55.	3.7	1.6	1.6
			50 kph	110.	7.5	1.8	1.9
			85 kph	400.	21.	2.2	2.3
11/9/82	EM-527-F	SASOL	Idle	7.4	1.5	1.0	1.2
			50 kph	30.	1.4	1.4	1.1
			85 kph	28.	4.8	1.4	1.7
11/12/82	EM-526-F	25% H-Coal	Idle	47.	5.9	1.6	1.8
			50 kph	41.	17.	1.5	2.2
			85 kph	81.	7.3	1.7	1.9

TABLE 12. SUMMARY OF VISIBLE SMOKE DATA

	Smoke Opacity, %, by Fuel		
Condition	329	527	526
Cold Start Peak	21.2	54.0	61.0
Cold Idle, avg. (after start)	0.2	0.7	0.5
1st Accel. Peak	28.2	39.0	54.5
Idle at 125 secs., Avg.	0.7	0.1	0.5
Accel. at 164 secs., Peak	37.5	24.5	56.2

E. Particulate Size Distribution

Data from impactor runs were analyzed, and are presented as percentage of the total particulate mass by stage in Table 13. These data show that, as observed earlier(7), over half the particulate mass was composed of particles smaller than 0.2 μm. In the case of the SASOL fuel, almost 75 percent of the particulate mass was under 0.2 μm.

TABLE 13. PARTICULATE SIZE DISTRIBUTION

Run No.	Fuel Code	Fuel Description	Percent of Total Particulate									Vehicle Total Particulate g/cycle[a]
			Stage 3 9.5 μm[a]	Stage 4 5.8 μm[a]	Stage 5 3.7 μm[a]	Stage 6 2.1 μm[a]	Stage 7 1.2 μm[a]	Stage 8 0.8 μm[a]	Stage 9 0.5 μm[a]	Stage 10 0.2 μm[a]	Filter	
1	EM-329-F	Base DF-2	4.9	2.7	6.3	4.4	8.2	5.0	6.1	7.9	55.	5.81
2	EM-329-F	Base DF-2	6.8	6.3	2.0	2.3	5.7	2.3	2.7	6.7	65.	6.05
1	EM-527-F	SASOL	5.8	2.3	1.4	5.9	2.3	3.2	3.2	1.3	74.	5.13
1	EM-526-F	25% H-Coal	2.5	3.8	3.9	6.8	4.8	3.2	5.1	5.2	65.	7.21

[a] Based on 47 mm Pallflex for 4-bag FTP

F. Analysis of Particulate Composition

This subsection includes data on major elements and trace elements. Carbon and hydrogen analyses were performed on particulate collected using 47 mm glass fiber filters. Particulate collected on 47 mm Fluoropore filters was analyzed for trace elements.

Carbon and hydrogen data are listed in Table 14. As seen in earlier studies(3,7), the data show fairly high carbon and low hydrogen content, indicative of "dry" or soot-like particulate material. The analyses on the SASOL and 25 percent H-Coal blend were performed approximately a year later

TABLE 14. CARBON AND HYDROGEN IN EXHAUST PARTICULATE MATTER

Fuel Code	Fuel Description	Cycle	Weight Percent	
			Carbon	Hydrogen
EM-329-F	Base DF-2	FTP_c	81.6	2.8
		FTP_h	80.3	2.7
		HFET	83.6	2.9
EM-527-F	SASOL	FTP_c	92.8	2.7
		FTP_h	93.1	3.1
		HFET	91.4	2.9
EM-526-F	25% H-Coal	FTP_c	91.1	3.0
		FTP_h	92.5	3.1
		HFET	84.0	2.6

than those reported in the earlier study.(7) Results from both studies do not indicate any trends. As stated in other studies(3,6,7), the technique used to analyze carbon and hydrogen content of particulate collected on glass fiber filters appears somewhat questionable. A new procedure is needed to insure correct and accurate analysis of particulate collected on glass fiber filters.

Date on trace elements are given in Table 15. As a whole, these elements made up 0.3 to 2.1 percent of the particulate mass. The trace elements found most commonly in the particulate matter were sulfur, iron, nickel, calcium, and zinc. Possible sources of iron and nickel are wear products from the engine and exhaust system. Suflur, calcium, and zinc can probably be attributed to fuel sulfur and lubricating oil additives. Of some interest was the presence of a measureable amount of lead when the SASOL fuel was used during the cold-start FTP. The earlier study(7) reported lead only with the 25 percent SRC-II blend (a non-upgraded coal-derived liquid).

TABLE 15. PERCENT TRACE ELEMENTS IN PARTICULATE MATTER

Elements	Weight Percentage of Particulate Matter by Fuel and Cycle								
	EM-329-F Base			EM-527-F SASOL			EM-526-F 25% H-Coal		
	FTP_c	FTP_h	FET	FTP_c	FTP_h	FET	FTP_c	FTP_h	HFET
Mg	0.018	0.011	0.004	0.016	0.007	0.013	0.016	0.013	0.010
Al	0.025	0.009	0.003	0.012	0.005	0.005	0.014	0.004	0.005
Si	0.048	0.022	0.005	0.006	0.000	0.000	0.015	0.007	0.000
P	0.039	0.029	0.009	0.017	0.008	0.014	0.038	0.023	0.033
S	0.741	0.427	0.254	0.176	0.051	0.071	0.727	0.527	0.849
Cl	0.003	0.005	0.001	0.003	0.000	0.006	0.000	0.000	0.000
Ca	0.082	0.035	0.007	0.020	0.013	0.012	0.028	0.016	0.015
Ti	0.005	0.000	0.001	0.000	0.000	0.000	0.003	0.003	0.003
Fe	0.388	0.145	0.029	0.448	0.154	0.150	0.688	0.387	0.437
Zn	0.051	0.040	0.009	0.029	0.000	0.032	0.051	0.033	0.051
Sn	0.008	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.002
Ba	0.004	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000
Cr	0.000	0.008	0.000	0.020	0.000	0.000	0.000	0.000	0.000
Pb	0.000	0.000	0.000	0.088	0.000	0.000	0.000	0.000	0.000
Mn	0.000	0.000	0.000	0.006	0.000	0.000	0.000	0.000	0.000
Br	0.000	0.017	0.000	0.044	0.000	0.000	0.000	0.000	0.000
Cd	0	0	0	0	0	0	0	0	0
K	0.009	0.003	0.001	0.000	0.000	0.000	0.000	0.000	0.000
Cu	0	0	0	0	0	0	0	0	0
Ni	0.096	0.016	0.005	0.092	0.000	0.020	0.058	0.019	0.021
V	0.000	0.000	0.001	0.008	0.000	0.008	0.000	0.008	0.006
Sb	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mo	0	0	0	0	0	0	0	0	0
Total Percentage of Particulate	1.517	0.770	0.329	1.410	0.643	1.012	2.152	1.557	1.838

G. Composition of Organic Solubles in Particulate Matter

The organic soluble portion of the particulate was obtained from particulate samples collected on 20x20 inch Pallflex filters, using a Soxhlet extraction procedure (methylene chloride as solvent). A portion of the organic soluble material was analyzed for carbon and hydrogen. The results are given in Table 16. All of the elemental data for the FTP are indicative of hydrocarbon-like materials (numeric H/C ratio approximately 1.80). The SASOL and 25 percent H-Coal solubles yielded a numeric H/C ratio of about 1.5 during the HFET. This ratio is somewhat lower than reported in other studies.(3,6,7) Since extractions are performed with a relatively non-polar solvent (methylene chloride), the material extracted should be hydrocarbon-like. A pure hydrocarbon yielding a numeric H/C ratio of 1.15 would be made up of approximately 91 percent carbon and 9 percent hydrogen, with an emperical formula similar to benzene. The sum of carbon and hydrogen for the HFET's is approximately 88 percent. The remaining 12 percent could be speculated to be oxygen, but the aldehydes, phenols, and the analysis of the total particulate do not support this speculation.

TABLE 16. COMPOSITION OF THE ORGANIC SOLUBLE PORTION OF THE PARTICULATE

Fuel Code	Fuel Description	Cycle[a]	Weight Percent	
			Carbon	Hydrogen
EM-329-F	Base DF - 2	FTP	85.2	12.9
		HFET	85.5	12.9
EM-527-F	SASOL	FTP	84.3	12.0
		HFET	80.9	7.7
EM-526-F	25% H-Coal	FTP	82.8	11.0
		HFET	81.9	8.2

[a] "4-bag" FTP's

H. Gas Chromatograph "Boiling Range" Analysis of Organic Solubles

The organic soluble portion of particulate matter resembles a very heavy oil or a varnish. A high-temperature GC-simulated boiling point distribution, with an internal standard, was run on organic soluble material from particulate generated with each fuel. Table 17 summarizes the results for samples generated during both the FTP and HFET. The chromatograms for all of the samples summarized in Table 17 are located in Appendix C, Figures C-3 through C-6.

Both FTP and HFET results show that solubles from tests on the SASOL and 25 percent H-Coal test fuels show slightly lower boiling ranges as compared to the base fuel. The SASOL fuel gave a boiling range similar to that observed with the Broadcut fuel tested in the earlier study.(7)

TABLE 17. CHROMATOGRAPH ANALYSIS OF ORGANIC SOLUBLES IN PARTICULATE MATTER

	Boiling Temperature, °C, at Distillation Point by Fuel during 4-Bag FTP		
Fuel Description	Base DF-2	SASOL	25% H-Coal
Fuel Code	EM-329-F	EM-527-F	EM-526-F
IBP	318	253	269
10% point	365	342	337
20% point	388	377	353
30% point	416	406	395
40% point	451	428	420
50% point	494	452	449
60% point	537	479	482
70% point	605	512	522
80% point	-	564	603
90% point	-	-	-
EP	-	-	-
%Recovery @ 640°C	70.0	83.8	79.6

	Boiling Temperature, °C, at Distillation Point by Fuel during HFET		
Fuel Code	EM-329-F	EM-527-F	EM-526-F
IBP	325	278	262
10% point	374	353	341
20% point	400	396	376
30% point	429	418	410
40% point	462	438	437
50% point	492	460	464
60% point	526	482	493
70% point	582	510	530
80% point	-	555	603
90% point	-	-	-
EP	-	-	-
%Recovery @ 640°C	71.7	84.5	80.3

I. Fraction by Relative Polarity

Composition of the soluble organic fraction of the particulate is complex, and its separation into individual compounds is very difficult. Fractionation of the organic solubles by high performance liquid chromatography (HPLC) separates the soluble portion into a series of fractions of increasing molecular polarity. This procedure(14) is not quantitative, but provides a method to collect fractions with generally different polarities. All samples were analyzed at the same ratio of organic extract and carrier solvent. Therefore, the results can be compared to one another on a relative basis to estimate increases or decreases of compound classes which differ from each other by molecular polarity. Figures 2 through 5 show the HPLC chromatographic outputs for direct comparison of the relative response of increasingly polar compounds at the wavelengths discussed in Section IV, Part E-5 of the report.

Each figure contains three traces, one representing the carrier solvent composition, a second representing the ultraviolet detector response, and the

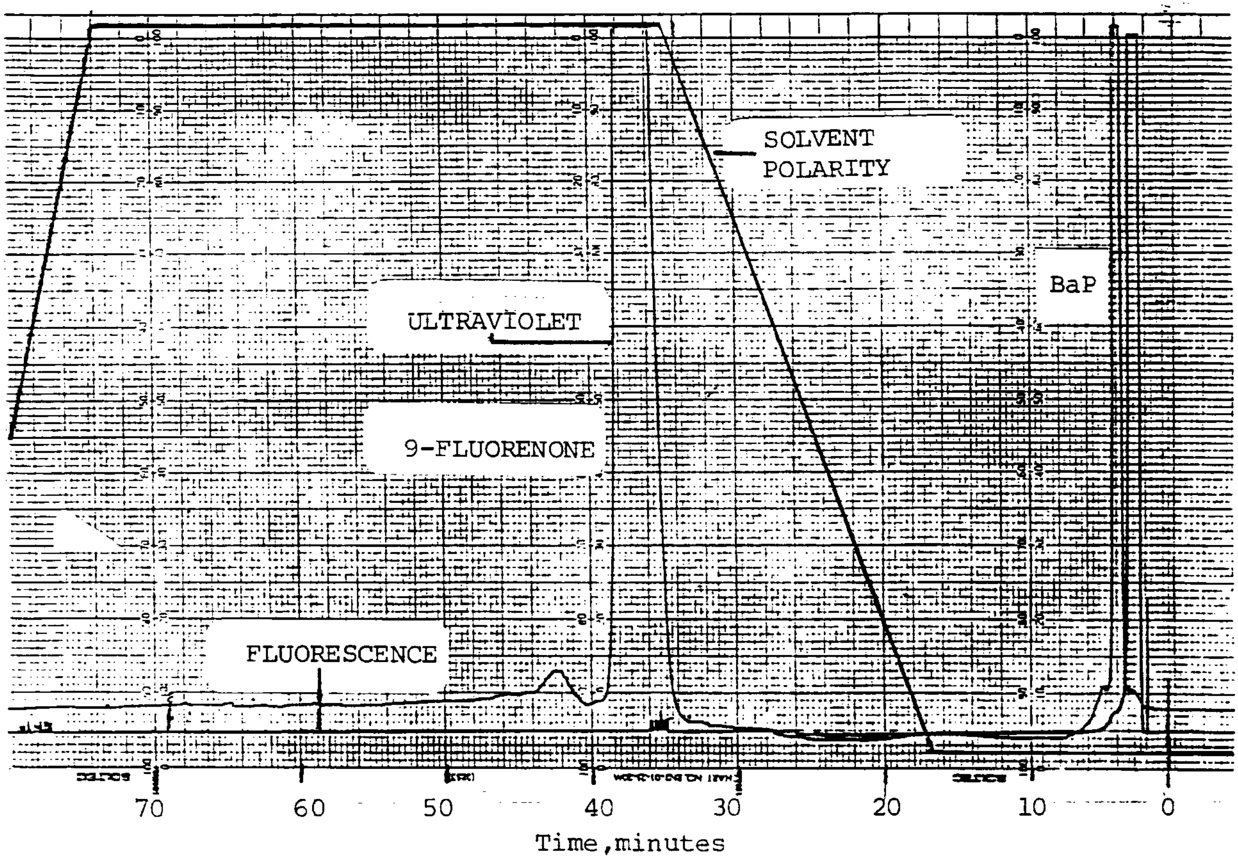

Figure 2. HPLC response to BaP and 9-fluorenone

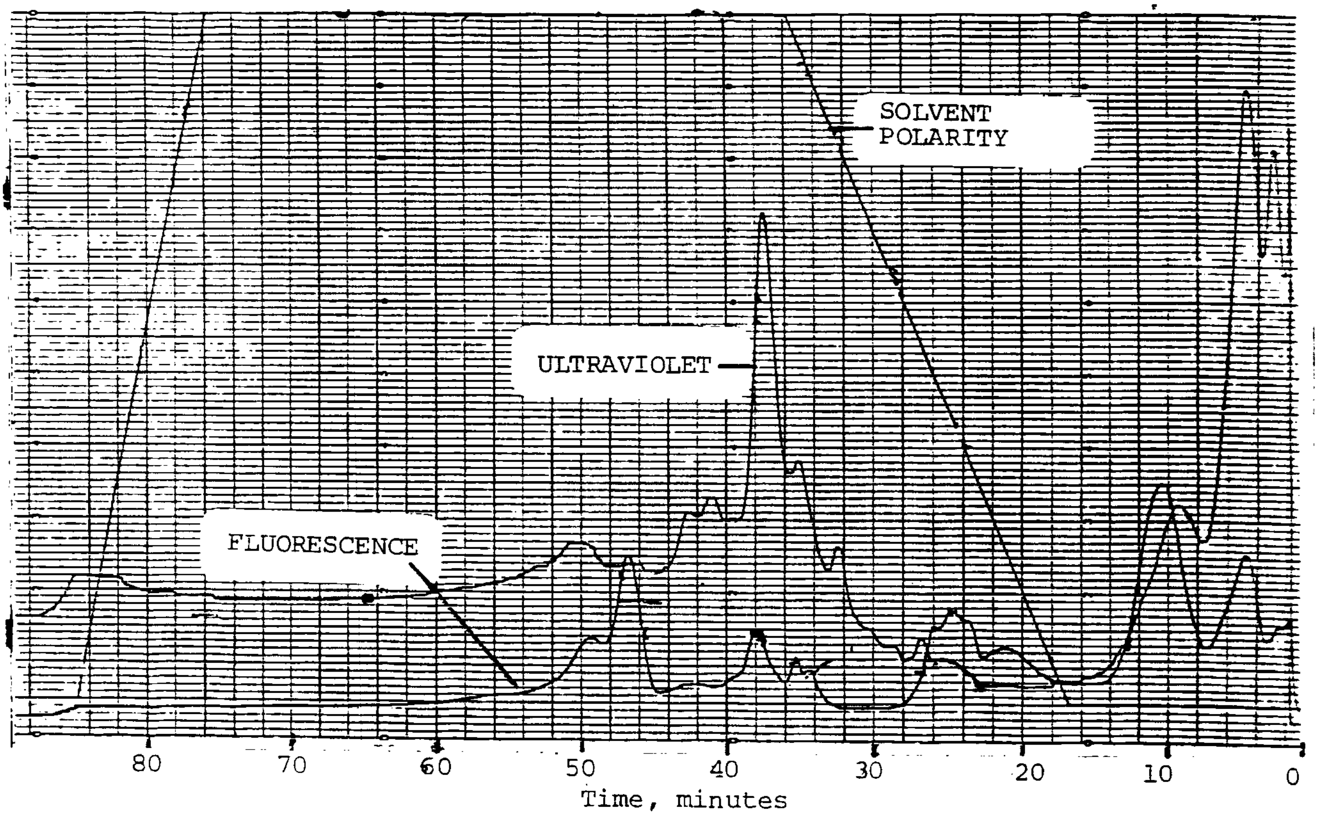

Figure 3. HPLC response to extract generated from base DF-2

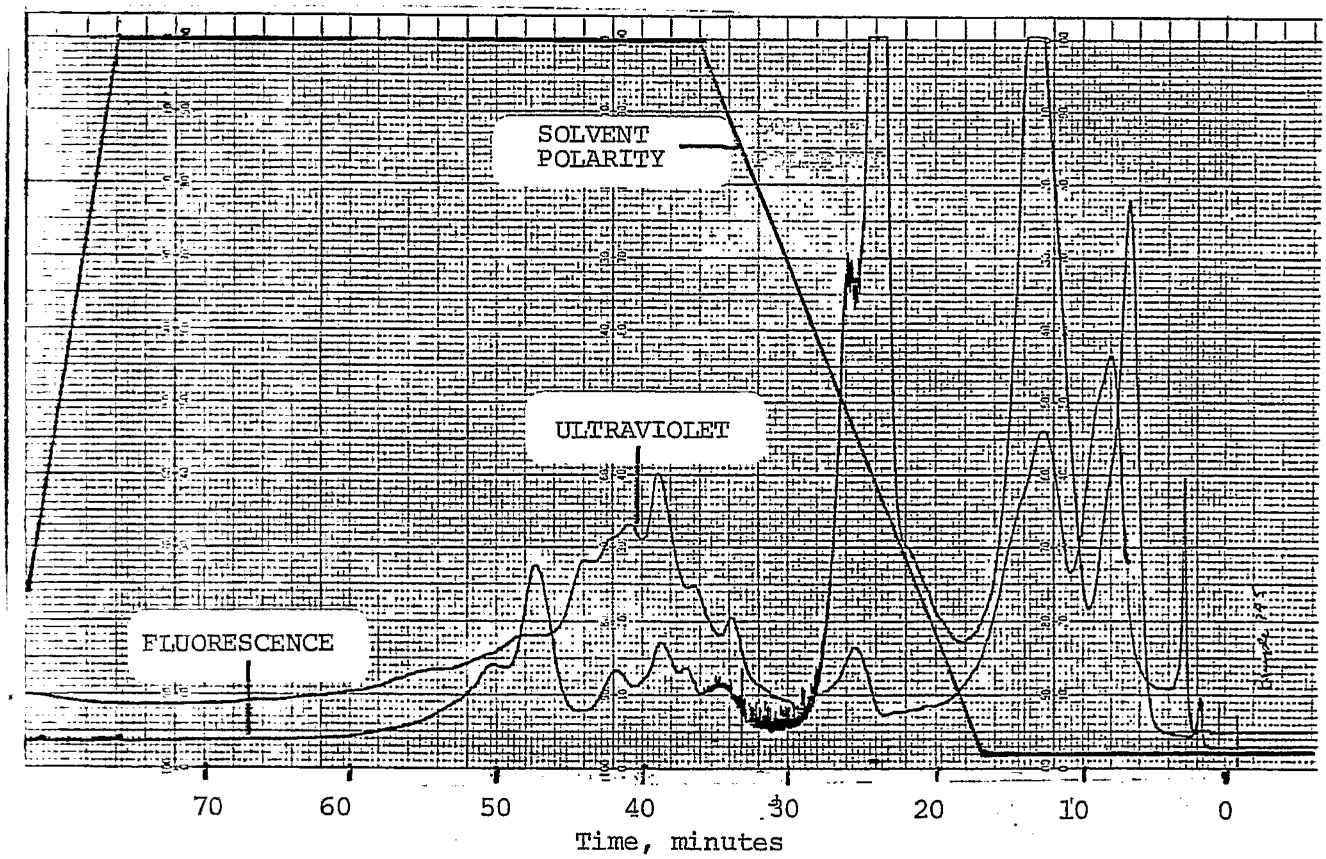

Figure 4. HPLC response to extract generated from SASOL middle distillate

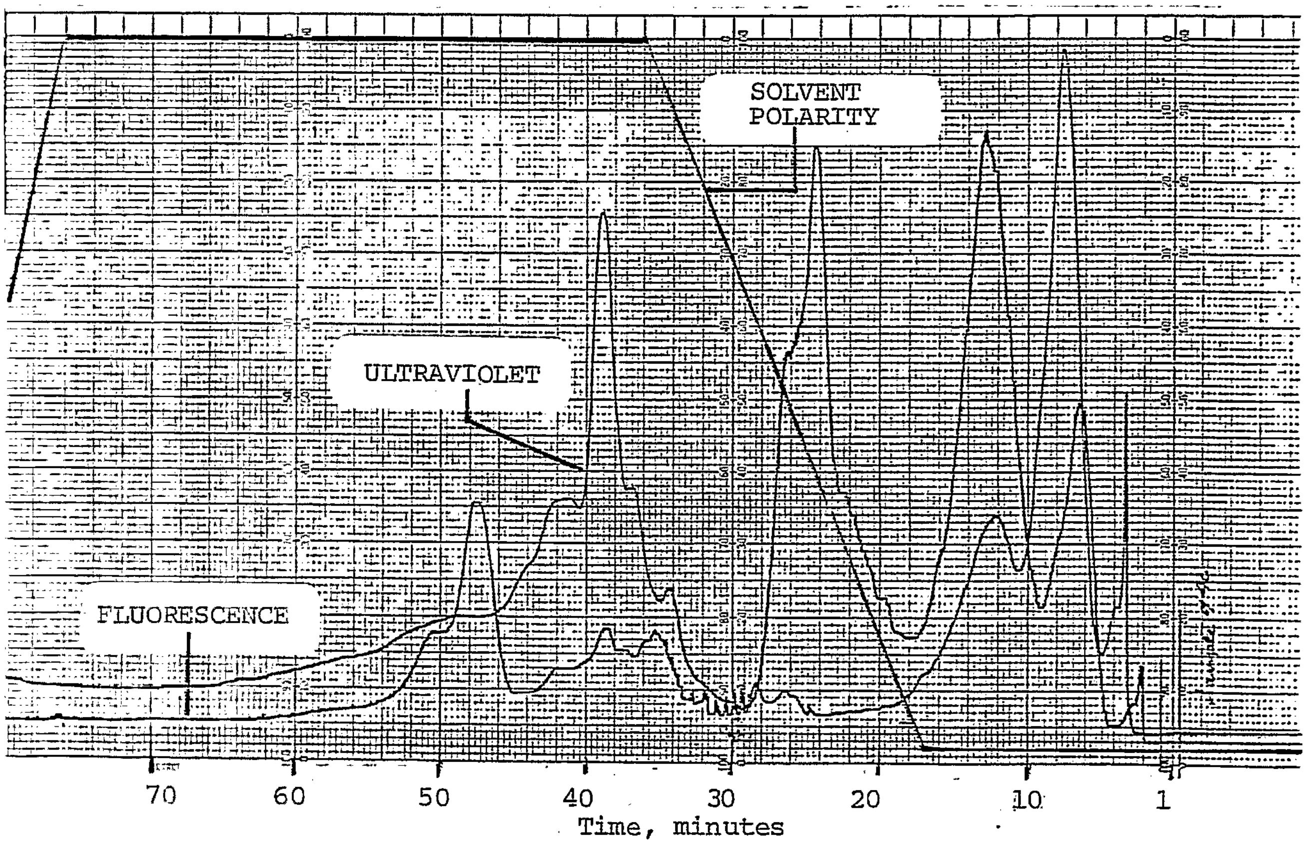

Figure 5. HPLC response to extract generated from 25% H-Coal

third representing the fluorescence detector response. Figure 2 shows the response of BaP and 9-fluorenone. BaP and similar compounds elute in this non-polar region. Near the end of the transition period (i.e., solvent polarity now polar), 9-fluorenone elutes. With 100 percent methylene chloride, even more polar compounds elute. For example, acridine elutes during this polar period (at about 70 minutes).

A CRC study(14) indicated that compounds which fluoresce in the transition fraction (at 20 to 30 minutes elution time, a fraction of intermediate polarity) yielded the highest Ames response (i.e., mutagenic activity). During this period, 20.9 percent of the Ames activity was associated with 2.5 weight percent of the organic soluble material. The greatest fluorescence response in this fraction (20 to 30 minutes elution time) was associated with the SASOL fuel. In the earlier study(7), the Paraho JP-5 (a shale oil fuel) yielded the highest fluorescence response. The H-Coal response was similar to the SRC-II blend reported earlier.(7) In summary, based on the results of the aforementioned CRC data and this study's fluorescence data, increases in Ames activity as compared to the base fuel might be projected for both the SASOL and the 25 percent H-Coal blend.

J. Benzo(a)pyrene (BaP) in Organic Solubles

BaP results are presented in Table 18 along with percentage of organic solubles in particulate matter. The BaP present in the organic soluble portion of the particulate for the fuels tested is substantially higher (about a factor of 10) than that found in other studies.(3,6,17) These results are consistent with those observed in the earlier study(17) using the same vehicle.

TABLE 18. BaP PRESENT IN ORGANIC SOLUBLES DURING $FTP_c + FTP_h$

Fuel Code	Fuel Description	Filter No.	Particulate g/km[a]	Percentage Extractables	% BaP in Extract	BaP µg/km
EM-329-F	Base DF-2	P20-82,83	0.25	14.6	0.042	14.9
EM-527-F	SASOL	P20-9,10	0.23	15.3	0.057	19.6
EM-526-F	25% H-Coal	P20-18,19	0.28	16.9	0.039	19.0

[a] based on 47 mm Pallflex

The BaP emissions for both the SASOL and 25 percent H-Coal blend were about 30 percent higher than those observed with base fuel. BaP emissions for most of the other alternate-source fuels tested earlier(7) were generally twice to three times the baseline levels.

K. Mutagenic Activity by Ames Testing

An additional amount of organic solubles representing each fuel tested was reserved for Ames bioassay analysis. The Ames test refers to a bacterial mutagenesis plate assay with Salmonella typhimurium according to the method of Ames.(13) The original test plan called for the Ames analysis to be performed by an outside laboratory under a separate EPA contract. Funding for this analysis was not included under Contract 68-03-3073, so it can not be performed at this time. It is anticipated that a new contract will be issued to complete these analyses, but it has not yet been finalized at this writing.

VII. STATISTICAL ANALYSIS OF FUEL AND EMISSIONS DATA

This report section discusses the application of several statistical computer programs to fuel and emissions variables. The principal goal was to determine, in a broad sense, the degree to which variation in alternate-source fuels affects exhaust emissions as compared to variation in petroleum fuels.

A. Statistical Methodology

Several approaches were developed to analyze data taken in the study and the data available in the literature. Alternate-source data from an earlier EPA study$^{(7)}$, this study, data available in previous EPA fuel variables work, and published literature were normalized to evaluate whether or not changes in emissions are affected by the source of the fuel (coal, shale, petroleum, etc.).

Originally, the prediction equations developed under EPA Contract 68-03-2707$^{(3)}$ were to be used in conjunction with the properties of the alternate-source fuels to yield predicted emissions, as if the alternate-source fuels were petroleum fuels. This study$^{(3)}$ used a Mercedes Benz 240D to evaluate petroleum fuel variation effects on exhaust emissions. The data from that study were subjected to multiple linear regression analysis to yield exhaust emission prediction equations as functions of fuel properties.

Requests to insert alternate-source fuel properties into petroleum fuel regression equations developed under Contract No. 68-03-2707 could not be answered straightforwardly without several critical assumptions. Due to the test designs of the two studies, they are essentially unrelated to each other because of vehicle differences (VW vs. Mercedes). Normalization of the Mercedes prediction equations would have involved a third study, in which both a Mercedes and a Volkswagen Rabbit were tested on the same fuels. This third study could have been used to determine the relationship between the two vehicles by determining a vehicle response factor, or equation which, when applied to Mercedes petroleum fuel prediction equations, would have resulted in petroleum fuel prediction equations for the VW. Insertion of alternate-source fuel properties into the VW equations would have yielded predicted emissions as if the fuels were petroleum-based. Comparison between these predicted values and the actual observed values using alternate-source fuels would have been used to determine if alternate-source fuel property variations were responsible for greater, lesser, or similar changes in emissions as compared to petroleum fuel property variations.

Determination of a vehicle response factor would have been difficult. In order to minimize the cumulative errors that would have occurred, the stuty conducted should have contained as many similarities as possible in terms of engine size, inertia settings, sample acquisition, analytical techniques, etc., to both the study which developed the Mercedes prediction equations and this current study. One study, performed at SwRI under Contract No. 68-03-2440$^{(6)}$, incorporated the identical Mercedes 240D used to develop prediction equations. The VW used in Contract No. 68-03-2440 was a different vehicle model year, although the engine displacement, inertia, horsepower setting, and transmission shift points were identical. Comparison of FTP emissions from the two VW Rabbits, both operated on "National Average" No. 2 diesel fuel (but different lots), showed that the vehicles did not respond similarly. If an assumption were made that the response difference was due to different diesel fuel lots, and that both VW's would respond identically if the exact same fuel were used, then the VW used in Contract No. 68-03-2440 could be used to determine a relationship between the Mercedes (petroleum-based prediction equation study) and the VW used in the alternate-source study.

Several other more critical assumptions would have been necessary. A vehicle response factor for each emission concerned would have been developed. The study under Contract No. 68-03-2440 did not result in prediction equations for most of the emissions with which we are concerned. At a minimum, the data in Contract No. 68-03-2440 would have been utilized again to establish some relationship between fuel properties and exhaust emissions for the Mercedes and VW Rabbit. If the relationships yielded equations containing the same fuel properties as variables, high R-squares, and low standard deviations, then the two vehicles could have been linked by some factor. If the resulting regression equations for the two vehicles were parallel, then a single vehicle response factor would have resulted. If the regression equations yielded non-parallel lines, then the vehicle response factor itself would have been in the form of another equation. Without this exercise to determine regression equations, a vehicle response factor for a particular point (i.e., one fuel property value) would have resulted. This resulting factor would have only been applicable to one point of the alternate-source fuel data, and general trends could not have been determined. Even if regression equations for both vehicles could have been determined, any error associated with each equation would have been cumulative, and would have eventually affected the final calculated VW prediction equations.

Assuming success to this point, two approaches existed. First, the vehicle response factor would have been applied to the Mercedes prediction equations determined in Contract No. 68-03-2707 to yield VW prediction equations. The accuracy of the Mercedes equations themselves would have to be verified first. Brief evaluation of the Mercedes prediction equations had shown poor prediction capabilities, however, due to a lack of population dispersion for fuels in that study.(6) Using these equations would have introduced additional error. The second approach involved using the prediction equations generated from the Mercedes/VW study (Contract No. 68-03-2440)(3), assuming that prediction equations were obtainable and that the 1977 model VW generated emission trends identical to the 1980 model VW, and inserting alternate-source properties into these equations to yield emissions as if the fuels were petroleum-based. This approach would have avoided probable errors that would have been introduced if vehicle factors had to be determined and then applied to the questionable Mercedes prediction equations. In any case, the procedures thus far discussed make many assumptions and introduce errors that may be large enough to invalidate any conclusions reached.

An alternate approach was reviewed to satisfy the objective of determining whether or not alternate-source materials affect exhaust emissions in the same way as petroleum fuels. This approach involved reviewing data available in previous EPA fuel variables work and other published literature to select studies that had some common element between the alternate-source study and petroleum studies. For example, studies chosen would incorporate a "base" fuel that is similar in properties. This criterion would reduce the number of studies to a workable matrix. The data from selected studies (about 12 were anticipated) would be grouped according to similar fuel property/exhaust emission interactions. For example, those studies which have shown a relationship between fuel aromatics and particuate emissions would be grouped together. Studies which resulted in a viscosity/particulate relationship would be in another group.

Each group would be treated separately. The data from each study within a particular group would be normalized to the "base" fuel for that study. The resulting normalization would express the various emissions data in terms of percent change from baseline data. The alternate-source study data would be treated similarly to determine if comparable changes in fuel properties would affect exhaust emisisons more, less, or the same as the results seen in studies dealing with petroleum base stocks.

In order to better visualize this approach, Table 19 presents mock data from studies reviewed and the alternate-source study. The following discussion is an example of what the table may be describing.

> "Table 19 shows the results of fuel aromatic content on particulate emissions. It should be noted that although an attempt was made to choose studies that began with a base fuel of similar properties, this was not the case for study D's aromatic content (study D was chosen for another fuel property matrix). Due to the apparent sensitivity of additional aromatics after a critical level, study D's results are not considered representative and comparable to the other petroleum fuel studies. Its data were therefore not included in averaging."

> "Another point to consider is that only study B incorporated a VW Rabbit. The other studies used different vehicles. The average, therefore, is affected by a variation in vehicle combustion characterisitics. Direct comparison between the average data from the alternate-source study with a VW Rabbit and the petroleum fuel study (study B) with a VW Rabbit showed that aromatic increases in the alternate-source materials did not affect particulate emissions."

The advantages of this approach would have been that no prediction equations were used directly (avoiding potentially high errors), vehicle response factors were not required, few assumptions were necessary, and a greater number of outside studies could have been used. Some disadvantages would have been that studies chosen may have had diverse base fuels which were not similar in properties. This situation would not have been apparent

TABLE 19. PARTICULATE EMISSIONS VERSUS FUEL AROMATIC CONTENT, MOCK DATA

	Particulate Emissions % Δ from Baseline Study						
Aromatic Content % Δ from Base	Alternate Source VW	Mercedes 240D	A	B	C	D[a]	Average[b]
1-25	0.1	0		0.5	--	10.	0.25
26-50	0.9	--	-1.0	5.	--	--	2.
51-75	4.	--	--	7.	--	40.	7.
76-100	8.	20.	10.	10.	10.	--	12.5
101-150	--	--	20.	30.	25.	--	25.
151-200	50.	--	--	40.	70.	--	55.
Average	12.6	--	--	12.5[c]	--	--	15.4[c]

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[a] Study D base fuel's aromatic content was twice that of other studies

[b] Study D is not included in the average

[c] Average does not include 101-150% Δ aromatic content

"Conclusions:"

1. At each range of Δ aromatic content, the alternate-source materials were associated with a smaller increase in particulate emissions as compared to the average results of petroleum based fuel studies.

2. On the average throughout the aromatic content range, the alternate-source fuels were associated with about 18% less particulate emissions as compared to the average of all the petroleum-based fuel studies. Comparing the alternate-source study (VW) with study B (VW) shows that the alternate-source fuels did not affect particulate emissions.

3. Study D exhibited the greatest increase of particulate emissions with minimal change in aromatic content. Probable cause was the initially high aromatic levels of that study's base fuel.

when reviewing the table. Other parameters such as engine displacment and driving schedules would also have been "buried" in the table. The range of a particular fuel property may not have been evenly spaced to cover each study properly. These potential inconsistencies may have resulted in a table which contained only a few elements, and in any case, would have not shown any type of population dispersion.

A third approach, which incorporated some of the techniques of the two aforementioned approaches, involved both a visual representation and a prediction equation. Due to the wide variety of vehicles, fuels, test cycles, and measurement techniques used in previous studies, a method to relate all these studies in terms of general trends was adopted. This method involved reviewing each study dealing with petroleum fuels for emission trends. Those studies which indicated similar fuel property-exhaust emission relationships (primarily one-to-one relationships) were grouped together. The data from each study were normalized to a predetermined fuel property level (similar to National Average No. 2D). The normalized data set for each study was plotted on a common graph. The resulting graph showed emission trends as a function of petroleum fuel property with a variety of vehicles, base fuels, and driving cycles. A band encompassing the plotted data represented a population dispersion of petroleum-based fuel effects studies. Data from the alternate-source fuel study were also normalized and plotted on the same graph. Where the alternate-source study's line fell in relation to the petroleum-based fuel's band described the comparative effects of using alternate-source fuels.

Data from the petroleum-based fuel studies' band were subjected to linear regression analysis to determine an equation which represented all of the studies evaluated. This equation was used in conjunction with the alternate-source fuel study's fuel properties to yield predicted emissions based on petroleum fuel trends. Comparisons between predicted emissions and observed emissions from the alternate-source study were analyzed using chi-square test for goodness-of-fit, and conclusions were reached about alternate-source fuel effects on emissions as compared to average trends seen in petroleum-based fuel studies.

Other options may have existed to satisfy the objectives of this project. It was our opinion, however, that the third approach satisfied the objectives without involving too many assumptions or possible misrepresentation of the data. In addition, the third approach allowed for inclusion of as many studies as desired without their having to meet restrictive criteria. During a November 2, 1982 meeting at SwRI, the Branch Technical Representative approved the third approach. Past studies have shown that fuel property-exhaust emission relationships are not simple one-to-one correlations. Unless a test plan has been designed essentially without compromise, statistical analysis should not be overly complex, but should only be used in general terms to describe trends.

At the request of the Branch Technical Representative, an expanded discussion of the third approach to the statistical analysis (from a statistician's perspective) was written. Dr. Robert L. Mason of SwRI's Department of Fuels and Lubricants Technology assisted in the expansion and discussion of the third approach. His discussion is located in Appendix D, pages D-2 through D-5, for reference.

B. Raw Data Acquisition

Raw data representing the alternate-source fuels were obtained by combining results generated in this study with results reported in the earlier study.(7) Raw data representing petroleum fuels were obtained by performing a library literature search dealing with diesel fuel effects on emissions from light-duty vehicles. The initial search resulted in a listing of 37 references. These references were reviewed along with other available materials to determine which studies met basic criteria. Criteria for selection were: more than one petroleum-based fuel evaluated, adequate fuel analysis, exhaust emissions measurements, and use of a light-duty 4-stroke engine (<7 liters displacement). For example, studies dealing with the effects of methanol were not useful in satisfying the objective of this study. After review, a total of 9 references met the criteria. In those nine, a total of 15 test cases were available (some studies used multiple vehicles, and each vehicle was considered a test case). Studies used are listed as references 3, 6, and 18 through 24.

The statistical packages used for analysis of the data were SPSS (Statistical Package for the Social Sciences)(25) and BMDP (Biomedical Computer Programs).(26) Selected programs for each of these packages were used to evaluate the data.

C. Selection of Variables and Study Identification

The total number of fuel property and exhaust emission variables was too large to form a reasonable test matrix. During the November 2, 1982 meeting at SwRI, the Branch Technical Representative approved 8 fuel properties and 9 exhaust emission variables for further consideraiton. Fuel properties chosen were: density, aromatics, olefins, cetane number, gum, nitrogen content, 90 percent boiling point, and 10 percent boiling point. Exhaust emissions selected were: HC, CO, NO_x, particulate, fuel consumption, organic solubles, aldehydes, phenols, and BaP. Gum was later deleted from further consideration because only one study reported gum values for the fuels tested. This matrix was filled by data from the fuel studies selected.

In the nine petroleum-fuel studies, there were a total of fifteen cases of fuel property effects on exhaust emissions. The raw data for the studies available are listed in Appendix D, pages D-6 through D-8. At the request of its author, the raw data for Study H were not published; however, the normalized data were approved for publication. Each case was identified as a "Study ID" number. Cases conducted under the same study were identified by "Study Info". For example, B1 and B2 are both from the same study, but represent two different vehicle types, and therefore, two separate cases. Study K1 consists of data representing the alternate-source fuels.

The raw data from the petroleum fuels studied in each case were subjected to a bivariate correlation procedure to generate Pearson's correlation coefficients. Coefficients were determiend for "fuel property-fuel property", "emission-emission," and "fuel property-emission" relationships. All the coefficients were reviewed to determine trends depicted in all the test cases. Coefficients less than 0.700 were not considered as representing a usable correlation. A summary of the occurrence of coefficients greater than 0.700 is listed in Tables 20 through 22. The complete computer printout is too voluminous to include in this report.

Primary interest was in the fuel property-exhaust emission relationships. Another bivariate correlation procedure was performed on the alternate-source data. Raw data for this study are located in Appendix D, page D-8, as Study K. The fuel property-emission matrices for this study are shown as Table 23. Criteria for selecting fuel property-emission data pairs for further analysis were as follows:

1. Alternate-source study's data pairs which yielded coefficients greater than 0.700.
2. Data pairs in Table 20 which contained a large number of studies.
3. Data pairs which intuitively may have been related, but did not yield high coefficients.

Based on the above criteria, the fuel property-exhaust emission data pairs are shown in Table 24. The combination of data pairs covers most of the original fuel properties and exhaust emissions originally selected. Phenols were not analyzed further because only one petroleum study contained phenol analysis. Table 25 lists the Pearson correlation coefficients of the data pairs in Table 24 for all the studies.

D. Data Normalization

In order to account for the wide variety of vehicles, fuels, test cycles, and measurement techniques used in the various test cases, a method to relate all these cases in terms of general trends was developed. The exhaust emission data from all test cases were normalized to each of the selected fuel properties. The fuel property level was based on an average of several Phillips 2D Emissions Grade control fuel lot analyses. Averages were rounded for ease of insertion into calculations and data discussion. Fuel property analyses of the Phillips control fuel are listed in Table 26.

None of the test cases evaluated a fuel with the exact fuel property levels listed in Table 26. Therefore, linear regression analysis was performed on each of the selected fuel property-exhaust emission data pairs for each study case. The resulting equations were used in conjunction with the appropriate fuel properties from Table 26 to yield prediction of emissions. The prediction for each data pair and case was used to normalize (by division) the corresponding raw emissions data. This process could have resulted in

TABLE 20. NUMBER OF PEARSON CORRELATION COEFFICIENTS GREATER THAN 0.700 FOR FUEL PROPERTIES VS. EMISSIONS

	Number of Studies Where Coefficients were >0.9(1st digit), 0.9-0.8(2nd digit), 0.8-0.7 (3rd digit)								
	HC(9)[a]	CO(9)	NO_x(9)	Part.(9)	Fuel(9)	BaP(4)	Aldehydes(5)	Phenols(1)	Solubles(7)
Cetane(11)[a]	2,3,1	3,2,1	2,0,0	1,0,1	1,0,1	0,1,1	1,0,1	0,0,0	0,1,0
Density(11)	1,1,2	1,0,2	1,0,5	2,4,1	0,1,1	0,0,1	1,1,0	0,0,0	0,2,0
Nitrogen(3)	1,0,0	1,0,1	0,0,1	1,0,0	1,0,1	1,0,1	1,1,0	0,0,0	1,1,0
Aromatics(11)	2,0,1	3,1,0	2,0,0	1,5,2	1,0,1	0,1,1	1,1,2	0,0,0	0,0,1
Olefins(7)	1,0,2	1,1,2	0,1,2	1,0,1	1,0,2	0,0,0	0,1,0	0,0,0	0,0,1
BP 10%(11)	1,0,1	0,2,1	1,0,3	0,1,0	0,0,2	0,0,0	1,1,0	0,0,0	0,0,0
BP 90%(11)	1,0,2	0,1,1	2,0,1	0,0,1	0,1,1	0,0,0	1,1,0	0,0,0	0,0,0

[a] Number in parentheses is number of studies containing particular fuel property or emission

TABLE 21. NUMBER OF PEARSON CORRELATION COEFFICIENTS GREATER THAN 0.700 FOR FUEL PROPERTIES VS. FUEL PROPERTIES

	Number of Studies Where Coefficients were >0.9(1st digit), 0.9-0.8(2nd digit), 0.8-0.7(3rd digit)						
	Cetane(11)[a]	Density(11)	Nitrogen(3)	Aromatics(11)	Olefins(7)	BP 10%(11)	BP 90%(11)
Cetane(11)[a]	---[b]	---[b]	---[b]	---[b]	---[b]	---[b]	---[b]
Density(11)	0, 1, 3	---[b]	---[b]	---[b]	---[b]	---[b]	---[b]
Nitrogen(3)	0, 2, 1	0, 0, 0	---[b]	---[b]	---[b]	---[b]	---[b]
Aromatics(11)	1, 2, 0	4, 7, 0	0, 0, 0	---[b]	---[b]	---[b]	---[b]
Olefins(7)	1, 1, 0	1, 0, 2	0, 0, 0	0, 0, 2	---[b]	---[b]	---[b]
BP 10%(11)	0, 1, 0	2, 2, 0	0, 0, 0	1, 0, 1	5, 0, 0	---[b]	---[b]
BP 90%(11)	0, 1, 0	3, 0, 4	0, 0, 0	2, 0, 1	3, 0, 0	4, 0, 2	---[b]

[a] Number in parentheses is number of studies containing particular property

[b] Redundant values omitted

TABLE 22. NUMBER OF PEARSON CORRELATION COEFFICIENTS GREATER THAN 0.700 FOR EMISSIONS VS. EMISSIONS

	Number of Studies Where Coefficients were >0.9(1st digit), 0.9-0.8(2nd digit), 0.8-0.7(3rd digit)								
	HC(9)[a]	CO(9)	NO_x(9)	Part.(9)	Fuel(9)	BaP(4)	Aldehydes(5)	Phenols(1)	Solubles(7)
HC(9)[a]	---[b]	---[b]	---[b]	---[b]	---[b]	---[b]	---[b]	---[b]	---[b]
CO(9)	5,4,0	---[b]	---[b]	---[b]	---[b]	---[b]	---[b]	---[b]	---[b]
NO_x(9)	2,1,0	2,2,2	---[b]	---[b]	---[b]	---[b]	---[b]	---[b]	---[b]
Part.(9)	1,0,1	2,0,0	0,1,3	---[b]	---[b]	---[b]	---[b]	---[b]	---[b]
Fuel(9)	0,2,1	2,2,0	3,1,1	1,1,1	---[b]	---[b]	---[b]	---[b]	---[b]
BaP(4)	1,1,0	1,0,0	0,0,0	1,0,1	0,1,0	---[b]	---[b]	---[b]	---[b]
Aldehydes(5)	3,0,0	1,1,1	2,0,1	1,0,1	1,1,0	1,0,1	---[b]	---[b]	---[b]
Phenols(1)	0,0,0	0,0,0	0,0,0	0,0,0	0,0,0	0,0,0	0,0,0	---[b]	---[b]
Solubles(7)	1,0,1	1,0,1	0,0,0	2,0,1	1,1,0	1,0,0	0,1,0	0,0,0	---[b]

[a] Number in parentheses is number of studies containing particulate emissions
[b] Redundant values omitted

TABLE 23. FUEL PROPERTY - EXHAUST EMISSION CORRELATION FOR THE ALTERNATE-SOURCE FUEL STUDY

	Pearson Correlation Coefficients							
	HC	CO	NO_x	Part.	Fuel	BaP	Aldehyde	Solubles
Cetane	-0.8873	-0.9221	-0.3262	-0.2938	-0.0669	-0.0800	0.1104	-0.5069
Density	-0.0563	-0.0123	0.7390	0.8059	-0.6205	-0.0365	-0.4577	0.4921
Nitrogen	0.6696	0.6556	0.5871	0.6672	-0.2254	0.0681	-0.3332	0.8149
Aromatic	-0.0864	0.0404	0.6483	0.8030	-0.6387	-0.0806	-0.7479	0.4817
Olefins	-0.2625	-0.3172	0.1202	0.2565	0.2369	0.2607	0.4099	0.0320
BP 10%	-0.6800	-0.6387	0.3149	0.4490	-0.4838	0.0583	-0.3021	0.0368
BP 90%	-0.1407	-0.1980	-0.0795	-0.0875	-0.4892	-0.1264	-0.5701	0.1157

TABLE 24. SELECTED FUEL PROPERTY-EXHAUST EMISSION DATA PAIRS

Fuel Property	Exhaust Emission
Cetane	HC
Cetane	CO
Cetane	Solubles
Density	HC
Density	NO_x
Density	Particulate
Density	Fuel
Nitrogen	CO
Nitrogen	BaP
Nitrogen	Solubles
Aromatics	HC
Aromatics	CO
Aromatics	NO_x
Aromatics	Particulate
Aromatics	BaP
Aromatics	Aldehydes
Olefins	Fuel
10% B.P.	HC
10% B.P.	NO_x
10% B.P.	Particulate
90% B.P.	HC
90% B.P.	Particulate

TABLE 25. PEARSON'S CORRELATION COEFFICIENTS FOR SELECT FUEL PROPERTY - EXHAUST EMISSION DATA PAIRS

Fuel Property	Exhaust Emission	Study Identification															
		A1	B1	B2	C1	D1	F1	F2	G1	G2	H1	I1	I2	J1	J2	J3	K1
Cetane	HC	-0.7618	-0.6425	-0.8297	0.9864	-0.6934	-0.9623	1.0000	-0.2962	0.8014	-0.3599			1.0000	1.0000	1.0000	-0.8873
Cetane	CO	-0.5405	-0.6213	-0.8848	0.9806	-0.8660	-0.9632	1.0000	-0.4325	0.7337	--	--	--	1.0000	1.0000	1.0000	-0.9221
Cetane	Solubles	-0.2560	0.5026	-0.8766	1.0000	--	--	--	-0.1599	0.1557	-0.2926	-0.1807	-0.2153	1.0000	1.0000	1.0000	-0.8873
Density	HC	0.7524	0.8307	0.6675	0.6990	-0.9265	0.7473	0.2842	0.2028	-0.6027	-0.2295	--	--	1.0000	1.0000	1.0000	-0.0563
Density	NO_x	0.7217	0.7273	0.1886	0.7780	0.9449	-0.2080	0.7125	-0.0262	-0.0387	-0.0974	--	--	1.0000	1.0000	1.0000	0.7390
Density	Particulate	0.8888	0.9870	0.8011	0.5553	-0.0751	--	--	0.0221	0.8915	0.4711	0.9233	0.7349	1.0000	1.0000	1.0000	0.8059
Density	Fuel	-0.0878	0.3993	0.4891	0.9513	0.4740	-0.8665	0.6533	-0.2198	-0.0766	0.2362	--	--	1.0000	1.0000	1.0000	-0.6205
Nitrogen	CO	0.0605	0.7342	0.9846	--	--	--	--	--	--	--	--	--	1.0000	1.0000	1.0000	0.6556
Nitrogen	BaP	-0.0313	0.7269	0.9744	--	--	--	--	--	--	--	--	--	1.0000	1.0000	1.0000	0.0681
Nitrogen	Solubles	-0.3506	-0.3042	0.9819	--	--	--	--	--	--	--	--	--	1.0000	1.0000	1.0000	0.8149
Aromatics	HC	0.7965	0.6360	0.6914	0.2487	-0.9993	0.9599	-0.2402	0.3877	-0.5090	-0.1339	--	--	1.0000	1.0000	1.0000	-0.0864
Aromatics	CO	0.9131	0.2347	0.5854	0.2739	-0.9494	0.9195	0.3542	0.8321	-0.3510	--	--	--	1.0000	1.0000	1.0000	0.0404
Aromatics	NO_x	0.6955	0.4237	0.2745	0.2608	0.9999	-0.6170	0.9696	-0.4444	-0.0711	0.2317	--	--	1.0000	1.0000	1.0000	0.6483
Aromatics	Particulate	0.8740	0.8939	0.8315	0.9084	-0.4102	--	--	-0.1657	0.7432	0.3697	0.8875	0.7058	1.0000	1.0000	1.0000	0.8030
Aromatics	Aldehydes	-0.3742	0.7120	0.8413	0.3866	0.9349	--	--	--	--	--	--	--	1.0000	1.0000	1.0000	-0.7479
Aromatics	BaP	0.1493	0.8568	0.7085	1.0000	--	--	--	--	--	--	--	--	1.0000	1.0000	1.0000	-0.0806
Olefins	Fuel	0.6246	-0.5565	-0.2942	-0.9698	-0.9999	-0.7033	-0.5684	--	--	0.2792	--	--	1.0000	1.0000	1.0000	0.2369
10% B.P.	HC	-0.4500	0.6997	0.3464	0.7088	-0.9707	-0.6874	1.0000	-0.4152	0.1499	-0.3230	--	--	1.0000	1.0000	1.0000	-0.6800
10% B.P.	NO_x	-0.0354	0.7283	0.5578	0.7962	0.9820	0.7225	-0.4617	0.4864	-0.0489	-0.2956	--	--	1.0000	1.0000	1.0000	0.3149
10% B.P.	Particulate	0.0735	0.8218	0.4826	0.5275	-0.2168	--	--	0.0880	0.3823	0.4420	0.2617	0.1076	1.0000	1.0000	1.0000	0.4490
90% B.P.	HC	0.0005	0.4973	0.1829	0.7481	-0.9794	0.7400	-0.1043	0.4744	-0.0734	-0.1842	--	--	1.0000	1.0000	1.0000	-0.1407
90% B.P.	Particulate	0.0817	0.7273	0.3294	0.5626	-0.2550	--	--	-0.2186	0.4946	0.4070	0.5768	0.4331	1.0000	1.0000	1.0000	-0.0875

TABLE 26. ANALYSES OF PHILLIPS 2D DIESEL FUEL LOTS

Property	EPA Specification	Phillips Lot No.			Average	Rounded
		C-345	C-504	C-747		
Cetane No.	42-50	47.8	46.3	47.5	47.2	47.
Distillation Range						
IBP, °C	171-204	196	200	197	198	200
10% point, °C	204-238	223	224	221	223	220
50% point, °C	243-282	264	257	263	262	260
90% point, °C	288-321	299	296	302	299	300
End point, °C	304-249	315	323	321	319	320
Gravity, °API	33-37	34.8	35.7	35.8	35.4	35.0
Density, g/mℓ		0.8509	0.8463	0.8458	0.8478	0.8500
Sulfur, %	0.2-0.5	0.30	0.25	0.20	0.25	0.25
Hydrocarbon Composition						
Paraffins, vol. %	---	65.	69.0	---	67.3	68.
Olefins, vol. %	---	5.	1.2	---	3.1	2.
Aromatics, vol. %	27 min	30.0	29.8	29.1	29.6	30.
Flash Point, °C min	54.4	79.4	75.0	69.4	74.4	74.
Viscosity, cs, 40°C	2.0-3.2	2.56	2.44	2.50	2.50	2.50
Nitrogen, ppm	---	---	80	---	80	80

a total of 352 normalization factors (16 cases, (15 petroleum + 1 alternate-source) x 22 selected fuel property-exhaust emission pairs). However, some studies did not report some of the selected fuel properties or exhaust emissions, so the actual total of normalization factors was 262. The normalization factors are listed in Table 27.

Application of the normalization factors to each raw data set (about two thousand simple divisions, plus re-establishment and storage of data files) was performed by a computer program written specifically for that purpose. The normalized exhaust emission data for each selected fuel property are listed in Appendix D, pages D-9 through D-29.

E. Scattergrams of Select Variables

The normalized data from each study were plotted on a common graph showing the emission of interest versus a specific fuel property. The petroleum-based fuel study data were plotted using the plot symbol "A", and the alternate-source study data used "B". A linear regression analysis was performed on the petroleum-based fuel data from all the studies to yield a single equation. This equation was used to superimpose a line on the common plot, representing the relationship between a particular petroleum-based fuel property and one exhaust emission variable. Similarly, a line representing the alternate-source fuels was also drawn on the plot. In addition, each plot contained a horizontal line representing a normalized emission value of 1.0, along with a vertical line representing the fuel property level to which the data were normalized. The effects of using alternate-source fuels were determined by observing where the alternate-source fuel line fell relative to the petroleum-based fuel line.

In addition, the normalized emissions data from each individual study were fitted with a least squares regression line using a specified fuel property as the independent variable. An equation was used similarly to fit the alternate fuel data. These lines were plotted on a common graph. The lines from the petroleum fuel data formed a region representing the dispersion for such studies. The effects of using alternate-source fuels were determined by observing where the alternate-source fuel line fell relative to the petroleum-based fuel band defined by the individual-study lines.

In all cases, the regression equation representing all the petroleum-based fuel data points was used (with the fuel property data from the alternate-source study) to obtain <u>predicted</u> emission values for comparison to the <u>observed</u> emission data from the alternate-source study. This comparison was accomplished using a goodness-of-fit statistic, defined as:

$$X^2 = \sum_{i=1}^{n} \frac{(\text{Observed} - \text{Predicted})^2}{\text{Predicted}}$$

Although "X^2" (as used here) is not a true chi-square statistic (as would occur in a single experiment with random observations), it is similar to the

TABLE 27. EMISSION NORMALIZATION FACTORS FOR SELECT FUEL PROPERTY - EXHAUST EMISSION DATA PAIRS

Fuel Property	Exhaust Emissions	Study Identification															
		A1	B1	B2	C1	D1	F1	F2	G1	G2	H1	I1	I2	J1	J2	J3	K1
Cetane	HC	0.124	0.148	0.318	0.200	0.240	0.875	0.479	0.101	0.260	0.771	--	--	0.369	0.329	0.135	0.333
Cetane	CO	0.576	0.639	0.592	0.790	0.880	1.022	1.213	0.418	0.762	--	--	--	1.251	1.047	0.709	1.095
Cetane	Solubles	27.811	29.807	34.614	71.600	--	--	--	26.086	39.439	37.27	181.473	68.590	163.619	101.976	41.338	45.244
Density	HC	0.151	0.169	0.388	0.288	0.169	1.722	0.434	0.130	0.033	0.428	--	--	0.353	0.305	0.131	0.398
Density	NO_x	1.053	0.833	0.608	1.536	0.844	0.411	1.099	0.963	0.818	2.019	--	--	0.873	1.259	0.651	0.732
Density	Particulate	0.311	0.342	0.277	0.300	0.179	--	--	0.117	0.176	13.233	0.563	0.255	0.282	0.209	0.276	0.299
Density	Fuel	9.560	8.985	5.883	8.958	7.917	4.918	12.877	10.125	11.552	128.30	--	--	8.596	10.219	10.636	6.357
Nitrogen	CO	0.521	0.625	0.550	--	--	--	--	--	--	--	--	--	--	--	--	1.106
Nitrogen	BaP	0.480	0.383	1.454	--	--	--	--	--	--	--	--	--	--	--	--	23.095
Nitrogen	Solubles	26.753	30.321	30.155	--	--	--	--	--	--	--	--	--	--	--	--	38.934
Aromatics	HC	0.123	0.168	0.418	0.264	0.197	1.094	0.367	0.125	0.098	0.660	--	--	0.330	0.269	0.125	0.400
Aromatics	CO	0.608	0.645	0.637	0.860	0.782	1.168	1.170	0.505	0.644	--	--	--	1.103	0.909	0.670	1.163
Armoatics	NO_x	0.938	0.826	0.597	1.412	0.834	0.409	1.047	0.946	0.818	2.145	--	--	0.844	1.265	0.645	0.718
Aromatics	Particulate	0.235	0.347	0.289	0.323	0.179	--	--	0.116	0.158	12.982	0.595	0.264	0.267	0.183	0.254	0.285
Aromatics	BaP	0.523	0.503	2.278	0.985	--	--	--	--	--	--	--	--	1.560	2.224	0.398	23.480
Aromatics	Aldehydes	0.974	19.794	35.948	33.247	28.621	--	--	--	--	--	--	--	11.462	7.296	0.807	6.494
Olefins	Fuel	9.592	8.757	5.787	8.426	7.563	4.150	10.738	--	--	124.69	--	--	8.494	10.409	10.709	6.474
10% B.P.	HC	0.085	0.171	0.357	0.288	0.178	0.240	0.648	0.080	0.269	0.209	--	--	0.309	0.240	0.119	0.356
10% B.P.	NO_x	0.854	0.840	0.619	1.533	0.840	0.492	0.936	1.054	0.816	1.939	--	--	0.821	1.271	0.539	0.721
10% B.P.	Particulate	0.188	0.345	0.268	0.299	0.178	--	--	0.118	0.160	13.176	0.522	0.226	0.254	0.163	0.236	0.292
90% B.P.	HC	0.101	0.149	0.300	0.270	0.249	0.785	0.372	0.130	0.198	0.638	--	--	0.345	0.292	0.127	0.405
90% B.P.	Particulate	0.209	0.319	0.245	0.291	0.181	--	--	0.115	0.153	12.878	0.436	0.220	0.276	0.199	0.269	0.278

chi-square; and the chi-square table was used to provide guidelines for determining whether or not the observed and the predicted values differed. A percentile value of $X^2_{.95}$, based on 9 degrees of freedom, was chosen from tables of the chi-square distribution to serve as a guideline value. If these had been true random observations, from a normal distribution, this value (16.9) would mean that decisions on whether petroleum-based fuel and alternate-source fuel effects were statistically different would have a 5 percent error rate.

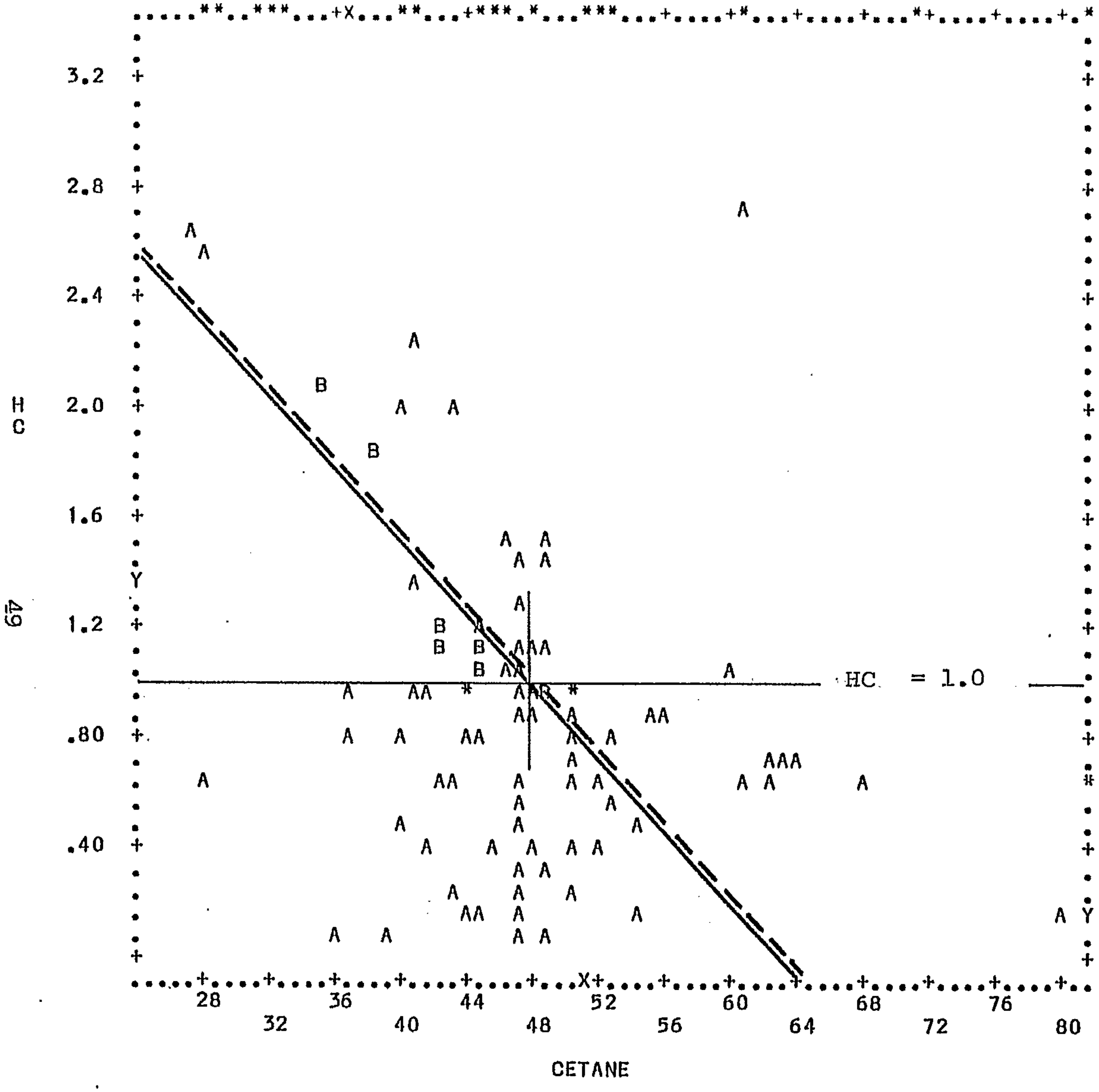
As stated in the Work Plan for this Assignment, the extent of statistical analysis possible depended on the funding available at the initiation of the data analysis portion of the work. As the analysis task began, it was apparent that a detailed statistical analysis was not possible due to efforts expended on the Q/A Project Plan and on attempts to formulate statistical approaches to analyze a greater number of fuel property/exhaust emission data pairs than originally anticipated. All the aforementioned analyses and data are included in this report as Appendix E. A detailed discussion of all the selected fuel property/exhaust emission data pairs was not feasible. Discussion on the regulated emissions (HC, CO, NO_x, and particulate) along with a few of the more interesting other results are presented using the goodness-of-fit technique to determine whether or not alternate-source fuels are different in affecting exhaust emissions as compared to petroleum-based fuels.

1. Hydrocarbons

Figure 6 shows the normalized data for both the petroleum-based fuels (A) and the alternate-source fuels (B) plotted in a common frame. The slopes of both lines are very similar, indicating that hydrocarbons respond to fuel cetane number independent of the type of fuel. The low correlation coefficient of the petroleum-based fuel data reflects variation by the individual study line plots among the petroleum-based fuel studies used; and this variation is further illustrated in Figure 7. These lines show that the alternate-source study K1 (dashed line) fell within the spread of the various petroleum-based studies.

Figure 6 includes the linear regression equation which represents data points from all the petroleum-based fuel studies. Using this equation and data from the alternate-source study, predicted emission values were calculated and compared to the observed emission data from the alternate-source study. Table 28 presents these results. The calculated "chi-square" (or goodness-of-fit, in this case) was 0.2376. The percentile value for a chi-square distribution with 9 degrees of freedom (number of data points - 1) for $X^2_{.95}$ is 16.9. Since 0.2376 is much smaller than 16.9, the "fit" of the data is very good, and therefore the observed values and predicted values do not appear to be different.

Figures 8 through 11 show the hydrocarbon data as a function of aromatics, density, 10 percent boiling point, and 90 percent boiling point, respectively. The line plots of the individual studies (similar to Figure 7) are located in Appendix E. Table 29 presents the goodness-of-fit (chi-square)



Petroleum
Solid Line

```
N=   85
COR=-.276

      MEAN      ST.DEV.     REGRESSION LINE        RES.MS.
X    47.424     8.3294    X=-1.1745*Y+ 48.644     64.882
Y    1.0390     1.9545    Y=-.06467*X+ 4.1058     3.5724
```

Alternate
Dashed Line

```
N=   10
COR=-.887

      MEAN      ST.DEV.     REGRESSION LINE        RES.MS.
X    44.000     4.9889    X=-11.360*Y+ 57.713     5.9547
Y    1.2072     .38969    Y=-.06931*X+ 4.2568     .03633
```

Figure 6. Normalized HC versus cetane.

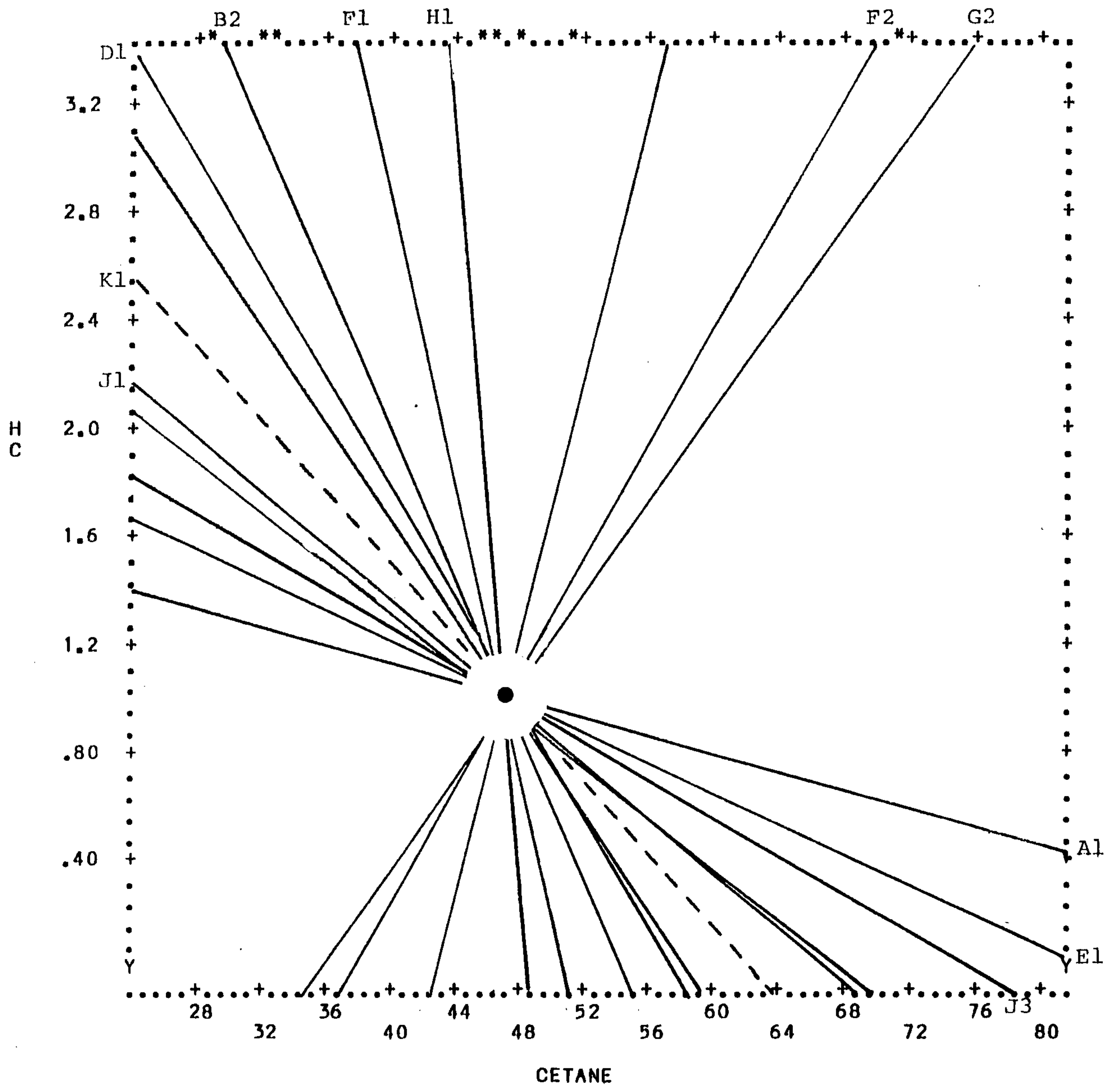
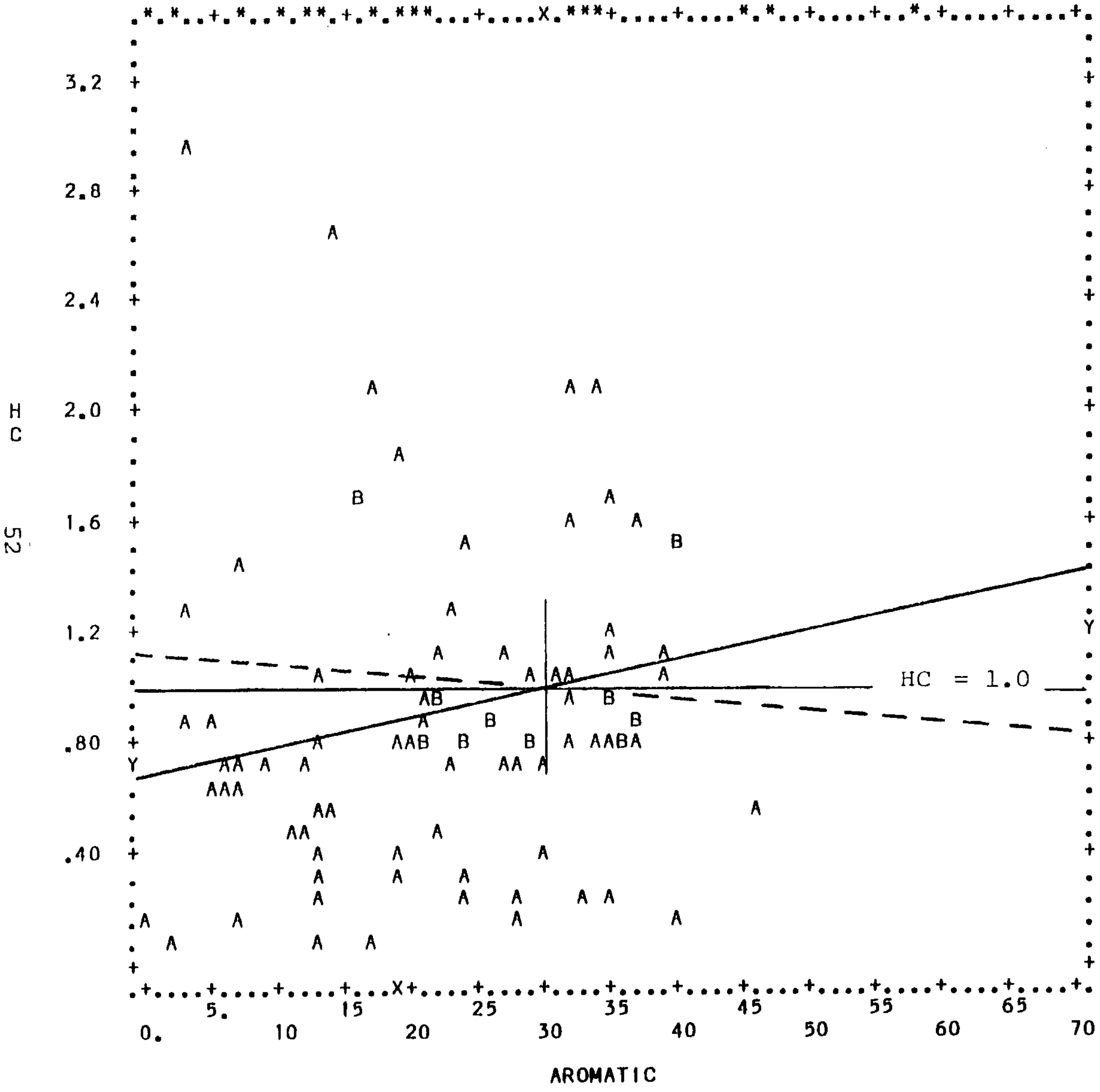


Figure 7. Normalized HC versus cetane by individual study.

TABLE 28. COMPARISON OF OBSERVED VERSUS PREDICTED HYDROCARBONS AS A FUNCTION OF FUEL CETANE USING PETROLEUM-BASED FUEL STUDY EQUATION AND ALTERNATE-SOURCE FUEL DATA

Cetane No.	Observed HC	"J" Predicted HC	"K" (Observed-Predicted)^2	"K"/"J"
50	0.9309	0.8723	0.0034	0.0039
49	0.9309	0.9730	0.0003	0.0003
45	1.1411	1.1957	0.0030	0.0025
42	1.1712	1.3897	0.0477	0.0343
35	2.0402	1.8424	0.0399	0.0217
38	1.8018	1.6483	0.0235	0.0143
44	0.9910	1.2603	0.0725	0.0575
45	1.0210	1.1957	0.0305	0.0255
50	0.9610	0.8723	0.0079	0.0091
42	1.0811	1.3897	0.0952	0.0685

$$X^2 = \Sigma \frac{\text{"K"}}{\text{"J"}} = 0.2376$$



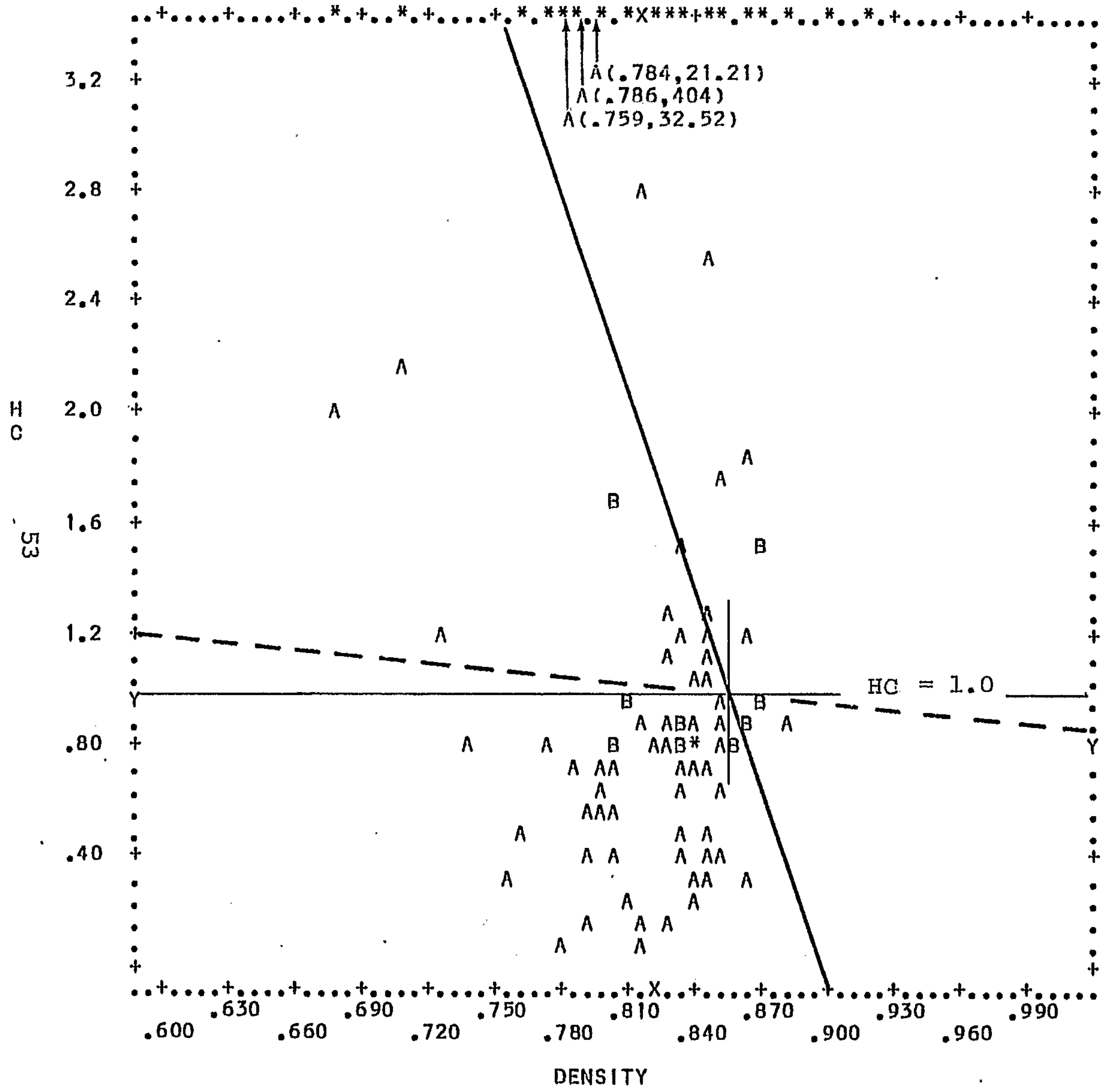
Petroleum
Solid Line

```
N=   83
COR= .141

     MEAN     ST.DEV.    REGRESSION LINE      RES.MS.
X   21.430    11.289   X= 2.7817*Y+ 18.968    126.46
Y   .88527    .57197   Y= .00714*X+ .73224    .32461
```

Alternate
Dashed Line

```
N=   10
COR=-.086

     MEAN     ST.DEV.    REGRESSION LINE      RES.MS.
X   28.590    8.0524   X=-2.1452*Y+ 30.746    72.401
Y   1.0050    .32442   Y=-.00348*X+ 1.1046    .11752
```

Figure 8. Normalized HC versus aromatics.



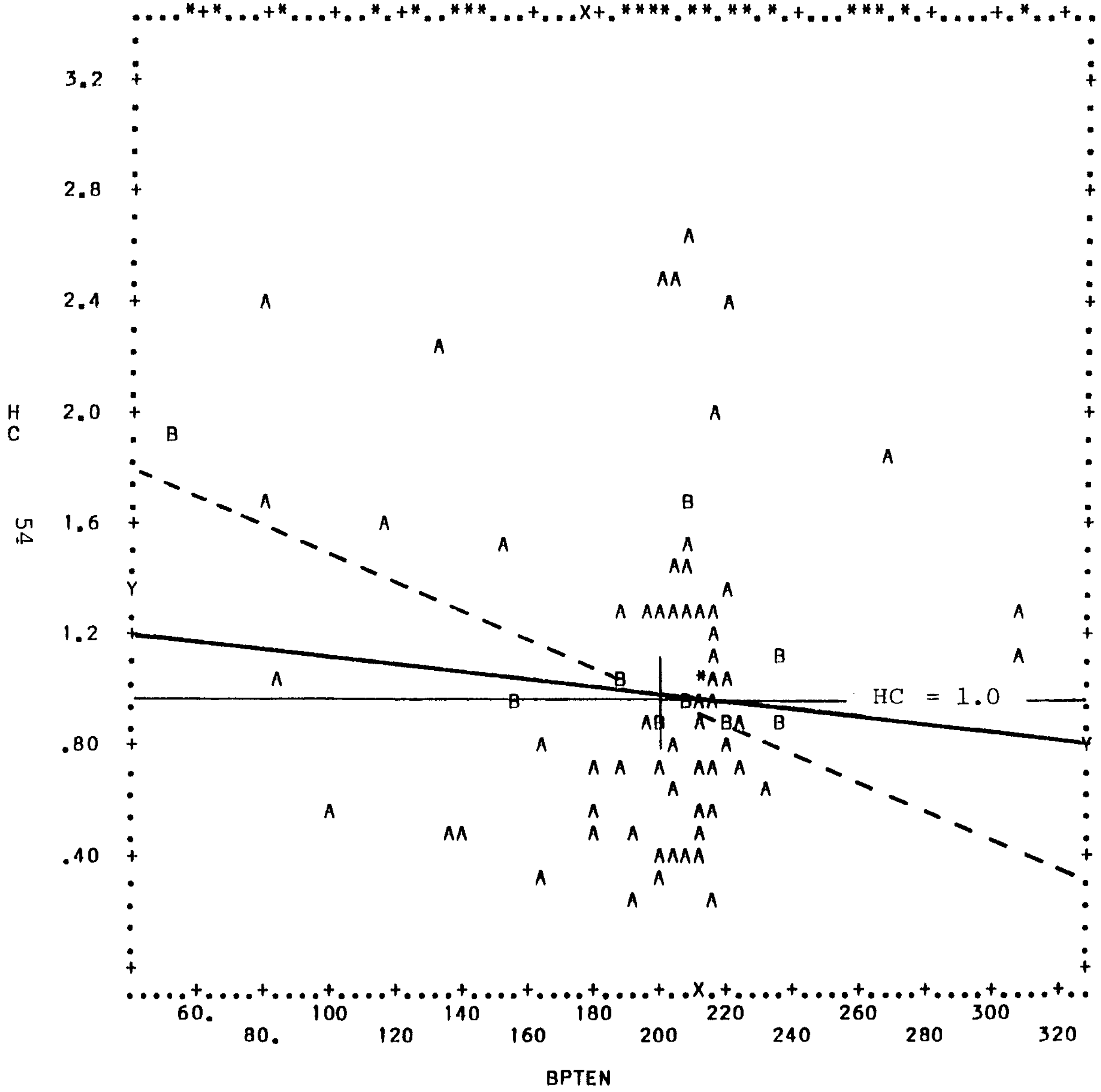
Petroleum
Solid Line

```
N=   86
COR=-.220

     MEAN      ST.DEV.     REGRESSION LINE      RES.MS.
X   .81541     .03993    X=-.00209*Y+ .81939    .00154
Y   1.9074     4.2128    Y=-23.261*X+ 20.875    17.085
```

Alternate
Dashed Line

```
N=   10
COR=-.056

     MEAN      ST.DEV.     REGRESSION LINE      RES.MS.
X   .83770     .02546    X=-.00440*Y+ .84214    727E-6
Y   1.0100     .32604    Y=-.72142*X+ 1.6144    .11921
```

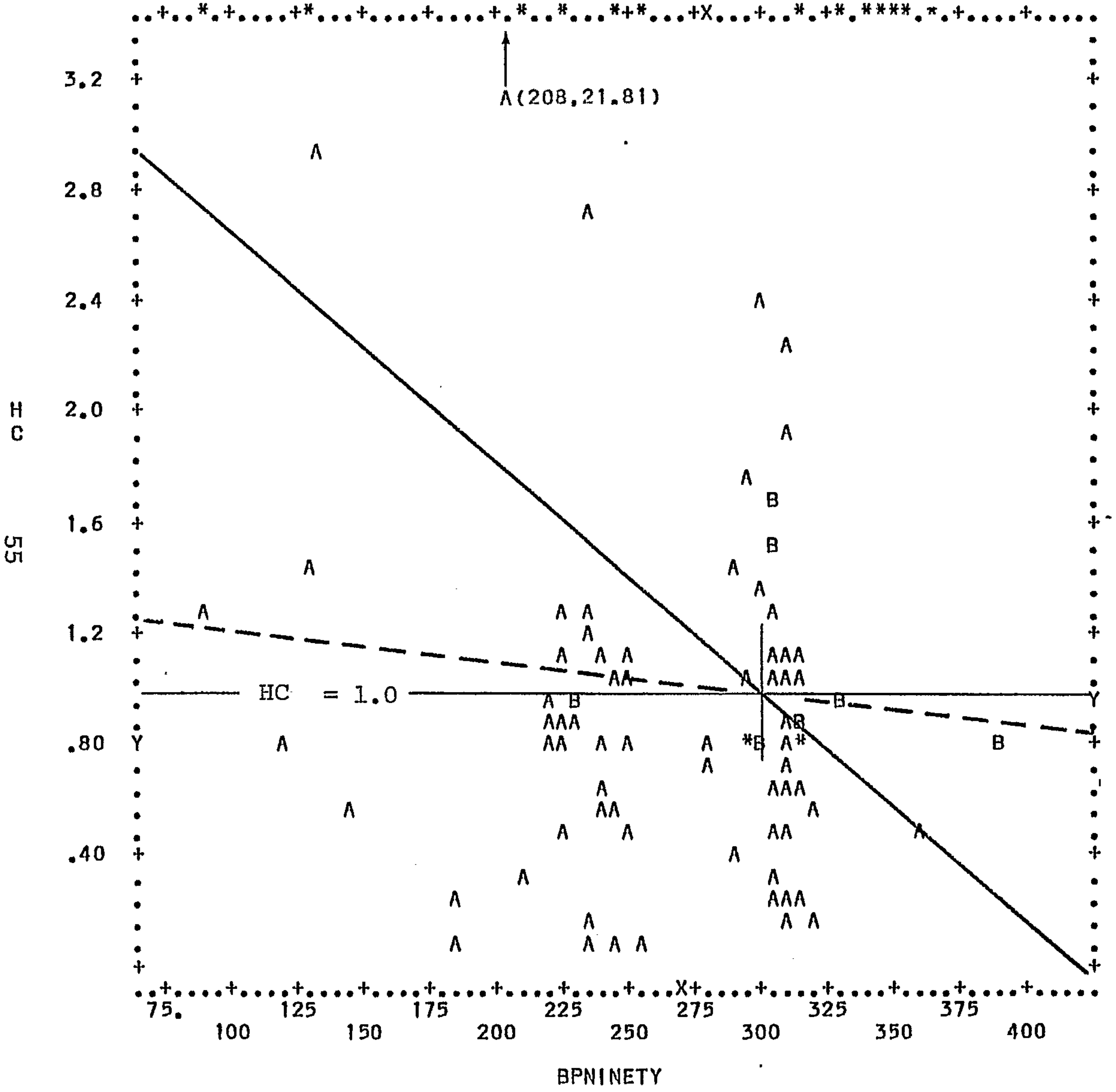
Figure 9. Normalized HC versus density.



```
                                   Petroleum
                                   Solid Line
N=    76
COR=-.077

      MEAN     ST.DEV.    REGRESSION LINE      RES.MS.
X    200.24    41.010   X=-5.5852*Y+ 206.08    1694.5
Y    1.0470    .56361   Y=-.00105*X+ 1.2583    .32005
```

```
                                   Alternate
N=    10                           Dashed Line
COR=-.680

      MEAN     ST.DEV.    REGRESSION LINE      RES.MS.
X    191.60    53.707   X=-100.19*Y+ 304.74    1744.6
Y    1.1292    .36451   Y=-.00462*X+ 2.0135    .08036
```

Figure 10. Normalized HC versus 10% boiling point.



```
Petroleum
Solid Line

N=    96
COR=-.160

     MEAN      ST.DEV.     REGRESSION LINE      RES.MS.
X   267.07     56.353   X=-4.0542*Y+ 271.82    3127.2
Y   1.1710     2.2251   Y=-.00632*X+ 2.8590    4.8754
```

```
Alternate
Dashed Line

N=    10
COR=-.141

     MEAN      ST.DEV.     REGRESSION LINE      RES.MS.
X   308.70     39.936   X=-17.543*Y+ 326.11    1758.7
Y   .99259     .32042   Y=-.00113*X+ 1.3412    .11322
```

Figure 11. Normalized HC versus 90% boiling point.

values for all the hydrocarbons-fuel property data pairs. The calculated "chi-square" values were compared to the $X^2_{.95}$ percentile value to determine if substitution of alternate source fuel properties into petroleum-based fuel prediction equations yielded statistically different results than emissions observed while using alternate-soruce fuels.

TABLE 29. HYDROCARBON DATA PAIRS GOODNESS-OF-FIT

Data Pair	Calculated "Chi-Square"	Petroleum vs. Alternate Statistically Different
HC - Cetane	0.238	No
HC - Aromatics	1.19	No
HC - Density	3.53	No
HC - 10% Boiling Point	0.920	No
HC - 90% Boiling Point	1.63	No

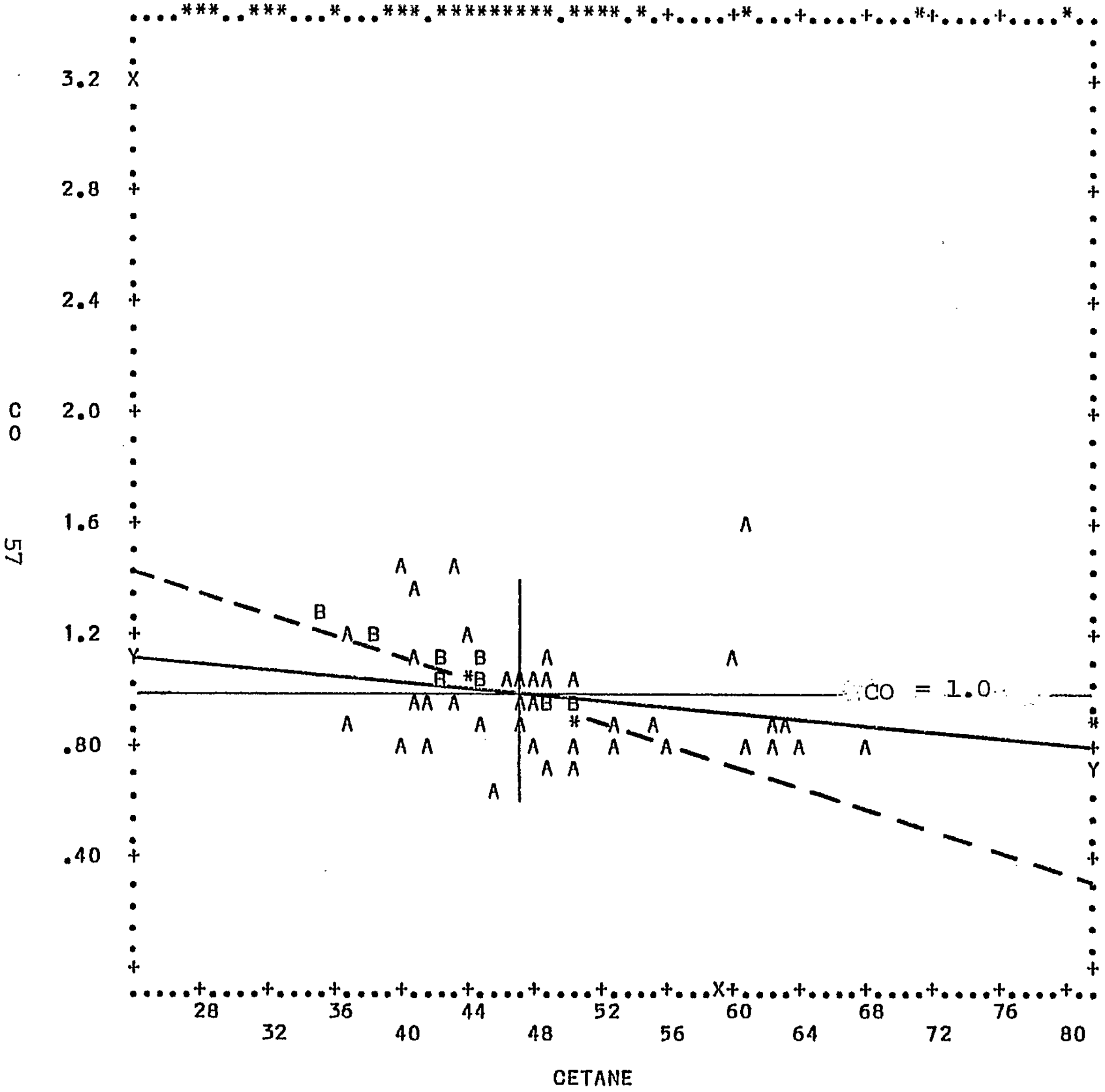
In summary, the effects of fuel aromatic content, cetane number, density and 90 percent boiling point on hydrocarbon emissions were about the same, independent of the source (petroleum-based or alternate-source). Although goodness-of-fit indicated that the 10 percent boiling point affected HC regardless of the source, the plot of the individual study lines showed a wide variation of HC response to petroleum-based fuels. This wide variation does not allow for a clear trend to be interpreted. Figure 9 shows the petroleum-base fuel line forced to reach a few points off-scale. It appears that without these points, the petroleum-based fuel line would be similar to that of the alternate-source line.

2. Carbon Monoxide

Figures 12 through 14 present the carbon monoxide data as functions of cetane number, aromatics, and nitrogen. The individual line plots for each study (in common frame) are located in Appendix E. Table 30 presents the goodness-of-fit values for each of the CO-fuel property data pairs. As before, the "chi-square" values were compared in the $X^2_{.95}$ percentile to determine if statistical similarities existed. All the scattergrams and goodness-of-fit calculations indicate that the effects of fuel cetane number, aromatic content, and nitrogen content on CO emissions are similar regardless

TABLE 30. CO DATA PAIRS GOODNESS-OF-FIT

Data Pair	Calculated "Chi-Square"	Petroleum vs. Alternate Statistically Different
CO - Cetane	0.116	No
CO - Aromatics	0.117	No
CO - Nitrogen	0.061	No



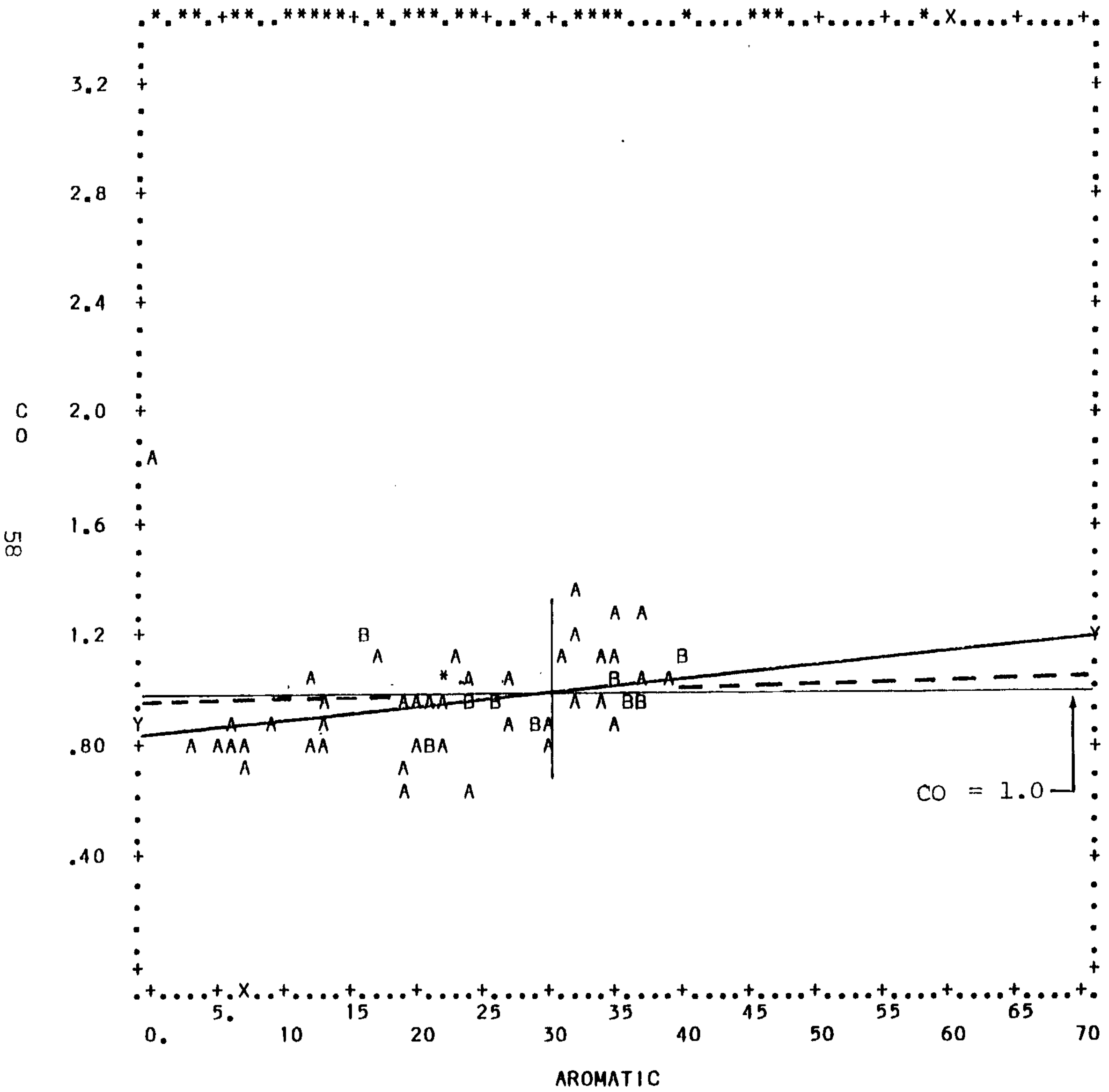
Petroleum
Solid Line

```
N=   54
COR=-.200

     MEAN     ST.DEV.     REGRESSION LINE     RES.MS.
X   48.815    7.1153   X=-7.4838*Y+ 56.042    49.541
Y   .96567    .18998   Y=-.00534*X+ 1.2261    .03532
```

Alternate
Dashed Line

```
N=   10
COR=-.922

     MEAN     ST.DEV.     REGRESSION LINE     RES.MS.
X   44.000    4.9889   X=-41.380*Y+ 87.911    4.1923
Y   1.0612    .11117   Y=-.02055*X+ 1.9653    .00208
```

Figure 12. Normalized CO versus cetane.



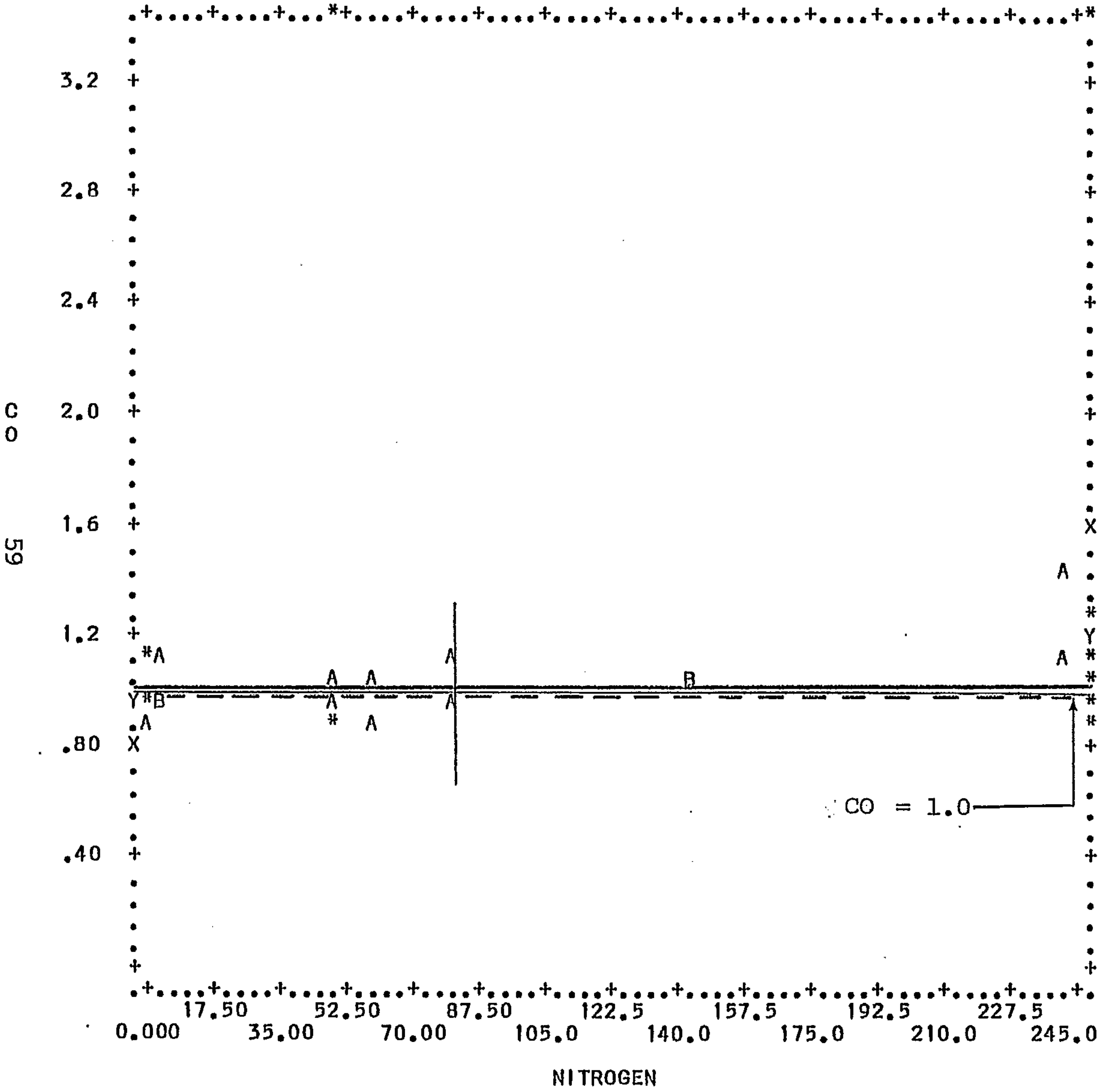
Petroleum
Solid Line

```
N=    56
COR= .272

      MEAN     ST.DEV.      REGRESSION LINE     RES.MS.
X   21.979      10.717   X= 14.688*Y+ 7.9194    108.34
Y   .95719      .19825   Y= .00503*X+ .84671    .03708
```

Alternate
Dashed Line

```
N=    10
COR= .040

      MEAN     ST.DEV.      REGRESSION LINE     RES.MS.
X   28.590      8.0524   X= 3.0995*Y+ 25.493    72.828
Y   .99913      .10467   Y= 524E-6*X+ .98416    .01230
```

Fiugre 13. Normalized CO versus aromatics.



Petroluem
Solid Line

```
N=   21
COR= .138

      MEAN     ST.DEV.     REGRESSION LINE      RES.MS.
X    171.00    263.07   X= 245.15*Y-78.175     71458.
Y    1.0164    .14813   Y= 777E-7*X+ 1.0031    .02266
```

Alternate
Dashed Line

```
N=   10
COR= .656

      MEAN     ST.DEV.     REGRESSION LINE      RES.MS.
X    604.40    742.46   X= 4422.9*Y-4042.4     353645
Y    1.0506    .11004   Y= 972E-7*X+ .99189    .00777
```

Figure 14. Normalized CO versus nitrogen.

of the fuel source.

3. Oxides of Nitrogen

The NO_x data as functions of aromatics, density, and 10 percent boiling point are shown in Figures 15 through 17. Appendix E contains the same data plotted as individual lines representing each study. Table 31 lists the goodness-of-fit values for each of the NO_x data pairs. Comparing the "chi-square" values in Table 31 to $X^2_{.95}$ (16.9) indicates that the effects of fuel aromatics, density, and 10 percent boiling point on NO_x emissions are similar regardless of the fuel source. Figure 16 shows a sharper slope for the alternate-source data than the petroleum data. This slope can be misleading in that the alternate-source data points do not exhibit a wide population dispersion and are located quite near the fuel density value to which the NO_x data were normalized.

TABLE 31. NO_x DATA PAIRS GOODNESS-OF-FIT

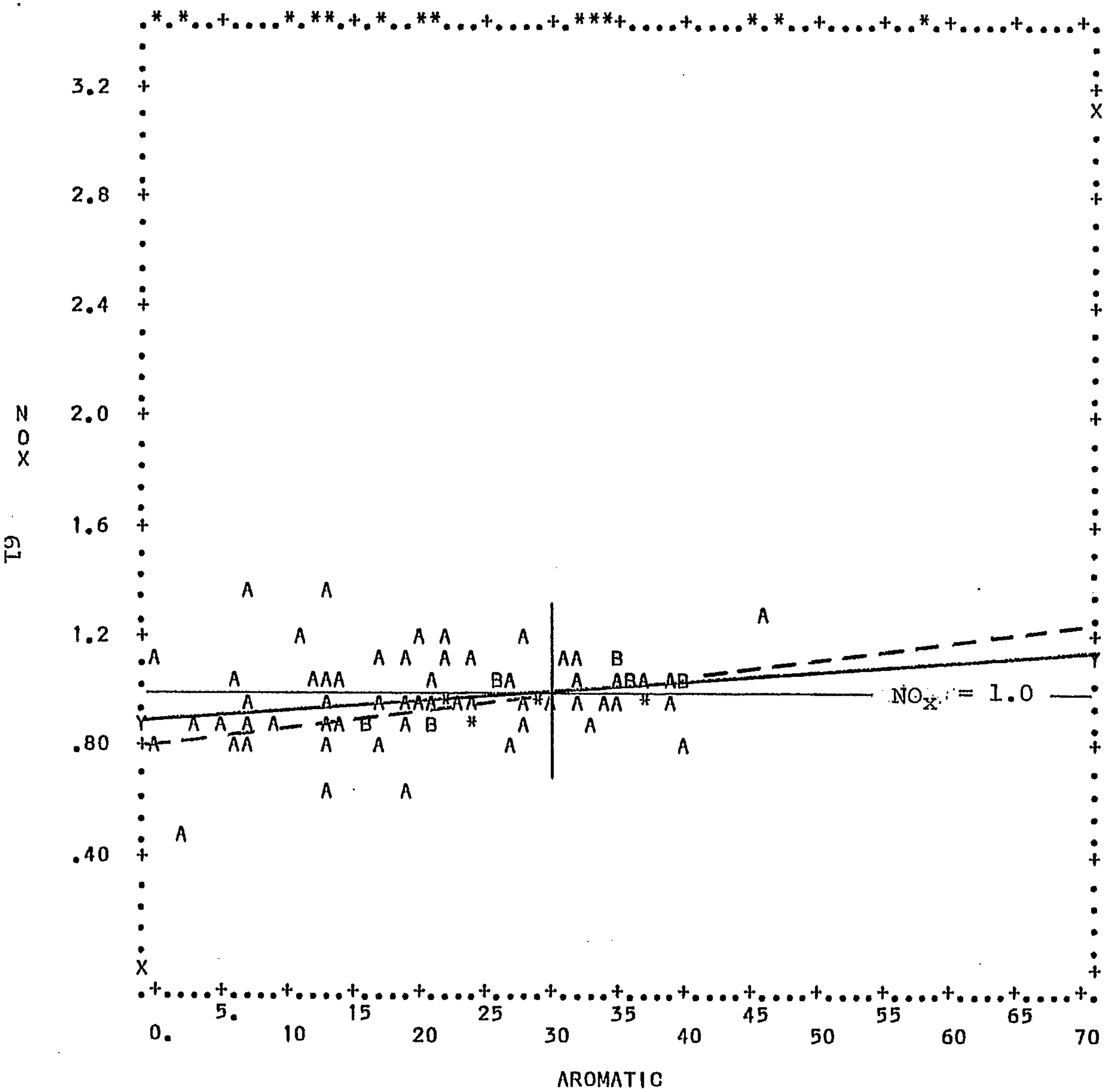
Data Pair	Calculated "Chi-Square"	Petroleum vs. Alternate Statistically Different
NO_x - Aromatics	0.045	No
NO_x - Density	0.062	No
NO_x - 10% Boiling Point	0.640	No

4. Particulate

Figures 18 through 21 present particulate data as a function of fuel aromatics, 90 percent boiling point, density, and 10 percent boiling point. Individual regression lines representing each study, in common graphs, are located in Appendix E. Table 32 gives the goodness-of-fit values for each of the particulate-fuel property data pairs. Calculated "chi-squares" indicate that fuel aromatics, 90 percent boiling point, density, and 10 percent boiling point affect particulate emissions similarly for both petroleum-based fuels and alternate-source fuels. Although the calculated "chi-square" value for the 10 percent boiling point is the highest of all the particulate-fuel property data pairs (1.713), the slopes of the alternate-source study and the

TABLE 32. PARTICULATE DATA PAIRS GOODNESS-OF-FIT

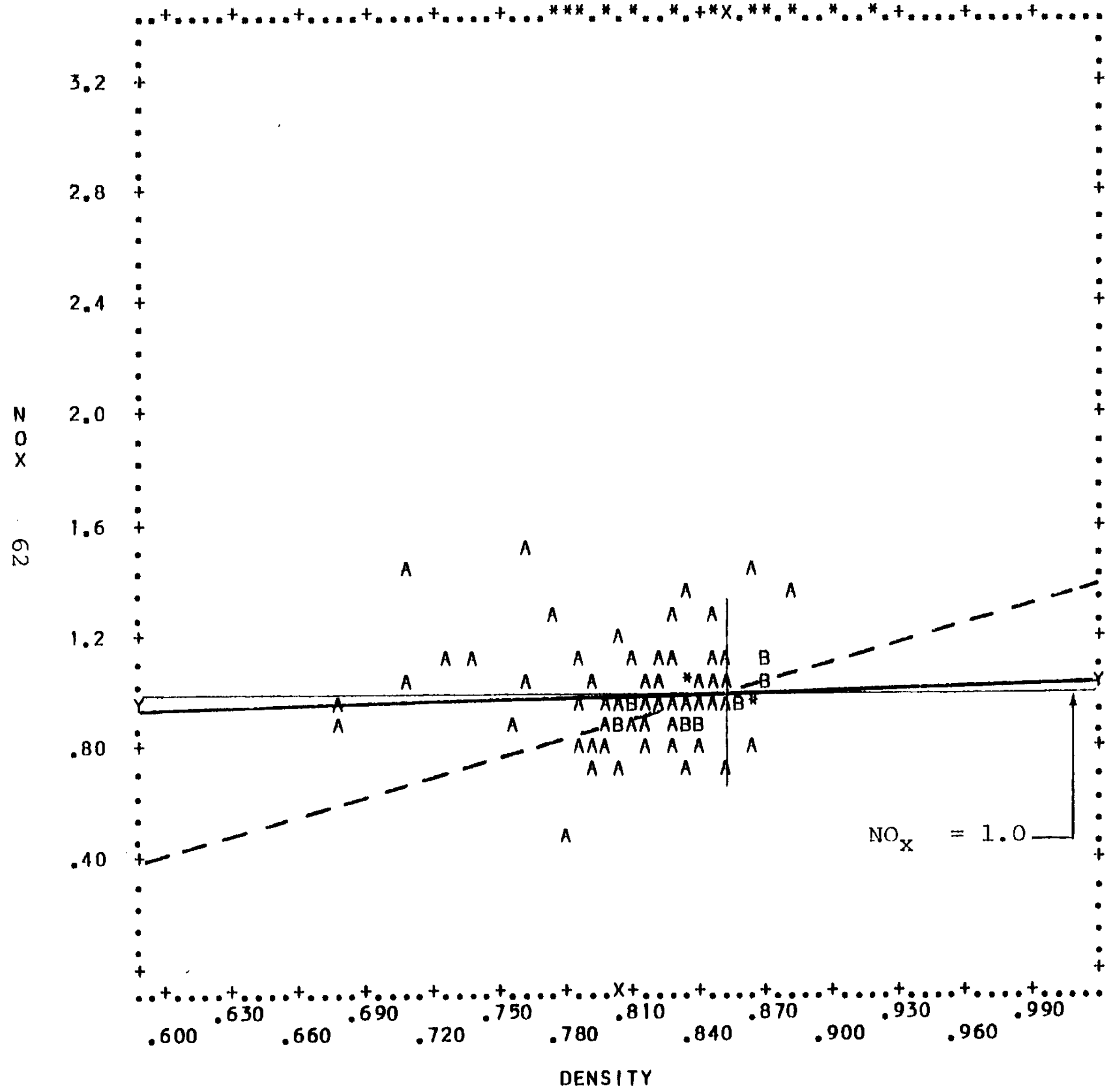
Data Pair	Calculated "Chi-Square"	Petroleum vs. Alternate Statistically Different
Particulate - Aromatics	0.133	No
Particulate - 10% Boiling Point	0.421	No
Particulate - Density	0.127	No
Particulate - 90% Boiling Point	1.713	No



```
                Petroleum
                Solid Line
N=    87
COR= .256

      MEAN      ST.DEV.     REGRESSION LINE      RES.MS.
X     20.895    11.396    X= 21.231*Y+ .21010    122.79
Y     .97428    .13739    Y= .00309*X+ .90980    .01785
```

```
                Alternate
                Dashed Line
N=    10
COR= .648

      MEAN      ST.DEV.     REGRESSION LINE      RES.MS.
X     28.590    8.0524    X= 62.390*Y-33.192     42.279
Y     .99025    .08368    Y= .00674*X+ .79760    .00457
```

Figure 15. Normalized NO_x versus aromatics.



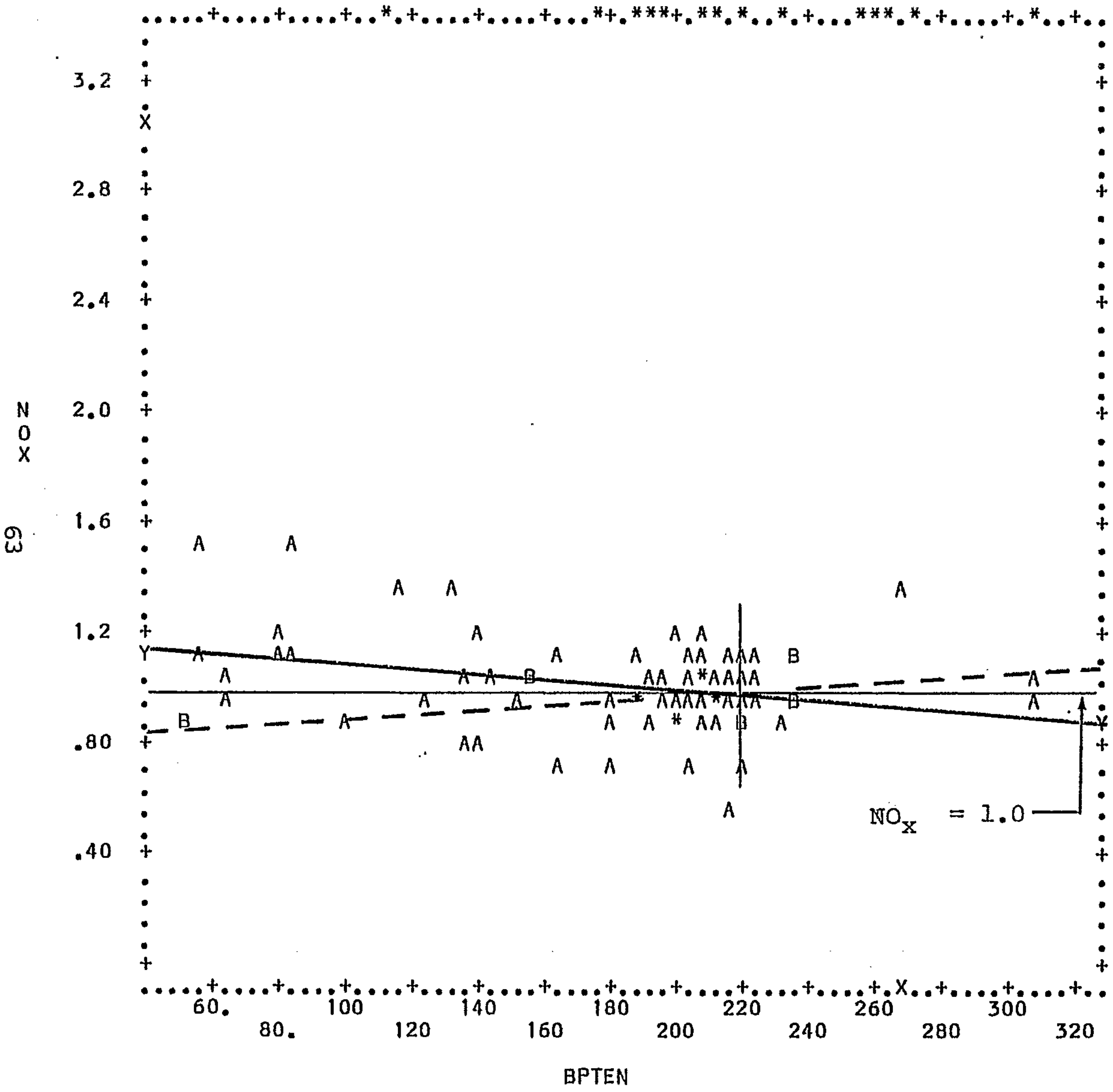
Petroleum
Solid Line

```
N=    87
COR= .043

       MEAN      ST.DEV.     REGRESSION LINE        RES.MS.
X     .81523     .03974    X= .00988*Y+ .80542      .00159
Y     .99281     .17358    Y= .18852*X+ .83913      .03043
```

Alternate
Dashed Line

```
N=    10
COR= .739

       MEAN      ST.DEV.     REGRESSION LINE        RES.MS.
X     .83770     .02546    X= .22911*Y+ .61516     331E-6
Y     .97132     .08210    Y= 2.3831*X-1.0250      .00344
```

Figure 16. Normalized NO_x versus density.



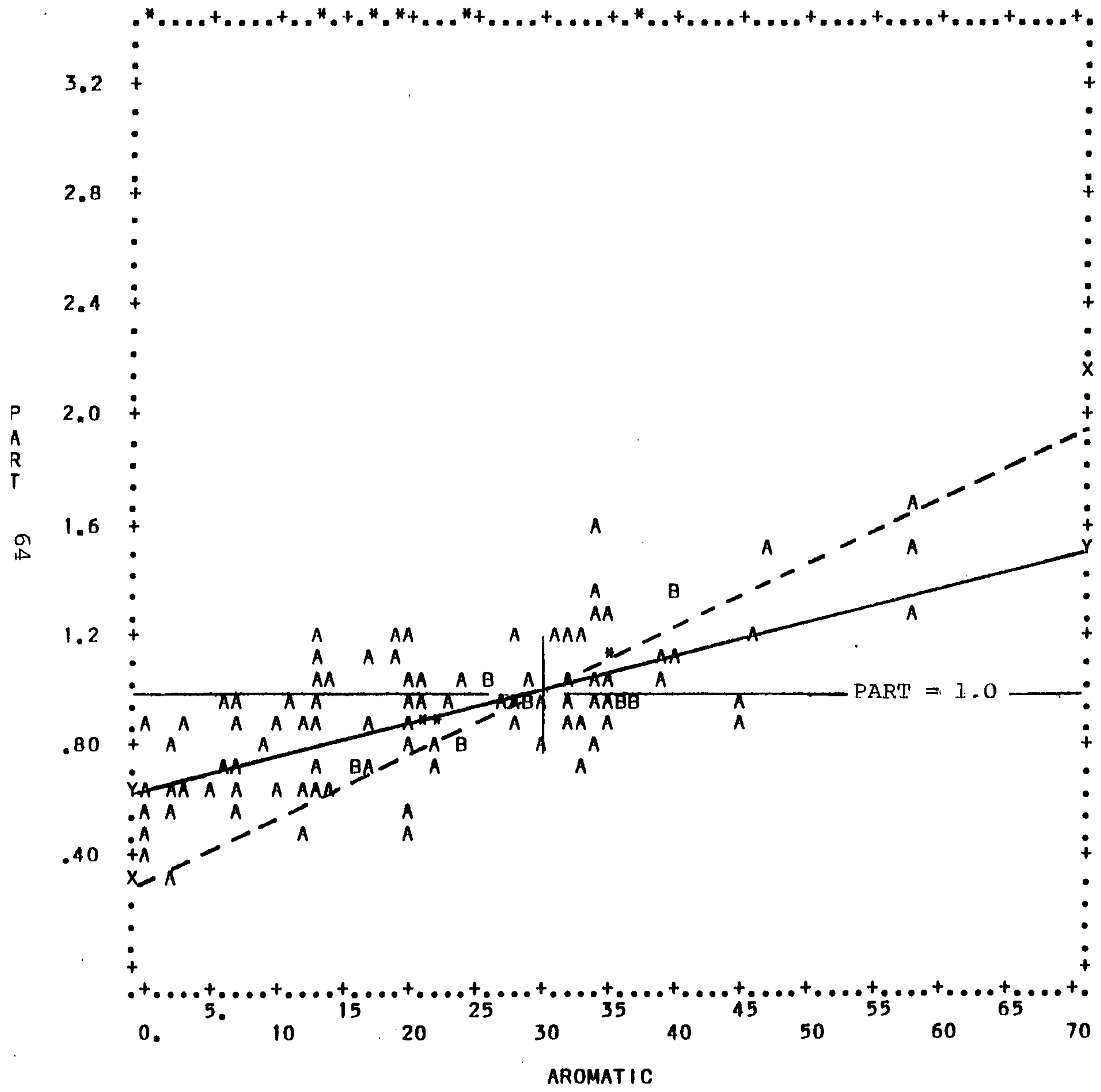
Petroleum
Solid Line

```
N=   87
COR=-.246

       MEAN      ST.DEV.     REGRESSION LINE      RES.MS.
X     189.66     51.422   X=-80.717*Y+ 270.78     2513.6
Y     1.0050     .15664   Y=-749E-6*X+ 1.1471     .02332
```

Alternate
Dashed Line

```
N=   10
COR= .315

       MEAN      ST.DEV.     REGRESSION LINE      RES.MS.
X     191.60     53.707   X= 203.01*Y-8.5940      2923.1
Y     .98614     .08333   Y= 489E-6*X+ .89250     .00704
```

Figure 17. Normalized NO$_x$ versus 10% boiling point.



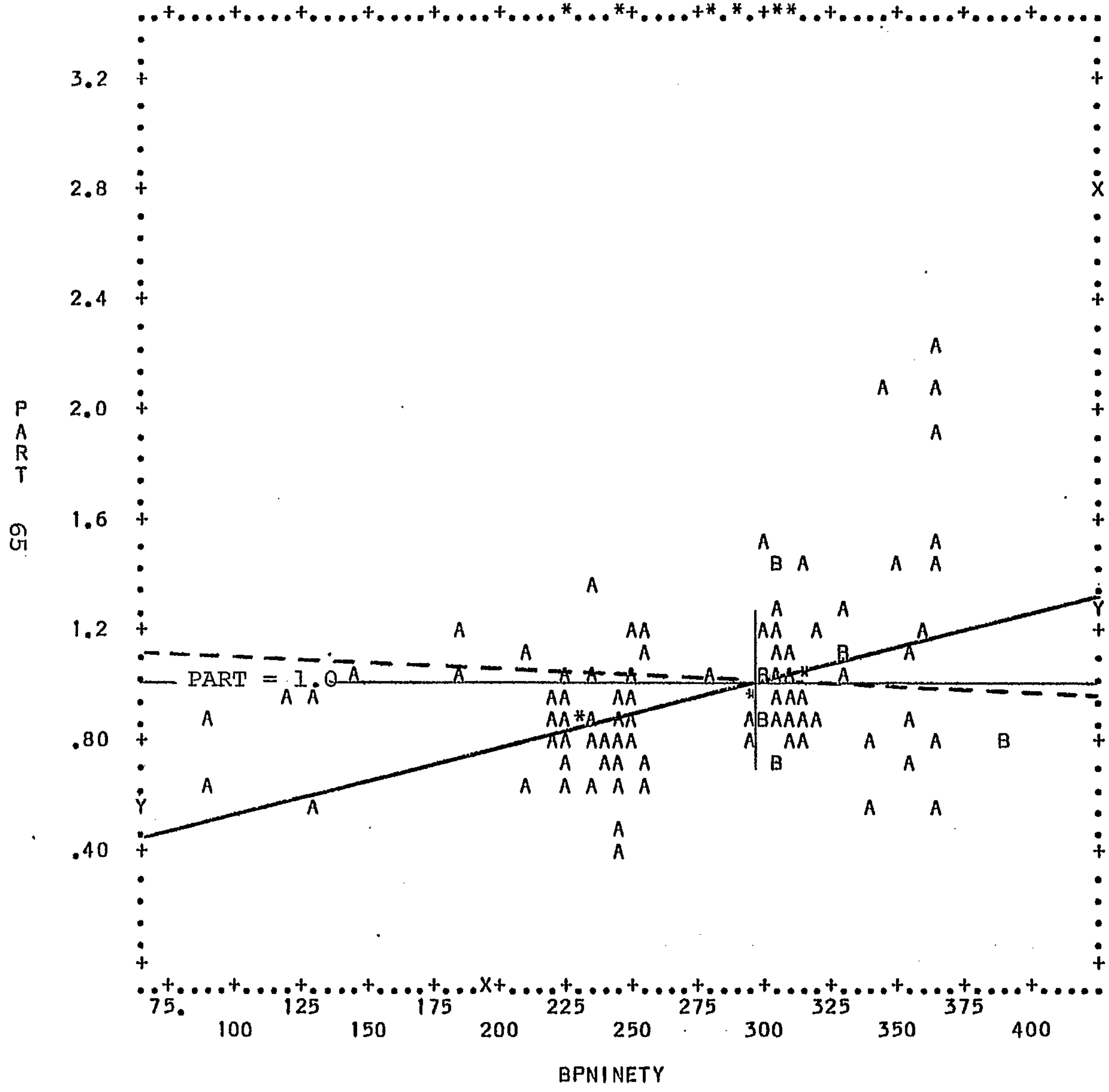
Petroleum
Solid Line

```
N=  112
COR= .701

      MEAN     ST.DEV.    REGRESSION LINE      RES.MS.
X    21.012    14.112   X= 38.669*Y-13.856     102.33
Y    .90169    .25567   Y= .01269*X+ .63500    .03359
```

Alternate
Dashed Line

```
N=   10
COR= .803

      MEAN     ST.DEV.    REGRESSION LINE      RES.MS.
X    28.590    8.0524   X= 34.579*Y-5.1281     25.902
Y    .97509    .18701   Y= .01865*X+ .44188    .01397
```

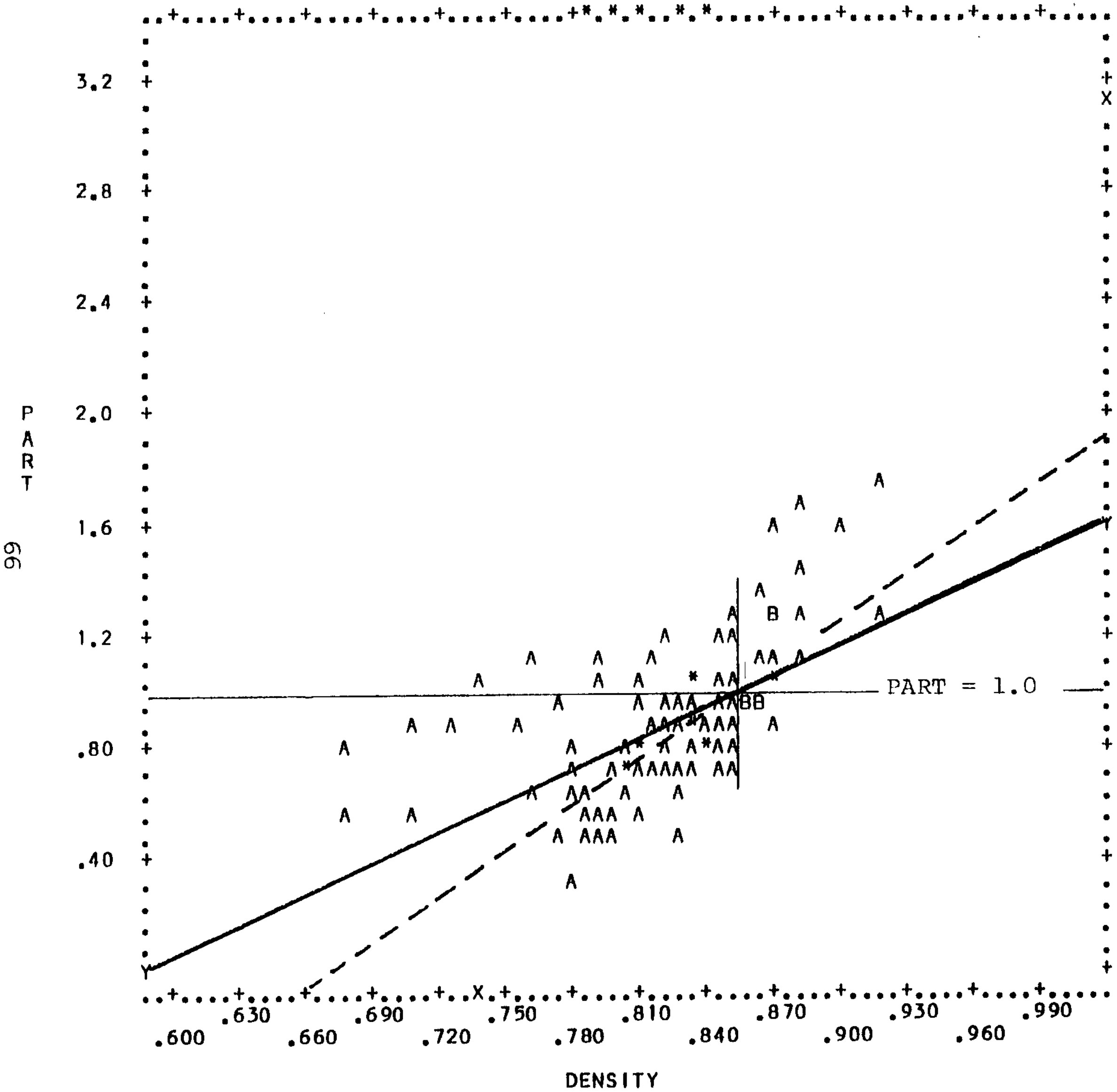
Figure 18. Normalized particulate versus aromatics.



```
N=  112                  Petroleum
COR= .432                Solid Line

      MEAN      ST.DEV.     REGRESSION LINE       RES.MS.
X    276.96     61.310    X= 82.100*Y+ 195.17     3086.3
Y    .99628     .32235    Y= .00227*X+ .36770     .08532
```

```
N=    10                 Alternate
COR=-.087                Dashed Line

      MEAN      ST.DEV.     REGRESSION LINE       RES.MS.
X    308.70     39.936    X=-18.213*Y+ 326.91     1780.5
Y    .99965     .19170    Y=-420E-6*X+ 1.1292     .04103
```

Figure 19. Normalized particulate versus 90% boiling point.



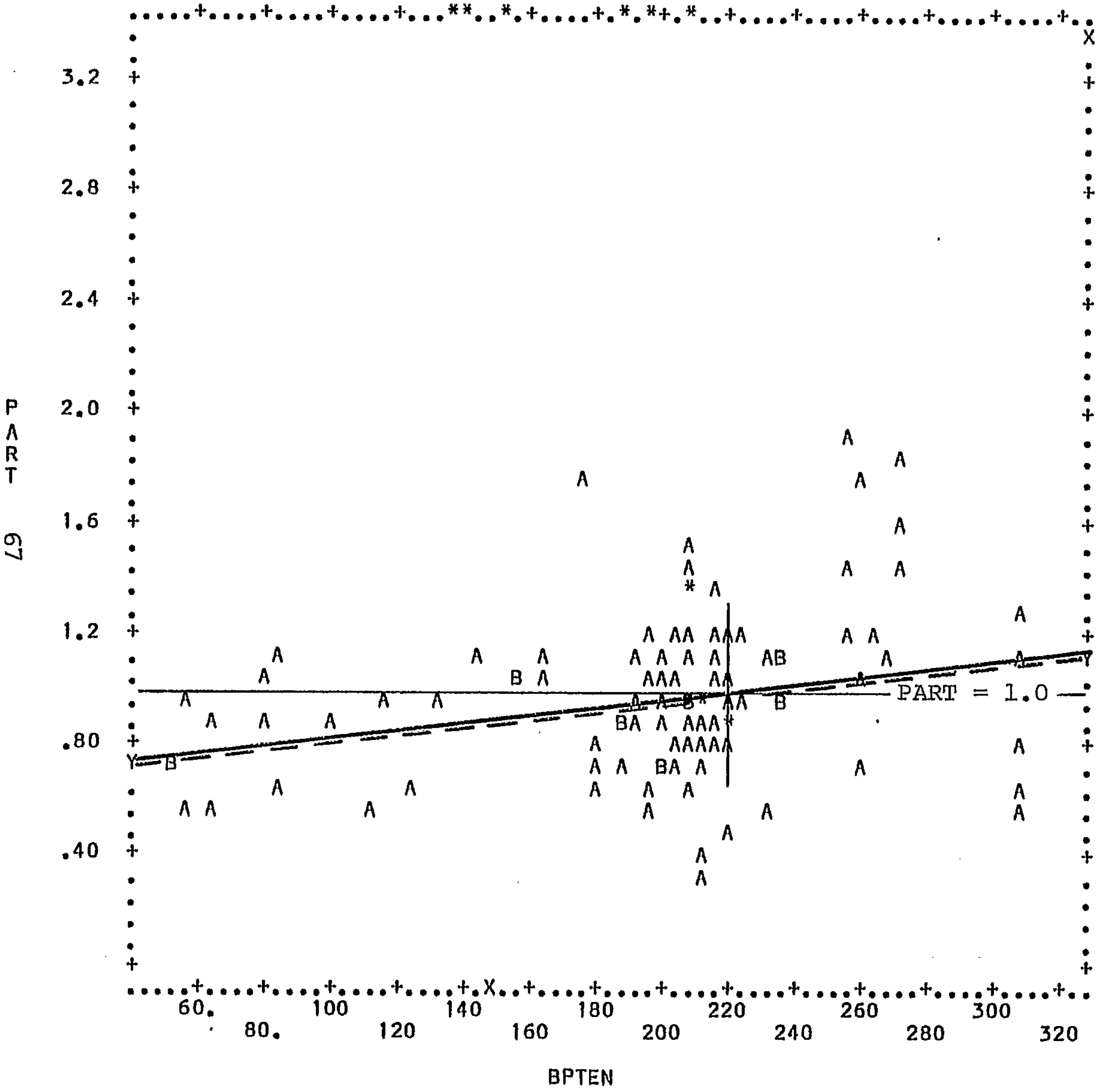
Petroleum
Solid Line

```
N=  112
COR= .565

      MEAN     ST.DEV.     REGRESSION LINE     RES.MS.
X    .82167    .04249   X= .08736*Y+ .74464    .00124
Y    .88174    .27503   Y= 3.6602*X-2.1258     .05192
```

Alternate
Dashed Line

```
N=   10
COR= .806

      MEAN     ST.DEV.     REGRESSION LINE     RES.MS.
X    .83770    .02546   X= .11511*Y+ .73072   256E-6
Y    .92943    .17823   Y= 5.6425*X-3.7973    .01253
```

Figure 20. Normalized particulate versus density.



Petroleum
Solid Line

```
N=  112
COR= .273

       MEAN     ST.DEV.     REGRESSION LINE      RES.MS.
X     203.20    52.199   X= 50.185*Y+ 154.81     2544.8
Y     .96412    .28379   Y= .00148*X+ .66271     .07522
```

Alternate
Dashed Line

```
N=   10
COR= .449

       MEAN     ST.DEV.     REGRESSION LINE      RES.MS.
X     191.60    53.707   X= 132.13*Y+ 65.847     2590.7
Y     .95171    .18252   Y= .00153*X+ .65934     .02992
```

Fiugre 21. Normalized particulate versus 10% boiling point.

petroleum-based studies are almost identical (Figure 21). This apparent anomaly is due to the poor fit of the regression lines caused by scattered data. The data was scattered similarly in both cases to yield similar slopes.

5. Unregulated Emissions

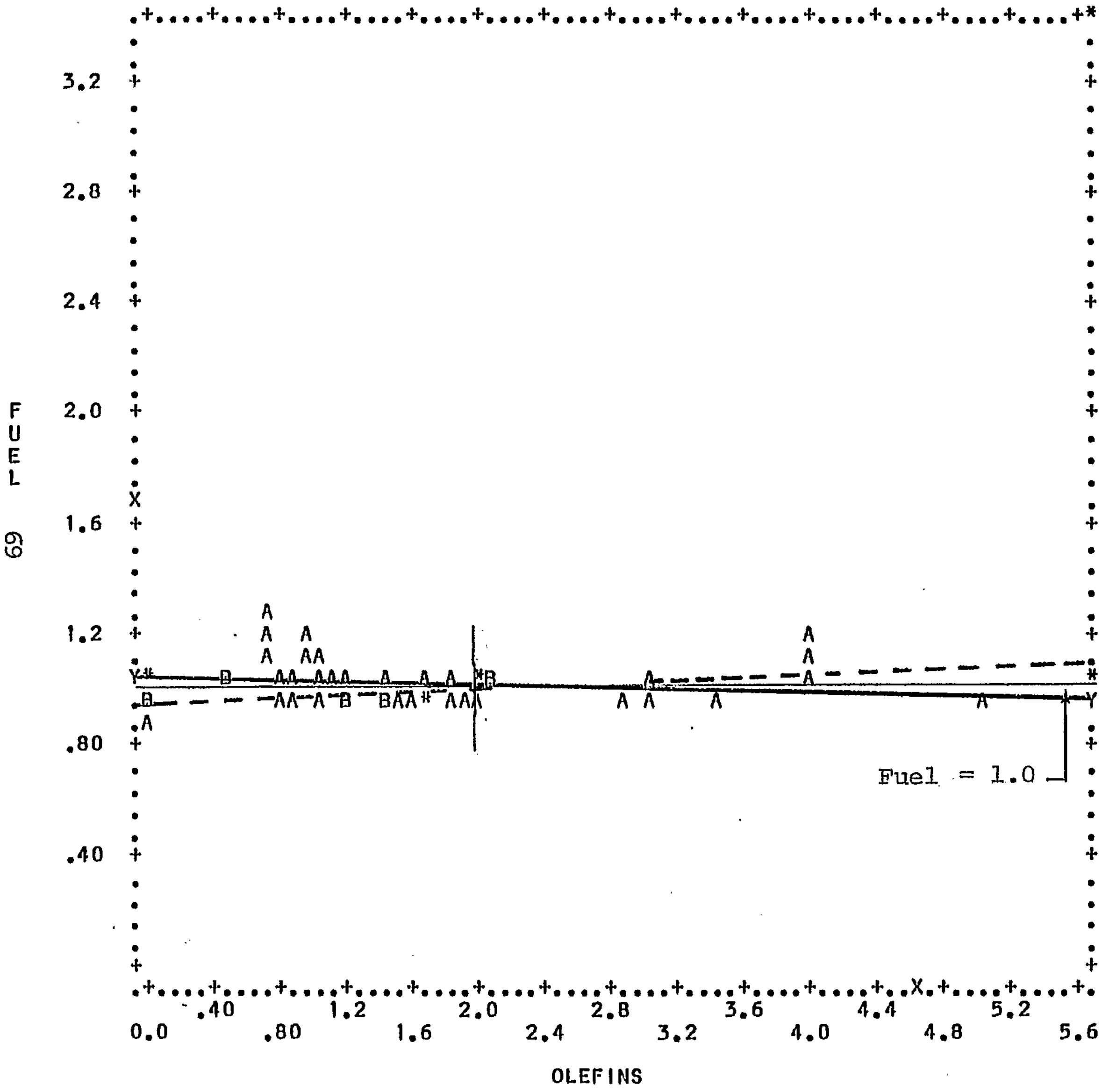
The remaining selected fuel property-exhaust emission data pairs are shown in Figures 22 through 28. Again, the individual regression lines representing each study in a common frame (for each fuel property-emission variable pair) are located in Appendix E. Table 33 shows the goodness-of-fit for each fuel property-exhaust emission data pair. Calculated "chi-square" values do not indicate any statistically different between petroleum-based and alternate-source fuel effects on the exhaust emissions listed in Table 33.

TABLE 33. UNREGULATED EMISSION DATA PAIRS GOODNESS-OF-FIT

Data Pair	Calculated "Chi-Square"	Petroleum vs. Alternate Statistically Different
Fuel Consumption - Olefins	0.033	No
Fuel Consumption - Density	0.012	No
BaP - Nitrogen	1.96	No
BaP - Aromatics	2.25	No
Aldehyde - Aromatics	3.65	No
Solubles - Cetane	1.45	No
Solubles - Nitrogen	0.482	No

F. Additional Comments

In many cases, the scattergrams of the fuel property-exhaust emission data pairs did not visually support the trends determined by goodness-of-fit calculations. It should be noted that all the scattergrams contained regression lines representing both petroleum-based fuels and alternate-source fuels, regardless of the bivariate correlation coefficient values. Bivariate correlation coefficients less than 0.7 are not considered to represent a good fit of the data. In most cases, the coefficients were <0.7. Therefore, the lines themselves may be misleading. A detailed statistical analysis would have included an error band to show the range within which the lines could have fallen. As used in this study, goodness-of-fit does not imply good linear fit of the ata. In the case of this study, the goodness-of-fit shows that petroleum-based fuel data yield prediction equations which, when used in conjunction with alternate-soruce data, results in a scatter of predicted results that are statistically similar to the scattered results observed.



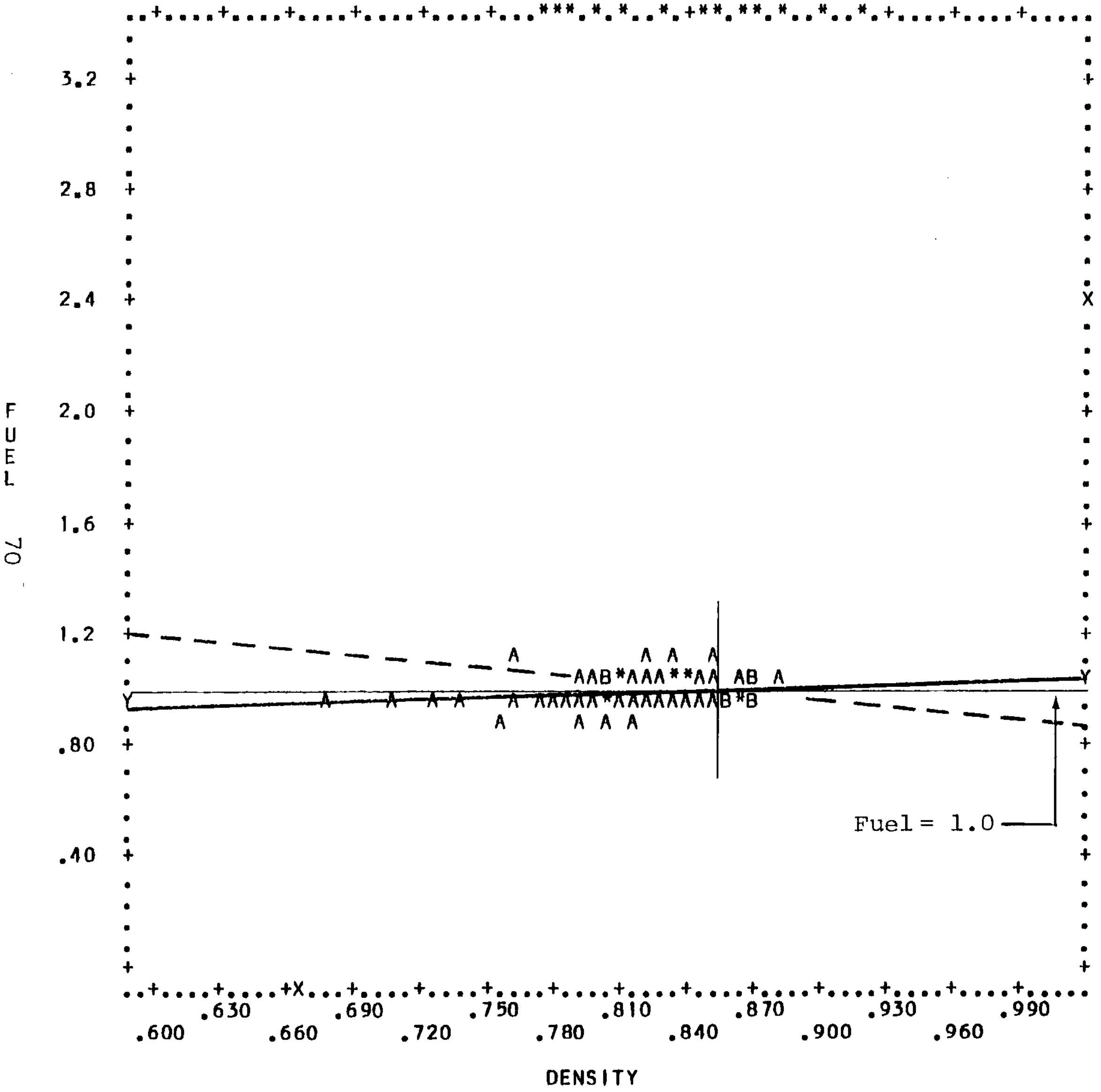
Petroleum
Solid Line

```
N=   69
COR=-.238

       MEAN     ST.DEV.     REGRESSION LINE        RES.MS.
X     1.8116    1.1309    X=-3.5767*Y+ 5.4825     1.2244
Y     1.0263    .07529    Y=-.01585*X+ 1.0551     .00543
```

Alternate
Dashed Line

```
N=   10
COR= .237

       MEAN     ST.DEV.     REGRESSION LINE        RES.MS.
X     1.0100    .82926    X= 6.3767*Y-5.3105      .73005
Y     .99119    .03086    Y= .00883*X+ .98227     .00101
```

Figure 22. Normalized fuel versus olefins.



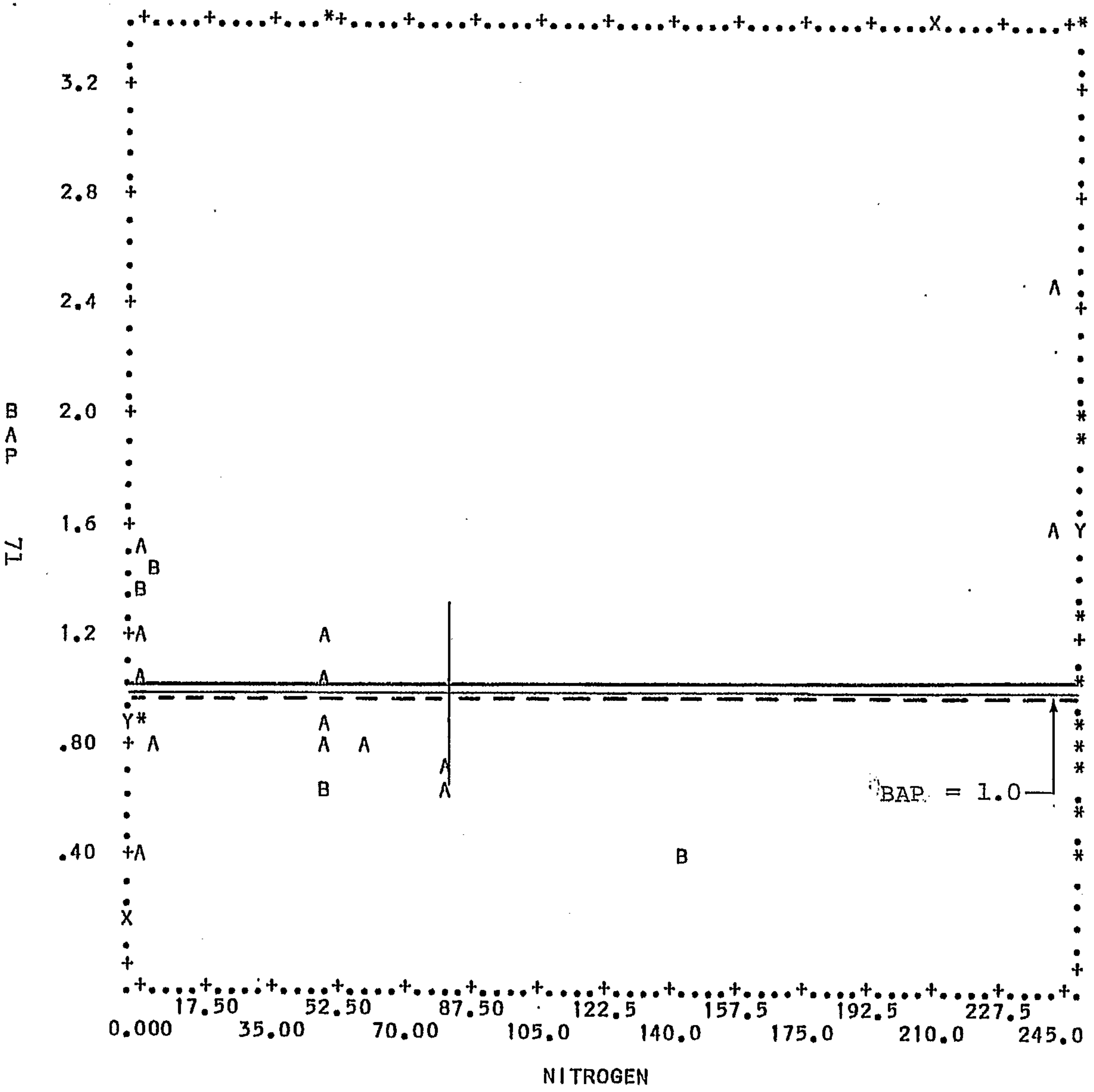
Petroleum
Solid Line

```
N=   85
COR= .195

       MEAN     ST.DEV.      REGRESSION LINE      RES.MS.
X     .81565    .04006   X= .15468*Y+ .66181     .00156
Y     .99455    .05062   Y= .24700*X+ .79309     .00249
```

Alternate
Dashed Line

```
N=   10
COR=-.621

       MEAN     ST.DEV.      REGRESSION LINE      RES.MS.
X     .83770    .02546   X=-.50251*Y+ 1.3450     448E-6
Y     1.0094    .03144   Y=-.76657*X+ 1.6516     684E-6
```

Figure 23. Normalized fuel versus density.



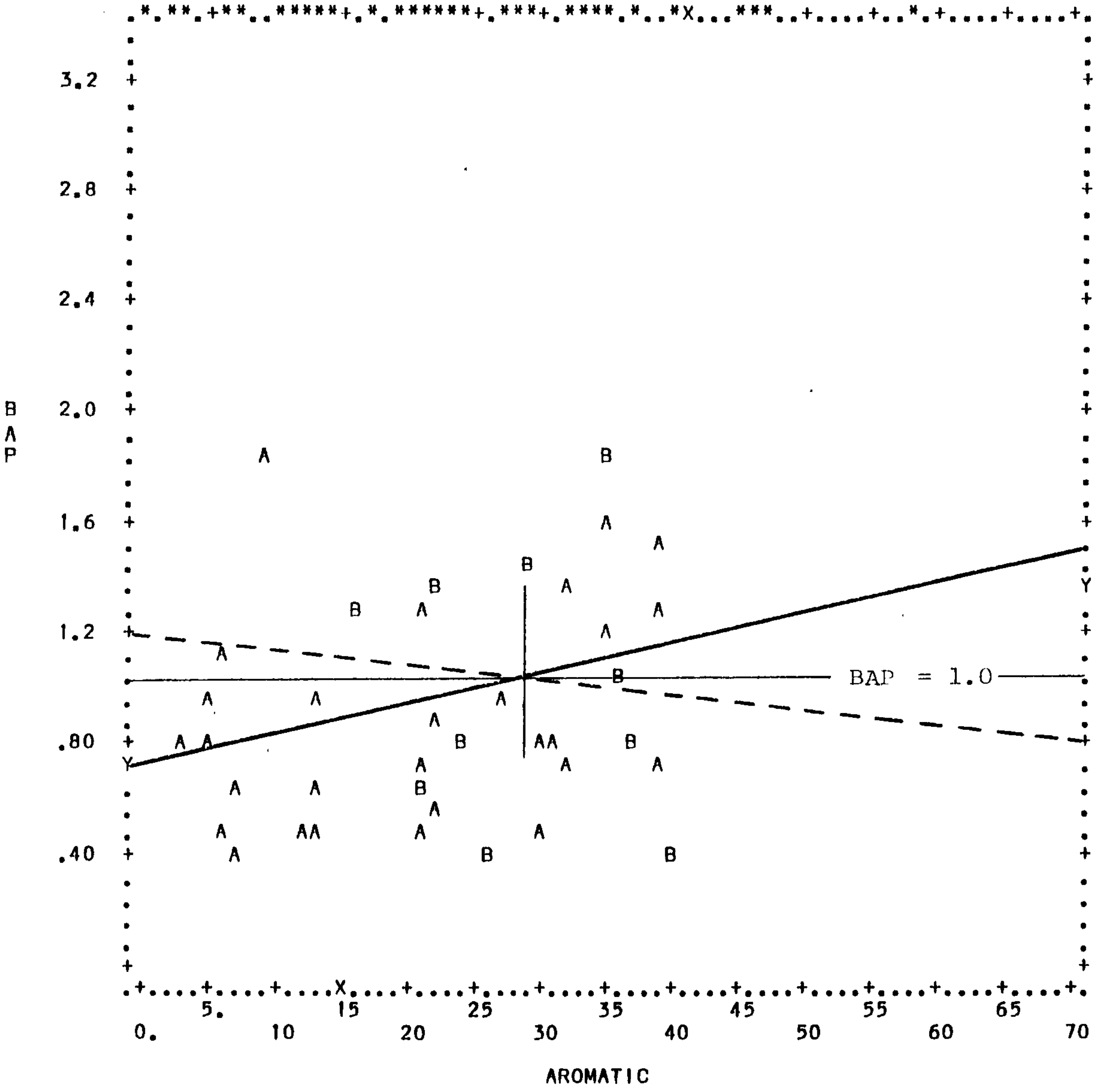
Petroleum
Solid Line

```
N=    21
COR= .077

        MEAN     ST.DEV.     REGRESSION LINE     RES.MS.
X     171.00     263.07   X= 40.591*Y+ 128.59    72410.
Y     1.0448     .50174   Y= 148E-6*X+ 1.0195    .26341
```

Alternate
Dashed Line

```
N=    10
COR= .068

        MEAN     ST.DEV.     REGRESSION LINE     RES.MS.
X     604.40     742.46   X= 103.02*Y+ 498.95    617273
Y     1.0236     .49078   Y= 450E-7*X+ .99640    .26972
```

Figure 24. Normalized BaP versus nitrogen.



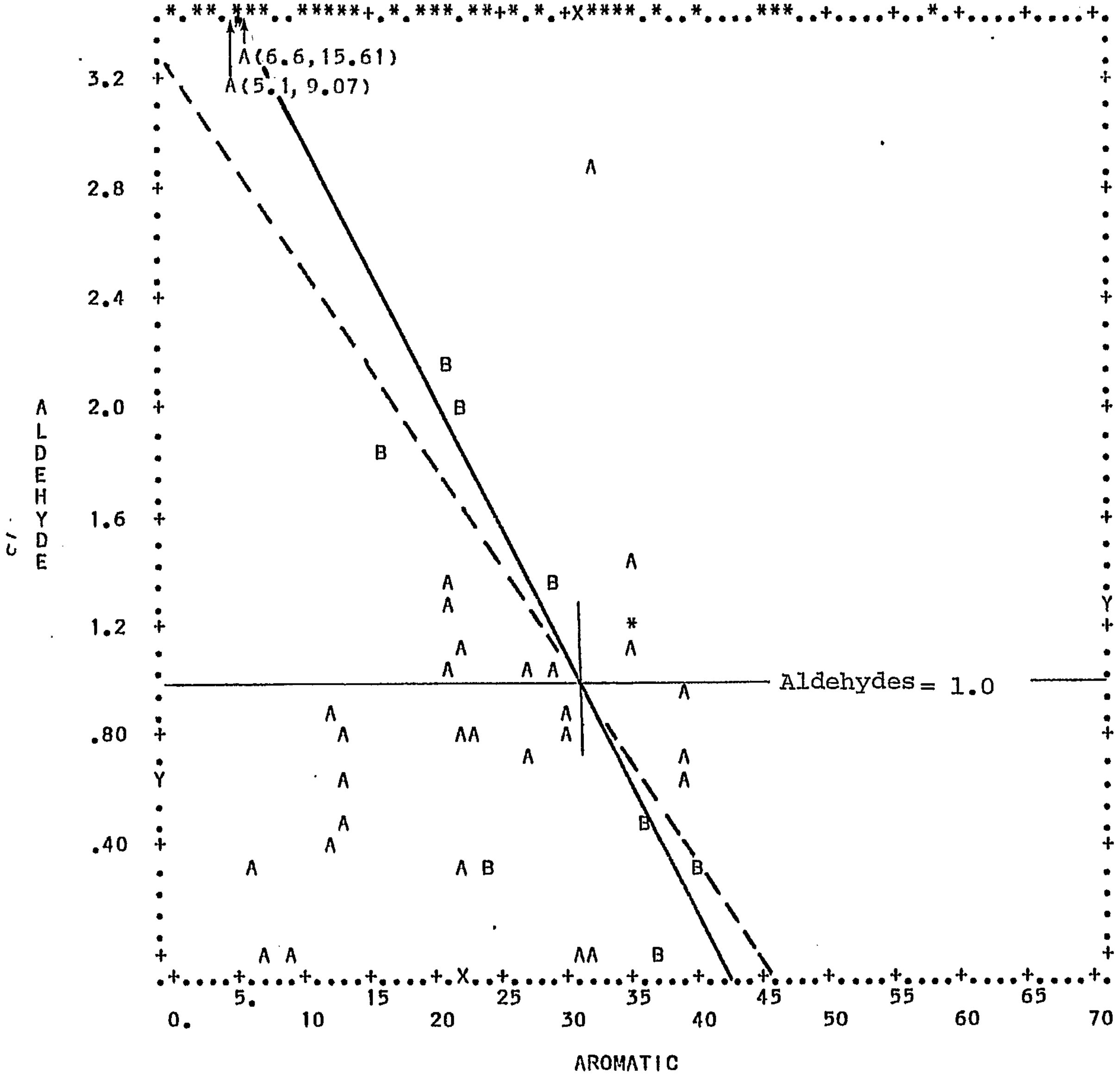
Petroleum
Solid Line

```
N=    29
COR= .327

     MEAN     ST.DEV.    REGRESSION LINE     RES.MS.
X    20.162   12.020   X= 10.271*Y+ 11.060   133.83
Y    .88624   .38263   Y= .01041*X+ .67642   .13560
```

Alternate
Dashed Line

```
N=    10
COR=-.081

     MEAN     ST.DEV.    REGRESSION LINE     RES.MS.
X    28.590   8.0524   X=-1.3445*Y+ 29.944   72.472
Y    1.0068   .48273   Y=-.00483*X+ 1.1450   .26045
```

Figure 25. Normalized BaP versus aromatics.



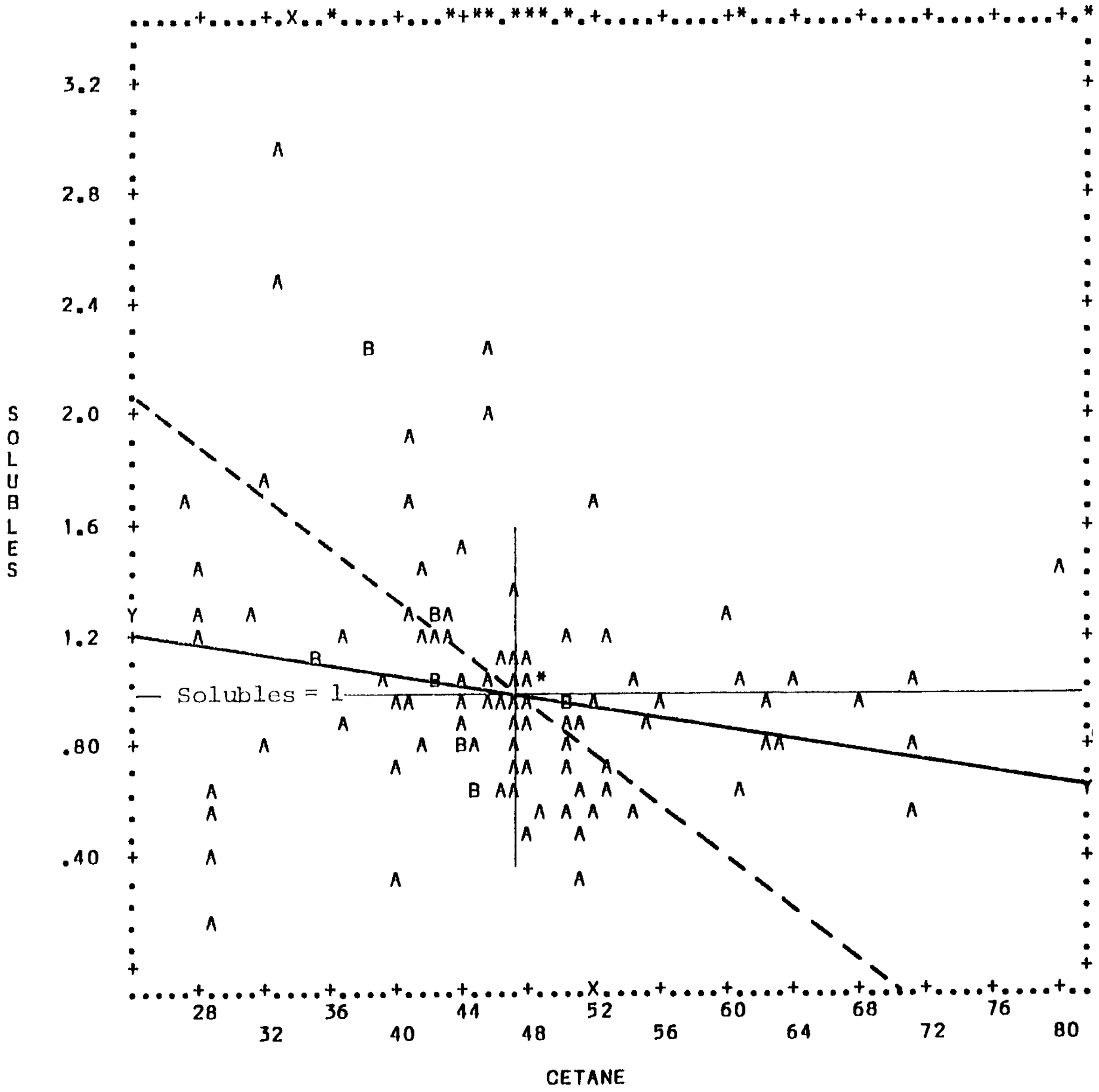
Petroleum
Solid Line

```
N=    34
COR=-.398

       MEAN     ST.DEV.     REGRESSION LINE      RES.MS.
X     21.176    11.500   X=-1.4345*Y+ 23.795    114.73
Y     1.8256    3.1943   Y=-.11068*X+ 4.1694    8.8519
```

Alternate
Dashed Line

```
N=     9
COR=-.748

       MEAN     ST.DEV.     REGRESSION LINE      RES.MS.
X     28.933    8.4629   X=-7.6660*Y+ 37.197    36.067
Y     1.0779    .82565   Y=-.07297*X+ 3.1891    .34329
```

Figure 26. Normalized aldehyde versus aromatics.



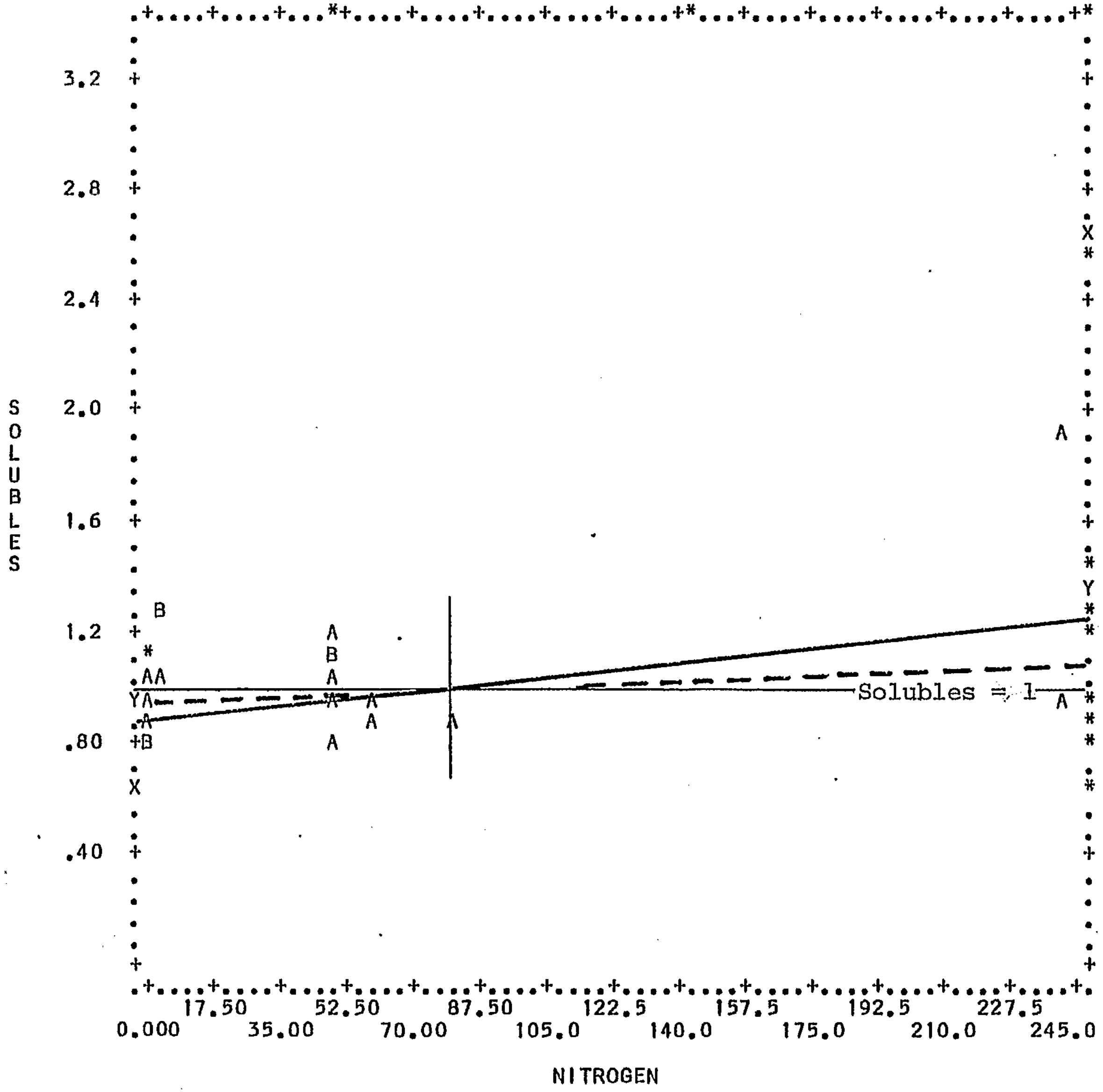
Petroleum
Solid Line

```
N=   105
COR=-.219

      MEAN      ST.DEV.      REGRESSION LINE      RES.MS.
X    46.810     9.8833   X=-5.0690*Y+ 51.851     93.911
Y    .99450     .42644   Y=-.00944*X+ 1.4362     .17483
```

Alternate
Dashed Line

```
N=     9
COR=-.507

      MEAN      ST.DEV.      REGRESSION LINE      RES.MS.
X    43.889     5.2784   X=-5.9836*Y+ 50.672     23.658
Y    1.1336     .44719   Y=-.04295*X+ 3.0186     .16982
```

Figure 27. Normalized solubles versus cetane.



Petroleum
Solid Line

```
N=    17
COR= .492

     MEAN      ST.DEV.     REGRESSION LINE       RES.MS.
X   57.118     74.904   X= 144.73*Y-91.980      4538.4
Y   1.0302     .25442   Y= .00167*X+ .93482     .05236
```

Alternate
Dashed Line

```
N=     9
COR= .815

     MEAN      ST.DEV.     REGRESSION LINE       RES.MS.
X   655.78     768.41   X= 1205.0*Y-931.56      226661
Y   1.3173     .51968   Y= 551E-6*X+ .95590     .10367
```

Figure 28. Normalized solubles versus nitrogen.

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