SECOND ANNUAL REPORT
ON

GASOLINE COMPOSITION AND VEHICLE EXHAUST GAS POLYNUCLEAR AROMATIC CONTENT

Period Ending April 15, 1971

CRC-APRAC Project No. CAPE-6-68
APCO/EPA Contract CPA-70-104

Submitted to
The Coordinating Research Council, Inc.
and
Environmental Protection Agency

Esso Research and Engineering Company
Products Research Division
Linden, New Jersey 07036

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Submitted to

The Coordinating Research Council, Inc.

c/o

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SECOND ANNUAL REPORT

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Note:

The following personnel changes will be in effect for the start of the third-year program of this Project:

1) Mr. J. S. Ninomiya, Ford Motor Co., new member of the Project Group.

2) Dr. J. H. Somers, Environmental Protection Agency, replaces Mr. T. W. Stanley as Project Officer.

1. SUMMARY

Fuel composition, engine deposits and vehicle emission-control systems have been studied as variables affecting the exhaust emissions of phenols and of polynuclear aromatic hydrocarbons (PNA, measured as benzo-(a)pyrene (BaP) and benz(a)anthracene (BaA)). This program was the second-year continuation of research supported jointly by the Coordinating Research Council, Inc., and the Environmental Protection Agency.

The exhaust from uncontrolled (1966) and engine-modification (EM) (1968 and 1970) vehicles in 7-mode cyclic tests with cold starts was cooled and filtered to collect PNA and phenols. Emission rates, per gallon of fuel, ranged from 74 to 776 milligrams of phenol, 3 to 165 micrograms of BaP, and 13 to 276 micrograms of BaA. Standard deviations for single determinations were estimated to be 38 milligrams of phenol, and 25% and 11% for BaP and BaA emissions, respectively. Standard calculated emission results for CO, HC, and NO were obtained concurrently with the PNA tests. Based on first-year results, PNA emissions from the 1966 and 1968 vehicles were corrected to a uniform CO level for each vehicle. For the 1970 vehicle, smaller variations in CO emission made PNA corrections unnecessary.

Fuel composition variables affecting emissions were found to have both direct effects, which were observed in short-term tests over existing engine deposits, and indirect effects, which appeared as emission differences between different engine deposits. The fuel-composition variables that were studied with typical-volatility fuels in direct-effect tests included aromatics content at 11-12%, 28%, and 46%; fuel PNA (as BaP, 0 and 3 ppm); fuel lead (0, 0.5, and 3 grams/gal.); and the content of a high-boiling naphtha (0 and 16% at 12% aromatics, 0 and 2% at 46% aromatics). Engine deposits were formed with commercial gasoline which provided a high lead level with phosphorus and, using a different base fuel and in only two vehicles, low-lead and no-lead levels without phosphorus. Comparable tests in the three vehicles provided data on the performance of emission control systems in controlling PNA and phenol emissions.

PHENOL EMISSION

Phenol emission from each vehicle correlated linearly with fuel aromatics, approaching zero at very low aromatics; other fuel variables had no effect. At typical aromatics levels, phenols from the 1970 vehicle were down 30% from the nearly-equal 1966 and 1968 vehicles. Engine-deposit type had no effect on phenol emission.

PNA EMISSION

PNA emissions from the 1968 and 1970 vehicles (EM) were similar at an average of only 30% of the PNA from the 1966 uncontrolled vehicle. The CO emissions were also similar at 0.6-0.8%, against 1.5% in the 1966

vehicle; emissions of CO and PNA correlated. This implies that more-nearly typical (higher-CO) 1966 and 1968 vehicles would emit more PNA than was observed here.

In the 1966 and 1968 test vehicles, increasing fuel aromatics from 11% to 46% caused PNA emissions to increase by an average of 134%, with BaP emission increasing more rapidly than BaA emission. In the 1970 vehicle, the effect of increased aromatics on PNA emission was not statistically significant.

Increasing fuel PNA content (as BaP, from 0 to 3 ppm, i.e., the field maximum) caused a 32% increase in BaA emission and a small, non-significant increase in BaP emission.

A high-boiling naphtha (catalytically cracked naphtha + polymer, FBP 419°F by ASTM D-86) present at 2% in a 46%-aromatic fuel did not significantly affect the emission of BaP or of BaA. When present at 16% in a 12%-aromatic fuel, this naphtha apparently caused substantial PNA-emission changes. However, increases in two vehicles were offset by decreases in the third, with no conclusive over-all effect for the naphtha.

The presence of antiknock lead in fuel had variable effects on PNA emission; both increases and decreases were observed, compared with tests using unleaded fuels. Limited data at 0.5 grams Pb/gallon indicated average decreases of 26% (BaA emission) to 43% (BaP emission). More extensive data at 3 grams/gallon indicated no significant BaP change and a 17% BaA increase.

While tests in the 1966 and 1968 vehicles showed that increases in fuel aromatics caused substantial increases in PNA emission, tests in the same vehicles showed that changes in fuel-derived engine deposits also affected PNA emission by a factor of more than two. As a part of these tests, high-aromatic fuels produced PNA emissions which were not higher than the PNA emissions from low-aromatic fuels under different, higher-emission, deposit conditions. The essential properties of fuels for forming low-emission or high-emission deposits are not clearly identified at this time.

2. INTRODUCTION AND OBJECTIVES

The first year of research on vehicular emission of polynuclear aromatics (PNA) and phenols under CRC-APRAC Project CAPE-6-68 resulted in a number of conclusions[1] (references are given in Appendix A) which influenced the definition of objectives for the second-year research program. Second-year objectives also reflected an increased interest in the use of low-lead and lead-free gasolines. In reflecting these influences, the second-year objectives unavoidably continued deferring action on some of the original objectives in areas such as vehicle operating modes, oil consumption, warm-up, spark timing, etc., which had been outlined in the original program plans but were not undertaken in the first year.

As a background for the second-year objectives, it is appropriate to review briefly the highlights of the first-year conclusions as to the effects of different controlled variables on the emission of PNA [benzo(a)pyrene (or BaP) and benz(a)anthracene (or BaA)] and phenols. Generally, these conclusions were based on comparing results obtained in test pairs which differed in respect to the variable under study, and each variable was usually evaluated by several available test pairs. The concurrently measured carbon monoxide (CO) emissions in the two tests of a pair commonly differed, and this difference was shown to affect the PNA emissions of the tests and thereby to influence the apparent effect of the variable being studied. A formula was developed to take this CO effect into account within a given vehicle and the conclusions reached are believed to be reasonably independent of this source of error. However, where the variable was "emission control system" and the "effect" is the difference between the PNA emissions of two vehicles which differ as to the presence of a control system for CO and HC emission, it was recognized that the difference in CO between the two vehicles was, in fact, part of the variable itself, rather than a source of error. Therefore, the CO-correction approach was not applied to the between-vehicle studies. (In the present report, the observed CO emission for every test in both years is used, together with the first-year formula, to convert all observed PNA emissions from a vehicle (1966 or 1968 only) to a standard CO level for that vehicle, and even between-vehicle comparisons are then on a more uniform basis.)

The highlights of the first-year studies, particularly as they influenced second-year plans, were:

1) Increases in fuel aromatics increased PNA emission, but to an apparently lesser degree in a 1968 Chevrolet (with EM control) than in a 1966 Plymouth without emission control (NC).

2) A high-aromatic fuel emitted less PNA, other things being equal, when it contained more C_7 aromatics, at the expense of C_{9-10} aromatics; i.e., volatility or molecular weight played a part.

3) The presence, in a low-aromatic test fuel, of a small amount of a high-boiling naphtha (a polymer/heavy catalytic naphtha mixture) was suspected as the cause of a relatively high PNA emission from the low-aromatic fuel and a consequent appearance of relatively low sensitivity to increased aromaticity, per se. This component was not rich in PNA content (i.e., BaP), however.

4) The presence, in a fuel, of PNA (measured as BaP) at the maximum field level found in gasolines resulted in PNA emission about 25% greater than if the fuel BaP content were near zero, and this relative effect was nearly constant over different fuels in two different vehicles (NC and EM), i.e., over a wide range of emission levels. Very little of even a large amount of BaP present in the fuel actually survived and was emitted, or caused the emission of other BaP that would appear to have survived from the fuel.

5) The presence of lead (3 ccs TEL/gallon) in fuel apparently caused little or no change in BaP emission and an increase of about 30% in BaA emission.

6) Accumulation of lead-free deposits in previously-cleaned combustion chambers caused no consistent effect on PNA emission. The deposits were accumulated in programmed city/suburb/highway operation on a dynamometer, with an average speed of 30 mph.

7) Conversion of these lead-free deposits to leaded deposits (with lead and phosphorus present in a different base fuel) slightly more than doubled the emission of PNA. These were single-vehicle, three-fuel results, and could be due to base-fuel composition, and/or lead, and/or phosphorus.

8) Emission of PNA from leaded fuel used in the presence of leaded (+ phosphorus) deposits was about double that from lead-free fuel and lead-free deposits; the effect was apparently due largely to the deposit change, in line with the preceding item. Tests of only two fuels in one vehicle were available for data on this point, and the result could derive either from lead, from phosphorus, or from the use of two different base fuels for deposit formation.

9) The PNA emission from a 1968 (EM system) Chevrolet was about 30% as great as from a 1966 (NC) Plymouth, with comparable deposits present in both and with five fuels tested in both vehicles. The CO emissions of both vehicles were relatively low, for the model years, so that PNA may have been relatively low as well, but the relative between-vehicle comparisons of PNA should remain valid.

10) An increase of 0.5% CO in the 7-mode cyclic test result from a given vehicle was associated with an apparent 45% increase in PNA emission.

11) Phenol emission more than tripled on increasing fuel aromatics from 12% to 46%; lead appeared to have a small suppressing

action on phenols, while deposit accumulation increased phenols. The 1968 emission control system decreased phenols only slightly, if at all, compared to the 1966 uncontrolled case. PNA in fuel, and fuel volatility at constant aromatics, did not affect phenol emission.

Most of these results, particularly as they relate to PNA emission, are in at least directional agreement with findings by Begeman,[2, 3, 4] by Griffing(5) and by others. The most unexpected, and significant, results were those relating to a direct (but small) effect of lead, to an effect of deposits, and to a suspected effect of high-boiling materials (aromatics?) in fuels, lying between the single-ring aromatics and the 4-ring or 5-ring polynuclear aromatics. The apparent reduction in PNA (but not phenol) by the 1968 emission-control system, while not expected, was judged important enough to justify tests in an additional controlled vehicle and to encourage testing in advanced experimental low-emission vehicles.

The second-year objectives developed from these considerations included the study, with respect to emissions of PNA and phenols, of the following factors:

1) The effects of lead antiknock (a) instantaneously, as a result of its presence in the test fuel, with a low, non-zero, level included, and (b) long-term, as lead residues appear in deposits, or disappear by extended use of reduced-lead and zero-lead gasolines.

2) The effects of fuel aromatics content, including an intermediate level around 30%.

3) The effects of fuel PNA content.

4) The effects of high-boiling aromatics, as distinct from total aromatics, such as might occur in heavy catalytic naphthas or heavy catalytic reformates and which are not PNA but may act as PNA precursors.

5) The effects of current exhaust emission control systems, extending the study of the above factors beyond the 1966 (NC) and 1968 (EM) vehicles to a 1970 EM vehicle.

6) The effects of advanced low-emission experimental systems (thermal and catalytic) as means of providing control on PNA and phenol emission; this heading also includes the effect, on PNA and phenols, of systems, either the same or separate, for controlling nitrogen oxide emissions.

It was foreseen that these objectives would be approached by the use of new test-fuel blends prepared without the high-boiling naphtha that was previously used, and including a cross-blend at an intermediate aromatics level. It was further foreseen that the lead-level experiments required should use this cross-blend as a base fuel, with "no-lead," "low-lead," and "high-lead" levels represented. Deposit studies would employ similar lead levels but in necessarily different base fuels. As far as possible, the second-year work was to be comparable with results already obtained in the first year. In the first year, however, deposits had been changed from no-lead to leaded in one car, while for the second year the change was to be in the opposite direction (leaded to no-lead), and in two or more cars.

Most of these objectives have been attained in, at least, a limited way. In few cases can it be assumed that work is complete, however, and no vehicles with experimental low-emission control systems were available for use.

The results obtained with the 1970 vehicle present a number of inconsistencies compared to earlier results, so that certain earlier conclusions from the first two vehicles are now less clear than they appeared to be initially. Specifically, the 1970 vehicle, with relatively leaner carburetion and with a retarded spark, emits less phenol than the earlier vehicles, and its PNA emisssions are less sensitive to some fuel compositional variables. Only one deposit condition was studied for the 1970 vehicle.

Two additional objectives have been achieved, although they were not formally specified for the second year: (1) The PNA accumulated in a vehicle muffler (three different vheicles) during a test has been evaluated (see Appendix C) in relation to the PNA emitted at the tailpipe. (2) The analytical methods for PNA have been converted to the GC/UV method developed by CAPE-12-68 (Appendix E), so that results are available on a larger variety of PNA species in each test. Data interpretation is still based on the emission of BaP and BaA, however, since these are the only PNA results for earlier tests.

3. EXPERIMENTAL

3.1 Test Fuels

The considerations involved in preparation of the test fuels used for first-year work are given at length in Section 4 and Appendix B of the First-Year Report(1). Prominent among these considerations was the requirement for volatility (Engler D86 distillation) properties, including the 90%-FBP range, that were commercially typical.

For the second year (see Appendix B of this report) these considerations continued to apply but presented new problems because the second-year objectives required that blends be prepared which were as similar as possible to the first-year blends but which did not contain the high-boiling naphtha (heavy catalytic naphtha/polymer/pentanes) that was used in the first-year blends. Appendix B of this report gives the compositions used, with identically the same components other than the heavy naphtha, to prepare the new (1970) basic blends for comparison with the earlier (1969) blends. Appendix B also contrasts the distillation and other properties of the two sets of blends, as summarized below:

FUEL PROPERTIES

Aromatics:	Low		Mid	High	
Year:	1969	1970	1970	1969	1970
RVP	10.6	10.5	10.2	10.7	10.5
IBP °F	82	92	91	84	92
10%, °F	112	116	116	112	116
50%	218	215	217	220	222
90%	320	296	310	332	322
FBP, °F	400	384	383	387	381
% Arom.	12	11	28	46	46
% Olef.	6	1	2	5	1

The second-year (1970) blends match the 1969 blends reasonably well except around the 90% - FBP range of the low-aromatic fuel. Here the exclusion of the heavy naphtha was only partly compensated by the increases made in certain aromatic fractions (see Appendix B). The 1970 base gasolines (11% and 46% aromatics) were low in PNA content, as were the 1969 fuels. PNA addition, when required, was done in both years by adding a 384+° FVT reformate bottoms, at 22 grams per gallon, thus adding 8000 μg of BaP per gallon and substantial amounts of other PNA species. (The 8000 μg BaP level was approximately the maximum found (First-Year Report) by Esso Research in a field sampling study, not at CAPE-6 expense, and

disclosed to CAPE-6 for guidance in preparing the blends.) Lead contents of 0, 0.5, and 3 gms./gallon were used in the 1970 fuels; the 0.5 level was used only in the mid-aromatic fuel, and the low-aromatic fuel was tested only with lead at the 3-gm. level.

The exclusion of the high-boiling naphtha (HBN) in formulating the second-year (1970 set) test fuels was prompted by the suspicion that its presence at 16% in the first-year (1969) low-aromatic (12%) fuels was causing misleadingly high PNA emissions. These, in turn, caused misleadingly small apparent effects for increasing fuel aromatics from 12% to 46%, since only 2% of the HBN was present in the 1969 46%-aromatic test fuel. When this suspicion was confirmed (Section 4) by the finding of lower emissions for the 1970 low aromatic (no HBN) fuels than for the 1969 fuels, the 1970 set became the basic reference blends for evaluating fuel variables in the present report, and data from the 1969 fuel set provided a measure of the effect of the presence of the high-boiling naphtha.

Different fuels, in larger quantities, were used for deposit accumulation or modification by operation of the test vehicles for periods of 1000-4000 miles on a Mileage-Accumulation Dynamometer (see Appendix C.) Where "leaded" deposits were specified in the first-year report (see footnote on page 9 of that report) the fuel used contained about 2.5 gms. of Pb per gallon, along with 0.2 theories of phosphorus, and was a commercial leaded premium fuel, or a prototype blend of that type. In this report, this fuel is coded as C3P. At the beginning of the second year, the 1966 and 1968 test vehicles contained such lead + phosphorus deposits, as did the 1970 vehicle when it was first used during the year. During this year, low-lead and lead-free fuels were also used for deposit changes in the 1966 and 1968 vehicles. These fuels, which were free of phosphorus, were based on a commercially-available, high-aromatic, (35-40%) lead-free premium gasoline, coded as fuel A in this report. Motor Mix TEL was added, at 0.5 gms. of Pb/gallon, to a portion of this fuel to prepare the "low-lead" blend with the code symbol A.5. Thus the high-lead deposits were invariably associated with one type of base gasoline and had phosphorus present. Conversely, the low-lead and no-lead deposits were invariably formed from a different type of base fuel and did not contain phosphorus. These distinctions as to phosphorus and as to base fuel in addition to lead level may be important in interpreting the deposit-effect results in this report, and exploration of their significance is one part of the third-year program. At the same time, any deposit effects from either base fuel, lead, or phosphorus can be detected, so that concurrent changes in all the variables is the most efficient procedure for initial studies.

3.2 Production of Samples

The procedure and equipment for sample production were unchanged from the first year and are fully described in the first annual report. The test vehicle is operated on a Clayton chassis dynamometer in three cold-start blocks of twelve 137-second, 7-mode cycles each. The vehicle drives about 29 miles and uses about 2-2.4 gallons (weighed) of fuel.

The total exhaust, except a sidestream for infrared gas analysis, is cooled and filtered and the condensed water is recovered. The samples for analysis include the water condensate (90+% of all phenols), the filter media, and the solvent washings of all surfaces from the inlet end of the vehicle muffler to the outlet side of the filter; most of this surface is on the walls of the 84-tube heat-exchanger. The side-stream scrubber tower on the filtered exit gas was not used in the second year, because first-year results showed it to be of doubtful value for PNA or phenols. As shown in Appendix C of the present report and on the basis of 18 tests, the muffler sample might often be omitted with little loss, but the need to clean the muffler anyway means the sample may as well be included and this is normally done.

3.3 Analysis Of Samples

Analytical techniques for phenols were unchanged in the second year from the descriptions in the previous report. The aqueous condensate ususally contains over 90% of all the phenols, while the Soxhlet extract of the fiber glass filter media contains no phenols. Although many different phenols are present, the data are reported in terms of phenol, i.e., the parent compound. CRC-APRAC-CAPE 12-68 at Esso Research is currently studying techniques for estimating individual phenols in the sample.

Analyses for PNA in exhaust samples in the early part of the second year (through Test 32) continued to be done with a TLC (thin-layer chromatography) finishing step, as described in the first-year report. Concurrently, CAPE-12-68 analyzed samples from twelve CAPE-6 tests by the GC/UV method which they had developed. The data by the two methods are compared in Appendix D, and Appendix E, prepared by CAPE-12, is a detailed description of the procedure for the GC/UV method. The regression equations for the data in Appendix D are

BaP by GC = 8.61 + 0.997 (BaP by TLC), with R = 0.997,
and BaA by GC = 15.36 + 0.830 (BaA by TLC), with R = 0.990.

Viewed differently, averaging the ratios of GC/TLC leads to

BaP by GC = 1.16 (TLC), and
BaA by GC = 0.94 (TLC).

These comparisons indicate reasonable agreement between the methods. (The BaA by GC is probably more accurate than by TLC, according to CAPE-12 studies, because the TLC band for BaA, when analyzed by mass spectroscopy, includes the methyl derivatives.) However, it appears preferable to compare results within a given method, where this is possible, in examining the effect of a controlled variable.

Tests earlier than number 26 include five tests covering a range of yields, for which both TLC and GC analyses were done (see Appendix D); for 26-32, both methods were used, and for tests 33-59 only GC analyses are available. Test 26 marked the beginning of a study of lead levels, using the 28%-aromatic fuel. In order to avoid ambiguity in the data that might arise over the choice of analytical results, this report uses GC/UV results for PNA yields on test 26 and all tests thereafter. However, previously-issued quarterly reports used TLC data through test 31, and GC results thereafter. Thus certain values here are slightly different from those previously reported. Another, smaller, variation from the quarterly report data also occurs because the present data, in some cases, reflect higher-precision radiotracer counting data than were used in previously issued reports.

The GC/UV method of exhaust-sample PNA analysis makes available the yield data on up to eleven different PNA species. In the earliest tests (26-31), only BaP and BaA were determined, but six species are known for most tests through number 54, with eleven species assayed thereafter. In some of the earlier tests, some GC peaks were not successfully trapped and yield results are missing in these cases. The available results are included in Appendix D, along with the calculated ratios between certain species. These ratios may suggest some differences in sample composition that is related to other variables, but no clear-cut conclusions are now available in this area.

3.4 Test Vehicles

A detailed discussion of the test vehicles appears in Appendix C. At this point, it is appropriate to compare the three vehicles briefly as to exhaust-gas composition (CO and oxygen) and temperature (at the muffler exit). These factors appear likely to influence the survival of PNA in the exhaust system and its ultimate emission. The importance of CO (expressed as the cyclic-test results) was demonstrated in the first-year report and is emphasized again in a later section of this report. Fundamentally, the presence of CO is to be taken as a symptom of an oxygen-deficient condition that should favor the formation and survival of PNA. The CO levels found for the 1966 and 1968 vehicles were only about half of the typical values for these model years, so their PNA may also be relatively low. Exhaust oxygen (as %) was estimated for each vehicle from average values of the computer-recorded correction factors used in cycle-test calculations to force % CO + % CO_2 to 15.00. The correction factors were taken as measures of air dilution and the oxygen contents calculated accordingly. Exhaust temperatures (muffler exit, Table C-44) were taken as the average of hot-cycle maximum values at the peak of the 15-50 MPH acceleration mode. The table on the next page compares the vehicles with respect to CO, O_2, and the exhaust temperature; reference to the differences will be made at a later point in this report.

VEHICLE EXHAUST CONDITIONS

Vehicle	Avg. % CO (Fed. Test)	Est. Avg. % O_2	Avg. Max.°F. Muffler Exit
1966 Plymouth	1.49	1.2	568
1968 Chevrolet	0.74	1.8	599
1970 Chevrolet	0.65	2.6	706

Oil consumption rates of the vehicles were observed (Appendix C) in each operation for mileage accumulation in changing engine deposits. The consumption rates remained low, at around 0.5 quarts/1000 miles; high oil consumption could be expected to influence PNA emission, according to the results reported by Begeman (4).

4. RESULTS

A summary of data on all tests for the second contract year is presented in Table 1. This table includes data on observed emission rates of benzo(a)pyrene (BaP), benz(a)anthracene (BaA), and phenols (as phenol), all per gallon of test fuel consumed. Fuel consumption, aqueous condensate recovery, ambient weather, and computed Federal cycle emissions results (1968-1969 model-year method) are also included.(a) Tables C-3 through C-43 in Appendix C present average results from one to three test blocks for each mode in six of the twelve cycles that form a block in a sample-production operation. The extreme right-hand columns of these Appendix C tables present the Federal cycle results that appear in Table 1.

Table 2 provides a test-number key to all the PNA/Phenol emissions tests since the start of Project CAPE-6-68, with the exception of a few tests specified in a footnote on the table. Reference to Table 2 will immediately indicate whether a given vehicle/deposit/test fuel case has been tested and specify the number of the test. All test pairs whose comparison can serve to evaluate a given controlled variable can be readily selected from this table. Similarly, sets of tests can be selected whose data can form a matrix for statistical analysis. Finally, this same format, with yields/gallon of fuel inserted in place of test numbers, can provide useful tabulations (in three tables) of emission rates for phenol, BaP, and BaA, within which the same selections of test pairs, etc., can be made. In the following, the effects of variables will be discussed in terms of data from both contract years, rather than from only the second year.

4.1 Phenol Emission

The format of Table 2 is used in Table 3 to present the phenol emission data for both contract years. Inspection of the data immediately indicates a dependence on fuel aromatics content, as was shown in the first year, and it also appears that the 1970 vehicle emits phenol at a lower level, for a given fuel, than the 1966 or 1968 vehicles. The early data in the 1966 Plymouth show a deposit effect which was interpreted, in the first year, as meaning that leaded deposits (C3P) caused higher emission than the (preceding) unleaded deposits (A). Newer data, in both the 1966 and 1968 vehicles, examine the phenol level after returning from C3P deposits, through low-lead (A.5), to the no-lead (A) condition, and it is clear that this change did not reduce phenol emission in either vehicle. It now appears more likely that the deposits for the early no-lead (A) tests, which

(a) For consistency, results from all three vehicles (1966, 1968, and 1970) are presented on the basis of concentrations (ppm or %). For the 1970 vehicle (4000-lb. class), the factors of 23.8 and 0.0127, respectively, will convert the tabulated % CO and ppm HC to the basis of grams/mile.

Table 1

CRC-APRAC PROJECT CAPE-6-68 - SECOND YEAR REPORT

SUMMARY DATA SHEET

Test No.	Test Vehicle	Deposit-Fuel Codes	Test Fuel[a] % Ar.	BaP	TEL	Year	Emission Rate/Gal. of Fuel[d] BaP, µg	BaA, µg	Phenol, mg	Fuel Used, Gal.	Aq. Cond. Lb.	Fed. Cycle Emissions[b] CO, %	HC (C_6IR)	NO, ppm	Bar. Pr. "Hg	Humidity Gr./Lb.
20	'66 Plymouth 318 (NC)	C3P	46	0	0	69	104	163	732	1.84	9.97	1.31	563	2400	30.33	20
22		C3P	11	0	3	70	45	99	113	1.90	11.45	1.40	729	2207	30.42	23
23		C3P	11	8K	3	70	35	128	110	1.99	11.40	1.45	752	2267	29.81	14
27		C3P	28	0	0	70	72	120	350	1.95	11.25	1.42	629	2375	29.99	33
28		C3P	28	0	0.5	70	67	92	424	2.00	12.55	1.57	623	2007	30.06	59
26		C3P	28	0	3	70	54	143	379	1.90	10.94	1.40	671	2268	30.28	23
34		A.5	28	0	0	70	37	51	279	1.99	11.77	1.54	549	1957	30.13	56
32		A.5	28	0	0.5	70	20	34	389	1.99	12.83	1.66	568	1590	30.11	92
37		A.5	28	0	3	70	31	49	334	1.98	12.44	1.57	592	1738	30.00	67
41		A	28	0	0	70	37	49	435	1.93	13.08	1.45	519	1352	30.14	108
42		A	46	0	0	69	51	73	772	1.93	12.07	1.38	496	1297	30.00	113
43		A	46	0	0	70	45	76	776	1.92	10.85	1.20	491	1721	30.08	39
54[c]		A	28	0	0	70	128[c]	195[c]	446	2.04	11.93	1.61	503	1861	30.29	23
21	'68 Chevrolet 307 (EM)	C3P	46	0	0	69	26	48	685	1.95	11.52	0.66	272	1391	29.94	21
24		C3P	11	0	3	70	9.7	37	78	2.07	13.24	0.72	415	1116	30.16	17
25		C3P	11	8K	3	70	13	75	88	2.04	13.23	0.79	419	1033	29.56	31
30		C3P	28	0	0	70	8.8	23	380	2.05	13.25	0.60	300	1094	30.05	65
31		C3P	28	0	0.5	70	9.8	22	406	2.15	13.26	0.91	283	1148	30.35	42
29		C3P	28	0	3	70	38	78	348	2.15	13.23	0.85	312	1098	30.21	36
35		A.5	28	0	0	70	14	15	346	2.14	13.45	0.80	264	1057	30.09	74
33		A.5	28	0	0.5	70	3.4	13	370	2.07	13.93	0.77	315	1087	30.18	82
36		A.5	28	0	3	70	2.8	12	401	2.05	13.38	0.60	301	1145	30.26	67
38		A	28	0	0	70	14	16	314	2.07	13.96	0.76	273	991	29.97	79
39		A	46	0	0	69	10.5	23	691	2.02	12.31	0.70	193	1136	30.11	66
40		A	46	0	0	70	9.9	19	607	2.02	12.60	0.62	185	1037	30.07	77
45[c]	'70 Chevrolet 350 (EM)	C3P	11	0	3	70	37[c]	58[c]	91	2.46	18.15	0.78	221	803	30.17	84
51[c]		C3P	11	0	3	70	103[c]	123[c]	81	2.38	16.06	0.66	273[c]	948	30.35	36
51B		C3P	11	0	3	70	19	57	78	2.71	17.37	0.73	238	1025	30.09	30
44		C3P	11	8K	3	70	20	70	123	2.42	16.85	0.63	227	953	30.32	56
52		C3P	11	8K	3	70	34	72	74	2.62	17.19	0.65	242	1033	30.42	31
47		C3P	12	0	3	69	12	28	107	2.49	16.85	0.70	222	979	30.41	36
58		C3P	12	0	3	69	20	31	119	2.35	15.40	0.60	177	991	30.73	11
46		C3P	12	8K	3	69	10.5	38	106	2.48	17.03	0.67	215	983	30.60	45
53		C3P	46	0	0	70	26	60	420	2.43	14.08	0.60	133	1170	30.00	20
48		C3P	46	0	3	69	29	52	434	2.38	13.86	0.60	135	1174	29.69	60
49		C3P	46	0	3	70	17	42	460	2.40	15.64	0.64	138	1034	30.31	68
50[c]		C3P	46	8K	3	70	122[c]	110[c]	426	2.50	15.03	0.55	107[c]	1141	30.20	25
59		C3P	46	8K	3	70	28	63	485	2.28	13.68	0.60	132	1100	29.72	22
57		C3P	28	0	0	70	48	70	287	2.33	14.32	0.76	153	989	29.46	15
56		C3P	28	0	0.5	70	36	61	259	2.59	16.05	0.84	201	1113	29.96	11
55		C3P	28	0	3	70	26	51	256	2.46	15.60	0.62	180	1091	30.23	25

(a) BaP level is near-zero or 8000 µg/gal, added as reformate still-bottoms (other PNA also present); TEL as ccs/gal, Motor Mix; year refers to fuel compositions in Table B-1, see text also.

(b) Average of computed results from first 7 cycles of two or more of 3 12-cycle (4 cold + 8 hot) blocks used for PNA/phenol sample. See detailed modal-emission data, Appendix C.

(c) Reservations as to the validity of PNA emissions from Tests 45, 50, 51, and 54 are discussed in Appendix C.

(d) PNA data for tests through Test 25 are by TLC/UV analysis; 26 and later tests are by GC/UV analysis.

Table 2

CAPE -6-68 -SECOND YEAR REPORT

KEY TO TEST NUMBERS

(Covering Tests for Two Years(a))

Test Fuel				Number of PNA/Phenol Test for Indicated Test Vehicle and Engine Deposits(b)								
				1966 NC Plymouth					1968 EM Chev.			1970 EM Chev.
Fuel Set	% Arom.	BaP, µg./g.	TEL cc./g.	No Deposit	A	C3P	A.5	A	C3P	A.5	A	C3P
1969	12	0	3			17			13			47,58
		8K	0	3	9							
			3	4	12	16			7			46
	46	0	0	1	8	20		42	21		39	
			3	2	11	19			5,6			48
		8K	3			18			14			
1970	11	0	3			22			24			51B
		8K	3			23			25			44,52
	28	0	0			27	34	41	30	35	38	57
			0.5			28	32		31	33		56
			3			26	37		29	36		55
	46	0	0					43			40	53
			3									49
		8K	3									59

(a) Test 10 (special fuel) and tests of doubtful validity (see Table 1) are omitted.

(b) Engine deposits are specified by the fuel used for deposit formation. A commercial leaded premium fuel with phosphorus (Code C3P), a commercial unleaded premium (A), and the latter with 0.5 grams Pb/gallon (A.5) are included.

Table 3

CAPE -6-68 -SECOND YEAR REPORT

SUMMARY OF PHENOL EMISSION DATA

(Covering Tests for Two Years(a))

Test Fuel				Phenol Emission, mg./gal., for Indicated Test Vehicle and Engine Deposits(b)								
				1966 NC Plymouth					1968 EM Chev.			1970 EM Chev.
Fuel Set	% Arom.	BaP, µg./g.	TEL cc./g.	No Deposit	A	C3P	A.5	A	C3P	A.5	A	C3P
1969	12	0	3			165			116			107,119
		8K	0	117	154							
			3	117	148	179			165			106
	46	0	0	498	565	732		772	685		691	
			3	358	487	689			663,667			434
		8K	3			663			663			
1970	11	0	3			113			78			78
		8K	3			110			88			123, 74
	28	0	0			350	279	435	380	346	314	287
			0.5			424	389		406	370		259
			3			379	334		348	401		256
	46	0	0					776			607	420
			3									460
		8K	3									485

(a) Test 10 (special fuel) and tests of doubtful validity (see Table 1) are omitted.

(b) Engine deposits are specified by the fuel used for deposit formation. A commercial leaded premium fuel with phosphorus (Code C3P), a commercial unleaded premium (A), and the latter with 0.5 grams Pb/gallon (A.5) are included.

were formed from 4,000 miles of operation after the clean-chamber tests, were not at equilibrium; i.e., that additional miles on the no-lead (A) fuel would have caused greater emission of phenol. Evidently, deposit accumulation to an equilibrium level does increase phenol emission, but the equilibrium phenol emission level is not strongly affected by the composition of the deposits. On this basis, linear regressions of all the data (phenol yield vs. % aromatics) for each vehicle except the first two columns of data from the 1966 vehicle have been calculated, making the implicit additional assumption that other variables, such as TEL and PNA, are not important.

The regression equations take the form

$$\text{Phenol} = a + b\ (\%\ \text{Aromatics}),$$

where a and b are constants and phenol is expressed in mg./gallon of fuel burned. The results of the analyses for the three vehicles are summarized below and are presented graphically in Figure 1.

PHENOL REGRESSIONS

	Test Vehicle		
	1966 NC	1968 EM	1970 EM
Number of points	16	17	13
Intercept, a	-82.0	-74.4	-15.2
Slope, b	17.2	15.9	10.1
Std. error in b	1.03	0.58	0.39
Std. error of estimate	53.3	31.4	20.8
Correlation coefficient	0.976	0.990	0.992
Variance due to regression, %	95.2	98.0	98.4

The negative intercepts predicted by linear regression suggest that the true relationships are not linear. It is more likely that phenol emission approaches zero asymptotically as aromatics content decreases toward zero. Aromatics levels below 11% were not tested. The regressions against aromatic content explain over 95% of the total variance in the data from each car, so it appears that no other variable (TEL, PNA, etc.) is important, as long as equilibrium deposits are present. The 1966 and 1968 vehicles are apparently equivalent in terms of their phenol emissions, since their regressions are not significantly different. The 1970 vehicle, however, emits only about 70-75% as much phenol as the 1968 vehicle when typical fuels are considered:

	Phenol, mg./gal.		
	1968	1970	
Fuel Aromatics	Estimate	Est.	% of 1968
10%	85	86	101
20	244	187	77
30	403	288	71
40	562	389	69

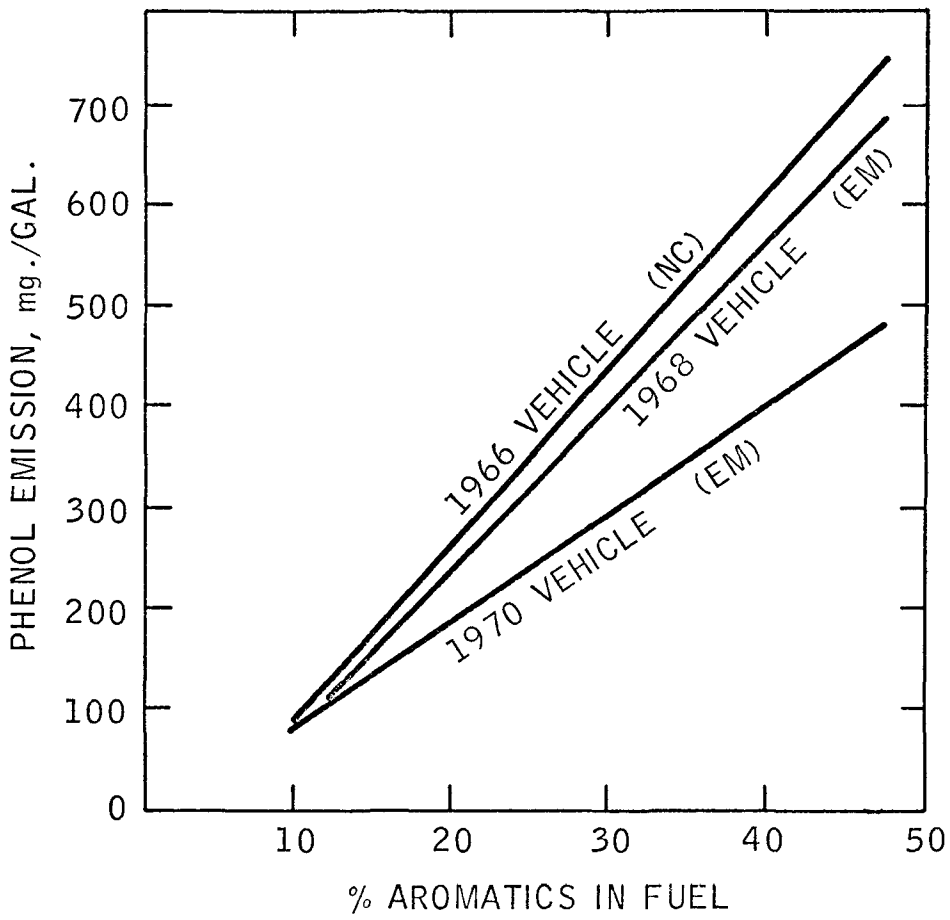

Figure 1

Effects Of Fuel Aromatics And Emission
Control Systems On Phenol Emission

According to the regressions, phenol emissions from all three vehicles are equal at about 10% aromatics in the fuel, i.e., just below the lower limit of the data. The 30% reduction in phenol that is found for the 1970 vehicle at higher aromatics contents, where the phenol levels of all vehicles are substantially higher, is clearly the more important conclusion, however.

4.2 Statistical Treatment Of PNA-Emission Data

In the first-year report for Project CAPE-6-68, the emission of PNA was shown to be correlated with the level of carbon monoxide (CO) emission, and the interpretation of first-year data was substantially improved by taking this effect into account. The Federal cycle % CO result, as determined at least once in each PNA emission test, was apparently a suitable measure of CO for the purpose. It was observed that if, between two PNA tests which differed as to some controlled variable, there was also an increase in CO, then the apparent relative PNA emission affect of the variable was unduly increased along with the CO change; the converse was also true. Where several measures of the relative PNA effect of a variable were available, along with associated between-test differences in CO emission, the results could be correlated to define a best estimate of the effect of the variable as that effect which appeared likely to occur if there were no attendant change in CO emission. By this means, an estimate of the change in PNA emission for any change in CO emission was obtained for use within a given vehicle (1966 Plymouth or 1968 Chevrolet) and with other factors constant. The relationship found (page 38 of reference 1) was

$$Y_s = Y_t/(1 + 0.9(C_t - C_s)),$$

where Y_s and Y_t are respectively the PNA yield rates (μg./gal.) at the standard CO level (C_s, in %) and at the emission-test CO level (C_t). This relation was applicable to both BaP and BaA yield rates, but presumably not beyond differences of about ± 0.5% CO from a selected standard. This relationship can be used to calculate correction factors for converting PNA yield rates to a standard CO level, as typified in the following table.

PNA CORRECTION FACTOR FOR CO-LEVEL VARIATION

	Lean Mixture			Rich Mixture		
$C_t - C_s$, %:	-0.6	-0.4	-0.2	+0.2	+0.4	+0.6
Corr. Factor:	2.17	1.56	1.22	0.85	0.74	0.65

The use of a correction factor of this type agrees directionally with the reports by Begeman (4), Griffing (5), and Gofmekler (6) that rich mixtures result in increased PNA emission.

Table 4

CAPE-6-68 SECOND-YEAR REPORT

CORRECTED[a] PNA DATA FOR 1966 PLYMOUTH AND 1968 CHEVROLET FOR TWO CONTRACT YEARS

			PNA Emission, µg./gal.			
			BaP		BaA	
	Test No.	% CO	Observed	Corr.	Observed	Corr.
'66 Plym.	1	2.08	54	36	142	94
	2	1.92	118	86	264	193
	3	1.67	49	43	168	146
	4	1.78	91	73	214	171
	8	1.52	55	54	96	94
	9	1.56	59	56	133	126
	10	1.47	38	39	80	82
	11	1.62	60	54	138	124
	12	1.95	79	56	219	155
	16	1.43	85	91	198	212
	17	1.39	70	78	164	182
	18	1.27	131	165	219	276
	19	1.70	149	127	303	258
	20	1.31	104	125	163	196
	22	1.40	45	50	99	109
	23	1.45	35	37	128	134
	26	1.40	54	59	143	157
	27	1.42	72	78	120	130
	28	1.57	67	63	92	86
	32	1.66	20	18	34	30
	34	1.54	37	36	51	49
	37	1.57	31	29	49	46
	41	1.45	37	39	49	51
	42	1.38	51	57	73	82
	43	1.20	45	62	76	104
'68 Chev.	5	0.68	29	32	67	75
	6	0.64	27	32	54	63
	7	0.75	26	27	81	85
	13	0.96	28	25	59	52
	14	0.85	38	36	89	85
	21	0.66	26	30	48	55
	24	0.72	9.7	10.5	37	40
	25	0.79	13	13	75	75
	29	0.85	38	36	78	75
	30	0.60	8.8	11	23	28
	31	0.91	9.8	8.9	22	20
	33	0.77	3.4	3.5	13	13
	35	0.80	14	14	15	15
	36	0.60	2.8	3.4	12	15
	38	0.76	14	15	16	17
	39	0.70	10.5	12	23	25
	40	0.62	9.9	12	19	23

[a] Corrected to 1.5% CO for 1966 Plymouth and 0.8% CO for 1968 Chevrolet. Data through Test 25 by TLC analysis, then GC/UV analysis.

Table 5

CAPE -6-68 -SECOND YEAR REPORT

SUMMARY OF BENZO(a)PYRENE DATA
(Covering Tests for Two Years(a))

Test Fuel				BaP Emission, µg./gal., for Indicated Test Vehicle and Engine Deposits(c)								
				1966 NC Plymouth(b)					1968 EM Chev.(b)			1970 EM Chev.
Fuel Set	% Arom.	BaP, µg./g.	TEL cc./g.	No Deposit	A	C3P	A.5	A	C3P	A.5	A	C3P
1969	12	0	3			78			25			12,20
		8K	0	43	56							
			3	73	56	91			27			10.5
	46	0	0	36	54	125		57	30		12	
			3	86	54	127			32,32			29
		8K	3			165			36			
1970	11	0	3			50			10.5			19
		8K	3			37			13			20,34
	28	0	0			78	36	39	11	14	15	48
			0.5			63	18		8.9	3.5		36
			3			59	29		36	3.4		26
	46	0	0					62			12	26
			3									17
		8K	3									28

(a) Test 10 (special fuel) and tests of doubtful validity (see Table 1) are omitted.

(b) PNA yields from the 1966 NC and 1968 EM vehicles are corrected to standard levels of CO emission, by equations based on first-year data.

(c) Engine deposits are specified by the fuel used for deposit formation. A commercial leaded premium fuel with phosphorus (Code C3P), a commercial unleaded premium (A), and the latter with 0.5 grams Pb/gallon (A.5) are included.

Table 6

CAPE -6-68 -SECOND YEAR REPORT

SUMMARY OF BENZ(a)ANTHRACENE DATA

(Covering Tests for Two Years(a))

Test Fuel				BaA Emission, µg./gal., for Indicated Test Vehicle and Engine Deposits(c)								
				1966 NC Plymouth(b)					1968 EM Chev.(b)			1970 EM Chev.
Fuel Set	% Arom.	BaP, µg./g.	TEL cc./g.	No Deposit	A	C3P	A.5	A	C3P	A.5	A	C3P
1969	12	0	3			182			52			28,31
		8K	0	146	126							
			3	171	155	212			85			38
	46	0	0	94	94	196		82	55		25	
			3	193	124	258			75,63			52
		8K	3			276			85			
1970	11	0	3			109			40			57
		8K	3			134			75			70,72
	28	0	0			130	49	51	28	15	17	70
			0.5			86	30		20	13		61
			3			157	46		75	15		51
	46	0	0					104			23	60
			3									42
		8K	3									63

(a) Test 10 (special fuel) and tests of doubtful validity (see Table 1) are omitted.

(b) PNA yields from the 1966 NC and 1968 EM vehicle are corrected to standard levels of CO emission, by equations based on first-year data.

(c) Engine deposits are specified by the fuel used for deposit formation. A commercial leaded premium fuel with phosphorus (Code C3P), a commercial unleaded premium (A), and the latter with 0.5 grams Pb/gallon (A.5) are included.

However, it is doubtful that such a relationship will be useful for vehicles carburetted near, or leaner than, stoichiometric. For this reason, and lacking data suitable for demonstrating its validity, this relation is not regarded as applicable to the recently-obtained PNA data from the 1970 Chevrolet test vehicle. Instead, the PNA emitted by the 1970 vehicle may reflect exhaust oxygen content and temperature. As pointed out earlier in Section 3.4, the average oxygen content of the 1970 vehicle's exhaust was estimated at 2.6%, compared with 1.8% for the 1968 vehicle, even though the CO contents were similar. The higher oxygen content in the 1970 vehicle exhaust resulting from leaner carburetion, together with a hotter exhaust, resulting from retarded spark timing, suggests that some PNA formed in the engine may be destroyed before being emitted from the exhaust system; this could, in turn, introduce an added source of variability in PNA results from the 1970 vehicle.

All PNA emission-rate data, from both contract years, for the 1966 and 1968 vehicles have now been "corrected," by the above equation, to the expected rates at standard (near-average) CO levels of 1.5% and 0.8% for the 1966 and 1968 test vehicles, respectively. The CO levels used are the composite computed results from Federal 7-mode tests, averaged over from one to three of the three 12-cycle blocks used to form a PNA sample. The resulting "corrected" PNA yields can be compared directly, without the need to quality the comparisons by noting concurrent change in % CO. The corrected PNA data are listed in Table 4. Tests 15 (see first year report) and 54 (see Appendix C, this report) are omitted, as they do not provide useful data.

These corrected PNA yield data, for both years, are presented in Tables 5 (BaP) and 6 (BaA) in the same format that is used for Tables 2 (Test Numbers) and 3 (Phenols). The tables also include PNA data from the 1970 Chevrolet test vehicle. These latter data are not corrected for CO variation, for reasons given above. Tables 5 and 6 provide the data base for statistical analysis and for the presentation of the effects of different variables on PNA emission. Data from both years are used where applicable. Where replicate tests are listed, the average result is used.

Statistical analyses were used to identify and quantify the significant variables in PNA emission; BaP and BaA emissions were analyzed separately. The variables were found to have fairly constant relative (%-change) effects, so that the effect of a variable could be appropriately stated as the geometric mean of ratios between the results from a number of test pairs with the variable at two levels. Statistical analyses using the data in logarithmic form for all pairs related to each variable then lead directly to the geometric mean ratios as best estimates of the effect of each variable. All mean ratios (R_M) reported here are geometric means of ratios observed in from two to fifteen pairs of tests. Where a need was apparent, three-factor analyses of variance were used to detect interactions, such as the effectiveness of a variable in two vehicles but not in a third vehicle; parts of the data were then analyzed in smaller two-factor analyses to redefine the geometric mean ratios.

In presenting the results for different variables, each geometric mean ratio is accompanied by a statement of the 95%-confidence interval. The interval assists in determining what effects are significant and whether two mean ratios are meaningfully different. Each interval results from multiplying, and dividing, the geometric mean ratio by a factor based on the number of pairs in the mean, and on the estimated standard deviation in the determination of the logarithm of a single BaP (or BaA) yield, in μg/gallon.

These estimates of standard deviations in $\log_{10}$ of the yield were initially based on four replicate-test pairs. Three other pairs were added as replicates after being shown to be internally equivalent. Table 7 lists the replicate pairs used for the estimates. Reference to Table 2 indicates that designating Tests 8 and 42 as replicates, in the first line of the table of replicates, implies that emissions for deposits from a given fuel are reproducible even if other deposits have intervened. The next three lines represent true replicates, while the last three lines include three test pairs that were classified as replicates after data-analysis showed no difference between the PNA from 46%-aromatic fuels with, or without, 2% of a high-boiling naphtha (see Section 3.1). The estimates of standard deviation are for single determinations of the $\log_{10}$ of the yield in μg/gallon. These correspond, approximately, to standard deviations of 25% and 11% for one determination of the BaP and BaA yields, respectively. The relatively poor repeatibility for BaP is due to three test pairs from the 1970 vehicle.

4.3 Effects Of Vehicle Emission-Control Systems On PNA Emission

The effects on PNA emission of using emission-control-equipped vehicles were measured by comparing results from the 1966 vehicle (no control) with fifteen comparable results from the 1968 vehicle and with ten comparable results from the 1970 vehicle. Relevant data are given in Table 8. Within the 95% confidence limits, the two control-system vehicles were equivalent and emitted 30% as much of both PNA species as was emitted by the 1966 uncontrolled vehicle; i.e., a 70% reduction in PNA emission is indicated for the production-vehicle control systems. It should be recalled (Section 3.4) that the average CO emissions of the 1966 and 1968 vehicles were about half of typical or permitted levels. It follows that more typical vehicles for these years might show somewhat higher emissions of both CO and PNA, but the relative rates (for 1968/1966) should remain similar to those found here.

Table 7

REPEATABILITY OF PNA EMISSION TESTS

Vehicle Year	Test Nos. In Replicate Pair	Emission Rates In Repeat Tests, μg/gallon BaP	BaA
Fully-replicate pairs:			
1966	8, 42(a)	54, 57	94, 82
1968	5, 6	32, 32	75, 63
1970	44, 52	20, 34	70, 72
1970	47, 58	12, 20	28, 31
Est. of s, $\log_{10}$ of μg/gal.		0.1134	0.0377
Pairs shown to be internally equivalent:			
1966	42, 43	57, 62	82, 104
1968	39, 40	12, 12	25, 23
1970	48, 49	29, 17	52, 42
Est. of s, $\log_{10}$ of μg/gal. based on seven pairs		0.1062	0.0478

(a) Deposits present were from the same deposit fuel, with other deposits intervening.

Table 8

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EMISSION CONTROL SYSTEM EFFECTS ON PNA EMISSION[a]

Benzo(a)pyrene µg./gallon			Benz(a)anthracene µg./gallon		
Uncontrolled	EM System		Uncontrolled	EM System	
1966 Vehicle	1968 Vehicle	1970 Vehicle	1966 Vehicle	1968 Vehicle	1970 Vehicle
125	30	26	196	55	60
127	32, 32	17, 29	258	63, 75	42, 52
165	36	28	276	85	63
78	11	48	130	28	70
63	8.9	36	86	20	61
59	36	26	157	75	51
50	10.5	19	109	40	57
37	13	20, 34	134	75	70, 72
78	25	12, 20	182	52	28, 31
91	27	10.5	212	85	38
36	14	--	49	15	--
18	3.5	--	30	13	--
29	3.4	--	46	15	--
54, 57, 62	12, 12	--	94, 82, 104	25, 23	--
39	15	--	51	17	--
	1968/1966	1970/1966		1968/1966	1970/1966
Ratio, R_M[b]	0.25	0.30		0.32	0.32
95% Interval for R_M	0.21 to 0.30	0.24 to 0.38		0.30 to 0.35	0.29 to 0.36

(a) Data on each line relate to a common fuel and engine-deposit condition.

(b) Geometric mean ratio of PNA emissions, emission-controlled/uncontrolled.

Table 9

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EMISSIONS FROM LOW-AND HIGH-AROMATIC FUELS

Test Vehicle	Fuel PNA, as ppm BaP	Benzo(a)pyrene Emission, µg./gal. 11% Ar.	Benzo(a)pyrene Emission, µg./gal. 46% Ar.	Benzo(a)pyrene Ratio,[a] 46%/11%	Benz(a)anthracene Emission, µg./gal. 11% Ar.	Benz(a)anthracene Emission, µg./gal. 46% Ar.	Benz(a)anthracene Ratio[a] 46%/11%
1966	0	50	127	2.54	109	258	2.37
	3	37	165	4.46	134	276	2.06
1968	0	10.5	32, 32	3.05	40	75, 63	1.72
	3	13	36	2.77	75	85	1.13
1970	0	19	17, 29	1.21	57	52, 42	0.82
	3	20, 34	28	1.04	70, 72	63	0.89

(a) Replicate data were averaged for ratios.

Table 10

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EFFECTS OF FUEL AROMATICS ON PNA EMISSIONS

Test Vehicles	No. of Ratios in Mean	Geometric Means of Ratios of Emission at 46% Aromatics to Emission at 11% Aromatics: Benzo(a)pyrene Mean Ratio	Benzo(a)pyrene 95% Interval	Benz(a)anthracene Mean Ratio	Benz(a)anthracene 95% Interval
1966	2	3.37	2.07-5.49	2.21	1.77-2.76
1968	2	2.91	1.79-4.75	1.39	1.11-1.74
1970	2	1.12	0.69-1.82	0.86	0.69-1.08
1966, 1968	4	3.12	2.63-3.71	1.76	1.63-1.90

4.4 Immediate Effects of Fuel Composition on PNA Emission

The reduction in PNA emission that was observed in the two control-system vehicles does not completely eliminate the value of studies on the effects of fuel variables, because the PNA from vehicles in current use does vary with fuel changes. The present section relates to immediately-observable PNA-emission effects where different test fuels were used; a later section discusses indirect effects that occurred after extended use of deposit-forming fuels.

4.4.1 Fuel Aromatics Content

Test fuels with 11%, 28%, and 46% aromatics were used in PNA emission tests in the 1966, 1968, and 1970 test vehicles. In order to simplify the presentation, tests with 11% and 46% aromatics will be reviewed here; the 28%-aromatic data are available in Tables 5 and 6. Two test pairs are available for each vehicle to illustrate the effect of increasing aromatics from 11% to 46%. The data are presented in Table 9, with the second data line for each vehicle representing tests in which PNA (BaP at 3 ppm) had been added to the test fuels.

The ratios of emission at 46% aromatics to emission at 11% aromatics, as given in Table 9, range from 0.82 to 4.46. The geometric mean ratios for each vehicle are given in Table 10, and, in view of the 95% confidence intervals, it is clear that the PNA emission from the 1970 vehicle was not sensitive to fuel aromatics. Excluding this vehicle, the last line of Table 10 indicates the geometric mean ratios, with confidence intervals, for the 1966 and 1968 vehicles. The confidence intervals are based on the statistical discussions given in a previous section.

The mean ratios show that, in the 1966 and 1968 vehicles increasing fuel aromatics from 11% to 46% caused average increases in emissions of BaP and of BaA amounting to about 212% and 76%, respectively. BaP emission was apparently more than twice as sensitive as BaA emission, although more data on this point appear to be needed. The mean ratios for each vehicle also show a trend, particularly in BaA emission: the sensitivity of the emission rate to increases in fuel aromatics decreased between vehicles in the order of 1966>1968>1970 i.e., the more recent vehicles were less sensitive to aromatics.

4.4.2 Fuel PNA Content

At a given level of fuel aromatics (11% or 46%), the presence of PNA (BaP, BaA, and other species) already in the fuel can affect the emission of PNA. The emission-test fuels were prepared with near-zero PNA contents, and PNA was added, as reformate still-bottoms, to increase BaP content to the field-maximum level of 8000 μg. of BaP/gallon, or about 3 ppm. Comparisons of PNA emissions from fuels with and without PNA addition are available in Table 11. Two low-aromatic fuels and one high-aromatic fuel were used to provide three test pairs in each of three vehicles, with fuel PNA content as the only within-pair variable. The ratios do not differ significantly between base fuels or between vehicles. The geometric means of two sets of nine ratios each are given, with the 95% confidence intervals, in Table 12. An increase of 32% in BaA emission is demonstrated by the data but the 8% apparent increase in BaP emission is not statistically significant.

Table 11

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PNA EMISSIONS FROM LOW- AND HIGH-PNA FUELS[a]

Test Vehicle	Benzo(a)pyrene Emission, µg/gal. 0 BaP	Benzo(a)pyrene Emission, µg/gal. 3 ppm BaP	Benzo(a)pyrene Ratio, 3/0	Benz(a)anthracene Emission, µg./gal. 0 BaP	Benz(a)anthracene Emission, µg./gal. 3 ppm BaP	Benz(a)anthracene Ratio, 3/0
1966	78	91	1.17	182	212	1.16
	50	37	0.74	109	134	1.23
	127	165	1.30	258	276	1.07
1968	25	27	1.08	52	85	1.63
	10.5	13	1.24	40	75	1.88
	32, 32	36	1.12	75, 63	85	1.23
1970	12, 20	10.5	0.66	28, 31	38	1.29
	19	20, 34	1.42	57	70, 72	1.24
	17, 29	28	1.22	52, 42	63	1.34

(a) Fuel PNA content is expressed as ppm BaP; replicates are averaged for ratios.

Table 12

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EFFECT OF FUEL PNA ON PNA EMISSION

	Geometric Means of Ratios of Emissions at 3 ppm BaP to Emission at 0 ppm	
	BaP Emission	BaA Emission
Means of Nine Ratios	1.08	1.32
95% Interval	0.85 to 1.35	1.19 to 1.48
Significant Effect?	No.	Yes.

4.4.3 High-Boiling Naphtha

Tests with and without a high-boiling naphtha component in the test fuels showed that its presence caused changes in PNA emission which varied with the amount present and with test-vehicle identity. The component used was a mixture of pentanes, heavy catalytic naphtha and polymer gasoline. Its presence in test fuels did not significantly affect the content of aromatics or of PNA. The effect of the naphtha on PNA emission was tested in all three vehicles, using two concentration levels: 2% in a 46%-aromatic fuel, and 16% in an 11% - aromatic fuel. Olefin content was maintained at about 1% without the naphtha, and at 6% when it was present at either concentration level. The PNA emissions data, with and without the component present, are summarized in Table 13. Parallel statistical analyses of the logarithms of the yield data for BaP and for BaA in the first three lines (2% naphtha) of the table showed no significant effects on either BaP or BaA emission at even 90% confidence for 2% of the naphtha, either as a main effect or as an effect showing interaction with vehicle identity. The error mean squares used in these analyses were the variances calculated from four replicate test pairs. The three test pairs relating to 2% of the naphtha in the above table were thereafter treated as additional replicate pairs and thus increased the available replicates to seven.

Statistical analyses of the data on 16% naphtha showed an interaction effect: the naphtha effect depends on the vehicle identity, being reversed in the 1970 vehicle from its effect in the 1966 and 1968 vehicles. Analysis of the data for the 1966 and 1968 vehicles only yielded the results in Table 14. The ratios imply increases of about 109% in BaP emission and 40% in BaA emission for the presence of 16% high-boiling naphtha. These results are clearly restricted to the particular tests included in the analysis. No explanation is available for the reversed effect of the naphtha in the 1970 vehicle, and the overall picture is not clear.

4.4.4 Antiknock Lead

The effect of lead antiknock (tetraethyllead as Motor Mix) on PNA emission can be examined by comparing emissions from ten tests using lead-free fuels with the emissions from ten tests with lead present at 3 grams/gallon and with five tests with lead at 0.5 grams/gallon. The 3-gram tests included fuels with 11%, 28%, and 46% aromatics, but the 0.5-gram tests were all in the 28%-aromatic fuel; all three test vehicles were used in the tests and gave similar results. The emissions data are summarized in Table 15. The geometric mean ratios for the effect of lead, together with the 95% confidence intervals, are given in Table 16. The effects for the presence of 3 grams of lead included a non-significant small decrease in BaP emission and a small, but significant, increase in BaA. With 0.5 gram of lead, the decreases observed are statistically significant but are based on a smaller number of tests using only one base fuel. Further testing appears necessary in order to clarify and establish this complex set of effects for the use of lead.

Table 13

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PNA EMISSIONS WITH A HIGH-BOILING NAPHTHA PRESENT

Vehicle	% Ar. in Fuel	Benzo(a)pyrene Emission, µg/gal. 0% HBN	2% HBN	Ratio 2%/0%	Benz(a)anthracene Emission, µg/gal. 0% HBN	2% HBN	Ratio 2%/0%
1966	46	62	57	0.92	104	82	0.79
1968	46	12	12	1.00	23	25	1.09
1970	46	17	29	1.71	42	52	1.24
		0% HBN	16% HBN	16%/0%	0% HBN	16% HBN	16%/0%
1966	11	50	78	1.56	109	182	1.67
	11	37	91	2.46	134	212	1.58
1968	11	10.5	25	2.38	40	52	1.30
	11	13	27	2.08	75	85	1.13
1970	11	19	12, 20	0.84	57	28, 31	0.52
	11	20, 34	10.5	0.39	70, 72	38	0.54

Table 14

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EFFECT OF HIGH-BOILING NAPHTHA ON PNA EMISSION
(Low-aromatic Fuels in Two Vehicles)

	Geometric Means of Ratios of Emission for 16% Naphtha to Emission for 0%	
	BaP Emission	BaA Emission
Means of Four Ratios	2.09	1.40
95% Confidence Intervals	1.48 to 2.95	1.20 to 1.64

Table 15

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PNA EMISSIONS WITH VARYING LEAD CONCENTRATION

Test Vehicle	% Arom. in Fuel	Emission, µg./gal., Lead in grams/gal. 0	0.5	3.0	Ratios 0.5/0	3/0
		Emission of Benzo(a)pyrene				
1966	11	56	--	56	--	1.00
	28	78	63	59	0.81	0.76
	28	36	18	29	0.50	0.81
	46	125	--	127	--	1.02
	46	54, 57, 62	--	54	--	0.93
1968	28	11	8.9	36	0.81	3.27
	28	14	3.5	3.4	0.25	0.24
	46	30	--	32, 32	--	1.07
1970	28	48	36	26	0.75	0.54
	46	26	--	17, 29	--	0.88
		Emission of Benz(a)anthracene				
1966	11	126	--	155	--	1.23
	28	130	86	157	0.66	1.21
	28	49	30	46	0.61	0.94
	46	196	--	258	--	1.32
	46	94, 82, 104	--	124	--	1.33
1968	28	28	20	75	0.71	2.68
	28	15	13	15	0.87	1.00
	46	55	--	63, 75	--	1.25
1970	28	70	61	51	0.87	0.73
	46	60	--	52, 42	--	0.78

Table 16

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EFFECT OF LEAD ON PNA EMISSIONS

	Geometric Means of Ratios of Emission with Lead to Emission without Lead			
	BaP Emission		BaA Emission	
	Lead at 0.5	Lead at 3	Lead at 0.5	Lead at 3
Geometric Mean	0.57	0.86	0.74	1.17
95% Interval	0.42 to 0.78	0.70 to 1.08	0.64 to 0.85	1.06 to 1.29
Effect Significant?	Yes.	No.	Yes.	Yes.

4.5 Long-Term (Deposit) Effects of Fuel Composition on PNA Emission

The comparisons of tests, or groups of tests, that have been made up to this point have been between results from different fuels or from different vehicles. In every comparison, the engine deposits have been constant, i.e., they were deposits formed under programmed cyclic city-suburb-highway conditions with essentially the same deposit-formation fuel. Deposits, as characterized by the fuel from which they were formed, are the only remaining test variable on which data are available.

The effect of deposits on PNA emission was studied initially by tests in the 1966 vehicle; the studies were later expanded to include the 1968 vehicle, but no deposit studies have been done in the 1970 vehicle. After cleaning the combustion chambers in the 1966 vehicle, lead-free deposits (fuel A) were accumulated as the first step in the deposit sequence shown in Table 17. The choice of deposit fuels for steps 1 and 2 of the 1966 vehicle was intended to allow a decision on whether lead-free and leaded deposits give different PNA emissions. However, when a difference was seen between deposits from the two marketed gasolines, a conclusion relating specifically to lead could not be reached confidently because, in addition to lead, the two deposit fuels differed as to phosphorus and base-stock composition. The next deposit steps, using A.5 and A fuels, were intended to overcome this objection, by using a single base fuel, but the effect of lead, via deposits, was tested at the new low-lead level of 0.5 g./gal. rather than at 3 grams; two vehicles were used. The program also allowed a test of the reversibility of deposit effects in the 1966 vehicle, i.e., could the conditions of step 1 be reached again in step 4 after two other deposit conditions?

The test results obtained with deposits from fuels A and A.5, in two vehicles, are summarized in Table 18. Two conclusions may be drawn from the data, although each conclusion is based on emission tests with only one fuel: (1) a deposit condition, as measured by the PNA emission level, was re-established after other deposits and emission tests had intervened, i.e., the PNA effects of deposits were reversible; and (2) this specific deposit fuel formed deposits with the same PNA emission levels, whether it was lead-free or leaded at 0.5 g. Pb/gallon. Additional tests of lead effects, using more lead and other base fuels for deposit formation, appear necessary in order to generalize any conclusion as to the effect of deposit lead on PNA emission. Within the present data, however, data from A and A.5 deposits can be combined as representing results characteristic of A-based fuel deposits.

Table 17

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SEQUENCE OF ENGINE-DEPOSIT FUELS

Step No. for Vehicle		Deposit Fuel	
1966	1968	Code	Description
1	--	A	Commercial lead-free premium.
2	1	C3P	Commercial leaded (2-3 g/gal.) prem. with phosphorus additive.
3	2	A.5	Commercial lead-free as above, + 0.5 g. Pb/gal.
4	3	A	Commercial lead-free as at start.

Table 18

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PNA EMISSIONS WITH DEPOSITS FROM BASE A FUELS

Vehicle	% Ar.-PNA-Pb	Emissions, μg./gal., with deposits from Base A leaded, as shown, in g./gal.			
		Benzo(a)pyrene		Benz(a)anthracene	
		0	0.5	0	0.5
1966	46 - 0 - 0	54	--	94	--
	46 - 0 - 0 [a]	57	--	82	--
	46 - 0 - 0 [b]	62	--	104	--
	28 - 0 - 0	39	36	51	49
1968	28 - 0 - 0	15	14	17	15

(a) This test is a repeat of the test on the line above and occurred after two intervening deposit conditions in the 1966 vehicle.

(b) This fuel, and the 28%-aromatic fuels, contain no high-boiling naphtha.

Comparisons (seven in the 1966 vehicle and five in the 1968 vehicle) of results from A-base deposits with results from C3P deposits are listed in Table 19 along with ratios, A/C3P of emissions from each test pair. The geometric mean ratios given in the table make it clear that deposit-fuel identity caused greater than two-fold differences in PNA emission from a variety of emission-test fuels.

Fuel C3P differed from A and A.5 in respect to lead content, phosphorus content, and hydrocarbon base fuel. The broad fact that the base fuels (hydrocarbons) were different implies the possibility of a variety of more specific differences, such as aromaticity, olefinicity, traces of high-boiling species present, etc. At the present time, it is not clear which of these factors, or a combination of the factors, is important in controlling the PNA-emission character of deposits.

Information on this point may be a matter of some practical interest, because in the course of the deposit studies, PNA emissions were observed from high-aromatic fuels, used with A-fuel deposits, which were similar to, or lower than, the emissions from fuels of appreciably lower aromatic content used in the presence of C3P deposits.

Table 19

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EFFECT OF DEPOSIT-FUEL COMPOSITION ON PNA EMISSION

		Emission, μg./gal.					
	Test	Benzo(a)pyrene			Benz(a)anthracene		
Test Vehicle	Fuel % Ar.	Deposit A	Deposit C3P	Ratio, A/C3P	Deposit A	Deposit C3P	Ratio, A/C3P
1966	46	54, 57, 62	125	0.46	94, 82, 104	196	0.47
	28	39	78	0.50	51	130	0.39
	12(a)	56	91	0.62	155	212	0.73
	46	54	127	0.43	124	258	0.48
	28	36	78	0.46	49	130	0.38
	28	18	63	0.29	30	86	0.35
	28	29	59	0.49	46	157	0.29
1968	46	12, 12	30	0.40	23, 25	55	0.44
	28	15	11	1.36	17	28	0.61
	28	14	11	1.27	15	28	0.54
	28	3.5	8.9	0.39	13	20	0.65
	28	3.4	36	0.09	15	75	0.20
Geometric Mean Ratios				0.46			0.44
95% Confidence Intervals				0.38 to 0.57			0.40 to 0.48

(a) With high-boiling naphtha, TEL, and high PNA content.

5. DISCUSSION

The origin and emission of polynuclear aromatic hydrocarbons in vehicle exhaust has been studied in numerous laboratories since attention was directed to their presence and possible medical significance in the 1950's, and many of the factors governing the exhaust concentration of PNA have been examined. A smaller number of similar studies on phenol emission has also appeared.

5.1 Effect of Carburetion

Several investigators (4, 5, 6, 7) have shown that vehicles with progressively higher air/fuel ratios and lower emissions of CO will also emit less PNA, and measures that control CO are apparently one of the most effective single approaches to minimizing PNA. Intuitively, however, the presence of CO in exhaust gas is much less likely to be a direct cause of PNA formation and emission than it is to be a symptom of an oxygen-deficient environment, in the engine, that is favorable to the synthesis and survival of PNA and of the free radicals that must combine for PNA synthesis. Radiotracer BaP experiments (5, 7,) have, in fact, shown that PNA are destroyed by oxidation or pyrolysis to an appreciable degree even in an exhaust with substantial CO content. Other experiments (4, 7) have shown the value of exhaust system oxidation with air-injection systems to reduce the amount of PNA that is emitted, as well as the value of engine-modification systems to combine the benefits of reduced CO and of whatever oxidation of PNA may occur from available exhaust oxygen. Also, reports have appeared recently of PNA control with an "advanced" emission control system (7) using a thermal reactor, exhaust recirculation, and particulate traps, and of PNA destruction in a prototype exhaust catalytic system (10). Paralleling or accompanying these reports on opportunities for control of PNA through engine design, adjustments, and the use of devices, there have been reports (2, 4, 7, 10, 11) of the effects of fuel compositional variables on PNA emission. In general, it appears that these reports of fuel effects are based on data obtained in tests characterized by the presence, in the exhaust, of appreciable CO; emissions of CO at a level of less than 1% (i.e., within the standard for a 4000-lb. 1970 vehicle) are not common in the reports on the effects of fuel factors on PNA.

The situation with respect to publications on exhaust phenols is somewhat different. Early tests (2, 12, 13) had implicated fuel aromatics as potent sources of exhaust phenols, using tests conducted under almost assuredly fuel-rich conditions. Now, a recent report (14) presents a convincing correlation of fuel aromaticity and exhaust phenol yields from three vehicles, of which two were 1970 models and must be assumed to have emitted less than 1% CO in the standard test.

The studies presented in the present report may be viewed as complementing the existing literature for both polynuclear aromatics and phenols. The three test vehicles that were used include one (1966) without emission controls and two (1968 and 1970), with engine-modification control. The vehicles were adjusted for relatively lean mixtures (Section 3.4), and operated in the near-stoichiometric range of air/fuel ratio, where relatively

little published information on the effects of fuel factors on PNA has been obtained.

With respect to phenol emission, we confirm the recently published results on fuel factors, as obtained with lean carburetion (1970) vehicles), and we extend the study of fuel factors toward a slightly higher CO level.

The existence of carbon monoxide emissions from an engine was referred to above as a symptom of an environment in which PNA or PNA precursors might form and survive, rather than being destroyed by oxidation or pyrolysis. Two other exhaust-gas factors, oxygen content and temperature, will obviously also play roles in PNA survival and emission. Phenols, as species capable of being oxidized, should also be sensitive to the same variables. It is thus appropriate, before reviewing our emission results, to note that both CO content, oxygen content, and temperature were different between the three vehicles (Section 3.4). We feel that these tabulated characteristics typify a progressively changing environment, between the three vehicles, that influenced the emission of PNA and phenols from the vehicles and also influenced the sensitivity of the vehicles, in terms of PNA and phenol emission, to changes in fuels. The influence on PNA emissions of even small changes in CO, between tests in a given vehicle, was sufficiently evident to provide a basis for a correlation to correct PNA data for CO variation, as discussed in a preceding part of this paper.

5.2 Phenol Emission

The three regression equations, developed from the data on each vehicle, for the emission of phenols as a function of fuel aromatics, explained over 95% of the variance in phenol rates (mg./gallon of fuel); as a result, no other within-vehicle variables (fuel composition, A/F ratio, etc.) are likely to be found significant, either statistically or practically. The equations do indicate substantial differences between the two nearly equivalent earlier vehicles (1966 and 1968) and the 1970 vehicle. The differences are typified by the phenol rates in Table 20, which were calculated from the equations that describe each vehicle. Our results for the 1970 vehicle are in good agreement with the recent report by Hinkamp (14) on phenol emission with fuels of varying aromaticity, as observed in two 1970 vehicles and one 1968 vehicle. The fact that phenol emission depended strongly on fuel aromatics in all three of our test-vehicles, but was lower in our 1970 vehicle than in the nearly-equal 1966 and 1968 vehicles, suggests that phenol formation depends on a reaction involving aromatic molecules that is independent of CO level, while phenol destruction or oxidation depends on an adequate oxygen supply and sufficiently high temperatures.

If the 30% decrease in phenol emission from our 1970 test vehicle, relative to the 1966 and 1968 vehicles, is assumed to be typical, it suggests

Table 20

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PHENOL EMISSION RATES

	Test Vehicle		
	1966 NC	1968 EM	1970 EM
Emission Rate, mg./gal.			
28% aromatic fuel	400	371	268
46% aromatic fuel	709	657	449
Slope, mg./gal./% aromatics	17.2	15.9	10.1

that phenol emission has not been reduced as effectively, in reaching the 1968 and 1970 stages of emission control, as have the emissions of other pollutants.

5.3 Emission-Control System Effects on PNA Emissions

The 1968 and 1970 vehicles, both equipped with engine-modification control systems, emitted an average of about 30% as much PNA (BaP or BaA) as was emitted by the 1966 uncontrolled vehicle. The 70% reduction (range, 29% to 88%) agrees generally with results published by Begeman (4) and by Hoffman (7). The range of reductions in BaP emissions reported by Begeman was 66% to 96%, relative to the same engines with the control system inoperative or replaced by a no-control configuration. Hoffman reported on eleven 1964-1966 vehicles and seven 1968 (controlled) vehicles, with two fuels tested in each vehicle. The average BaP emissions of the seven controlled cars were reduced by 79%, for one fuel, and 67%, for the other, from the average BaP emissions, on the same fuels, in the uncontrolled group. For both of these reports, the % CO (emission-test result) was generally 2% to 4% in the "uncontrolled" tests and was still, usually, a little greater than 1% in the "controlled" tests. By contrast, our 1966 vehicle and 1968 vehicle average CO levels were 1.49% and 0.75%, i.e., each was about half to two-thirds as great as in the other published studies, or as is typical for those years. We interpret this as meaning that our 1966 and 1968 vehicles perform correctly relative to each other, but that the PNA from both may be on the order of 50% low. The other published studies do not include comparable data in 1970 vehicles, which, as a class, were required to meet lower emission standards for CO (typically, 1% vs. the prior 1.5%). Our 1970 vehicle shows no difference in PNA emission from our 1968 vehicle, but we attribute this to the fact, indicated above, that both the 1966 and 1968 test vehicles had depressed emissions because their carburetion was abnormally lean.

In the preceding discussion of phenol emissions from our test vehicles, we proposed, in effect, that about 30% of the phenols formed in the 1970 vehicle engine were oxidized in the exhaust system so that it emitted less phenol than did the 1966 and 1968 vehicles. It is reasonable, if this is true, to expect that PNA from this engine would also be oxidized to some extent. Yet we find that the 1970 and 1968 vehicles have very similar emissions of PNA. We conclude either that the expected oxidation of PNA did not occur in the 1970 vehicle exhaust, or that it did occur but that relatively more PNA was initially formed, for unknown reasons.

5.4 Immediate Fuel Effects on PNA Emission

Changes in PNA emission rates with changes in fuel composition can occur in two ways. An immediate effect may occur as soon as a change is made in fuel composition, or the extended use of any one fuel will result in engine deposits which may influence the emission of PNA, just as deposit accumulation is known to affect the emission of unburned hydrocarbons. In this program, the two types of change have been studied independently by examining several fuels in each of several successive

deposit conditions, and the two types of change will be discussed separately. In no case were the deposit fuels and the emission-test fuels identical.

5.4.1 Fuel Aromatics Content

The effects of increasing fuel aromatics from 11% to 46% were observed in two test pairs (which differed in PNA content) in each of three vehicles, and both BaP and BaA emission data were obtained. The summary of geometric mean ratios in Table 9 showed trends with vehicles and with the species of PNA detected. The 1970 vehicle could not significantly detect the effect of increased aromaticity, while the 1966 vehicle was the most sensitive. Sensitivity to fuel aromatics was also greater for BaP emission than for BaA. The overall geometric mean ratio for two PNA species in only the two earlier vehicles is 2.34, indicating a 134% PNA emission increase for increasing aromatics from 11% to 46%.

The finding that increased fuel aromatics increases PNA emission is in agreement with numerous other studies (2, 7, 11, 12). Only rarely [Griffing (5), and Padrta (10)] have cases been reported in which there was not a clear PNA relation to aromatics content. Hoffman (7) has reported on uncontrolled and 1968-model controlled vehicles, with each car in both groups testing low- and high-aromatic fuels. In contrast to our finding, the PNA emissions of the controlled vehicles displayed fully as much relative response to increased fuel aromatics as did the emissions of the uncontrolled vehicles. Hoffman also reports experiments in which two different control systems were added to a 1966 uncontrolled car. Again the response of PNA emission to aromatics changes did not decrease with the use of controls, nor was BaA emission less sensitive to aromatics than BaP emission. These tests were conducted at generally higher CO levels than were present in our work, however.

It would appear to be very desirable to know from a larger sample whether or not the PNA emissions of vehicles with lean carburetion and retarded spark, such as the 1970 test vehicle used here, are sensitive to fuel aromatics. However, the question is one of differences in PNA emissions which are already reduced substantially from earlier levels because of the emission control systems.

5.4.2 Fuel PNA Content

The presence of PNA in fuel, commonly expressed in terms of BaP content in μg./gallon, or ppm, where 1 ppm is about 2800 μg./gallon, has been shown to cause increased emission of exhaust PNA. Distillation to remove the high-boiling material from a gasoline that initially contained 0.7 ppm of BaP was reported by Hoffman (7) to have caused an 87% decrease in BaP emission. Begeman (4) found that Indolene, with about 4 ppm BaP, gave four to five times as much PNA emission as a regular-grade gasoline with 1.1 ppm.

The present studies find much smaller effects for PNA addition to fuels of initially low PNA content. The PNA added was the still-bottoms from careful distillation of a large quantity of catalytic reformate. This approach seemed preferable, in studying fuel PNA, to either distilling

a finished fuel, with the chance of removing materials other than PNA, or to comparing fuels that may differ in other ways than their analyzed PNA contents. The distillate from the reformate was used for test-fuel blends, which had about 0.015 ppm BaP, and the bottoms were added as required to introduce 2.9 ppm BaP. This BaP level was near the field maximum found in a small-scale survey (1). A composite of nationwide premium and regular gasoline samples obtained separately would have about one-tenth of this maximum BaP level (1). Hoffman (7) suggests that most fuel BaP derives from catalytic reformate.

The effect of adding PNA to introduce 2.9 ppm BaP was observed in two low-aromatic fuels and one high-aromatic fuel, with all three fuels used in three vehicles, and data were obtained on both BaP and BaA emissions. Neither vehicle identity nor fuel aromatics influenced the observed effects of fuel PNA, which were unexpectedly small: an 8% increase in BaP emission was not significant, and the increase in BaA emission was only 32%. These relatively modest effects for fuel PNA, compared to those reported in the other papers, are believed to be due to differences in details of the experiments that were carried out. The earlier studies were conducted in relatively rich, fully warmed-up laboratory engines with appreciably longer tests than were used here. Griffing (11) has reported that high-PNA fuels seem to deposit PNA that can persist into a later test with a low-PNA fuel, suggesting that longer tests might give greater emphasis to fuel PNA. Pending further data, our findings of a modest effect for fuel PNA appear correct for short-term effects in low-CO vehicles, but long-term effects and other engine conditions might change this picture.

5.4.3 High-Boiling Naphthas

The fuel PNA studied in the foregoing experiments was derived from the higher-boiling portion of a catalytic reformate and was rich in aromatic hydrocarbons. Other high-boiling materials can also be present in gasoline, for example, from the blending of heavy catalytic naphthas; this component is relatively common in regular-grade gasolines. In the studies described here, low-aromatic (11%-12%) fuels were compared, with or without 16% of a high-boiling naphtha (419°F end-point, ASTM-D86) that included heavy catalytic naphtha as one component. Fuel compositions and inspections in Appendix B show that blending the naphtha caused an increase of 16 degrees (F) in end-point; the fuel PNA level was very low and was not increased significantly by the naphtha. The data obtained were not entirely clear as to the effect of the naphtha on PNA emission, since the emissions were increased by the naphtha in the first two vehicles used, but were reduced in a third vehicle.

The data from the first two vehicles do suggest that a high-boiling naphtha may promote PNA emission under at least some circumstances. Griffing (5) has also noted that a low-aromatic, low-PNA fuel with a high end-point gave unexpectedly high BaP emission. Hoffman's data (7) indicate that the heavy catalytic naphthas which he inspected contained no BaP or BaA, and the blends we used with the naphtha present were low in PNA content. It appears that any effects of heavy catalytic naphthas on PNA emission may involve smaller molecules, or different species, than PNA. Further study of high-boiling materials in gasolines appears desirable.

In reviewing the fuel-composition studies on the PNA-emission effects of fuel aromatics, fuel PNA, and a high-boiling naphtha, it is noteworthy that these three variables are actually independent, and that each of them, under at least some circumstances, caused significant increases in PNA emission. Under these circumstances, experiments to evaluate the effect of any one variable must be carefully controlled as to the other variables. Furthermore, while they were not investigated here, it is reasonable to assume that within-class differences in potency as PNA precursors will exist. For example, C_7, C_8, C_9, and C_{10} aromatics are likely to differ, as are 2-ring, 3-ring, and 4-ring polynuclears, in potency as precursors for, say BaA, or BaP. Evidently, much more research is necessary before the different possible descriptions of fuel composition can be definitively related to PNA emission.

5.4.4 Antiknock Lead

The immediate effect of the presence of lead in gasoline on PNA emission has been examined in several laboratories. Begeman and Colucci (4) found both small increases and small decreases in PNA emission for the presence of lead in Indolene fuel. Hoffman (7) presents data showing more increases than decreases in PNA as a result of lead addition when testing several fuels in a 1966 engine (about 3% CO), but consistent substantial decreases in BaP emission, when lead was added, for tests conducted in two 1970, presumably fuel-lean, vehicles. Griffing (11), employing two different 1967 vehicles, found no effect for lead on BaP emissions. All of these studies compared results from fuels with 0 and 3 grams of lead (or ccs. of TEL/gallon).

Our tests included the 1966, 1968, and 1970 test vehicles and permit comparisons of PNA emissions obtained with lead at both 0.5 and 3 grams/gallon with corresponding lead-free tests. The effects observed for lead were not statistically different between the three vehicles, but there was a difference between the two lead levels in their effects on PNA emission. The results for 0.5 grams, which were fewer in number and limited to one fuel, showed decreases in PNA emissions due to lead, of 26% (BaA) and 43% (BaP). For 3 grams, with more tests and in three fuels, we found a non-significant 14% BaP decrease and a statistically significant 17% increase in BaA emission.

Our lead-effect results indicate that there may be complex effects of lead on PNA emission, varying with specific situations, but that these effects are relatively small. No large overall effect of lead on PNA emission is apparent in terms of the lead itself. As a material which may affect the presence of aromatics, and the composition of gasolines, in general, lead probably can have indirect effects.

5.5 Deposit Effects on PNA Emission

The possibility that fuel composition could influence PNA emission slowly by changes in engine deposits has received much less attention in the published literature than has been applied to the immediate PNA-emission effects of fuel changes. The Griffing (11)

observation of a carryover effect of fuel PNA on PNA emission has been previously noted; the implication of possible deposit effects was not apparently pursued, but steps were taken to avoid the problem presented. Hoffman (7) reports tests in two 1970 vehicles on the PNA-emission effect of lead in deposits. Four measurements of BaP emission in each deposit condition yielded data showing three increases and one decrease in BaP associated with lead in the deposits. The PNA emissions were described as "essentially the same" for leaded and unleaded deposits. It is not clear whether the lead-free and leaded deposit fuels were prepared from a single base fuel in this study.

Our approach to studying deposits was also directed, initially, to the question of "leaded" vs. "unleaded" deposits, and two commercial premium gasolines, lead-free and leaded (with phosphorus) were used for deposits. Thus, the base gasolines were not identical in this comparison. The PNA emissions from the leaded (+P) deposits were substantially higher than from the lead-free deposits, according to tests with three emission-test fuels in each deposit condition. This initial study of deposit effects, which was limited to the 1966 vehicle, was followed by additional deposit tests in both the 1966 and 1968 vehicles. In these tests, deposits from the commercial leaded (+P) premium gasoline were converted to low-lead, and then lead-free, deposits by the successive use of the same lead-free commercial premium gasoline, first with lead added to 0.5 grams/gallon, and then without lead.

For both vehicles, the PNA-emission levels from the low-lead and no-lead deposits were equivalent and these levels were only about one-half of the level that had been obtained with deposits from the leaded (+P) gasoline. The PNA emissions of the 1966 vehicle had returned to the same level that was observed in the first tests of the lead-free premium gasoline, before going to leaded deposits. Two distinct levels of emission, related to deposits, were thus established, but the evidence remains unclear, at this time, whether the effect observed was due to base-fuel composition, phosphorus, or lead level, or to interactions between these or other factors.

Lead, phosphorus, and fuel composition have all been examined in relation to some aspects of deposits by various investigators in the past. Although these studies did not include PNA-emission differences between deposits, the results that were obtained, and the fuel composition factors that were considered, may be relevant here. In studies of lead, at several levels from 0 to 3 grams/gallon, and of phosphorus with lead, Gagliardi (8) and Gagliardi and Ghannam (9) found that the emission of volatile hydrocarbons was elevated equally by any non-zero lead level, relative to the emission from lead-free deposits, while the use of phosphorus, with lead, did not affect hydrocarbon emission. Studies on the base-fuel composition aspects of deposits have been concerned primarily with combustion abnormalities, such as knock and surface-ignition, rather than with the emission of air pollutants. Differences in combustion, related to deposits, have been ascribed to increased overall fuel aromatics content at a constant lead level (15); thus overall deposit-fuel aromaticity should be considered as a possible factor in the effect of deposits on PNA emission. In addition to overall aromatics,

attention has been directed toward high-boiling components (15, 16) whose presence may be apparent from ASTM D-86 distillation data, and to high-boiling aromatics specifically, such as naphthalene (17). The latter, extending in principle to include trace amounts of PNA in fuels, may not appear in terms of distillation data, but are found in PNA analyses, such as our small-scale field survey (1) on the BaP content of several gasolines.

Thus the fuel composition factors that may affect PNA emission indirectly because of their effects on deposits may be somewhat the same fuel factors that appeared to influence PNA emission directly in the experiments described earlier. These factors were aromatics, high-boiling naphthas, and polynuclear aromatics (PNA, as BaP); within these broad classes there are likely to be hydrocarbons with widely differing potency for both directly, and indirectly, influencing PNA emission.

5.6 Areas For Further Study

Our studies are currently directed toward getting a better understanding of the fuel composition factors that influence PNA emission in current vehicles, with particular reference to higher-boiling materials. However, on the basis of the tests reported here, it appears that future low-emission vehicles will minimize the significance of any of these factors.

APPENDIX A

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Appendix B

TEST FUELS

The emission-test fuels used in the second-year program of CAPE-6-68 were blended from the same catalytic-reformate distillation fractions and other blending stocks used for the first-year blends. These components are described in detail in Appendix B of the first-year report; along with compositions and inspections of the first-year test fuels. In the following, selected first-year fuel information is repeated to permit comparison with second-year fuels. First-year fuels are designated as "1969" fuels and those for the second-year as "1970" fuels.

Section 6.3 of the first-year report indicated the intention to prepare, for the second year, new blends that would not contain a high-boiling stock (a mixture of heavy catalytic naphtha, polymer gasoline, and pentanes) that was present in the 1969 set; total fuel aromatics was to remain constant at each extreme. The purpose of the change was the elimination, particularly from the low-aromatic test fuel, of suspected high-boiling PNA-precursor materials that were thought to be responsible for relatively high PNA emission from the low-aromatic fuel and a resulting decrease in the apparent effect on PNA emission from increasing the overall fuel aromatics content from low (12%) to high (46%). A consequence of the change in fuel composition would be a decrease in final boiling-point, as measured by the ASTM-D86 method, as well as decreases in the distillation temperatures for the entire higher-boiling parts of the fuels. These effects could be partly compensated by using relatively more heavier aromatics, particularly in the low-aromatic fuel where the high-boiling naphtha represented 16% of the 1969 blend, against only 2% in the high-aromatic fuel.

The blend compositions used in both years are given in Table B-1 of this Appendix. The components used in the two years are identical materials except for the C_{10}-C_{11} aromatic solvent, where different batches manufactured to the same specification were used. As indicated in the table, essentially the same total aromatics were provided in both years, but the olefin content decreased from about 6% to 1% when the high-boiling naphtha was deleted. This change, which was unavoidable in the low-aromatic fuel, was matched in the high-aromatic fuel by decreasing the amount of light catalytic naphtha from 13% to 4% and then compensating with other components.

Routine inspections of the fuel blends for both years are compared in Table B-2. For the 1970 set, an equal-volume cross-blend of the high- and low-aromatic fuels is included, and the table also lists typical inspections for two fuels used for accumulating combustion-chamber deposits in test vehicles during both the first and second program years. The fuel codes for both years, as used in Table B-2 and at other points in this report, are listed as follows:

		FUEL CODE DESIGNATION				
		11-12% Arom.		Cross Blend	46% Arom.	
PNA	TEL	1969	1970	1970	1969	1970
Low	0		1L00	3000	5HOC[a]	5H00
	0.5			3000.5		
	3	100	1L03	3003	5HO	5HO3
High	0	108C				5H80
	3	108	1L83		5H8	5H83

[a] A similar fuel, 5LOC, is more volatile in the mid-fill region, and was used only in the first year.

This code includes certain fuels that were prepared but have not yet been tested. It also includes the cross-blend of the basic 1970 low-aromatic (1L00) and high-aromatic (5H00) fuels and indicates that this cross-blend was tested at low lead content (0.5 ccs. TEL, as Motor Mix, per gallon), as well as at zero and 3 ccs./gallon. The "low" and "high" PNA levels indicated in the code chart refer to the as-made fuels with less than 50μg. of benzo(a)pyrene (BaP) per gallon (low PNA) and to the fuels with PNA added, in the form of reformate still bottoms, in an amount sufficient to add 8000 μg. of BaP/gallon to the fuel. Further details on this PNA-additive material are in Appendix B of the first-year report.

The major differences in the inspections given in Table B-2 between the 1969 and 1970 fuels are in the distillation temperatures and the sulfur contents. It is clear that the expected decreases in back-end distillation temperatures have occurred, and that the low-aromatic fuel now distills, throughout its range up to the end-point, at lower temperatures than the high-aromatic fuel. It appears reasonable to assume from this that high-boiling PNA precursors have been minimized in the new fuels, although other more definitive inspections of the fuels would be more informative. The decrease in sulfur is also a predicted result of excluding the high-boiling naphtha. Its significance, if any, for PNA emission is unknown.

Table B-3 presents mass-spectrometer analyses of the two fuel sets, including also an analysis showing the changes observed when the reformate still-bottoms (PNA) is added. These analyses indicate appreciable decreases, between the 1969 and 1970 sets, in the amounts of C_{11} and C_{12} aromatics and indans, with only small changes in naphthalenes. As expected, "naphthenes + olefins" also decreased substantially because of the olefin decrease. The changes from 1969 to 1970 fuels appear reasonable, except that the decrease in C_{12} aromatics from 0.18-0.22% in the two 1969 fuels to zero in both of the 1970 fuels is not consistent with the quite modest change in composition between the 1969 and 1970 high-aromatic fuels

as against a large change between the low-aromatic fuels (see Table B-1, higher-boiling components).

Table B-4 presents GC analyses on the aromatic hydrocarbons present in the same basic fuels, in the two batches (essentially equal) of C_{10-11} aromatic solvent (see above), in the lead-free deposit-accumulation gasoline, and in the high-boiling naphtha used in the 1969 fuel set. These GC data apparently do not reach to as high a boiling-point as do the MS analyses; identification is essentially complete at C_{10}, so that C_{11} and C_{12} cannot be discussed adequately. Like the MS, the GC indicates decreased indan in 1970 fuels. However, the GC data are necessarily suspect when it is noted that the 1970 low-aromatic and high-aromatic fuels appear to have almost equal amounts of a variety of high-boiling aromatics, whereas the compositions (Table B-1) show the high-aromatic fuel has from 2 to 18 times as much of any of the reasonable sources of these aromatics as are present in the low-aromatic fuel. The GC analysis of the aromatic part of the high-boiling naphtha does not reveal any uniquely abundant species that would markedly diminish if this component were omitted from gasoline, yet the lower Engler (D86) final boiling points (Table B-2) for 1970 show that some high-boiling materials have indeed been excluded.

It appears from these analyses, both MS and GC, that techniques for getting better data on the higher-boiling materials in gasoline would be a distinct advantage in a study of PNA emission as a function of fuel composition.

TABLE B-1

FUEL COMPOSITIONS

Stock	Low Aromatic 1969	Low Aromatic 1970	High Aromatic 1969	High Aromatic 1970
n-Butane	4	4	8	7
Isopentane	16	17	15	19
Motor Alkylate	54	65	2	5
Lt. Cat. Naphtha	2	2	13	4
Toluene	1	1	3	3
155-220 Reformate	1	1	15	17
220-241 Reformate	1	1	15	18
241-298 Reformate	1	2	11	11
298-384 Reformate	1	3	9	9
C_{10-11} Aromatic Solvent	3	4	7	7
H. Cat. N. + Polymer + C_5's	16	None	2	None
% Aromatics	11.9	11.0	46.3	46.2
% Olefins	5.8	0.8	5.2	1.4

TABLE B-2

TEST FUEL INSPECTIONS

Fuel Code:	1969			1970			Commercial Fuels For Deposit Accumulation	
	100 Etc.	5 LOC	5 HO Etc.	1L00 Etc.	3000 Etc.	5 HOO Etc.	Lead-Free	Leaded[b]
RVP	10.60	10.62	10.68	10.50	10.15	10.48	11.87[a]	10.6[a]
IBP	82	82	84	92	91	92	87	97
°F. 5% (D+L)	100	97	98	104	105	105	95	116
10	112	112	112	116	116	116	108	126
20	134	135	135	134	136	136	130	145
30	158	161	161	159	162	162	157	165
40	192	194	197	193	194	196	190	186
50	218	216	220	215	217	222	219	208
60	231	233	240	225	231	237	236	226
70	244	248	257	236	243	254	252	245
80	263	270	283	252	260	277	274	269
85	284	291	304	267	278	298	290	286
90	320	324	332	296	310	322	312	307
95	368	364	364	352	352	352	338	343
FBP	400	390	387	384	383	381	378	394
Sulfur, ppm	115	55	60	15	12	10	60	80
% Ar.	11.9	46.0	46.3	11.0	27.6	46.2	37.4	27.9
% Olef.	5.8	5.2	5.2	0.8	1.7	1.4	2.2	9.5
°API	67.9	53.8	53.7	69.1	60.8	52.9	56.7	61.5
Clear RON	96.1	98.4	98.0	96.5	96.9	97.4	--	--
MON	87.5	86.2	86.0	91.0	88.5	87.2	--	--
3-TEL RON	103.9	103.7	103.8	106.3	105.5	104.4	--	--
MON	100.3	93.6	94.0	102.5	99.3	95.0	--	--

(a) Inspections of different batches may vary; those listed are believed to be typical.

(b) Typically with 2.5 grams Pb/gallon and 0.2 theories phosphorus.

Table B-3

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MASS SPECTROMETER ANALYSES OF TEST FUELS[a]

	WT. % OF TOTAL GASOLINE				
	Low Aromatic Fuels			High Aromatic Fuels	
	1969 Set	1970 Set As Made	1970 Set + PNA[b]	1969 Set	1970 Set
Benzene	0.31	0.29	0.30	3.78	4.41
Toluene	2.73	2.71	2.74	21.67	24.99
C_8 Aromatics	2.61	2.63	2.57	13.37	12.88
C_9 Aromatics	2.76	2.50	2.42	8.76	7.80
C_{10} Aromatics	3.32	3.40	3.50	6.47	6.36
C_{11} Aromatics	1.14	0.82	0.91	2.07	1.47
C_{12} Aromatics	0.18	0.00	0.09	0.22	0.00
Naphthalenes	0.19	0.14	0.34	0.52	0.45
Indans	1.07	0.54	0.65	1.40	1.08
Total Aromatics	14.35	13.06	13.56	58.30	59.46
Naphthenes + Olefins	10.18	3.88	4.18	7.27	3.15
Paraffins	73.80	82.37	81.53	32.27	36.60
Condensed Naphthenes	1.66	0.67	0.71	2.14	0.77
Total	99.99	99.98	99.98	99.98	99.98

(a) Mass-spectral analyses can be compared on a relative basis, but the total aromatics may be in error because the computer program used assumed no butane in the samples. Both non-aromatic and total-aromatic calculations are affected.

(b) PNA added as 384+° FVT reformate bottoms to add 8000 μg. of BaP/gallon.

TABLE B-4

GC ANALYSES OF AROMATIC FRACTIONS FROM SILICA-GEL SEPARATIONS OF TEST FUELS AND BLEND COMPONENTS

Compound	Wt. % of Total Gasoline					Wt. % of Aromatic Fraction		
	Low Aromatic		High Aromatic		Lead-Free	C_{10-11} Arom. Solv.		HCN + Poly.
	1969	1970	1969	1970	Comm. Pre.	1969	1970	+ C_5
Benzene	0.31	0.28	3.50	3.55	0.35	--	--	0.9
Toluene	3.40	2.75	21.96	24.88	20.40	--	--	7.4
Ethyl Benzene	0.49	0.56	2.86	3.21	1.53	--	--	2.9
m- & p-Xylene	1.79	1.67	7.94	6.89	6.10	--	--	15.2
o-Xylene	0.68	0.69	2.74	1.98	2.23	--	--	5.7
Benzene, i-C_3	<0.01	0.04	0.12	0.10	0.10	--	--	0.1
n-C_3	0.15	0.19	0.62	0.45	0.53	--	--	1.3
1 M, 3 E	0.94	0.85	2.86	1.87	2.63	--	--	9.0
1,3,5 TM	0.35	0.34	1.06	0.75	1.18	--	--	4.1
1 M, 2 E	0.19	0.18	0.56	0.42	0.66	--	--	2.1
1,2,4 TM	1.08	0.90	2.74	1.92	3.24	0.3	0.3	12.8
i-C_4	--	--	--	--	0.10	--	--	--
t-C_4	--	--	--	--	0.08	--	--	--
1,2,3 TM	0.21	0.18	0.48	0.36	0.61	0.9	0.6	2.4
1,3 DE	0.27	0.19	0.38	0.29	0.48	4.2	3.2	2.6
Indan	0.25	0.09	0.34	0.12	0.10	2.7	2.2	3.6
Benzene, n-C_4	0.15	0.18	0.22	0.25	0.35	2.5	2.1	--
1,3 DM, 5 E	0.25	0.19	0.38	0.29	0.53	3.7	2.6	2.6
1 M, 2 n-C_3	0.10	0.12	0.17	0.17	0.10	2.8	2.5	0.6
1,4 DM, 2 E	0.22	0.21	0.36	0.29	0.23	4.4	4.1	1.4
1,3 DM, 4 E	0.25	0.29	0.44	0.64	0.25	5.4	5.3	1.5
1,2 DM, 4 E	0.50	0.51	0.73	0.37	0.41	11.1	10.6	2.4
Unknown A	0.07	0.07	0.02	0.08	--	--	--	0.6
B	0.03	0.08	--	0.11	--	--	--	0.2
Benzene 1,3 DM, 2 E	0.21	0.09	0.23	0.10	0.04	3.0	3.1	1.6
1,2 DM, 3 E	0.10	0.19	0.19	0.22	0.07	3.8	4.3	0.5
1,2,4,5 TM	0.40	0.44	0.67	0.56	0.20	8.3	8.5	1.4
1,2,3,5 TM	0.56	0.64	1.06	0.82	0.29	12.2	12.5	1.9
Unknown C	0.06	0.06	--	0.07	0.04	1.4	1.5	0.5
D	0.04					0.2	0.2	0.1
E	0.10	0.13	0.05	0.14	0.12	2.2	2.3	0.9
F	0.06					0.8	0.7	0.5
G	0.09	0.06	0.08	0.10	--	1.1	1.3	0.7
H	0.25	0.15	0.25	0.19	0.11	3.5	3.6	2.1
I	0.02	--	--	--	--	0.5	1.2	0.6
J	0.07	0.05	--	0.07	--	0.5	0.6	0.8
Benzene, 1,2,3,4 TM	0.20	0.35	0.32	0.41	0.11	5.8	7.1	--
Unknown K	0.24	0.25	0.22	0.28	0.14	4.4	5.2	2.0
L	0.03	0.10	0.02	0.11	0.05	0.3	0.3	0.2
M	0.11	0.03	0.05	0.06	--	2.9	2.9	1.9
N	0.07	0.10	0.06	0.13	0.04	0.7	0.7	1.0
O	0.08	0.06	--	0.07	--	2.1	2.1	0.9
Naphthalene	0.37	0.34	0.49	0.57	0.39	6.5	6.7	1.6
Unknown P	0.03	0.06	--	0.06	--	--	--	0.8
Q	--	--	--	--	--	0.4	0.4	--
R	--	--	--	--	--	0.5	0.4	--
Methylnaphthalene	--	0.05	--	0.06	--	0.9	0.8	0.3
Total, Wt. % Aromatics	14.8	13.7	54.2	53.0	43.8	100.0	100.0	100.0

Appendix C

TEST VEHICLES AND TEST-OPERATIONS DETAILS

Appendices C and D of the First Annual Report described the essentials of test-vehicle preparation and operation, the test-stand facilities, the design and functioning of the PNA/phenol sample collector, and the recovery of the samples from the collector for analysis. Sample production continues to involve three cold-start blocks of 12 7-mode, 137-second test cycles, with substantially all the exhaust processed. In the second year of CAPE-6-68, there have been no major changes in any of these areas, except that a third vehicle has been incorporated in the test fleet. This vehicle, a 1970 350 CID Chevrolet V-8, has thus far yielded PNA data that appear less consistent than that from the earlier vehicles, and certain tests have had to be discounted on the basis of observed abnormalities.

Test Vehicles

The 1966 318 CID Plymouth without emission control (NC) and the 1968 307 CID Chevrolet (EM) that were used in the first-year work also supplied the majority of the second-year data. Both have undergone combustion-chamber deposit changes as part of their test use. Oil consumption (10W-40 commerical in all cases) apparently rose slowly in the Plymouth according to data obtained during vehicle operation on a mileage-accumulation dynamometer for deposit modification. However, recent third year data show this trend was due to an oil leak and that true oil consumption is near 0.5 qts./1000 miles. Oil consumption rates in the 1968 and 1970 Chevrolets have remained at low levels:

MAD Operation City/Suburb/Highway 30 MPH Average	Deposit Fuel Code	Quarts/1000 miles: Plymouth 1966 (b)	Chevrolets 1968 307 CID	Chevrolets 1970 350 CID
1000 miles, lead + P[a]	C3P	0.67	1.11[c]	0.32
4000 miles, no lead	A	0.46	--	
2000 miles, lead + P	C3P	0.53	--	
5000 miles, low TEL	A.5	0.65	0.56	
5000 miles, no lead	A	0.70	0.46	

(a) All vehicles had additional prior deposits from commercial leaded premium gasoline with phosphorus (Code C3P).

(b) Before initial tests (first year), deposits were removed from the Plymouth, and lead-free deposits were later introduced with a commercial lead-free premium.

(c) Affected by an oil leak.

The fuel indicated as "low TEL" was a commercially available lead-free premium, with 0.5 ccs. of TEL added per gallon, as Motor Mix, and without phosphorus. Without TEL or P, the same gasoline was used where "no lead" is indicated in the table.

The 1970 Chevrolet, in common with the other two vehicles, was loaned by Esso Research from its test fleet. Prior to CAPE-6 use it had been used in a program in which its exhaust emissions were within the 1970 standards. Vehicle preparation, similar to that described on p. 61 of the First Annual Report, was followed by a 1000-mile MAD operation (see above) and a regular emissions test for CO, HC and NO. However, repeated emissions tests (cold-start 7-mode) were required, interspersed with engine tuning and testing and, in some cases, replacement of parts related to the vacuum spark advance controls, intake-air heater controls, distributor spark advance schedule, ignition points, etc., in order to pass the emissions standards for a 1970 vehicle. The vehicle was ultimately accepted for PNA use when its composite cycle results were 0.58% CO (= 13.8 grams/mile), 178 ppm HC (= 2.2 grams/mile), and 853 ppm NO. The precise cause or causes of the initial difficulty in meeting 1970 emission standards are not known. The problem centered on HC emission in the deceleration modes, in most cases. In the course of subsequent PNA emissions testing, the vehicle malfunctioned on other occasions, with the loss or invalidation of certain PNA tests as a result. In one case, clean-up solvent was trapped in the laminated walls of the muffler and boiled out during the next test, causing very high apparent HC emissions and other abnormalities; the muffler had to be reconstructed with welded joints. In another case, the vacuum hose for vacuum spark advance became detached during a test, resulting in unusually high exhaust temperatures at speeds above about 23 mph. Other difficulties included an apparent binding or sticking in the automatic choke linkage, an apparent deviation in hot-idle RPM which resulted in high HC emissions in deceleration modes, and evidence of questionable performance of two resistor-type spark-plug cables. The net effects of such difficulties, together with other irregularities such as variations in choke action at start-up, were that three fuels had to be tested twice and one fuel three times in the course of the work reported here; single tests are normally used. The rejection or questioning of PNA results from certain of these tests is discussed further in Table C-1. Also listed in this table of rejected tests is a Test (No. 54) from the Plymouth vehicle that was carried out as a base-point test prior to a deposit change needed for third-year work. As noted in the table, this test had evident defects from the outset, and these are believed to have caused an abnormally high PNA-emission result. In this particular case, there appear to be factors above and beyond explanation in terms of the observed CO-emission level in the test. According to the first-year conclusion as to the effect of CO differences, the PNA yield in this test would be increased only about 15% above an earlier

equivalent test because of the observed CO-level difference between the first blocks of the two tests, with the later two blocks of the tests equal. In fact, the PNA difference shown in the table is much larger, but the cause is obscure. The long (4-month) idle period between tests, and the heavy dynamometer load at startup, are both potential explanations and represent situations to be avoided. The earlier test, which was consistent with other data, will have to be used as the base case for evaluating future results, and the results of Test 54 are rejected.

Test Operations Details

Table C-2 presents data on the average unburned hydrocarbon emissions (NDIR, C_6) from all three vehicles and in different deposit conditions over both contract years. Two facts are clear: (1) Depending on fuel aromaticity, the apparent HC emission can vary widely; this is at least partly an instrument sensitivity effect. (2) Deposit condition has a marked effect on HC emission, with the "lead + phosphorus" case, at least for the fuels used here, clearly giving the highest HC emission, and with the "lead-free" deposits giving less. It should be noted, however, that the "lead + P" and "lead-free" fuels used different base stocks, as well as differing in additive content. Evidently, the emissions of the 1970 Chevrolet (see above) would have been acceptable at the outset if a different choice of test fuel and deposits had been made. The corresponding vehicle emissions of CO and NO, as given in the data tables in the main text are not tabulated here in the same way, because, as shown in the first year (for the Plymouth), CO and NO were related (by regression equations) to ambient humidity rather than to fuel or deposits. Second-year Plymouth CO data fit the same humidity correlation until test 41, at which point carburetor service established a new relationship for subsequent tests.

Tables C-3 through C-43 of this Appendix show the average emission of CO, IRHC, and NO for each mode of each cycle in cycles 1-4 and 6-7 in each test of the second contract year. The values are based on "corrected" (to CO_2 + CO = 15) values from computer printout sheets, averaged over all available printouts for 1 to 3 of the 3 cold-start blocks that form a PNA emission test. As in the first-year work, the choke action of all three vehicles at startup was variable, so that starting mixture ratio and engine speed ranged over fairly wide limits in different tests or in different blocks of the same test.

Table C-44 records the maximum and minimum muffler-exit and heat-exchanger inlet gas temperatures observed in hot test cycles for all second-year tests. The 1968 Chevrolet exhaust is only slightly warmer than that from the 1966 Plymouth, while the 1970 Chevrolet is over 100 Fahrenheit degrees hotter. This higher muffler-exit temperature, for the 1970 car, combined with a slightly higher gas flow rate (measured at the PNA collector outlet) also results in higher exchanger-inlet temperatures; even the exchanger-outlet temperatures are about 5° higher for the 1970 vehicle. Examination of temperatures for individual tests in Table C-44 reveals some conspicuous departures from typical values. No explanation can be

offered for these variations; the likely causes, such as dynamometer loading and spark timing do not appear to be generally useful. In some, but not all cases, higher temperatures appear associated with higher fuel consumption, but the variations in fuel consumption are, in themselves, unexplained. In any case, it is likely that the higher average temperatures and fuel consumption for the 1970 Chevrolet, relative to the 1968 Chevrolet, are at least partly due to the lack of vacuum spark advance below 23 mph because of the action of the TCS (transmission-controlled spark) system in the 1970 vehicle.

Between-vehicle differences in exhaust-gas temperatures at the muffler might be expected to cause differences in the tendency of the mufflers of the different cars to retain PNA that is emitted from the engines in the course of a test. The data in Table C-45 suggest that this is indeed the case, and that at the temperature level of the 1970 Chevrolet it is not really necessary to include the muffler washings in a PNA-sample workup, even though cleaning the muffler between tests does appear to be in order. The data in this table were obtained by separate GC/UV analyses of muffler washings from 18 tests, covering a variety of fuels in three vehicles. The data are admittedly unbalanced in terms of vehicle identity, fuel TEL, engine deposits, etc., but no further separate analyses are planned. Muffler washings will continue to be added to the main samples for work-up. Muffler clean-out was improved, during the year, by drilling a small hole near the side of one end-wall of each muffler and extending its entire length. This hole promoted drainage of clean-up solvent from the muffler; it was closed by a screw plug when neither filling nor drainage of solvent was needed. With cover plates also blocking the gas inlet and outlet, each muffler could be charged with a small amount of solvent and mechanically rotated to ensure thorough washing. One problem encountered here was that cleanout solvent could penetrate into an insulation layer between the inner and outer shells of the 1970 Chevrolet muffler; the consequences are mentioned in Table C-1; the remedy was rebuilding the muffler and adopting, as the last step of clean-up, a procedure in which filtered air is drawn through the muffler while it is warmed with electric heating tape.

Table C-1

CAPE-6-68

TESTS OF DUBIOUS VALIDITY AS TO PNA

(Tests 45, 50, 51 in 1970 Chevrolet, 54 in 1966 Plymouth)

Test No.	Comment
45	Solvent from prior test trapped in laminated muffler wall, boiled out in early part of first block, caused off-scale HC results with other analyses normal. Aborted Block 1 after Cycle 3; choke was then open but oil and coolant not at equilibrium temps. Block 2 was run for 21 cycles, with oil at ~225°F for 9 cycles (20 minutes), where normally oil only reaches 220°F. at end of 12-cycle block. Sample from muffler dark yellow (abnormal), high in BghiP and BaP. Yields of phenol and BaA "normal," of BaP, high. Note: Similar HC retention in muffler wall in Test 46, but with the 3 standard 12-cycle blocks, showed low emission of all PNA and low muffler hold-up.
51	Same fuel as Test 45, no muffler abnormality. Incorrect idle speed setting is believed to be cause of abnormally high HC emissions in deceleration modes (modes 4 and 7). All PNA high except pyrene; samples dark colored, abnormal.
50	In third block, lost vacuum spark advance hose connection; suppressed NO, elevated peak exhaust temperatures ~ 80°F. at muffler exit; strongly oxidized exhaust HC, particularly in Mode 7. PNA yields are very high; muffler sample and main sample abnormally dark and dirty. BaP exceeds BaA (abnormal).
54	Vehicle was idle for 3.7 months. Dynamometer was pre-loaded for 16 BHP at 50 MPH, i.e., 2 x normal; reduced to near normal by approximately 12th minute of test. The entire first block of this test was rich, relative to the earlier test 41 which was expected to be matched:

Block:	% CO, Cycle Results 1	2	3	BaP/gal.	BaA/gal.	Fuel, gal.
Test 41	1.42	1.49	1.45	37	49	1.93
Test 54	1.89	1.50	1.44	128	195	2.04

Table C-2

NDIR HYDROCARBON EMISSIONS - CAPE-6-68 TESTS[a]

(Data of Both Contract Years)

Vehicle, Deposits	Fuel Aromatics: Fuel Set[b]	Average Hydrocarbons, C_6, ppm (No. of Tests) 11% - 12% 1969	11% - 12% 1970	28% 1970	46% 1969	46% 1970
'66 NC						
Clean		677(2)			590(2)	
Lead-free (A)		776(2)			600(2)	
Lead + P (C3P)		817(2)	740(2)	641(3)	624(4)	
Low-lead (A.5)				570(3)		
Lead-free (A)				511(2)	496(1)	491(1)
'68 EM						
Lead + P (C3P)		458(2)	417(2)	298(3)	285(4)	
Low-lead (A.5)				293(3)		
Lead-free (A)				273(1)	193(1)	185(1)
'70 EM						
Lead + P[c] (C3P)		205(3)	232(4)	178(3)	135(1)	134(3)

[a] Each value is the average of 1 to 4 test results, each of which is the average from results on 1 to 3 test blocks out of 3 blocks comprising a test. Deposit conditions listed in order of occurrence.

[b] Fuel sets (by year) are identified in Appendix B.

[c] Tests 50 and 51 (abnormal) omitted from averages. First blocks of certain other tests, in which muffler clean-out solvents affected apparent IRHC at startup, are also excluded; see Table C-1.

TABLE C-3

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 20

Data are averages from first 7 cycles of 2 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	1.26	1.75	2.34	5.76	2.92	1.45	6.78	
	2	4.52	1.97	1.28	5.72	4.42	1.19	6.54	
	3	4.67	1.39	0.37	4.52	4.08	0.46	4.45	
	4	2.02	1.14	0.47	2.32	3.82	0.36	3.96	
	Avg. 1-4	3.12	1.56	1.12	4.58	3.81	0.87	5.44	1.66
	6	1.68	1.10	1.00	2.07	4.30	0.48	3.62	
	7	2.02	1.20	1.02	2.04	4.30	0.48	3.54	
	Avg. 6-7	1.85	1.15	1.01	2.06	4.30	0.48	3.58	1.12
	Composite Test Result, % CO								1.31
IRHC, ppm (C_6)	1	595	487	463	918	514	443	1823	
	2	716	629	543	714	572	501	1610	
	3	658	573	492	591	555	482	1964	
	4	615	575	472	746	573	482	1940	
	Avg. 1-4	646	566	492	742	553	477	1834	564
	6	587	532	450	916	561	472	2050	
	7	583	526	449	953	552	458	2048	
	Avg. 6-7	585	529	450	935	557	465	2049	562
	Composite Test Result, ppm HC								563
NO, ppm	1	1053	1760	1611	586	638	2408	297	
	2	177	1868	2113	640	261	2757	380	
	3	211	2486	3067	850	324	3550	889	
	4	163	2243	2444	988	292	3562	1018	
	Avg. 1-4	401	2089	2309	766	379	3070	646	2279
	6	165	2381	1743	757	237	3554	994	
	7	134	2277	1713	725	190	3495	1023	
	Avg. 6-7	150	2329	1728	741	214	3525	1009	2466
	Composite Test Result, ppm NO								2400

TABLE C-4

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 21

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	3.52	3.08	4.34	3.40	2.99	1.18	3.85	
	2	1.47	0.41	0.19	2.80	0.72	0.20	3.40	
	3	1.82	0.40	0.18	2.09	0.52	0.19	2.84	
	4	1.80	0.40	0.20	1.89	0.48	0.19	2.60	
	Avg. 1-4	2.15	1.07	1.23	2.55	1.18	0.44	3.17	0.98
	6	1.71	0.36	0.19	1.98	0.51	0.20	2.72	
	7	1.72	0.43	0.20	2.05	0.63	0.20	2.61	
	Avg. 6-7	1.72	0.39	0.20	2.01	0.57	0.20	2.67	0.49
	Composite Test Result, % CO								0.66
IRHC, ppm (C_6)	1	385	346	322	312	309	299	457	
	2	351	300	244	272	243	267	553	
	3	353	290	239	258	225	259	497	
	4	354	293	235	257	220	259	513	
	Avg. 1-4	361	308	261	275	249	271	505	286
	6	349	290	239	271	217	252	504	
	7	353	289	228	259	213	248	499	
	Avg. 6-7	351	290	235	266	215	251	502	266
	Composite Test Result, ppm HC								272
NO, ppm	1	367	702	504	457	464	1705	411	
	2	369	1314	989	313	267	2002	471	
	3	211	1301	1035	333	276	2035	508	
	4	212	1325	961	327	263	1991	515	
	Avg. 1-4	289	1161	873	357	318	1934	477	1327
	6	227	1415	942	327	260	2027	535	
	7	220	1139	943	292	220	2041	509	
	Avg. 6-7	224	1377	943	309	240	2034	522	1426
	Composite Test Result, ppm NO								1391

TABLE C-5

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 22

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	6.50	4.34	1.98	5.44	3.57	2.17	6.46	
	2	4.73	2.66	1.11	4.84	4.24	1.69	5.77	
	3	4.46	1.72	0.37	3.99	4.00	0.49	3.51	
	4	1.81	1.05	0.33	1.81	4.07	0.53	3.27	
	Avg. 1-4	4.38	2.44	0.95	4.02	3.97	1.22	4.76	2.00
	6	1.97	1.17	0.48	2.10	4.25	0.43	3.35	
	7	2.10	1.18	0.55	2.21	4.33	0.54	3.40	
	Avg. 6-7	2.03	1.18	0.52	2.16	4.29	0.49	3.37	1.08
	Composite Test Result, % CO								1.40
IRHC, ppm (C_6)	1	1155	774	664	1196	801	661	1879	
	2	1039	806	661	898	819	657	1631	
	3	925	721	607	824	799	631	2133	
	4	739	679	578	1302	821	617	2189	
	Avg. 1-4	947	745	628	1055	810	642	1959	747
	6	712	646	566	1487	788	596	2225	
	7	691	630	556	1547	772	587	2335	
	Avg. 6-7	702	639	561	1518	780	592	2281	719
	Composite Test Result, ppm HC								729
NO, ppm	1	214	853	1608	603	301	1931	243	
	2	157	1433	1819	650	289	2293	325	
	3	203	2161	2539	736	316	3363	866	
	4	142	2181	2311	1008	305	3313	989	
	Avg. 1-4	179	1657	2069	744	303	2725	605	1972
	6	121	2112	1963	759	162	3400	991	
	7	113	2079	1856	718	164	3237	1031	
	Avg. 6-7	117	2096	1910	739	163	3319	1011	2333
	Composite Test Result, ppm NO								2207

TABLE C-6

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 23

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	3.71	3.67	2.33	5.45	3.19	2.09	6.52	
	2	4.73	2.63	1.24	5.27	4.39	1.90	6.34	
	3	4.87	2.28	1.11	2.83	4.42	1.04	5.36	
	4	4.50	1.35	0.49	2.57	4.11	0.56	3.61	
	Avg. 1-4	4.45	2.48	1.29	4.53	4.03	1.40	5.46	2.19
	6	2.24	1.02	0.56	2.44	4.14	0.37	3.55	
	7	2.27	1.22	0.53	2.48	4.29	0.43	3.55	
	Avg. 6-7	2.26	1.12	0.55	2.46	4.22	0.40	3.55	1.05
	Composite Test Result, % CO								1.45
IRHC, ppm (C_6)	1	1020	759	679	1231	805	653	2013	
	2	1047	832	714	973	845	691	1856	
	3	1010	791	673	866	813	648	1574	
	4	903	717	631	1297	823	640	2227	
	Avg. 1-4	995	775	675	1092	821	658	1917	772
	6	743	679	603	1509	802	613	2301	
	7	735	677	596	1532	757	600	2346	
	Avg. 6-7	739	678	600	1521	780	607	2324	742
	Composite Test Result, ppm HC								752
NO, ppm	1	391	1081	1451	479	479	1963	183	
	2	147	1561	2064	595	275	2279	253	
	3	171	1857	2065	591	272	2990	517	
	4	187	2195	2475	822	299	3226	937	
	Avg. 1-4	225	1674	2013	623	332	2615	473	1912
	6	110	2351	2125	809	199	3496	899	
	7	103	2095	2195	706	183	3428	915	
	Avg. 6-7	107	2224	2160	758	191	3463	908	2458
	Composite Test Result, ppm NO								2267

TABLE C-7

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 24

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	3.04	4.49	6.99	6.14	6.25	3.87	2.77	
	2	0.81	0.31	0.27	2.85	0.82	0.23	2.97	
	3	1.37	0.37	0.16	1.54	0.30	0.18	2.37	
	4	1.05	0.32	0.16	1.20	0.23	0.18	1.88	
	Avg. 1-4	1.57	1.38	1.90	2.93	1.90	1.12	2.40	1.45
	6	1.06	0.30	0.16	1.26	0.21	0.17	1.91	
	7	0.95	0.31	0.16	1.21	0.28	0.18	1.90	
	Avg. 6-7	1.01	0.30	0.16	1.24	0.24	0.18	1.91	0.34
	Composite Test Result, % CO								0.72
IRHC, ppm (C_6)	1	633	599	565	545	554	524	477	
	2	509	451	404	394	362	415	717	
	3	528	437	379	373	328	384	685	
	4	506	417	366	371	317	377	775	
	Avg. 1-4	543	476	429	421	391	425	663	445
	6	507	416	369	363	348	374	845	
	7	510	420	359	354	329	375	851	
	Avg. 6-7	509	419	364	359	339	375	848	399
	Composite Test Result, ppm HC								415
NO, ppm	1	267	276	99	101	104	491	421	
	2	463	999	874	269	233	1654	389	
	3	188	1083	749	271	257	1749	428	
	4	242	1161	785	283	273	1712	432	
	Avg. 1-4	291	880	627	231	217	1402	418	973
	6	250	1196	786	277	251	1658	475	
	7	261	1217	727	260	213	1676	486	
	Avg. 6-7	256	1207	757	269	233	1667	481	1193
	Composite Test Result, ppm NO								1116

TABLE C-8

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 25

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	6.23	6.54	6.46	5.53	5.09	2.65	3.72	
	2	1.94	0.61	0.18	3.26	1.01	0.22	3.61	
	3	1.85	0.49	0.16	2.27	0.34	0.19	2.74	
	4	1.52	0.42	0.16	1.74	0.24	0.17	2.22	
	Avg. 1-4	2.89	2.02	1.74	3.20	1.67	0.81	3.08	1.53
	6	1.39	0.37	0.15	1.65	0.34	0.15	2.10	
	7	1.26	0.33	0.16	1.74	0.31	0.18	2.06	
	Avg. 6-7	1.33	0.35	0.16	1.70	0.33	0.17	2.08	0.40
	Composite Test Result, % CO								0.79
IRHC, ppm (C_6)	1	613	597	535	519	524	500	742	
	2	553	481	410	424	372	416	813	
	3	539	444	380	382	323	385	742	
	4	521	431	376	385	319	387	861	
	Avg. 1-4	557	489	425	427	385	422	790	451
	6	519	427	368	364	301	376	891	
	7	511	421	373	379	307	379	917	
	Avg. 6-7	516	424	371	372	304	378	905	404
	Composite Test Result, ppm HC								419
NO, ppm	1	133	110	105	117	161	835	359	
	2	251	864	721	227	186	1351	351	
	3	142	939	727	234	229	1583	406	
	4	171	1039	740	238	219	1635	418	
	Avg. 1-4	175	738	574	205	199	1351	383	900
	6	187	1023	682	227	187	1628	391	
	7	198	1059	701	207	205	1571	456	
	Avg. 6-7	193	1042	692	217	196	1600	424	1105
	Composite Test Result, ppm NO								1033

TABLE C-9

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 26

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	3.96	3.99	2.73	6.04	3.48	1.61	6.63	
	2	4.39	2.44	1.11	5.42	3.87	1.34	6.34	
	3	4.58	2.18	0.65	4.49	3.89	0.69	5.18	
	4	3.36	1.20	0.30	3.25	3.95	0.55	4.20	
	Avg. 1-4	4.07	2.46	1.20	4.80	3.80	1.05	5.59	2.02
	6	1.45	1.14	0.60	1.94	4.21	0.54	3.40	
	7	1.54	1.17	0.50	1.88	4.42	0.55	3.32	
	Avg. 6-7	1.50	1.16	0.55	1.91	4.32	0.55	3.36	1.08
	Composite Test Result, % CO								1.40
IRHC, ppm (C_6)	1	709	627	591	1005	679	571	1923	
	2	871	744	608	783	675	593	1717	
	3	800	695	579	715	677	578	1777	
	4	751	659	539	789	687	580	1901	
	Avg. 1-4	783	682	580	823	679	581	1830	667
	6	695	628	543	1210	696	564	2211	
	7	677	623	530	1268	697	557	2251	
	Avg. 6-7	687	626	537	1239	697	561	2232	674
	Composite Test Result, ppm HC								671
NO, ppm	1	1081	1148	1477	461	436	2267	224	
	2	195	1621	2257	617	478	2661	331	
	3	210	1879	2529	727	435	3357	619	
	4	219	2387	2777	907	379	3199	831	
	Avg. 1-4	427	1759	2260	678	433	2871	501	2095
	6	143	2077	2091	791	273	3346	908	
	7	131	1949	2149	819	253	3359	988	
	Avg. 6-7	137	2014	2120	805	263	3353	949	2361
	Composite Test Result, ppm NO								2268

TABLE C-10

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 27

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	2.62	3.02	3.01	6.08	3.14	1.79	6.76	
	2	4.99	2.89	1.24	5.61	4.09	1.58	6.40	
	3	4.92	2.16	0.38	4.70	4.20	0.62	4.48	
	4	2.59	1.33	0.24	2.33	3.90	0.52	3.67	
	Avg. 1-4	3.78	2.35	1.22	4.68	3.83	1.13	5.33	2.01
	6	1.92	1.32	0.46	2.15	4.49	0.49	3.42	
	7	2.00	1.27	0.47	2.04	4.53	0.50	3.31	
	Avg. 6-7	1.96	1.30	0.47	2.10	4.51	0.50	3.37	1.12
	Composite Test Result, % CO								1.42
IRHC, ppm (C_6)	1	600	558	523	1261	632	523	2003	
	2	882	711	588	853	663	575	1799	
	3	813	669	561	733	665	549	1971	
	4	725	621	514	1036	647	520	2222	
	Avg. 1-4	755	640	547	971	652	541	1999	647
	6	653	564	479	1227	638	499	2331	
	7	638	549	469	1285	635	493	2341	
	Avg. 6-7	645	557	474	1256	637	496	2336	620
	Composite Test Result, ppm HC								629
NO, ppm	1	1337	1384	1432	506	677	2193	212	
	2	164	1495	2239	659	487	2509	309	
	3	177	1945	3420	876	461	3490	731	
	4	166	2162	3058	1125	447	3485	876	
	Avg. 1-4	461	1746	2538	791	518	2919	532	2160
	6	114	2035	2358	947	265	3569	949	
	7	105	2103	2223	879	262	3531	964	
	Avg. 6-7	110	2070	2291	913	264	3550	957	2491
	Composite Test Result, ppm NO								2375

TABLE C-11

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 28

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	2.12	1.68	2.69	5.75	3.25	1.89	6.70	
	2	4.99	2.96	1.49	5.64	4.68	1.81	6.36	
	3	4.99	2.64	0.53	4.67	4.26	0.88	4.87	
	4	3.44	1.57	0.31	2.37	4.12	0.77	3.64	
	Avg. 1-4	3.89	2.22	1.26	4.61	4.08	1.34	5.40	2.09
	6	2.21	1.49	0.45	2.38	4.57	0.71	3.48	
	7	2.32	1.49	0.65	2.42	4.76	0.70	3.48	
	Avg. 6-7	2.27	1.49	0.55	2.40	4.67	0.71	3.48	1.30
	Composite Test Result, % CO								1.57
IRHC, ppm (C_6)	1	748	608	515	1285	639	522	2025	
	2	883	747	574	932	679	568	1819	
	3	797	682	533	731	638	534	1680	
	4	691	609	485	1061	645	515	2043	
	Avg. 1-4	780	661	527	1003	651	535	1892	647
	6	604	568	455	1281	636	489	2130	
	7	601	560	457	1287	624	484	2167	
	Avg. 6-7	603	564	456	1284	630	487	2149	611
	Composite Test Result, ppm HC								623
NO, ppm	1	667	1525	1277	476	493	1835	241	
	2	144	1239	1776	610	293	2051	349	
	3	164	1487	2459	835	389	2829	638	
	4	191	1789	2597	1014	357	2816	839	
	Avg. 1-4	291	1510	2027	734	383	2383	517	1781
	6	113	1757	2095	790	266	2975	902	
	7	103	1773	2221	738	180	2984	871	
	Avg. 6-7	109	1765	2159	765	223	2980	887	2128
	Composite Test Result, ppm NO								2007

TABLE C-12

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 29

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	5.93	6.54	6.95	5.80	5.51	2.63	5.14	
	2	3.19	1.13	0.23	3.12	0.94	0.24	3.52	
	3	2.02	0.64	0.20	1.96	0.39	0.20	2.78	
	4	1.57	0.45	0.20	1.56	0.31	0.21	2.48	
	Avg. 1-4	3.18	2.19	1.90	3.11	1.79	0.82	3.48	1.62
	6	1.46	0.46	0.21	1.70	0.31	0.20	2.46	
	7	1.34	0.46	0.20	1.61	0.34	0.20	2.54	
	Avg. 6-7	1.40	0.46	0.21	1.65	0.33	0.20	2.50	0.45
	Composite Test Result, % CO								0.85
IRHC, ppm (C_6)	1	463	453	395	382	373	358	1162	
	2	477	415	322	325	279	317	849	
	3	415	355	280	287	245	283	741	
	4	389	332	261	279	233	285	808	
	Avg. 1-4	437	389	315	319	282	311	891	349
	6	379	317	257	270	221	269	747	
	7	369	312	246	272	213	265	811	
	Avg. 6-7	374	315	252	271	217	267	779	293
	Composite Test Result, ppm HC								312
NO, ppm	1	175	134	99	116	138	920	459	
	2	99	773	801	267	233	1581	469	
	3	157	909	788	273	268	1689	503	
	4	197	1087	795	276	248	1813	494	
	Avg. 1-4	157	725	621	233	222	1501	482	976
	6	209	1049	833	280	259	1701	476	
	7	199	1019	731	265	221	1686	531	
	Avg. 6-7	204	1034	783	273	240	1694	503	1165
	Composite Test Result, ppm NO								1098

TABLE C-13

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 30

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	4.63	4.61	1.59	1.01	0.80	0.27	3.97	
	2	2.57	0.77	0.21	1.99	0.36	0.21	2.58	
	3	1.64	0.47	0.21	1.67	0.38	0.20	2.40	
	4	1.60	0.49	0.22	1.66	0.36	0.24	2.26	
	Avg. 1-4	2.61	1.59	0.56	1.58	0.48	0.23	2.81	0.85
	6	1.57	0.50	0.25	1.54	0.43	0.22	2.36	
	7	1.48	0.51	0.23	1.54	0.32	0.21	2.44	
	Avg. 6-7	1.53	0.51	0.24	1.54	0.38	0.22	2.40	0.48
	Composite Test Result, % CO								0.60
IRHC, ppm (C_6)	1	403	380	295	292	309	332	1135	
	2	434	347	274	287	226	285	897	
	3	379	325	241	298	201	260	859	
	4	380	331	243	261	199	255	917	
	Avg. 1-4	399	347	263	285	235	283	952	315
	6	373	337	231	275	197	254	935	
	7	366	345	221	267	191	259	889	
	Avg. 6-7	369	341	226	271	194	257	912	293
	Composite Test Result, ppm HC								300
NO, ppm	1	299	280	526	549	573	1682	462	
	2	117	910	713	254	245	1483	487	
	3	175	1035	702	253	227	1575	524	
	4	189	1152	677	253	233	1671	535	
	Avg. 1-4	195	844	655	327	320	1603	502	1069
	6	190	1077	634	229	193	1617	553	
	7	194	1092	624	214	221	1559	551	
	Avg. 6-7	192	1085	629	222	207	1589	552	1108
	Composite Test Result, ppm NO								1094

TABLE C-14

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 31

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	5.51	6/56	6.80	5.78	5.76	2.82	5.41	
	2	3.50	1.06	0.26	3.44	1.20	0.28	3.69	
	3	2.34	0.68	0.30	2.34	0.52	0.20	3.18	
	4	2.12	0.60	0.22	2.03	0.38	0.20	2.52	
	Avg. 1-4	3.36	2/23	1.89	3.40	1.96	0.88	3.70	1.70
	6	1.60	0.45	0.19	1.74	0.37	0.20	2.50	
	7	1.76	0.53	0.19	1.85	0.47	0.18	2.64	
	Avg. 6-7	1.68	0.49	0.19	1.79	0.42	0.19	2.57	0.49
	Composite Test Result, % CO								0.91
IRHC, ppm (C_6)	1	430	423	377	361	359	335	1146	
	2	448	370	288	310	262	285	765	
	3	383	312	247	262	212	253	684	
	4	360	295	219	251	188	235	712	
	Avg. 1-4	406	350	284	296	255	277	827	314
	6	352	290	234	264	193	241	738	
	7	355	286	233	253	187	242	727	
	Avg. 6-7	354	288	234	259	190	242	733	268
	Composite Test Result, ppm HC								283
NO, ppm	1	232	143	110	122	131	823	420	
	2	92	920	861	271	215	1553	449	
	3	135	1025	860	228	245	1807	459	
	4	167	1080	901	271	277	1713	520	
	Avg. 1-4	157	792	683	223	217	1474	462	987
	6	191	1059	795	257	263	1853	474	
	7	181	1059	791	257	205	1817	441	
	Avg. 6-7	186	1059	793	257	234	1835	458	1235
	Composite Test Result, ppm NO								1148

TABLE C-15

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 32

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	2.14	1.86	2.22	5.42	3.63	2.16	6.53	
	2	5.21	2.71	1.11	5.20	4.36	1.58	5.88	
	3	4.69	2.03	0.33	4.25	4.32	0.73	3.69	
	4	2.17	1.33	0.69	2.57	4.38	0.73	3.63	
	Avg. 1-4	3.55	1.98	1.09	4.36	4.17	1.30	4.93	1.95
	6	2.64	1.57	1.30	2.69	4.79	0.71	3.64	
	7	2.71	1.68	0.82	2.71	4.84	1.02	3.73	
	Avg. 6-7	2.67	1.63	1.06	2.70	4.82	0.87	3.69	1.52
	Composite Test Result, % CO								1.66
IRHC, ppm (C_6)	1	677	557	439	1184	679	495	2005	
	2	787	634	497	825	611	501	1717	
	3	719	580	454	656	589	459	2119	
	4	531	505	443	1099	590	435	2166	
	Avg. 1-4	679	569	459	941	617	473	2002	581
	6	518	479	412	1353	597	432	2228	
	7	511	475	403	1481	603	427	2245	
	Avg. 6-7	515	477	408	1417	600	430	2237	562
	Composite Test Result, ppm HC								568
NO, ppm	1	231	1115	1030	396	327	1506	285	
	2	100	1154	1337	458	259	1913	351	
	3	139	1489	1749	537	219	2409	712	
	4	108	1562	1552	535	200	2463	715	
	Avg. 1-4	145	1330	1417	482	251	2073	516	1496
	6	93	1473	1161	506	132	2491	786	
	7	89	1391	1254	501	149	2292	702	
	Avg. 6-7	91	1433	1208	505	141	2392	745	1642
	Composite Test Result, ppm NO								1590

TABLE C-16

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 33

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	5.06	4.95	4.10	3.00	2.85	1.52	4.86	
	2	3.40	1.16	0.26	2.75	0.51	0.23	3.19	
	3	1.91	0.59	0.23	2.02	0.35	0.23	2.73	
	4	1.89	0.61	0.24	1.81	0.31	0.23	2.52	
	Avg. 1-4	3.07	1.83	1.21	2.40	1.01	0.56	3.33	1.24
	6	1.66	0.54	0.24	1.90	0.39	0.23	2.58	
	7	1.77	0.52	0.23	1.83	0.37	0.23	2.59	
	Avg. 6-7	1.72	0.53	0.24	1.87	0.38	0.23	2.59	0.53
	Composite Test Result, % CO								0.77
IRHC, ppm (C_6)	1	446	422	355	354	335	326	1219	
	2	469	381	300	328	271	299	948	
	3	407	327	275	307	242	273	900	
	4	397	317	269	303	232	271	955	
	Avg. 1-4	430	362	300	323	270	293	1006	334
	6	399	320	263	303	226	272	974	
	7	398	321	263	306	231	271	996	
	Avg. 6-7	399	321	263	305	229	272	985	306
	Composite Test Result, ppm HC								315
NO, ppm	1	266	277	323	360	377	1237	418	
	2	96	795	787	273	261	1519	457	
	3	145	1714	727	271	286	1683	470	
	4	150	1005	769	269	262	1608	490	
	Avg. 1-4	165	771	651	293	297	1513	459	1004
	6	159	949	685	232	223	1704	498	
	7	155	1011	634	238	227	1683	503	
	Avg. 6-7	157	980	660	235	225	1694	501	1132
	Composite Test Result, ppm NO								1087

TABLE C-17

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 34

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	1.55	1.66	1.82	5.34	3.56	2.10	6.47	
	2	5.20	3.06	1.24	5.26	4.47	1.82	5.94	
	3	4.82	2.17	0.36	4.46	4.37	0.76	5.10	
	4	4.41	1.43	0.28	4.00	4.24	0.63	4.16	
	Avg. 1-4	4.00	2.08	0.92	4.77	4.16	1.33	5.42	2.02
	6	2.66	1.30	0.29	2.56	4.66	0.70	3.82	
	7	2.68	1.34	0.38	2.80	4.74	0.66	3.89	
	Avg. 6-7	2.67	1.32	0.34	2.68	4.70	0.68	3.86	1.29
	Composite Test Result, % CO								1.54
IRHC, ppm (C_6)	1	706	526	407	1072	530	430	1970	
	2	770	628	484	889	573	474	1820	
	3	709	567	448	746	583	442	1643	
	4	625	499	384	693	555	410	1975	
	Avg. 1-4	703	555	431	850	561	439	1852	547
	6	618	490	379	1359	566	407	2205	
	7	591	477	407	1345	575	405	2233	
	Avg. 6-7	605	484	393	1352	571	406	2219	550
	Composite Test Result, ppm HC								549
NO, ppm	1	823	1529	1370	488	413	1749	317	
	2	107	1206	1633	523	279	2004	385	
	3	131	1601	2289	639	283	2885	575	
	4	167	1821	1958	521	222	2780	673	
	Avg. 1-4	307	1539	1813	543	300	2355	487	1733
	6	109	1798	1976	741	183	2877	797	
	7	109	1808	1907	689	166	2962	861	
	Avg. 6-7	109	1803	1942	715	175	2920	829	2077
	Composite Test Result, ppm NO								1957

TABLE C-18

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 35

Data are averages from first 7 cycles of 2 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	5.86	6.07	6.04	4.91	4.77	2.39	4.83	
	2	2.75	0.95	0.22	3.47	0.93	0.22	3.62	
	3	2.39	0.61	0.18	2.10	0.39	0.16	2.89	
	4	2.06	0.55	0.16	1.81	0.36	0.15	2.56	
	Avg. 1-4	3.26	2.05	1.65	3.07	1.62	0.73	3.47	1.50
	6	1.68	0.44	0.15	1.87	0.38	0.16	2.55	
	7	1.76	0.44	0.15	1.82	0.38	0.15	2.66	
	Avg. 6-7	1.72	0.44	0.15	1.85	0.38	0.16	2.61	0.44
	Composite Test Result, % CO								0.80
IRHC, ppm (C_6)	1	424	405	360	338	336	318	947	
	2	402	320	236	310	234	247	863	
	3	369	282	220	256	193	217	761	
	4	357	279	217	267	192	220	819	
	Avg. 1-4	388	322	259	293	239	250	848	291
	6	353	260	205	255	189	220	866	
	7	357	264	207	270	184	216	858	
	Avg. 6-7	355	262	206	263	187	218	862	250
	Composite Test Result, ppm HC								264
NO, ppm	1	146	137	133	154	168	863	369	
	2	139	754	891	237	207	1542	366	
	3	105	992	905	267	232	1649	445	
	4	135	1005	778	244	209	1669	479	
	Avg. 1-4	132	722	677	225	205	1431	415	947
	6	156	1038	776	256	206	1518	580	
	7	137	1000	748	230	207	1701	473	
	Avg. 6-7	147	1019	762	243	207	1610	527	1116
	Composite Test Result, ppm NO								1057

TABLE C-19

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 36

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	4.43	4.34	3.61	2.72	2.50	0.85	4.68	
	2	3.33	0.89	0.21	2.55	0.45	0.17	3.17	
	3	1.87	0.50	0.20	1.88	0.36	0.15	2.57	
	4	1.83	0.41	0.17	1.63	0.28	0.14	2.30	
	Avg. 1-4	2.86	1.54	1.04	2.20	0.90	0.33	3.18	1.01
	6	1.40	0.36	0.16	1.47	0.35	0.15	2.29	
	7	1.43	0.34	0.17	1.58	0.30	0.15	2.30	
	Avg. 6-7	1.42	0.35	0.17	1.53	0.33	0.15	2.30	0.39
	Composite Test Result, % CO								0.60
IRHC, ppm (C_6)	1	417	396	343	336	323	309	1126	
	2	464	372	307	322	267	289	883	
	3	397	312	273	283	233	259	857	
	4	387	307	265	283	233	259	900	
	Avg. 1-4	417	347	297	307	265	279	941	322
	6	376	297	258	284	225	252	930	
	7	376	299	270	284	237	261	912	
	Avg. 6-7	376	298	264	284	231	257	921	291
	Composite Test Result, ppm HC								301
NO, ppm	1	356	379	358	399	437	1545	409	
	2	97	981	765	273	254	1549	429	
	3	153	1051	819	245	266	1725	479	
	4	168	1124	809	269	259	1689	471	
	Avg. 1-4	195	883	688	297	305	1627	447	1089
	6	189	1107	716	232	226	1603	467	
	7	185	1225	783	244	234	1719	525	
	Avg. 6-7	187	1166	750	238	230	1661	331	1176
	Composite Test Result, ppm NO								1145

TABLE C-20

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 37

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	1.82	1.52	1.69	5.40	3.43	1.70	6.49	
	2	5.16	2.67	0.99	5.33	4.43	1.43	6.03	
	3	4.84	2.16	0.36	4.55	4.40	0.98	5.32	
	4	4.53	1.62	0.22	4.14	4.34	0.59	5.04	
	Avg. 1-4	4.08	2.00	0.82	4.86	4.15	1.18	5.72	1.94
	6	4.54	1.50	0.24	4.16	4.41	0.79	3.85	
	7	2.61	1.48	0.29	2.50	4.46	0.61	3.70	
	Avg. 6-7	3.58	1.49	0.27	3.33	4.44	0.70	3.77	1.38
	Composite Test Result, % CO								1.57
IRHC, ppm (C_6)	1	809	589	446	1184	569	473	2044	
	2	848	713	546	943	627	536	1867	
	3	771	652	501	727	603	515	1753	
	4	693	602	462	702	595	500	1715	
	Avg. 1-4	781	639	489	889	599	506	1845	612
	6	605	531	417	703	554	443	2243	
	7	716	574	425	1473	604	481	2244	
	Avg. 6-7	661	553	421	1089	579	462	2243	583
	Composite Test Result, ppm HC								592
NO, ppm	1	373	1231	1359	569	358	1771	354	
	2	101	1118	1697	629	305	2044	443	
	3	133	1502	2353	800	301	2389	617	
	4	136	1525	2111	681	231	2476	665	
	Avg. 1-4	187	1344	1879	671	299	2170	519	1614
	6	109	1565	1930	633	213	2422	865	
	7	85	1426	1769	739	186	2599	907	
	Avg. 6-7	97	1496	1850	687	199	2511	887	1806
	Composite Test Result, ppm NO								1738

TABLE C-21

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 38

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	4.31	4.48	3.93	2.78	2.47	0.93	5.18	
	2	3.78	1.21	0.24	3.21	0.69	0.22	3.70	
	3	2.45	0.67	0.25	2.41	0.50	0.22	3.18	
	4	2.39	0.57	0.23	2.17	0.47	0.20	2.98	
	Avg. 1-4	3.23	1.73	1.17	2.64	1.03	0.39	3.76	1.18
	6	2.01	0.53	0.22	2.12	0.51	0.21	2.76	
	7	1.86	0.47	0.24	2.10	0.52	0.20	2.79	
	Avg. 6-7	1.94	0.50	0.23	2.11	0.52	0.21	2.78	0.54
	Composite Test Result, % CO								0.76
IRHC, ppm (C_6)	1	385	369	321	305	296	280	1221	
	2	448	351	268	319	245	257	942	
	3	397	314	268	297	237	265	875	
	4	381	294	241	281	198	216	857	
	Avg. 1-4	403	332	275	301	244	255	973	303
	6	355	272	219	270	195	224	907	
	7	354	268	221	269	194	217	885	
	Avg. 6-7	355	270	221	271	195	221	897	257
	Composite Test Result, ppm HC								273
NO, ppm	1	345	289	283	323	357	1327	433	
	2	80	768	643	244	210	1315	456	
	3	113	880	702	260	219	1519	503	
	4	121	911	808	257	201	1476	487	
	Avg. 1-4	165	712	609	271	247	1409	470	933
	6	132	870	635	233	180	1524	527	
	7	141	928	625	240	205	1483	515	
	Avg. 6-7	137	899	630	237	193	1504	521	1022
	Composite Test Result, ppm NO								991

TABLE C-22

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 39

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	2.59	3.15	3.38	2.25	2.01	0.52	5.50	
	2	3.79	1.17	0.37	3.19	0.92	0.22	3.79	
	3	2.43	0.67	0.23	2.39	0.63	0.21	3.12	
	4	2.28	0.57	0.23	2.07	0.59	0.23	2.95	
	Avg. 1-4	2.77	1.39	1.05	2.48	1.04	0.29	3.84	1.01
	6	1.86	0.43	0.26	2.03	0.71	0.20	2.79	
	7	1.87	0.52	0.25	2.13	0.79	0.19	2.86	
	Avg. 6-7	1.87	0.48	0.26	2.08	0.75	0.20	2.83	0.54
	Composite Test Result, % CO								0.70
IRHC, ppm (C_6)	1	260	240	217	213	193	183	1179	
	2	391	292	203	272	203	193	794	
	3	353	245	177	236	167	171	633	
	4	285	213	159	197	147	159	629	
	Avg. 1-4	323	247	189	229	177	177	675	220
	6	256	197	161	189	141	150	643	
	7	249	195	149	179	137	146	645	
	Avg. 6-7	253	196	155	184	139	148	644	180
	Composite Test Result, ppm HC								193
NO, ppm	1	957	707	393	463	500	1686	459	
	2	93	855	737	266	214	1560	477	
	3	139	1017	820	275	237	1663	551	
	4	150	1040	749	261	239	1651	507	
	Avg. 1-4	335	905	675	317	298	1640	499	1108
	6	163	1130	720	266	185	1598	575	
	7	163	1080	756	267	179	1693	540	
	Avg. 6-7	163	1105	738	267	182	1646	558	1152
	Composite Test Result, ppm NO								1136

TABLE C-23

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 40

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	4.22	4.55	4.56	3.39	3.13	1.03	4.73	
	2	2.48	0.73	0.22	2.68	0.41	0.21	3.16	
	3	1.66	0.51	0.19	1.71	0.27	0.16	2.61	
	4	1.62	0.44	0.18	1.68	0.27	0.16	2.41	
	Avg. 1-4	2.50	1.56	1.29	2.37	1.02	0.39	3.23	1.08
	6	1.18	0.32	0.18	1.53	0.28	0.16	2.50	
	7	1.39	0.33	0.18	1.68	0.26	0.16	2.54	
	Avg. 6-7	1.29	0.33	0.18	1.61	0.27	0.16	2.52	0.39
	Composite Test Result, % CO								0.62
IRHC, ppm (C_6)	1	289	268	227	220	210	193	978	
	2	320	246	192	236	168	174	738	
	3	276	208	165	200	140	157	706	
	4	254	184	142	184	120	138	719	
	Avg. 1-4	284	226	182	210	160	166	786	205
	6	248	182	144	180	124	142	799	
	7	248	182	140	179	120	142	824	
	Avg. 6-7	248	183	142	180	122	143	812	175
	Composite Test Result, ppm HC								185
NO, ppm	1	405	331	254	304	334	1401	441	
	2	149	907	744	394	247	1394	497	
	3	148	887	775	296	272	1518	547	
	4	162	967	723	294	265	1491	564	
	Avg. 1-4	217	773	624	295	279	1451	513	976
	6	180	977	702	270	240	1586	575	
	7	163	1034	609	255	241	1475	609	
	Avg. 6-7	172	1006	656	263	241	1531	593	1070
	Composite Test Result, ppm NO								1037

TABLE C-24

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 41

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	6.32	3.80	2.16	4.88	3.58	2.05	5.64	
	2	4.13	2.54	1.39	4.32	3.91	1.52	4.77	
	3	3.51	1.57	0.55	2.80	3.29	0.56	3.40	
	4	2.56	1.23	0.62	2.39	3.48	0.53	3.40	
	Avg. 1-4	4.13	2.29	1.18	3.60	3.57	1.17	4.30	1.91
	6	2.78	1.34	0.56	2.64	3.54	0.58	3.42	
	7	2.65	1.32	0.63	2.62	3.84	0.69	3.48	
	Avg. 6-7	2.72	1.33	0.60	2.63	3.60	0.64	3.45	1.22
	Composite Test Result, % CO								1.45
IRHC, ppm (C_6)	1	539	446	370	887	488	393	2071	
	2	623	563	486	672	587	441	1846	
	3	535	498	477	864	570	411	2151	
	4	515	474	420	1031	537	395	2195	
	Avg. 1-4	553	495	438	864	545	410	2066	520
	6	519	453	425	1108	525	384	2269	
	7	541	459	421	1197	515	381	2271	
	Avg. 6-7	531	456	411	1153	508	383	2270	519
	Composite Test Result, ppm HC								519
NO, ppm	1	186	751	845	353	273	1322	323	
	2	81	888	1087	361	263	1595	436	
	3	97	1239	1296	435	305	2073	669	
	4	99	1261	1213	451	245	2131	668	
	Avg. 1-4	116	1035	1110	400	271	1781	523	1250
	6	91	1216	1075	403	186	2121	734	
	7	91	1185	943	387	156	2003	688	
	Avg. 6-7	91	1201	1009	395	171	2065	710	1407
	Composite Test Result, ppm NO								1352

TABLE C-25

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 42

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	5.35	3.02	2.55	4.87	3.25	1.37	5.69	
	2	4.04	2.35	1.74	4.59	3.95	1.38	4.94	
	3	3.28	1.52	0.44	2.32	2.86	0.54	3.45	
	4	2.40	1.35	0.44	2.21	3.08	0.64	3.30	
	Avg. 1-4	3.77	2.06	1.29	3.50	3.29	0.98	4.35	1.74
	6	2.54	1.34	0.74	2.31	3.44	0.74	3.23	
	7	2.57	1.26	0.66	2.18	3.43	0.62	3.21	
	Avg. 6-7	2.56	1.30	0.70	2.25	3.44	0.68	3.22	1.20
	Composite Test Result, % CO								1.38
IRHC, ppm (C_6)	1	443	372	323	899	418	336	2093	
	2	651	597	490	707	496	428	1865	
	3	558	543	458	870	509	418	2116	
	4	559	495	417	917	473	391	2153	
	Avg. 1-4	553	502	423	849	474	393	2057	507
	6	527	448	389	1052	470	368	2187	
	7	504	439	379	1050	461	359	2219	
	Avg. 6-7	516	445	385	1051	466	364	2203	492
	Composite Test Result, ppm HC								496
NO, ppm	1	341	943	788	305	298	1421	400	
	2	94	916	959	361	299	1633	543	
	3	115	1147	1245	527	361	2024	603	
	4	117	1152	1243	491	309	1959	685	
	Avg. 1-4	167	1040	1059	421	317	1759	558	1243
	6	104	1157	910	395	214	1879	699	
	7	107	1145	872	400	200	2001	794	
	Avg. 6-7	106	1151	892	398	208	1941	725	1327
	Composite Test Result, ppm NO								1297

TABLE C-26

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 43

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	6.03	3.56	1.93	5.11	2.16	1.06	5.95	
	2	3.60	1.94	1.56	4.92	3.71	1.11	5.60	
	3	3.54	2.41	0.51	3.48	3.08	0.47	3.91	
	4	2.22	1.09	0.22	2.18	2.70	0.49	3.43	
	Avg. 1-4	3.85	2.08	1.05	3.93	2.91	0.78	4.73	1.65
	6	2.04	1.06	0.26	2.01	2.99	0.49	3.26	
	7	2.10	1.16	0.33	1.95	3.10	0.46	3.29	
	Avg. 6-7	2.07	1.11	0.30	1.99	3.05	0.48	3.28	0.96
	Composite Test Result, % CO								1.20
IRHC, ppm (C_6)	1	436	359	311	904	405	338	1999	
	2	608	571	465	692	477	423	1898	
	3	568	542	477	506	465	427	1935	
	4	510	497	438	754	459	402	2051	
	Avg. 1-4	531	492	416	714	451	398	1971	495
	6	470	439	386	858	454	389	2144	
	7	480	451	375	966	486	385	2127	
	Avg. 6-7	475	445	381	912	471	387	2136	490
	Composite Test Result, ppm HC								491
NO, ppm	1	292	963	1177	519	559	2064	416	
	2	111	1225	1403	541	423	2175	601	
	3	143	1667	1770	676	526	2546	784	
	4	145	1581	1928	759	563	2532	829	
	Avg. 1-4	173	1309	1569	624	518	2329	658	1652
	6	128	1473	1720	723	353	2441	907	
	7	1468	1506	632	294	2490	887	887	
	Avg. 6-7	125	1471	1613	678	324	2466	897	1758
	Composite Test Result, ppm NO								1721

TABLE C-27

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 44

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	.31	2.36	2.43	1.29	.86	2.95	1.94	
	2	.79	.87	.16	.53	.22	.70	.61	
	3	.29	.76	.15	.24	.14	.72	.45	
	4	.28	.67	.15	.24	.13	.73	.45	
	Avg. 1-4	.42	1.17	.72	.58	.34	1.28	.86	1.02
	6	.35	.59	.14	.27	.13	.56	.49	
	7	.31	.60	.15	.28	.13	.53	.53	
	Avg. 6-7	.34	.60	.15	.28	.13	.55	.51	.44
	Composite Test Result, % CO								.63
IRHC, ppm (C_6)	1	732	488	431	359	193	279	579	
	2	216	199	315	294	141	209	677	
	3	194	175	321	289	123	199	652	
	4	188	175	296	287	128	201	691	
	Avg. 1-4	333	260	341	307	145	222	650	261
	6	179	165	277	269	105	197	649	
	7	172	166	309	267	101	189	708	
	Avg. 6-7	176	165	294	268	103	193	679	209
	Composite Test Result, ppm HC								227
NO, ppm	1	430	613	1119	697	228	558	564	
	2	183	630	1567	725	251	1144	785	
	3	246	686	1639	820	251	1151	820	
	4	244	696	1621	791	245	1200	840	
	Avg. 1-4	277	657	1487	759	245	1014	752	887
	6	244	608	1564	767	232	1269	832	
	7	263	647	1541	755	240	1198	789	
	Avg. 6-7	254	628	1553	761	236	1234	811	989
	Composite Test Result, ppm NO								953

TABLE C-28

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 45

Data are averages from first 7 cycles of 2 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	3.56	4.16	2.33	1.26	.85	2.26	1.58	
	2	.94	1.13	.16	.37	.31	.80	.51	
	3	.40	.80	.13	.24	.13	.81	.43	
	4	.37	.78	.13	.30	.13	.77	.47	
	Avg. 1-4	1.31	1.72	.69	.54	.36	1.16	.75	1.13
	6	.46	.80	.14	.33	.20	.78	.55	
	7	.44	.76	.14	.39	.14	.78	.55	
	Avg. 6-7	.45	.78	.14	.36	.17	.78	.55	.60
	Composite Test Result, % CO								.78
IRHC, ppm (C_6)	1	387	323	438	330	197	288	492	
	2	250	226	341	340	164	228	597	
	3	208	186	296	296	116	208	524	
	4	191	173	307	263	110	210	507	
	Avg. 1-4	259	228	345	307	147	234	530	252
	6	183	169	269	246	102	206	553	
	7	178	169	266	252	96	194	542	
	Avg. 6-7	181	169	268	249	100	201	548	205
	Composite Test Result, ppm HC								221
NO, ppm	1	147	181	822	621	228	594	480	
	2	159	487	1225	609	195	1029	673	
	3	220	540	1288	651	227	958	694	
	4	228	593	1296	668	233	1113	710	
	Avg. 1-4	189	451	1158	638	221	924	639	741
	6	214	542	1368	718	212	1058	669	
	7	234	570	1316	704	230	954	756	
	Avg. 6-7	225	556	1343	712	222	1006	713	837
	Composite Test Result, ppm NO								803

TABLE C-29

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 46

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	2.17	3.59	2.90	1.55	1.36	3.32	1.85	
	2	.69	.79	.18	.58	.23	.71	.52	
	3	.24	.62	.14	.22	.16	.67	.35	
	4	.21	.61	.14	.19	.15	.60	.38	
	Avg. 1-4	.49	1.40	.84	.63	.48	1.33	.78	1.14
	6	.32	.56	.16	.27	.16	.55	.43	
	7	.31	.55	.15	.24	.13	.48	.41	
	Avg. 6-7	.32	.56	.16	.25	.15	.52	.42	.42
	Composite Test Result, % CO								.67
IRHC, ppm (C_6)	1	607	515	442	353	205	281	591	
	2	219	194	297	283	153	216	522	
	3	177	166	260	279	118	205	603	
	4	174	164	283	250	117	197	563	
	Avg. 1-4	294	260	321	292	149	225	570	256
	6	167	155	255	269	109	193	545	
	7	167	154	253	228	106	180	574	
	Avg. 6-7	167	155	254	249	108	187	560	195
	Composite Test Result, ppm HC								215
NO, ppm	1	283	554	858	677	197	382	538	
	2	184	613	1570	757	241	1257	807	
	3	241	721	1556	786	219	1324	832	
	4	261	689	1430	739	227	1295	888	
	Avg. 1-4	243	645	1354	740	222	1065	766	888
	6	247	670	1519	775	229	1388	879	
	7	252	711	1563	801	236	1207	883	
	Avg. 6-7	251	691	1542	789	233	1298	881	1035
	Composite Test Result, ppm NO								983

TABLE C-30

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 47

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	4.25	4.76	2.48	1.90	1.42	3.12	1.80	
	2	.68	.80	.15	.54	.25	.65	.59	
	3	.24	.69	.12	.19	.11	.62	.38	
	4	.25	.66	.12	.20	.11	.64	.37	
	Avg. 1-4	1.36	1.72	.72	.71	.47	1.26	.79	1.20
	6	.28	.64	.12	.24	.14	.58	.38	
	7	.35	.62	.12	.25	.09	.57	.36	
	Avg. 6-7	.32	.63	.12	.25	.12	.58	.37	.45
	Composite Test Result, % CO								.70
IRHC, ppm (C_6)	1	619	509	434	368	224	307	443	
	2	225	200	296	279	147	216	422	
	3	192	175	287	302	129	192	527	
	4	207	185	288	255	127	201	538	
	Avg. 1-4	311	267	326	301	157	229	482	259
	6	181	168	253	243	123	199	491	
	7	177	166	250	267	109	196	524	
	Avg. 6-7	179	167	252	255	119	198	508	203
	Composite Test Result, ppm HC								222
NO, ppm	1	297	549	1007	709	230	538	581	
	2	209	627	1639	771	287	1274	824	
	3	258	695	1554	838	263	1132	898	
	4	270	730	1665	905	275	1231	919	
	Avg. 1-4	259	650	1467	806	264	1044	805	902
	6	265	694	1622	865	276	1339	915	
	7	271	579	1643	839	281	1174	894	
	Avg. 6-7	269	637	1633	852	279	1257	905	1022
	Composite Test Result, ppm NO								979

TABLE C-31

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 48

Data are averages from first 7 cycles of 2 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	2.09	3.87	2.34	1.55	.55	2.41	3.30	
	2	1.07	.75	.22	.77	.28	.53	1.04	
	3	.45	.58	.17	.38	.17	.56	.60	
	4	.39	.45	.17	.35	.19	.50	.56	
	Avg. 1-4	1.00	1.41	.73	.76	.30	1.00	.94	1.00
	6	.46	.52	.16	.41	.16	.42	.63	
	7	.46	.52	.18	.44	.22	.44	.75	
	Avg. 6-7	.46	.52	.17	.43	.19	.43	.69	.40
	Composite Test Result, % CO								.60
IRHC, ppm (C_6)	1	442	362	363	390	172	219	351	
	2	176	151	213	209	118	140	282	
	3	150	128	187	183	104	128	291	
	4	132	114	178	184	93	123	280	
	Avg. 1-4	225	189	236	242	123	153	301	180
	6	126	109	162	186	65	96	282	
	7	108	92	150	137	65	98	288	
	Avg. 6-7	117	101	156	162	65	97	285	112
	Composite Test Result, ppm HC								135
NO, ppm	1	634	592	879	697	329	683	482	
	2	265	752	2054	993	348	1319	814	
	3	319	830	2157	1041	356	1404	918	
	4	338	904	2104	1057	347	1510	889	
	Avg. 1-4	389	769	1798	947	345	1229	776	1072
	6	337	909	2000	950	349	1470	844	
	7	332	902	1996	889	311	1446	782	
	Avg. 6-7	335	906	1998	920	330	1458	813	1230
	Composite Test Result, ppm NO								1174

TABLE C-32

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 49

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	1.95	3.87	1.58	1.31	.75	2.34	2.73	
	2	.89	.76	.23	.59	.43	.77	.61	
	3	.31	.60	.22	.30	.20	.67	.51	
	4	.31	.56	.22	.30	.24	.56	.47	
	Avg. 1-4	.86	1.45	.56	.63	.41	1.09	1.08	1.01
	6	.39	.57	.22	.37	.19	.57	.58	
	7	.43	.58	.22	.45	.19	.50	.61	
	Avg. 6-7	.41	.58	.22	.41	.19	.54	.60	.44
	Composite Test Result, % CO								.64
IRHC, ppm (C_6)	1	320	309	259	216	122	165	321	
	2	142	123	185	198	98	132	384	
	3	125	112	203	199	82	130	443	
	4	120	102	201	179	81	116	426	
	Avg. 1-4	177	162	213	198	96	136	394	160
	6	114	99	166	210	74	116	406	
	7	120	103	165	168	74	113	488	
	Avg. 6-7	117	101	166	190	74	115	448	128
	Composite Test Result, ppm HC								138
NO, ppm	1	445	621	1035	725	288	621	478	
	2	223	673	1637	736	298	1314	697	
	3	281	785	1505	729	289	1342	743	
	4	293	776	1561	729	291	1347	753	
	Avg. 1-4	311	714	1435	730	291	11157	668	960
	6	296	705	1647	773	308	1387	797	
	7	292	709	1601	727	299	1321	765	
	Avg. 6-7	294	707	1624	751	204	1355	781	1075
	Composite Test Result, ppm NO								1034

TABLE C-33

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 50

Data are averages from first 7 cycles of 3 12-cycle blocks. (a)

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	2.56	4.26	3.02	1.84	.60	2.13	2.80	
	2	.87	.79	.20	.59	.20	.61	.65	
	3	.24	.49	.16	.25	.13	.50	.43	
	4	.21	.50	.17	.26	.17	.49	.40	
	Avg. 1-4	.97	1.51	.89	.73	.28	.93	1.07	1.00
	6	.21	.41	.17	.34	.14	.36	.49	
	7	.22	.40	.16	.24	.14	.39	.47	
	Avg. 6-7	.22	.41	.17	.29	.14	.38	.48	.31
	Composite Test Result, % CO								.55
IRHC, ppm (C_6)	1	305	285	215	170	109	150	257	
	2	135	115	139	136	69	105	215	
	3	104	95	115	122	67	97	259	
	4	106	96	117	111	65	90	226	
	Avg. 1-4	163	148	147	135	78	111	239	139
	6	101	94	123	123	61	95	228	
	7	98	87	114	115	57	93	226	
	Avg. 6-7	100	91	119	119	59	94	227	98
	Composite Test Result, ppm HC								107
NO, ppm	1	857	677	847	586	363	802	447	
	2	243	815	1581	649	350	1427	694	
	3	309	905	1553	682	329	1427	711	
	4	319	1033	1550	665	320	1495	725	
	Avg. 1-4	433	858	1383	645	341	1288	645	1049
	6	323	923	1517	691	321	1635	773	
	7	329	921	1489	709	303	1426	753	
	Avg. 6-7	326	922	1503	700	312	1531	763	1192
	Composite Test Result, ppm NO								1141

(a) In the third block, failure of the vacumn advance system of the distributor severely depressed the emission of HC and NO above about 23 MPH in the test cycle. Gas temperature at the muffler exit, and fuel consumption, were increased. All three blocks are included in the averages above.

TABLE C-34

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 51

Data are averages from first 7 cycles of 2 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to CO + CO_2 = 15

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	.21	3.46	2.17	1.74	.99	1.98	1.84	
	2	.57	.88	.20	.30	.75	.62	.48	
	3	.16	.66	.16	.22	.16	.71	.45	
	4	.16	.65	.15	.23	.13	.68	.41	
	Avg. 1-4	.28	1.41	.67	.62	.51	1.00	.80	.94
	6	.25	.67	.16	.31	.18	.67	.46	
	7	.25	.61	.17	.32	.16	.69	.54	
	Avg. 6-7	.25	.64	.17	.32	.17	.68	.50	.52
	Composite Test Result, % CO								.66
IRHC, ppm (C_6)	1	814	413	459	396	208	279	988	
	2	248	207	351	523	188	226	1605	
	3	254	196	301	558	139	210	1373	
	4	233	184	293	461	116	196	1458	
	Avg. 1-4	387	250	351	485	163	228	1356	297
	6	227	184	286	539	129	221	1380	
	7	238	177	279	490	118	204	1497	
	Avg. 6-7	233	181	283	515	124	213	1439	262
	Composite Test Result, ppm HC								273
NO, ppm	1	75	201	952	397	193	726	426	
	2	114	668	1625	474	121	1451	599	
	3	156	647	1055	439	157	1276	690	
	4	168	574	1201	449	171	1219	671	
	Avg. 1-4	129	523	1208	440	161	1168	596	858
	6	183	680	1199	473	197	1452	684	
	7	180	588	1285	521	181	1316	652	
	Avg. 6-7	182	635	1243	497	190	1370	669	997
	Composite Test Result, ppm NO								948

TABLE C-35

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 51B

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	3.89	4.95	2.27	1.84	.49	2.16	1.66	
	2	.60	.78	.17	.41	.23	.74	.42	
	3	.25	.68	.15	.24	.18	.61	.43	
	4	.22	.77	.15	.28	.13	.72	.47	
	Avg. 1-4	1.24	1.80	.68	.69	.26	1.06	.75	1.11
	6	.41	.67	.16	.34	.14	.69	.55	
	7	.40	.76	.15	.36	.14	.68	.56	
	Avg. 6-7	.41	.72	.16	.35	.14	.69	.56	.54
	Composite Test Result, % CO								.73
IRHC, ppm (C_6)	1	615	466	427	385	193	281	587	
	2	234	207	320	349	149	230	639	
	3	197	176	287	283	125	198	653	
	4	189	179	273	257	109	204	689	
	Avg. 1-4	309	257	327	319	144	229	642	260
	6	191	164	297	282	105	206	746	
	7	259	203	301	274	119	214	659	
	Avg. 6-7	225	184	299	278	112	210	703	226
	Composite Test Result, ppm HC								238
NO, ppm	1	256	295	1099	462	263	752	560	
	2	188	667	1469	652	239	1314	747	
	3	241	704	1560	752	243	1291	817	
	4	259	773	1614	775	251	1290	811	
	Avg. 1-4	236	609	1436	661	249	1162	734	928
	6	255	683	1601	751	260	1375	845	
	7	267	708	1546	724	266	1393	835	
	Avg. 6-7	261	696	1575	738	263	1384	840	1077
	Composite Test Result, ppm NO								1025

TABLE C-36

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 52

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	2.50	3.51	3.10	2.34	1.40	1.72	1.98	
	2	.68	.86	.14	.43	.15	.68	.49	
	3	.22	.61	.13	.22	.15	.59	.38	
	4	.27	.67	.12	.24	.16	.65	.43	
	Avg. 1-4	.92	1.42	.87	.81	.46	.91	.82	.98
	6	.36	.70	.12	.31	.11	.67	.57	
	7	.42	.61	.12	.34	.10	.59	.55	
	Avg. 6-7	.39	.66	.12	.33	.11	.63	.56	.49
	Composite Test Result, % CO								.65
IRHC, ppm (C_6)	1	649	565	476	424	227	290	572	
	2	244	224	317	307	158	243	615	
	3	217	197	311	291	143	217	612	
	4	207	195	285	283	141	218	655	
	Avg. 1-4	329	280	348	327	168	242	614	277
	6	210	201	274	293	122	221	675	
	7	202	177	280	255	118	207	647	
	Avg. 6-7	206	189	277	275	120	214	662	224
	Composite Test Result, ppm HC								242
NO, ppm	1	175	412	942	433	226	895	549	
	2	183	683	1447	641	220	1383	796	
	3	237	754	1815	717	226	1419	795	
	4	235	743	1778	793	246	1396	805	
	Avg. 1-4	208	649	1496	646	230	1274	736	993
	6	239	711	1431	708	250	1379	837	
	7	239	673	1666	775	249	1317	820	
	Avg. 6-7	239	693	1549	742	250	1348	829	1055
	Composite Test Result, ppm NO								1033

TABLE C-37

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 53

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	3.26	4.22	2.75	2.65	.63	1.46	2.74	
	2	.72	.66	.13	.47	.14	.47	.65	
	3	.22	.53	.13	.25	.11	.51	.53	
	4	.26	.50	.14	.27	.14	.54	.50	
	Avg. 1-4	1.12	1.48	.79	.91	.25	.75	1.11	.91
	6	.37	.54	.14	.35	.16	.54	.72	
	7	.42	.57	.15	.40	.13	.60	.67	
	Avg. 6-7	.40	.56	.15	.38	.15	.57	.70	.45
	Composite Test Result, % CO								.60
IRHC, ppm (C_6)	1	323	291	287	249	133	170	280	
	2	152	136	180	193	98	133	357	
	3	129	122	162	169	93	129	361	
	4	118	110	160	151	82	115	377	
	Avg. 1-4	181	165	197	191	101	137	344	157
	6	118	104	153	149	77	117	333	
	7	107	101	150	142	75	117	341	
	Avg. 6-7	113	103	152	146	76	117	337	121
	Composite Test Result, ppm HC								133
NO, ppm	1	400	348	958	447	305	967	574	
	2	258	854	1771	803	356	1413	840	
	3	319	924	1761	890	387	1531	867	
	4	336	879	1900	882	347	1471	882	
	Avg. 1-4	329	751	1597	756	349	1346	791	1082
	6	339	819	1983	988	338	1519	907	
	7	339	814	1913	918	384	1441	936	
	Avg. 6-7	339	817	1949	953	362	1481	922	1218
	Composite Test Result, ppm NO								1170

TABLE C-38

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 54

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	6.47	3.65	2.17	4.93	3.14	1.60	6.50	
	2	3.99	2.46	1.53	4.67	3.86	1.37	5.59	
	3	3.68	1.44	0.21	2.90	3.38	0.53	4.34	
	4	2.95	1.29	0.48	3.09	3.84	0.65	4.28	
	Avg. 1-4	4.27	2.21	1.10	3.90	3.56	1.04	5.18	1.86
	6	3.35	1.42	0.65	3.37	4.35	0.83	4.48	
	7	3.43	1.53	0.72	3.44	4.35	0.74	4.38	
	Avg. 6-7	3.39	1.47	0.69	3.41	4.35	0.79	4.43	1.48
	Composite Test Result, % CO								1.61
IRHC, ppm (C_6)	1	635	531	418	950	538	456	1261	
	2	473	473	410	633	524	436	1303	
	3	593	497	377	668	514	407	1529	
	4	455	441	382	695	519	412	1522	
	Avg. 1-4	539	485	397	737	524	429	1404	492
	6	451	441	380	958	533	424	1782	
	7	513	476	394	1018	544	436	1750	
	Avg. 6-7	482	459	388	989	539	430	1766	510
	Composite Test Result, ppm HC								503
NO, ppm	1	154	953	1185	467	477	1861	204	
	2	103	1226	1525	495	423	2227	347	
	3	135	1698	1865	654	455	2905	598	
	4	133	1792	1848	652	352	2871	583	
	Avg. 1-4	131	1418	1606	566	427	2466	433	1730
	6	117	1768	1621	599	236	2737	658	
	7	118	1727	1421	583	231	2783	669	
	Avg. 6-7	118	1748	1521	591	234	2760	664	1933
	Composite Test Result, ppm NO								1861

TABLE C-39

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 55

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	1.41	3.22	2.53	2.09	.63	1.38	2.14	
	2	.62	.75	.14	.38	.17	.66	.50	
	3	.21	.65	.13	.22	.14	.60	.44	
	4	.26	.55	.14	.26	.13	.69	.47	
	Avg. 1-4	.63	1.29	.73	.74	.27	.83	.89	.87
	6	.41	.67	.15	.36	.13	.60	.59	
	7	.42	.69	.15	.38	.14	.62	.62	
	Avg. 6-7	.42	.68	.15	.37	.14	.61	.61	.49
	Composite Test Result, % CO								.62
IRHC, ppm (C_6)	1	347	390	336	320	164	215	429	
	2	183	167	237	275	118	170	540	
	3	162	147	210	218	107	150	529	
	4	159	141	206	216	103	163	489	
	Avg. 1-4	213	211	248	257	123	175	497	203
	6	151	134	195	205	94	155	584	
	7	200	153	202	217	99	160	533	
	Avg. 6-7	175	144	199	211	97	158	559	169
	Composite Test Result, ppm HC								180
NO, ppm	1	162	322	880	427	260	1013	557	
	2	202	697	1396	613	261	1395	769	
	3	273	820	1700	787	313	1359	823	
	4	282	825	1518	753	301	1481	823	
	Avg. 1-4	230	667	1374	645	284	1312	743	1004
	6	285	747	1621	783	313	1441	893	
	7	309	800	1623	805	315	1447	909	
	Avg. 6-7	298	773	1622	794	314	1444	901	1138
	Composite Test Result, ppm NO								1091

TABLE C-40

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 56

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	5.19	5.56	5.42	4.33	2.79	3.02	3.35	
	2	1.15	1.01	.16	.81	.17	.71	.68	
	3	.33	.59	.16	.32	.14	.67	.53	
	4	.37	.63	.16	.30	.14	.61	.55	
	Avg. 1-4	1.76	1.95	1.48	1.44	.81	1.25	1.28	1.43
	6	.44	.67	.16	.39	.15	.68	.67	
	7	.49	.64	.17	.44	.16	.67	.61	
	Avg. 6-7	.47	.66	.17	.42	.16	.68	.64	.53
	Composite Test Result, % CO								.84
IRHC, ppm (C_6)	1	911	875	825	755	784	803	571	
	2	215	199	235	250	128	173	431	
	3	156	140	192	201	101	152	462	
	4	150	137	193	201	106	142	513	
	Avg. 1-4	359	338	362	352	280	317	495	332
	6	136	121	164	215	71	122	505	
	7	113	103	147	168	68	115	431	
	Avg. 6-7	125	112	157	192	70	119	469	132
	Composite Test Result, ppm HC								201
NO, ppm	1	280	300	373	237	211	169	501	
	2	217	717	1901	851	372	1375	845	
	3	279	761	1859	894	366	1462	880	
	4	291	782	1850	882	337	1443	895	
	Avg. 1-4	267	641	1496	716	322	1225	781	982
	6	300	725	1895	859	343	1425	887	
	7	303	714	1983	946	372	1515	920	
	Avg. 6-7	302	721	1939	903	357	1471	904	1185
	Composite Test Result, ppm NO								1113

TABLE C-41

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 57

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	1.57	3.26	3.72	3.18	2.12	2.29	2.98	
	2	1.25	.98	.15	.68	.33	.74	.73	
	3	.36	.64	.14	.37	.17	.63	.56	
	4	.43	.70	.15	.35	.20	.63	.63	
	Avg. 1-4	.91	1.49	1.04	1.15	.71	1.07	1.23	1.14
	6	.59	.72	.18	.43	.20	.61	.71	
	7	.54	.76	.20	.44	.29	.71	.78	
	Avg. 6-7	.57	.74	.19	.44	.25	.66	.75	.57
	Composite Test Result, % CO								.76
IRHC, ppm (C_6)	1	423	294	309	275	166	200	368	
	2	179	156	201	229	107	153	483	
	3	125	110	164	182	69	116	439	
	4	119	109	171	193	82	129	488	
	Avg. 1-4	211	168	211	220	107	150	445	172
	6	127	116	177	192	85	134	558	
	7	136	113	191	177	79	123	508	
	Avg. 6-7	132	115	184	203	83	129	533	144
	Composite Test Result, ppm HC								153
NO, ppm	1	227	309	591	267	191	669	465	
	2	183	577	1607	685	265	1301	719	
	3	245	685	1666	767	277	1261	757	
	4	265	739	1695	807	270	1342	750	
	Avg. 1-4	230	577	1390	631	251	1143	673	904
	6	268	685	1645	743	277	1295	747	
	7	280	629	1583	774	261	1295	759	
	Avg. 6-7	275	671	1615	759	269	1295	754	1036
	Composite Test Result, ppm NO								989

TABLE C-42

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 58

Data are averages from first 7 cycles of 2 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	.34	2.92	1.45	1.67	.92	1.43	1.95	
	2	.70	.74	.17	.38	.16	.53	.48	
	3	.23	.57	.17	.26	.16	.57	.47	
	4	.31	.58	.19	.31	.15	.63	.46	
	Avg. 1-4	.39	1.20	.49	.65	.35	.79	.84	.79
	6	.41	.63	.21	.36	.16	.67	.59	
	7	.46	.75	.19	.37	.18	.57	.55	
	Avg. 6-7	.44	.70	.20	.37	.17	.63	.57	.51
	Composite Test Result, % CO								.60
IRHC, ppm (C_6)	1	477	320	299	249	122	181	436	
	2	156	135	224	333	89	144	857	
	3	150	128	211	291	78	146	728	
	4	164	143	237	265	101	168	710	
	Avg. 1-4	237	181	243	285	97	160	683	195
	6	144	120	243	236	78	150	750	
	7	140	122	192	238	66	143	862	
	Avg. 6-7	142	121	218	237	72	147	807	169
	Composite Test Result, ppm HC								177
NO, ppm	1	199	412	997	525	221	962	600	
	2	191	607	1251	588	250	1119	818	
	3	246	777	1381	689	241	1308	809	
	4	262	713	1460	691	239	1318	842	
	Avg. 1-4	225	627	1273	623	238	1177	768	177
	6	264	650	1373	707	260	1392	813	
	7	269	649	1554	725	248	1285	827	
	Avg. 6-7	267	650	1464	717	254	1339	820	1031
	Composite Test Result, ppm NO								991

TABLE C-4

CAPE-6-68

EXHAUST ANALYSIS DATA - TEST NO. 59

Data are averages from first 7 cycles of 3 12-cycle blocks.

Avg. Conc. in Secs. Read, Corr. to $CO + CO_2 = 15$

Mode No.		1	2	3	4	5	6	7	Corr. & Wtd.
Wtg. Factors		0.042	0.244	0.118	0.062	0.050	0.455	0.029	
% CO	Cycle 1	3.78	4.42	2.30	2.70	1.06	1.46	2.77	
	2	.84	.73	.16	.47	.18	.52	.56	
	3	.21	.64	.14	.21	.15	.48	.48	
	4	.19	.16	.21	.14	.52	.52	.48	
	Avg. 1-4	1.26	1.60	.69	.90	.39	.75	1.07	.95
	6	.32	.57	.14	.28	.15	.53	.55	
	7	.34	.55	.16	.28	.16	.56	.65	
	Avg. 6-7	.33	.56	.15	.28	.16	.55	.60	.43
	Composite Test Result, % CO								.60
IRHC, ppm (C_6)	1	277	251	257	225	128	169	331	
	2	134	116	172	167	83	116	412	
	3	131	122	167	177	97	126	479	
	4	125	107	173	191	74	105	455	
	Avg. 1-4	167	149	193	190	96	129	419	151
	6	121	103	156	164	71	111	499	
	7	110	91	153	188	67	107	519	
	Avg. 6-7	116	98	155	177	69	109	509	124
	Composite Test Result, ppm HC								132
NO, ppm	1	409	365	977	445	269	992	575	
	2	222	771	1667	730	301	1335	806	
	3	287	885	1666	893	298	1441	868	
	4	313	811	1615	774	299	1457	825	
	Avg. 1-4	308	709	1481	711	292	1307	769	1033
	6	311	745	1675	801	310	1473	839	
	7	314	720	1746	799	315	1408	814	
	Avg. 6-7	313	733	1711	800	313	1441	827	1137
	Composite Test Result, ppm NO								1100

Table C-44

MUFFLER EXIT AND EXCHANGER-INLET TEMPERATURES

(Hot Cycles)

Vehicle	Test No.	Muffler Exit, °F., min./max. Block 1	Block 2	Block 3	Exchanger Inlet, °F., min./max. Block 1	Block 2	Block 3
'66 Plym.	20	427/557	425/560	425/555	212/293	215/294	212/293
	22	417/550	417/547	417/547	217/292	217/292	217/291
	23	410/550	421/550	420/550	212/287	216/288	217/292
	26	416/549	419/550	422/550	207/279	207/280	210/280
	27	423/560	418/560	420/555	220/297	220/295	220/296
	28	--/--	451/586	452/585	225/310	228/311	230/310
	32	456/590	458/591	455/585	230/308	226/305	228/306
	34	447/565	454/565	450/570	--/--	234/303	230/300
	37	457/569	449/571	452/572	--/--	227/305	227/305
	41	452/575	452/575	457/577	--/--	--/--	222/300
	42	457/587	457/583	455/585	235/315	237/317	235/315
	43	450/577	450/577	452/580	220/300	222/300	225/304
	54	457/575	457/578	460/575	230/305	228/305	227/303
'68 Chev.	21	475/588	495/605	493/600	245/--	263/325	264/324
	24	485/595	485/593	478/585	259/322	260/320	257/315
	25	467/572	467/573	470/575	243/302	243/302	244/302
	29[a]	--/--	--/--	--/--	--/--	--/--	--/--
	30	480/590	496/610	492/610	250/305	260/320	257/318
	31	485/607	487/605	487/605	250/312	250/312	253/315
	33	499/615	497/615	489/612	265/330	263/325	258/322
	35	485/606	483/603	483/603	255/313	254/311	252/309
	36	485/602	490/606	487/605	254/311	258/317	256/317
	38	477/597	494/602	492/605	254/315	261/326	266/326
	39	475/590	485/600	485/599	256/319	260/325	262/325
	40	477/595	480/595	484/599	251/307	--/--	--/--
'70 Chev.	44	562/685	570/690	575/689	302/369	307/370	305/370
	45[b]	--/--	570/693	580/697	--/--	318/383	318/383
	46	577/701	577/698	574/704	303/372	307/373	307/373
	47	578/705	578/705	573/704	305/374	310/375	307/374
	48	570/708	570/710	572/705	307/373	310/375	310/375
	49	583/714	582/711	585/715	312/380	312/--	316/385
	50[c]	568/710	570/712	643/800	303/375	--/376	347/432
	51[d]	535/680	542/680	538/685	278/357	286/363	285/363
	51B	583/703	588/712	589/710	322/385	327/391	327/391
	52	585/710	590/702	587/700	317/380	323/385	327/385
	53	583/708	583/707	585/709	326/390	330/393	332/395
	55	607/735	607/735	607/734	--/393	322/395	324/397
	56	615/743	603/735	612/737	327/404	324/398	325/403
	57	575/700	567/685	567/685	300/370	293/364	293/360
	58	565/690	561/682	565/685	298/370	295/365	298/369
	59	565/698	563/698	568/706	298/365	298/368	301/372

[a] Defect in temperature recorder.

[b] First block aborted at Cycle 3; Block 2 was 21 cycles.

[c] Lost vacuum spark advance (above 23 MPH only) in Block 3.

[d] All temperatures low, reason unknown. Deceleration hydrocarbon high.

Table C-45

CAPE-6-68
MUFFLER RETENTION OF PNA SPECIES

Test No.	Test Vehicle	Fuel TEL	Muffler PNA content as % of Total PNA						
			BaP	BeP	BghiP	BaA	Chrysene	Pyrene	Triphenylene
34	'66 Plym.	0	18	--	--	17	14	10	10
37		3	10	3	--	6	3	--	4
41		0	8	3	10	5	4	3	--
42		0	5	3	7	4	2	0.2	--
43		0	12	6	15	8	6	0.1	--
38	'68 Chev.	0	17	2	--	4	2	--	6
39		0	3	10	--	4	7	--	4
40		0	5	1	7	3	2	1	2
44	'70 Chev.	3	2	1	0.7	0.6	0.4	0.4	--
45[a]		3	10	5	23	0.7	--	0.9	--
46		3	2	0.8	2	0.5	0.5	0.3	--
47		3	6	0.8	9	1	1	0.5	--
48		3	1	0.8	0.9	2	0.9	0.4	--
49		3	2	0.8	1	<1	0.5	0.2	--
50[a]		3	4	1	6	0.7	0.9	0.1	--
51[a]		3	2	0.1	2	1	--	1.1	--
51B		3	4	2	4	1	0.8	0.8	--
52		3	4	0.9	3	0.5	0.3	0.3	--

[a] Abnormalities in this test (see text) may influence the results reported here.

APPENDIX D

CORRELATION AND APPLICATION OF THE GC/UV PNA METHOD

During the second year of CAPE-6-68, CRC-APRAC Project CAPE-12-68, also at Esso Research, developed a GC/UV method for analysis of exhaust-tar solutions (CAPE-6 samples), gasolines, or oils for PNA content. The method is described in Appendix E. Major differences from the first-year procedures given in Reference (1) include resumption of the addition of radiotracer spikes before, rather than after, boildown, with new precautions to assay the exact amount of activity added, caustic extraction to remove possible interfering materials, a modified alumina-column separation and elution, use of the programmed GC separation to yield trapped peaks (in place of TLC separation and developing, sectioning, and extracting the TLC bands), and the availability of assays on eleven different PNA species (formerly, only BaP and BaA). The assays are more accurate for five of the species than for the remaining six, as indicated in a footnote on Table D-2; the analysis for benzo (g,h,i) perylene has been particularly likely to vary, or to be in error, according to a recent examination of standard-sample results.

Parallel analyses, by CAPE-12-68 using GC/UV and by CAPE-6-68 using the TLC method of the first year, were carried out on samples from 12 CAPE-6 tests. In certain tests, equal halves of the original sample have been independently spiked (after boildown, rather than before) with radiotracers, and two independent TLC analyses have been carried out on the two samples, with GC analysis of one. Table D-1 compares the test yields, in micrograms of BaP and BaA, calculated from results of the two methods. The regression equations relating these results, and the average ratios of results, were presented in Section 3.3 of the main text of this report. Following the results of this comparison, the GC/UV method was adopted for CAPE-6 use and gradually expanded to include up to eleven PNA species.

The available multiple-species analyses are given in Table D-2, covering 29 vehicle tests. The alkylated BaA, BaP, and BeP species are not precisely defined as to the points of substitution on the parent structures; it follows that if the UV spectra differ slightly between isomers, the absorptivity values (Appendix E) may not be precisely correct. Certain of these isomers elute in adjacent GC peaks which are separately trapped and the UV absorbances then added together. Moreover, where several species (BaA, chrysene, triphenylene) occur in one GC peak, the UV absorbance for one species at its selected wave-length may require correction for absorbance due to another species, which is assayed by the absorbance at some other wave-length.

Disregarding, of necessity, these sources of error, the ratios between some of the prominent PNA species have been calculated and are given in Table D-3. Each ratio has a fairly uniform value, with the exception of BeP/BaP (i.e., benzo (e) pyrene/benzo (a) pyrene).

This ratio is apparently higher in data from the 1970 Chevrolet than from the other two cars, and especially so if the data from "dubious" tests are excluded. It is not clear whether this represents a difference between carburetion or other characteristics of the vehicles, or a difference in the deposits present when the tests were run. For the data in the 1970 vehicle, the BeP/BaP ratios from low-aromatic fuels appear to be higher when the high-boiling naphtha was present (1969 fuel set) than when it was absent.

Because of the possibilities for error noted above, and on Table D-2, conclusions are probably not justified until more multiple-species analyses are available from future work.

Table D-1

PNA ANALYSES BY TLC AND GC METHODS

CAPE-6 Test No.	Sample No.	Yield from Test, μg BaP TLC	BaP GC	BaA TLC	BaA GC
16		172	184	402	361
19		279	281	567	464
22		86	95	189	162
23		70	89, 89	255	217, 239
24		20	24	77	60
26	1	105	--	270	--
	2	83	102	253	272
27		130	140	270	234
28	1	131	--	218	--
	2	129	133	213	183
29	1	68	--	209[a]	--
	2	73	82	164	167
30		12	18	46	48
31	1	10[a]	--	55	--
	2	16	21	45	47
32		39	40	62	68

[a] Value rejected as derived from low, or impure, UV spectrum on extract of TLC band.

Table D-2

CAPE-6-68 PNA EMISSION DATA

MULTIPLE-SPECIES ANALYSES OF EXHAUST SAMPLES
BY THE GC/UV METHOD OF CAPE-12-68[f]

CAPE-6 Test No.	Total Test Yield, Including Muffler Washings, µg.											Notes
	BaP	BeP	BghiP	BaA	Chrysene	Pyrene	Triphenylene	Me-BaA	DM/Et-BaA	Me-BaP	Me-BeP	
32	40	157	188	68	206	1727	71					(a)
34	73	--	127	102	167	1140	61					(d)
37	62	377	--	97	180	--	47					(d)
41	71	236	195	94	171	1220						
42	98	145	324	142	316	1283						
43	86	176	216	143	414	1514						
54	260	603	1318	398	862	3911	145					(e)
33	7.9	--	--	26	50	362	30					(b)
35	30	54	--	32	72	640	28					(d)
36	5.8	28	35	25	69	--	26					(d)
38	30	168	--	34	81	--	28					(d)
39	21	51	--	46	87	--	45					(d)
40	19	53	81	39	108	832	69					(d)
44	48	281	134	170	276	1088						(c)
45	91	186	208	144	201	533						(e)
46	26	247	45	94	182	757						
47	31	247	67	71	163	425						
48	70	392	115	124	232	568						
49	42	262	236	101	199	626	55					
50	305	1171	1254	275	560	1472						(e)
51	245	1057	1121	294	597	515						(e)
51B	52	306	334	154	238	665						
52	90	437	431	187	310	1496	73	116	25	36	293	
53	64	482	565	146	290	1273	76					
55	64	362	483	125	258	702	62	53	17	17	131	
56	92	507	278	158	330	1143	46	78	21	24	262	
57	112	518	766	163	310	1525	76	81	17	29	266	
58	48	467	54	74	175	552	46	22	6	11	71	
59	63	312	223	143	303	1386	72	61	12	9	104	

(a) All tests in this group are in the 1966 Plymouth.

(b) All tests in this group are in the 1968 Chevrolet.

(c) All tests in this group are in the 1970 Chevrolet.

(d) Analyst reports a contaminant (dioctylphthalate?) leading to lower precision in GC peaks and UV spectra and sometimes requiring additional column separations. Accuracies of BaA, chrysene, and triphenylene are particularly affected. The contaminant has now been avoided.

(e) Tests of doubtful validity for reasons discussed in Appendix C.

(f) BaP and BeP elute together, as do BaA, chrysene, and triphenylene. Both of these GC peaks contain tracers (BaP and BaA); the accuracy of these five species is thus superior to that of all other species, for which the tracer showing the greater recovery is the basis for scale-up to total yield, even though it occurs in a different GC peak than the species being estimated.

Table D-3

CAPE-6-68
RATIOS OF PNA SPECIES
IN EXHAUST SAMPLES

(GC/UV Analyses)

Test No.	Test Vehicle	Total-Yield Ratios			
		BeP/BaP	BaA/BaP	Chrysene/BaA	Triphenylene/BaA
32	'66 Plym.	3.92	1.70	3.03	1.04
34		--	1.40	1.64	0.60
37		6.08	1.56	1.86	0.48
41		3.32	1.32	1.82	--
42		1.48	1.45	2.23	--
43		2.05	1.66	2.90	--
54[a]		2.32	1.53	2.17	0.36
33	'68 Chev.	--	3.29	1.92	1.15
35		1.80	1.07	2.25	0.88
36		4.83	4.31	2.76	1.04
38		5.60	1.13	2.38	0.82
39		2.43	2.19	1.89	0.98
40		2.79	2.05	2.77	1.77
44	'70 Chev.	5.85	3.54	1.62	--
45[a]		2.04	1.58	1.40	--
46		9.50	3.62	1.94	--
47		7.97	2.29	2.30	--
48		5.60	1.77	1.87	--
49		6.24	2.40	1.97	0.54
50[a]		3.84	0.90	2.04	--
51[a]		4.31	1.20	2.03	--
51B		5.88	2.96	1.55	--
52		4.86	2.08	1.66	0.39
53		7.53	2.28	1.99	0.52
55		5.66	1.95	2.06	0.50
56		5.51	1.72	2.09	0.29
57		4.63	1.46	1.90	0.47
58		9.73	1.54	2.36	0.62
59		4.95	2.27	2.12	0.50

[a] Test of dubious validity. See Appendix C.

Appendix E

Analytical Procedures

(Adapted from CAPE-12-68 Description)

Introduction

This method was developed to determine polynuclear aromatic hydrocarbons in gasoline, crankcase oil, and tar from auto exhaust; the tar-sample preparation is described in Reference (1).

Scope

The method covers polynuclear aromatics (PNA) ranging from pyrene to benzo(g, h, i) perylene. As described herein, eleven PNA's are measured, including: Pyrene, benz(a)anthracene, chrysene, triphenylene, methylbenz(a)anthracene, dimethyl and/or ethylbenz(a)anthracene, benzo(a)-pyrene, (benzo(e)pyrene, methylbenzo(a)pyrenes, methylbenzo(e)pyrenes and benzo(ghi)perylene. Additional PNA's can be included. The procedure was successfully demonstrated for gasoline, exhaust tars and crankcase oils.

Summary

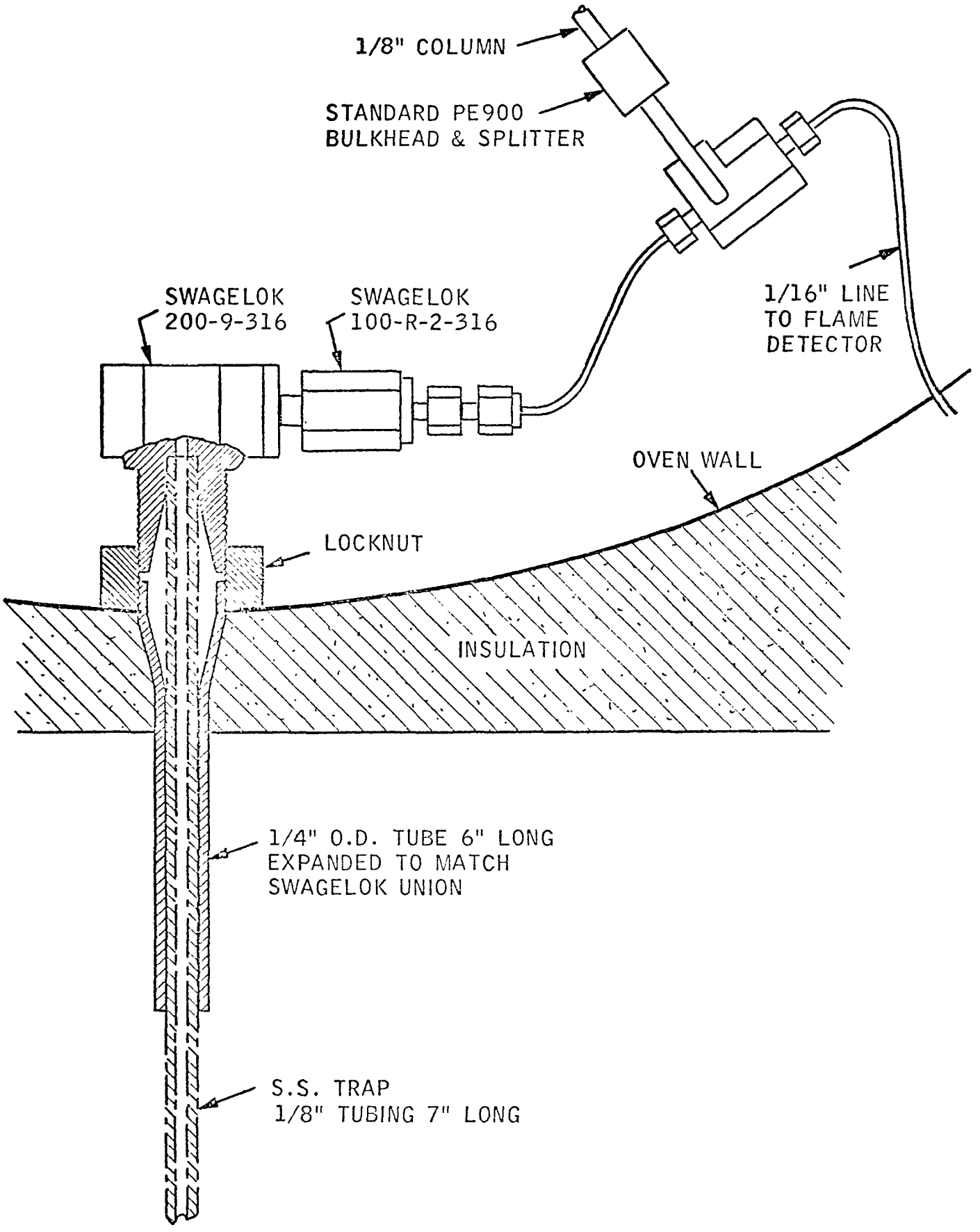
A sample to be analyzed is spiked with known quantities of carbon 14 labeled benzo(a)anthracene (BaA) and benzo(a)pyrene (BaP). A caustic treat is done and then PNA hydrocarbons are removed from the total sample by separation on a column of partially deactivated alumina. The solvents used are cyclohexane, cyclohexane-benzene, benzene, and benzene-methanol. The fraction containing the PNA's is reduced to a minimum volume by evaporation on a steam bath. An aliquot of this sample is injected into a gas chromatograph and fractions are collected at predetermined retention times. Quantitative measurement of each Pna is based on UV spectra of collected fractions.

Apparatus & Isotope Dilution

1. The Gas Chromatograph is equipped with a flame ionization detector, a linear temperature programmer and a flow controller. The injection port consisted of an aluminum block with a stainless steel tube insert (quartz sleeve). The chromatograph is modified by the addition of a by-pass and trap so that 15% of the effluent of the column will go to the detector and 85% to the trap. A Perkin-Elmer 900 chromatograph was used in the development of this method, but equivalent instruments should perform satisfactorily. A diagram of the trap is presented in Figure E-1.

Figure E-1

GAS CHROMATOGRAPH TRAPPING ASSEMBLY



2. Recorder, 0-1 millivolt, 2 min/inch chart speed.

3. Trapping Tubes, 20 or more stainless steel tubes 7" long by 1/8" diameter.

4. Column, Ten feet of 1/8" O.D. stainless steel tubing packed with 2 percent SE-30 (GC Grade) on Chromosorb G (acid washed and DMCS treated), 80/100 mesh. The prepared packing is available from Supelco Inc., Bellefonte, Pennsylvania, and other suppliers.

5. Syringe, 10 microliter. The syringes, Cat. #701N, manufactured by the Hamilton Co., P. O. Box 307, Whittier California 90608, and Model C of Precision Sampling Corp., P.O. Box 15119, Baton Rouge, La., are satisfactory.

6. Spectrophotometer, spectral range 225 nanometers-400 nanometers with spectral slit width of 2 nanometers or less. Under instrument operating conditions for these absorbance measurements, the spectrophotometer shall also meet the following performance requirements: absorbance repeatability, $\pm$ 0.01 at 0.4 absorbance; absorbance accuracy, $\pm$ 0.05 at 0.4 absorbance; wavelength repeatability, $\pm$ 0.2 nanometer; wavelength accuracy, $\pm$ 1.0 nanometer.

7. Spectrophotometric Cells, fused quartz cells having optical path lengths of 1.000$\pm$ 0.005 cm. and 5 cm. cells. The 5-cm cells are micro-cells and contain about 3 ml of solution.

8. Graduate Glass, 5 ml.

9. Vials, one- and three-dram with cap.

10. Steam Bath equipped with nitrogen outlet for purging vials.

11. Medicine Dropper, with tip drawn out.

12. Special Low UV Emission Room Lights, Westinghouse W-40-gold fluorescent lamps.

13. Chromatographic Column, two feet long 0.5 inch OD and 0.43 inch ID with 200 ml. receiving bulb on top and stopcock with Teflon barrel on the bottom.

14. Radiation Counters used are Intertechnique SL-20 and Packard Tri-Carb.

15. Counting Vials, 20 ml. with cap.

REAGENT AND MATERIALS

Regeant grade chemicals must be used throughout. The polynuclear compounds were used as purchased. Compounds of comparable purity from other suppliers may be employed.

1. Cyclohexane As a large amount of cyclohexane is used, it must be of highest purity. To check purity, evaporate 180 ml. down to 5 ml. Run a UV scan on this residue in a one-cm. cell from 280-400 nm. The absorbance should not exceed 0.01 units. To purify, percolate through activated silica gel, Grade 12, in a glass column, 90 cm. long and 5-8 cm. diameter. Satisfactory solvents may be purchased from several sources including Burdick and Jackson laboratories, Inc., Muskegon, Michigan 49442. Their products are called "Distilled in Glass Solvents."

2. Toluene.

3. Acetone.

4. Sodium hydroxide.

5. Hydrochloric Acid.

6. Benzene, Burdick and Jackson Laboratories, Inc.

7. Methanol, Burdick and Jackson Laboratories, Inc.

8. Benz(a)anthracene $C_{18}H_{12}$, MW 228, Eastman 4672.

9. Benzo(a)pyrene $C_{20}H_{12}$, MW 252, Eastman 4951, repurified by elution through deactivated alumina.

10. Pyrene $C_{16}H_{10}$, MW 202, Eastman 3627.

11. Benzo(g, h, i)perylene $C_{22}H_{12}$, MW 276, Columbia Organic.

12. Test Blend.

CAUTION

Exercise care when handling these compounds to avoid inhaling them or getting them on the skin. Wash hands thoroughly after handling.

Weigh exactly 25.0 mgs. of each of the four compounds listed as Items 4 through 7. Place in a 25-ml. volumetric flask, add 20 ml. of toluene and swirl until compounds are in solution. Then make up to volume. This will contain 1 microgram of each compound per microliter of solution. Pour into a small, narrow neck brown bottle and keep in a cool, dark place, preferably a refrigerator.

13. Organic Counting Solution 8 gm of BBOT in a liter of toluene.

METHOD

Precautionary Note: Because of the sensitivity of the test, the possibility of errors arising from contamination is great. It is of the greatest importance that all glassware be scrupulously cleaned to remove all organic matter such as oil, grease, detergent residues, etc. Examine all glassware, including stoppers and stopcocks, under ultraviolet light to detect any residual fluorescent contamination. As a precautionary measure it is recommended practice to rinse all glassware with purified isooctane immediately before use. No grease is to be used on stopcocks or joints. Great care to avoid contamination of samples in handling and to assure absence of any extraneous material arising from inadequate packaging or storing is essential. Because some of the polynuclear hydrocarbons sought in this test are very susceptible to photooxidation, the entire procedure is to be carried out under subdued light. Avoid use of fluorescent lamps. Special yellow lights are available. Tygon tubing must absolutely be avoided, to eliminate Di(iso)octyl phthalate (DOP) contamination which interferes in both the GC and UV.

Radioactive Materials must be handled and disposed by accepted methods. Glassware should be rinsed with chloroform-acetone solvent and washed in dichromate-sulfuric acid cleaning solution.

A. Distillation of Exhaust - Tar Solution

Before commencing the distillation prepare the radioactive BaA and BaP spikes. Add 50 λ of BaA to a 25 ml. volumetric flask and 50 λ of BaP to a second. Make up to volume with cyclohexane and remove duplicate 100 λ aliquots from each for counting. Pour the contents of the flasks into the still and rinse out well with cyclohexane and acetone Conduct the distillation as described in Reference (1).

B. Caustic Extraction

1. The volume of still bottoms will be about one liter. Take exactly one half of this and place in a one-liter separatory funnel.

2. Add 50 ml of 0.5 N aqueous sodium hydroxide solution, shake one minute, and remove lower aqueous phase.

3. Repeat the extractions with 30 and 20 ml portions of sodium hydroxide.

4. Wash with 50 ml of water, then 50 ml of 1/10 N HCl.

5. Finally wash with 25 ml of water.

6. Evaporate cyclohexane to about 150 ml and filter, if necessary.

7. Evaporate filtrate to below 50 ml, place in a 50 ml volumetric flask and make up to volume with cyclohexane.

8. Take 25 ml for placing on the alumina chromatographic column.

C. Column Chromatographic Separation.

1. A column of 2 ft. length and 0.43" I.D. is prepared with de-activated alumina. Seventy-five grams of Woelm Neutral alumina are dried at 150°C. in an oven 1 hour. The alumina is transferred to a bottle and allowed to reach room temperature. 1.50 ml of water are added dropwise with shaking. The bottle is capped and placed on a paint shaker for 15 minutes to obtain a uniform mixture.

2. A glass wool plug is placed in the end of the column and the alumina is poured in along with gentle tapping to pack the alumina. The column is filled to within one inch of the top and another glass wool plug is placed on top.

3. Ten ml. of cyclohexane are placed on top of the column and allowed to run into the column under nitrogen pressure of 2 pounds. The sample in cyclohexane is then poured into the 200 ml. bulb on top and allowed to run into the column. 100 ml cyclohexane is added to the bulb.

4. When the cyclyhexane has run into the column below the top glass wool plug, 100 ml of cyclohexane benzene (4:1) are added and run into the column. The first one hundred (cut #1) ml of cyclohexane is collected and set aside. The following solutions are collected in 3 dram vials and capped. Each should contain 10 ml of solution.

5. After the cyclohexane benzene (4/1) is below the top of the glass wool plug, 100 ml of benzene are added to the column. Collection of 10 ml fractions is continued.

6. After all the benzene has passed the top glass wool plug, 100 ml of benzene methanol (1:1) is added to the column. The benzene methanol front on the column is followed by the movement of an orange colored band usually in the sample. In addition, the front can be detected by a warm front moving down the column which is apparent to the touch or followed with UV lamp. When the front reaches the end of the column a two phase system becomes visible in the collecting vial. At this point, the remaining solution is collected in one large bottle and allowed to run off the column (cut 3). Column should not be stopped or allowed to run dry between solvent additions.

7. The solutions in the individual 3 dram vials are scanned in order of elution on a UV spectrophotometer. The peak at 340 nm is used as a guide in determining the start of elution of tetracyclic PNA compounds. The solution whose spectrum shows a significant 340-peak is the start and all remaining solutions are combined as the PNA fraction (cut #2).

D. Concentration of PNA's

1. Transfer the contents of the first 4 vials of cut #2 to a 150 ml beaker and rinse each vial twice with 1 to 2 ml of cyclohexane and combine with the contents of the beaker.

2. Place the 150 ml beaker on the steam bath under a small jet of nitrogen.

3. As evaporation progresses, add the contents of the remaining vials with similar rinsing to the beaker. Do not evaporate to less than two mls and in no case let the contents go to dryness.

4. Transfer the concentrated solution to a one-dram vial. Wash beaker with cyclohexane and add to vial. If it is necessary to obtain the weight of the extracted material, the tare weight of the vial should be determined to the nearest 0.1 milligram.

5. Place the vial in a 30 ml beaker for support. The beaker is placed on a steam bath under a gentle jet of nitrogen.

6. Rinse the 150 ml beaker with 3 or 4 small portions of cyclohexane (~1 ml) and combine with the contents of the one-dram vial as evaporation proceeds.

7. If, as is preferable, it is unnecessary to obtain the weight of the PNA residue, evaporate the solution down to about 50 µl (0.05 ml). Add about 0.5 ml of toluene and again evaporate to 50 µl.

8. If the weight of the residue must be obtained, exercise great care as the solution approaches dryness. Keep the vial under constant observation and the instant all the solvent has been removed, cool and weigh the vial.

9. Return the vial to the beaker under nitrogen for an additional minute, cool and reweigh. Repeat this procedure until a constant weight is reached. For the GC analysis add 10 to 20 microliters of toluene to lower the viscosity of the sample. Cap and save.

E. Gas Chromatographic Analysis

Parameters

The following parameters are employed in developing the gas chromatographic separation with the Perkin-Elmer 900. Other instruments might use different conditions.

Carrier Gas - Helium
Flow Rate - 30 ml./min.
Hydrogen and Air - at manufacturers recommendation, or optimum rates.
Injection Port - 300°C.
Detector - 340°C.
Program - 175°C to 300°C at 4° per minute. The temperature is held at 300° until all peaks are eluted, but in any case, for 20 minutes.

Dual columns are not used.

Column Conditioning

1. The Supelco Co. states that only minimum conditioning is needed on the column specified in (4) of apparatus. Connect the column to the inlet of the GC but not with the detector.

2. Pass helium through at 30 ml. per minute program at one degree per minute from 150°C to 275°C. Keep at 275 for 30 minutes. Cool and connect to the detector.

3. If SE 30 as supplied by the manufacturer is used in place of GC grade, connect as in (1). Purge with helium for 10 minutes and then put a cap on the exit end, keeping a helium pressure on the column.

4. Raise the oven to 350°C and bake for 3 hours.

5. Cool to room temperature, remove cap, pass helium through at 30 ml. per minute and continue conditioning column as shown below without attaching to the detector.

Temp., °C.	150	200	250	275
Time, Min.	30	30	30	60

6. Cool to room temperature and attach to detector. The column is now ready for use.

Performance Test

This test is used to measure retention times and demonstrate suitable recovery of individual PNA's. Recoveries of $\geq$ 83% are required. With the column conditioned and the parameters set as described in 1, prepare to inject a sample.

7. With the 10 µl syringe, take the Test Blend and flush out twice.

8. The third time fill the syringe and hold vertically point up. Stick the tip in a rubber septum and depress the plunger to compress air bubbles which rise to the top.

9. Now advance the plunger to the desired amount, for instance 2 µl; the rubber is removed, and the plunger retracted until the air-liquid meniscus enters the glass bore.

10. Note the volume from meniscus to plunger.

11. Insert the syringe up to the hilt in the GC injection port, depress the plunger. Start the recorder.

12. Remove the syringe from the port and retract the plunger.

13. Note the volume remaining (generally about 0.2 µl) and subtract from the previously noted volume (4) to determine the net volume injected.

14. Have stainless steel trapping tubes and one-dram vials available. The vials should be supported in small holes drilled in a board.

14A. An ice bath surrounds the stainless steel insert as a precaution.

15. As a peak approaches, insert a tube. Remove as the trace returns to the baseline. Mark the peak No. I and place the tube in a one-dram vial labelled I.

16. Continue taking cuts, putting each tube in a separate vial labelled 2, 3 etc.

17. Typical retention times obtained in setting up this method are shown in Table E-1.

Table E-1

OBSERVED RETENTION TIMES

Compound	Retention Time, Min.
Pyrene	13.6
Triphenylene	20.0
Benz(a)anthracene	20.1
Chrysene	20.4
Methylbenz(a)anthracenes	23.3
Dimethyl/ethylbenz(a)anthracenes	25.0
Benzo(e)pyrene	27.2
Benzo(a)pyrene	27.3
Methylbenzo(e)pyrenes[a]	29.0, 29.6, 30.7
Methylbenzo(a)pyrenes[a]	
Benzo(g,h,i)perylene	33.3

(a) Measured in three different peaks.

18. When the run is completed take the first tube and place in a 5-ml. graduate. With an elongated medicine dropper add enough cyclohexane through the top of the tube to fill the spectrophotometric cell to be used. In developing this method, 3.8 ml. was a convenient volume to employ, but all cuts must be made up to the same volume.

19. Pour the solution into the original vial, cap and protect from light. Rinse out the graduate with cyclohexane and use for the next tube. Save the fractions for UV, and calculation of recoveries.

20. When the run is completed, measure and record the retention time in minutes from injection point for each compound including the internal standard.

Analysis of Samples

21. From the vial containing the PNA concentrate from the alumina column, take 5-10 µl of sample and inject into the GC unit. Trap the cuts at the retention times obtained on the Test Blend runs and also trap any other peak that might be of interest. The cuts of the samples must be made up to the same volume employed for the test blend.

F. Ultraviolet Spectrophotometric Analysis

Calibration

1. Prepare solutions of known concentrations of each PNA in cyclohexane, e.g., 2.4 μg/ml.

2. With cyclohexane in the reference cell, obtain the spectrum of each solution from 400 to 225 nm.

3. Rinse the cell thoroughly with cyclohexane between spectra and remove the last traces of solvent by vacuum or a gentle jet of air.

4. From the spectra obtain the absorbances of the various compounds at the wavelengths shown in Table E-2. Calculate absorptivity from the known concentrations. Typical calibration data are also shown in the table.

Analysis of Samples

5. Obtain the UV spectrum of each selected fraction as directed in step C21. Measure the absorbance at the specified wavelength. Several of the trapped fractions will contain more than one PNA species. Triphenylene, benz(a)anthracene, and chrysene occur together and are analyzed in their common spectrum by determining BaA, then correcting the 269 nm (chrysene) absorbance for BaA and the 259 nm absorbance for both BaA and chrysene; the coefficients are given in Table E-2. The fractions for the methyl- and the dimethyl/ethyl-BaA isomers include the alkyl derivatives of chrysene and triphenylene; calibration data are lacking for the latter, but their presence does not interfere with determining the BaA derivatives with the tabulated coefficients. BaP and BeP are found together but do not interfere when absorbances at 383 and 333 nm, respectively, are used. Methyl-BaP and - BeP occur in three GC fractions yielding three UV spectra with slightly varying peak locations due to isomer effects; the three absorbances near 384 nm are added for MeBaP, and the three near 335 nm for MeBeP. Pyrene and benzo(ghi)perylene occur in peaks separated from interfering species.

6. One ml of the fraction containing BaA is placed in a counting vial along with 9 ml of toluene and 10 ml of counting solution. Counts per minute are measured using a scintillation counter. The same procedure is followed with one ml of the BaP fraction.

TABLE E-2

UV CALIBRATION DATA FOR SOME PNA HYDROCARBONS

Wavelength nm												
Peak	Base Line	Pyrene	BaA	Chrysene	Triphenylene	Methyl BaA	Dimethyl/ethyl BaA	BaP	BeP	Methyl BaP	Methyl BeP	Benzo-(g,h,i perylene
		Absorptivity (ml/μg-cm)										
336	327-343	0.240										
289	283-295		0.332									
269	263-277		0.039	0.464								
259	252-263		0.015	0.107	0.480							
293[a]	285-300					0.27						
293[a]	285-300						0.27					
383	373-390							0.092				
333	325-338								0.135			
384[b]	373-390									0.075		
335	325-340										0.110	
382	370-390											0.074

[a] Occurs in range, 290-293 nm, depending on isomers.

[b] Occurs in range, 383-385 nm, depending on isomers.

To calculate the amount of the various compounds in the entire sample, the aliquot factor (activity ratio) must be determined based on the radioactivity in 1 ml of the fractions containing the internal standards

$$M = \frac{QN}{(K-L)}$$

Q = activity added to sample, DPM[2]

M = activity ratio

K = average CPM[1] per ml

L = Background, CPM

N = counting efficiency CPM per DPM

(1) CPM is counts per minute

(2) DPM is disintegrations per minute (a measure of radioactivity).

The concentration of each component is determined from the UV absorbance.

$$D = \frac{A}{BC}$$

D = concentrations of each PNA (μg/ml)

A = absorbance of each PNA

B = absorptivity of each PNA (ml/μg-cm)

C = cell length (cm)

The weight of added radiotracer is determined,

$$X = \frac{Q}{S}$$

X = weight of radiotracer added, μg.

S = specific activity (DPM/μg)

Calculate weight of PNA in the sample

$$T = MD - X$$

T = weight of PNA in the sample.

Where more than one internal standard is used, all components eluting in the same peak with a standard are calculated based on that standard's activity ratio. All other components are calculated using the smallest activity ratio since this represents the maximum recovery of standard.

Calculations are now handled on an IBM 1800 for 11 of the PNA's.