EPA-AA-TSS-PA-86-03

Analysis of Fuel Samples from Baltimore, Detroit, and Philadelphia

(Report from Work Assignment 8, Contract 68-03-3192 with Southwest Research Institute)

Mary Ann Warner-Selph and Charles T. Hare
Southwest Research Institute
Craig A. Harvey and Jonathan Adler, EPA
July 1986

NOTICE

Technical Reports do not necessarily represent final EPA decisions or positions. They are intended to present technical analysis of issues using data which are currently available. The purpose in the release of such reports is to facilitate the exchange of technical information and to inform the public of technical developments which may form the basis for a final EPA decision, position or regulatory action.

Technical Support Staff
Emission Control Technology Division
Office of Mobile Sources
Office of Air and Radiation
U.S. Environmental Protection Agency

I. INTRODUCTION

The objective of this Work Assignment was to analyze samples of in-use gasoline from a representative selection of gasoline outlets that were not major (national) brands. The samples were obtained under Work Assignment No. 1 of Contract 68-03-3192 from three cities: Baltimore, Detroit, and Philadelphia. Thirty-nine fuel samples originated from Baltimore, 36 from Detroit, and 48 from Philadelphia, for a total of 123 samples. Single samples from most of the major brand outlets in each city were included for comparison.

Selection of "minor" (regional) outlets was done using a random selection weighted by sales volume as reported by the Lundberg Letter. In other words, each minor outlet listed by Lundberg for each of the three cities was assigned a probability of selection proportional to its reported sales volume. Then, using a random number generator, forty minor outlets from each city were selected so as to ensure that thirty currently operational outlets could be found during sample collection. (The Lundberg data were not fully up to date for some of the outlets, so some of the outlets no longer existed.) The major outlets (and ARCO Oxinol outlets) were chosen arbitrarily with some emphasis on selecting larger volume outlets of each brand. Premium Gasoline was chosen for every fourth sample; current data indicate that 25% of unleaded gasoline sold is premium grade.

Fuel samples were collected and stored in sealed cans as is done with MVMA fuel samples. For the first few months of storage these cans were kept in a refrigerated enclosure. Due to space limitations they were then moved to an underground unrefrigerated storage room with an estimated temperature of about 60°F.

These cities and this sampling bias toward non-major outlets were chosen for a combination of reasons. The MVMA national fuel survey includes mostly major brand outlets, while non-major outlets tend to have a greater use of alcohol blends, which EPA wished to characterize. Also, in Philadelphia, ARCO markets a gasoline/Oxinol[1] blend, and only one sample of this was included in the summer 1984 MVMA survey. Therefore eleven samples of this fuel were collected and analyzed in this program. Section V of this report provides a comparison of summer 1984 MVMA data with the results of this program.

---

[1] A fuel additive composed of methanol and tertiary butyl alcohol (TBA).

All samples were analyzed for Reid Vapor Pressure (RVP), distillation temperature curve, methanol, ethanol, tertiary butyl alcohol (TBA), water content, and lead content. In addition, the "Evaporative Index"[2] (EI) was calculated for each fuel. This parameter was developed by DuPont to correlate volatility characteristics of fuels to the evaporative emissions of vehicles. Fuel control and reference samples were also analyzed to fulfill quality assurance requirements for this Work Assignment. The reference fuel samples were used to determine procedural accuracy and repeatability. The control fuel samples were analyzed periodically to assure repeatability and reproducibility.

The test plan was written up as part of the Work Plan, which is included as Appendix A. The test plan describes the analysis sequence for control samples, reference samples, and fuel samples. Reference and control samples were analyzed in duplicate prior to fuel sample analysis. Batches of approximately twenty fuel samples were analyzed for RVP, distillation temperature curve, alcohols, water content, and lead content, alternating with duplicate analyses of control samples.

Fuel samples were originally scheduled for all analyses at the Engines, Fuels and Lubricants Division of Southwest Research Institute (SwRI). Due to scheduling difficulties, however, it became necessary to have the water and distillation analyses conducted at other laboratories. The measurement of water was conducted at the Fuels and Lubricants Research Division of SwRI. Fuel distillations were conducted by King Laboratories in San Antonio. All other analyses were conducted at SwRI by the Engines, Fuels and Lubricants Division.

II. ANALYTICAL PROCEDURES

The analytical procedures and calculations used in evaluating the gasoline samples are as follows:

REID VAPOR PRESSURE (RVP) - Automatic RVP Instrument Method. It has been determined by the ASTM that the conventional "wet-bomb" method (ASTM-D-323) is not satisfactory for analysis of gasoline-alcohol blends. The Automatic RVP Instrument, developed at SwRI and used to analyze all MVMA survey samples, has been found to be a satisfactory alternate method. This method is described in Appendix B.

[2] EI = 0.85 RVP + 0.14 (percent evaporated at 200°F) - 0.32 (percent evaporated at 100°F).

DISTILLATION - ASTM D-86.

METHANOL, ETHANOL, AND TERTIARY BUTYL ALCOHOL (Volume Percent) - Water Extraction/Gas Chromatography. There are currently no standard ASTM Procedures for determination of alcohols in gasoline. SwRI has developed a reliable analytical procedure based on extraction of the gasoline with 2 volumes of water and gas chromatography of the extract using a flame ionization detector. Full details are given in Appendix B. This method is used to analyze MVMA survey samples.

WATER (Weight Percent) - ASTM D-1533 Karl Fischer Automatic Titration (pyridine free), using the Photo Volt Aquatest IV instrument.

LEAD (Weight Percent) - ASTM D-3237, Atomic Absorption Spectrometry.

EVAPORATIVE INDEX (EI) - From RVP and distillation data:
EI = 0.85xRVP - 0.32x(% EVAP @100°F) + 0.14x(%EVAP @200°F)

III. RESULTS

A description of the fuel samples is given in Appendix C. The fuels, which were obtained from Baltimore, Detroit, and Philadelphia, are designated as either regular unleaded or premium unleaded. The locations of the gas stations where the fuel samples were obtained are also given in Appendix C.

Table 1 summarizes the average RVP data grouped by city and by alcohol content. The results of RVP, distillation, alcohol, water, and lead analyses are listed in Tables 2, 3, and 4 for fuel samples from Baltimore, Detroit, and Philadelphia, respectively. RVP was measured in psi, distillation in °F, alcohols (methanol, ethanol, and TBA) in percent by volume, water by weight percent, and lead in g/gal.

Fuel samples were collected in mid September, 1984, from Baltimore, Detroit, and Philadelphia. The recommended limits for RVP (as given in ASTM Designation: D439-83) of gasoline are based on the month of the year as well as location. The ASTM specification for maximum gasoline. RVP in Baltimore in September is 11.5 psi (Class C). The ASTM specification for maximum RVP in Detroit and Philadelphia in September is 13.5 psi (class C/D), but September is a transition month, so fuel conforming to the 11.5 psi standard may also be sold. The specification for both of these cities in August is 11.5 psi. Seventy-seven percent of the Baltimore fuel samples had measured RVP below 11.5 psi, ten percent had measured RVP between 12.4 and 12.7 psi, and thirteen percent were above 12.7

psi. Thirty-one percent of the Detroit samples and twenty-three percent of the Philadelphia samples (or 30% if the Oxinol samples are excluded) had RVP less than or equal to 11.5 psi. All the fuel samples from Detroit, and ninety-six percent of the Philadelphia fuel samples had measured RVP less than 13.5 psi. The highest RVP of any of the Philadelphia samples was 13.7 psi.

The average RVP for the samples in Philadelphia not containing alcohol (less than 3% total alcohol) was 11.9 psi, while the average RVP for the gasoline/alcohol blend samples was 13.3 psi. All of the samples in Philadelphia which contained alcohol were Oxinol samples. It is possible that all of the Oxinol samples were formulated to a class D specification, which would explain why their RVP's were so much higher than the other samples. For Detroit, the average RVP of samples with alcohol (all of which contained 7.7 - 10.5% ethanol) was 12.4 psi, while the average RVP for samples without alcohol was 11.8 psi.

Alcohol content and water content of the fuel samples appeared to be related variables. These values were plotted and are presented in Figure 1. Two major clusters of data are apparent: relatively low alcohol with low water and relatively high alcohol with high water. When total alcohol (methanol, ethanol, and TBA) was less than 1.0 percent (by volume) of the fuel sample, water content was less than or equal to 0.05 percent (by weight). When total alcohols exceeded 7.0 percent, water content was greater than or equal to 0.15 percent of the fuel sample. One fuel sample had a high water content relative to the other samples. Sample 70, with 8.0 percent total alcohol, had a water content of 0.48 percent.

The distillation curve data from the fuel samples are given in Tables 5, 6, and 7 for Baltimore, Detroit, and Philadelphia. In general, the samples which contained alcohol needed lower temperatures to achieve a given amount of evaporation than those which did not contain alcohol. The Evaporative Index was calculated from RVP and distillation curve data. These EI values are reported in Table 8. Figure 2 shows the frequency distributions of the EI values of the samples grouped by city and fuel type. The distillation values of some control samples, which were periodically analyzed with the three-city fuel samples, were out of the range specified in the Quality Assurance Plan. This situation is discussed in the Quality Assurance Assessment section, and should be taken into consideration when using the distillation and EI values for the sampled fuels.

The EPA specified maximum lead level in unleaded gasoline is 0.05 g/gal. All but one fuel sample had lead concentrations below this level. Fuel sample 58 contained 0.83 g/gal of lead.

Table 1 Summary of RVP Data, Grouped by City and Alcohol Content

City	Brand Distribution*	Avg. RVP (psi) less than 3% alcohol	Avg. RVP (psi) more than 3% alcohol
Baltimore	National	11.3	
	Regional	11.1	
Detroit	National	11.2	12.7
	Regional	12.0	12.4
Philadelphia	National	12.0	
	Regional	11.9	
	(Oxinol)		13.3

* Oxinol is considered separately from national and regional groups.

Table 2. RVP, Alcohol Fraction, Water Fraction, and Lead Content of Baltimore Fuel Samples

Sample Identification[a]	RVP, psi Automatic	% by Volume Methanol	Ethanol	TBA	Water, Wgt. %	Lead, g/gal
		NATIONAL				
1 AMOCO (R)	11.04	--[b]	--	0.42	0.01	0.005
2 ARCO (R)	11.20	--	--	0.14	0.01	0.006
3 BP Oil (R)	11.13	--	--	0.37	0.02	0.007
4 Exxon (P)	10.52	--	--	--	0.02	0.003
5 Getty (R)	12.46	--	--	--	0.01	0.001
6 Gulf (R)	11.21	--	--	0.11	0.01	0.004
7 Mobil (R)	11.37	--	--	0.19	0.01	0.007
8 Shell (P)	11.09	--	--	--	0.02	0.006
9 Sunoco (R)	11.93	--	--	0.15	0.02	0.003
10 Texaco (R)	11.21	--	--	0.54	0.02	0.008
		REGIONAL				
11 Merit (R)	11.50	--	--	--	0.01	0.007
12 Merit (P)	10.84	--	--	--	0.02	0.008
13 Crown (R)	10.47	--	--	--	0.01	0.004
14 Crown (R)	11.25	--	--	--	0.01	0.005
15 Crown (R)	10.99	0.12	--	--	0.02	0.005
16 Crown (P)	10.40	--	--	--	0.02	0.003
17 Citgo (R)	11.20	--	--	0.54	0.02	0.006
18 Merit (R)	10.96	--	--	--	0.02	0.010
19 Crown (R)	10.29	--	--	--	0.02	0.004
20 Hess (R)	11.43	--	--	--	0.02	0.006
21 Crown (P)	10.72	0.14	--	0.11	0.04	0.002
22 Crown (R)	10.36	--	--	--	0.05	0.005

Table 2. (Cont'd) RVP, Alcohol Fraction, Water Fraction, and Lead Content of Baltimore Fuel Samples

Sample Identification[a]	RVP, psi Automatic	% by Volume Methanol	Ethanol	TBA	Water, Wgt. %	Lead, g/gal
		REGIONAL				
23 Crown (R)	10.62	--	--	--	0.04	0.004
24 Crown (R)	10.79	--	--	--	0.05	0.004
25 Merit (P)	10.91	0.11	--	--	0.05	0.006
26 BP Oil (R)	12.62	--	--	--	0.03	0.004
27 Crown (R)	10.91	--	--	--	0.03	0.005
28 Merit (R)	11.61	--	--	--	0.04	0.006
29 Citgo (R)	12.51	--	--	--	0.04	0.004
30 Citgo (R)	10.86	0.15	--	0.15	0.03	0.005
31 Citgo (R)	10.73	0.17	--	0.15	0.03	0.010
32 BP Oil (R)	12.67	0.12	--	--	0.03	0.004
33 No Brand (R)	11.81	--	--	0.22	0.04	0.006
34 Big Red (R)	11.63	--	--	--	0.04	0.010
35 Crown (R)	10.23	--	--	--	0.04	0.004
36 BP Oil (P)	10.56	--	--	--	0.03	0.003
37 7-11 (R)	11.58	--	--	--	0.02	0.010
38 Merit (R)	11.49	--	--	--	0.04	0.006
39 Crown (P)	10.72	--	--	0.10	0.03	0.002
Avg. with alcohol[c]	0	0	0	0	0	0
Avg. without alcohol	11.2	0.02	0	0.08	0.03	0.005
S.D. with alcohol[c]	0	0	0	0	0	0
S.D. without alcohol	0.6	0.05	0	0.15	0.01	0.002

[a](R) = Regular, (P) = Premium
[b] =<0.1%
[c]Includes samples with >3% total alcohols

Table 3. RVP, Alcohol Fraction, Water Fraction, and Lead Content of Detroit Fuel Samples

Sample Identification[a]	RVP, psi Automatic	% by Volume Methanol	Ethanol	TBA	Water, Wgt. %	Lead, g/gal
		NATIONAL				
40 Boron (R)	12.11	--[b]	--	--	0.04	0.002
41 Shell (R)	11.06	--	--	--	0.03	0.002
42 Union 76 (R)	12.74	--	7.70	--	0.20	0.005
43 Sunoco (R)	11.22	--	--	--	0.01	0.001
44 Union 76 (R)	10.36	--	--	--	0.02	0.001
45 AMOCO (P)	11.32	--	--	--	0.04	0.003
46 Mobil (P)	11.05	--	--	--	0.04	0.002
		REGIONAL				
47 Total (R)	12.09	--	--	--	0.02	0.004
48 No Brand (R)	12.39	--	--	--	0.03	0.001
49 Speedway (P)	11.46	--	--	--	0.03	0.002
50 Martin (R)	12.09	--	--	--	0.02	0.005
51 No Brand (R)	10.88	--	10.1	--	0.20	0.001
52 Total (R)	11.02	--	--	--	0.02	0.004
53 Total (P)	12.27	--	10.3	--	0.19	0.016
54 Total (R)	12.00	--	--	--	0.02	0.004
55 Speedway (R)	12.40	--	--	--	0.02	0.001
56 Total (P)	11.97	--	10.1	--	0.21	0.004
57 Clark (R)	12.75	--	--	--	0.02	0.003
58 Citgo (R)	11.94	--	--	--	0.02	0.83[c]
59 Tulsa (R)	13.22	--	10.2	--	0.17	0.001
60 Total (P)	11.10	--	10.5	--	0.21	0.004

Table 3. (Cont'd) RVP, Alcohol Fraction, Water Fraction, and Lead Content of Detroit Fuel Samples

Sample Identification[a]	RVP, psi Automatic	% by Volume Methanol	Ethanol	TBA	Water, Wgt. %	Lead, g/gal
		REGIONAL				
61 Speedway (R)	12.19	--	--	--	0.04	0.001
62 Clark (R)	13.19	--	--	--	0.05	0.002
63 Total (R)	11.46	--	--	--	0.04	0.004
64 Pennzoil (R)	11.66	--	--	--	0.04	0.002
65 Clark (R)	12.89	--	--	--	0.04	0.002
66 No Brand (R)	13.06	--	9.22	--	0.18	0.003
67 Gas & Go (R)	12.23	--	--	--	0.04	0.002
68 Host (P)	12.41	--	9.38	--	0.22	0.005
69 Citgo (R)	13.34	--	9.83	--	0.19	0.004
70 Martin (R)	13.19	--	8.89	--	0.48	0.005
71 Tulsa (R)	12.38	--	9.86	--	0.20	0.002
72 Hi-Fy (P)	12.03	--	9.77	--	0.19	0.002
73 Clark (R)	11.64	--	--	--	0.04	0.002
74 Total (R)	11.85	--	--	--	0.04	0.005
75 Total (R)	10.46	--	0.16	--	0.04	0.003
Avg. with alcohol[d]	12.4	0	9.6	0	0.22	0.004
Avg. without alcohol	11.8	0	0.01	0	0.03	0.003
S.D. with alcohol[d]	0.8	0	0.8	0	0.08	0.004
S.D. without alcohol	0.7	0	0.03	0	0.01	0.001

[a](R) = Regular, (P) = Premium
[b] = <0.1%
[c]Sample 58 lead value not included in averaging
[d]Includes samples with > 3% total alcohols

Table 4. RVP, Alcohol Fraction, Water Fraction, and Lead Content of Philadelphia Fuel Samples

Sample Identification[a]	RVP, psi Automatic	% by Volume Methanol	Ethanol	TBA	Water, Wgt. %	Lead, g/gal
		NATIONAL				
76 BP Oil (R)	13.38	--[b]	--	--	0.02	<0.001
77 Gulf (R)	11.79	0.19	--	--	0.03	<0.001
78 Amoco (R)	11.71	--	--	2.08	0.08	0.009
79 Exxon (P)	10.66	0.21	--	--	0.03	0.003
80 Sunoco (R)	11.80	--	--	--	0.04	0.002
81 Mobil (R)	11.84	--	--	--	0.03	0.002
82 Texaco (R)	12.74	--	--	--	0.03	0.001
		REGIONAL				
83 Citgo (R)	12.48	--	--	0.40	0.03	0.002
84 Hess (R)	12.31	--	--	0.13	0.03	0.003
85 BP Oil (R)	12.81	--	--	--	0.02	0.001
86 Alert (P)	12.99	--	--	--	0.02	0.001
87 Merit (R)	11.91	--	--	0.13	0.03	0.003
88 Hess (R)	10.93	--	--	--	0.03	0.005
89 Hess (R)	10.58	--	--	--	0.02	0.005
90 Citgo (P)	12.22	--	--	1.60	0.04	0.005
91 Golden (R)	11.63	--	--	--	0.03	0.003
92 BP Oil (R)	11.40	0.18	--	0.18	0.03	0.005
93 7-11 (R)	12.37	--	--	0.64	0.03	0.002
94 BP Oil (P)	9.76	--	--	--	0.03	0.002
95 Citgo (R)	12.14	--	--	0.70	0.04	0.002

Table 4. (Cont'd) RVP, Alcohol Fraction, Water Fraction, and Lead Content of Philadelphia Fuel Samples

Sample Identification[a]	RVP, psi Automatic	% by Volume Methanol	Ethanol	TBA	Water, Wgt. %	Lead, g/gal
		REGIONAL				
96 Merit (R)	11.48	--	--	0.10	0.03	0.004
97 Merit (R)	11.08	--	--	--	0.03	0.004
98 Hess (P)	11.97	--	--	--	0.04	0.006
99 Merit (R)	11.47	--	--	0.10	0.04	0.005
100 T.F.C.O. (R)	12.08	--	--	0.11	0.05	0.006
101 Merit (R)	11.12	--	--	--	0.04	0.005
102 Hess (P)	12.04	--	--	--	0.05	0.007
103 Hess (R)	11.86	--	--	0.12	0.03	0.003
104 BP Oil (R)	13.11	--	--	--	0.03	0.001
105 Hess (R)	11.93	--	--	0.14	0.03	0.003
106 BP Oil (P)	13.01	--	--	--	0.04	0.001
107 Citgo (R)	12.31	--	--	0.45	0.04	0.002
108 Merit (R)	11.38	--	--	--	0.04	0.004
109 Alert (R)	12.53	--	--	--	0.04	0.001
110 Merit (P)	11.16	--	--	0.14	0.04	0.004
111 Citgo (R)	12.13	--	--	0.60	0.04	0.002
112 Wm. Penn (R)	12.02	--	--	--	0.04	0.002
		OXINOL				
113 ARCO (R)	13.38	4.13	--	3.76	0.16	0.002
114 ARCO (R)	13.61	4.03	--	3.75	0.19	0.002
115 ARCO (R)	13.52	4.00	--	3.65	0.17	0.002

Table 4. (Cont'd) RVP, Alcohol Fraction, Water Fraction, and Lead Content of Philadelphia Fuel Samples

Sample Identification[a]	RVP, psi Automatic	% by Volume Methanol	Ethanol	TBA	Water, Wgt. %	Lead, g/gal
		OXINOL				
116 ARCO (R)	13.48	4.18	--	3.77	0.16	0.002
117 ARCO (P)	12.71	4.32	--	3.96	0.15	0.002
118 ARCO (R)	13.19	4.06	--	3.72	0.17	0.002
119 ARCO (R)	13.46	3.94	--	3.61	0.17	0.002
120 ARCO (R)	13.74	4.03	--	3.72	0.16	0.003
121 ARCO (P)	12.90	4.06	--	3.64	0.16	0.002
122 ARCO (R)	13.19	3.81	--	3.67	0.23	0.002
123 ARCO (R)	13.16	4.20	--	3.76	0.15	0.002
Avg. with alcohol[c]	13.3	4.1	0	3.7	0.17	0.002
Avg. without alcohol	11.9	0.02	0	0.21	0.03	0.003
S.D. with alcohol[c]	0.3	0.1	0	0.1	0.02	0.000
S.D. without alcohol	0.8	0.05	0	0.44	0.01	0.002

[a](R) = Regular, (P) = Premium
[b] = <0.1%
[c]Includes samples with >3% total alcohols

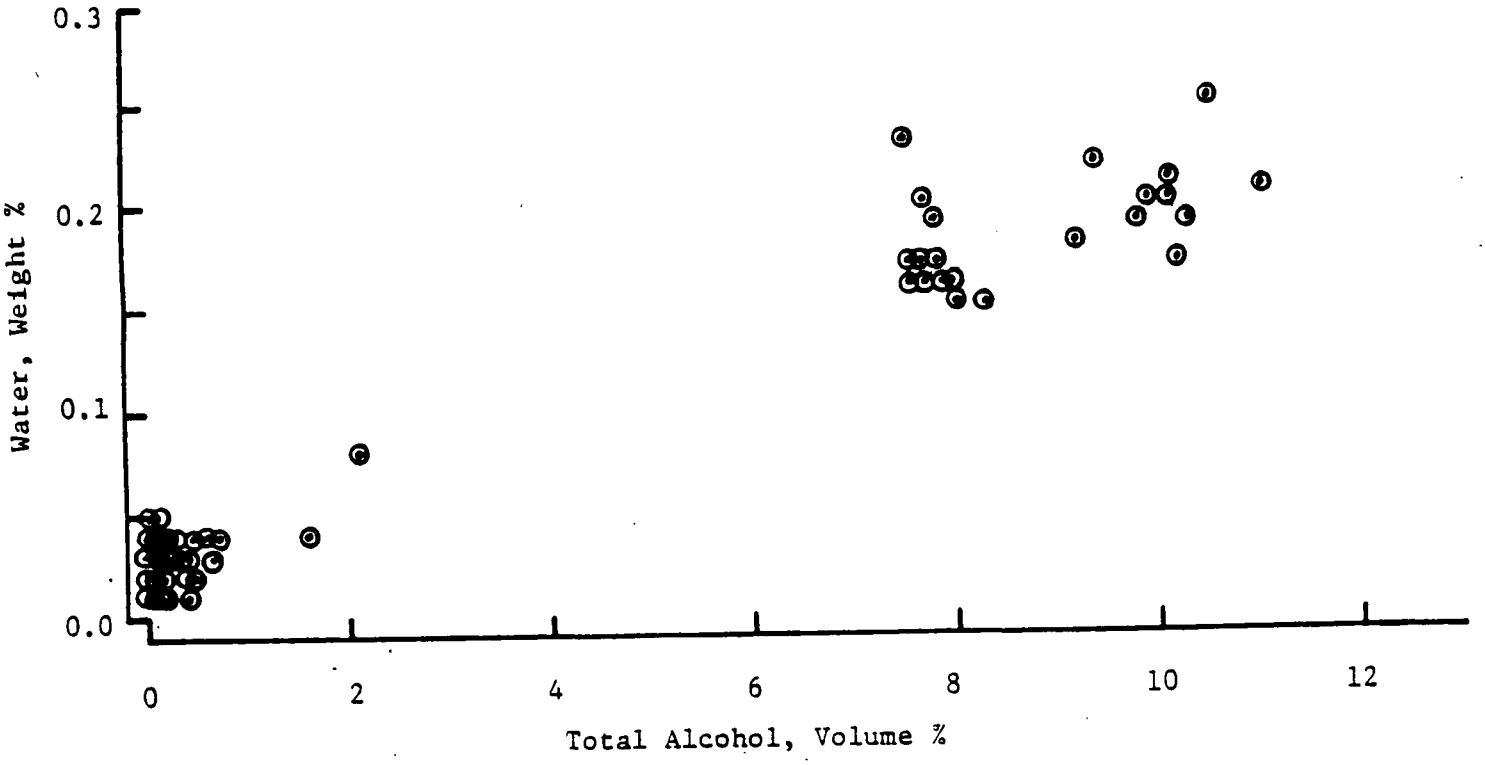

Figure 1. Comparison of Water Content and Alcohol Content of Fuel Samples

Table 5. Distillation Data from Baltimore Fuel Samples

Sample Number	Temperature, °F at % Evaporated															
	IBP	5%	10%	15%	20%	30%	40%	50%	60%	70%	80%	90%	95%	EP	Residue (%)	Recovered (%)
	National															
1	91	115	126	135	145	165	190	216	242	268	300	345	372	418	1.5	98.5
2	91	120	133	144	151	160	181	212	237	264	297	342	372	414	1.5	98.0
3	88	108	117	124	135	158	183	211	239	268	305	356	394	420	1.5	97.5
4	95	122	133	140	149	170	192	217	239	264	300	342	358	399	1.0	98.5
5	81	99	107	115	122	137	160	181	210	241	281	325	356	390	1.5	98.5
6	84	108	120	129	138	156	180	208	234	264	300	356	387	430	1.5	98.5
7	84	112	122	132	141	160	185	207	235	264	300	343	372	421	1.0	98.5
8	89	116	127	136	145	158	175	193	219	235	257	298	334	379	1.5	98.0
9	83	109	120	129	140	160	183	207	234	264	298	351	385	424	1.0	98.5
10	94	113	123	132	142	163	188	208	240	267	301	342	380	418	1.0	98.5
	Regional															
11	90	114	123	133	143	162	182	210	240	268	300	342	378	412	1.5	98.0
12[a]	87	106	120	131	141	161	187	214	233	248	271	305	343	385	1.0	98.0
13	90	124	138	147	156	172	190	210	234	262	295	338	365	417	1.5	98.0
14	89	115	126	136	148	169	193	216	233	266	298	345	376	421	1.0	98.5
15	93	122	133	144	154	175	195	214	241	268	302	343	380	424	1.0	98.5
16	93	122	135	147	158	176	192	219	241	263	297	330	361	402	1.0	98.5
17	99	122	129	136	147	167	190	216	242	271	306	352	390	419	1.5	98.0
18	100	124	131	140	149	171	194	221	246	273	306	349	376	423	1.5	98.0
19[b]																
20[b]																
21[a]	92	114	128	140	150	174	201	221	241	262	291	330	357	403	1.0	99.0
22	98	119	130	140	151	172	195	222	246	270	302	340	370	410	1.0	99.0
23	100	129	142	153	158	169	192	217	234	268	300	342	369	423	1.0	99.0
24	98	125	138	147	156	176	198	218	243	270	306	345	376	421	1.0	98.5
25	99	122	134	144	152	170	188	201	225	243	265	300	328	382	1.0	99.0
26	93	116	128	136	147	158	190	214	239	265	296	334	366	398	1.5	97.0
27	94	123	135	146	156	174	194	212	235	263	293	338	364	414	1.0	99.0
28	91	121	132	140	151	171	194	212	243	261	297	346	381	419	1.5	98.0
29	99	120	131	142	151	167	187	212	235	262	295	331	360	403	1.0	98.5
30	99	126	139	143	153	176	196	219	241	268	306	356	396	432	1.5	98.0
31	97	118	129	138	149	171	194	221	246	273	307	349	383	423	1.5	98.0
32[b]																
33	97	124	138	147	156	177	199	219	244	271	301	340	369	417	1.0	98.5
34	91	120	134	144	151	169	186	205	225	251	275	351	390	423	1.5	98.0
35	102	128	136	144	158	179	203	217	240	268	302	340	376	421	1.0	98.5
36	102	139	156	168	178	190	205	230	247	269	299	334	355	410	1.0	99.0
37	97	117	129	138	149	169	192	212	230	257	297	363	405	433	1.5	98.0
38	91	113	124	133	143	165	190	219	246	273	307	351	379	423	1.0	99.0
39	100	131	146	156	165	185	207	228	246	262	297	329	367	419	1.5	98.0

[a]Instrument #2
[b]No data

Table 6. Distillation Data from Detroit Fuel Samples

Sample Number	Temperature, °F at % Evaporated														Residue (%)	Recovered (%)
	IBP	5%	10%	15%	20%	30%	40%	50%	60%	70%	80%	90%	95%	EP		
	National															
40[a]	87	107	120	131	145	173	201	228	253	279	309	348	386	425	1.5	98.0
41	95	118	130	140	150	171	194	210	236	260	288	326	360	424	1.0	99.0
42	96	112	118	123	128	139	150	192	230	263	297	342	378	412	1.5	98.5
43	86	108	120	133	143	163	182	210	240	269	304	350	400	440	1.0	98.5
44	98	120	131	139	147	165	186	214	241	269	305	346	382	425	1.0	98.5
45	95	124	139	149	160	181	205	230	245	273	316	347	370	403	1.0	98.5
46[a]	89	116	135	153	170	203	218	230	243	263	298	337	372	421	1.5	98.0
	Regional															
47	89	108	119	130	140	158	184	214	240	269	302	340	369	429	1.0	99.0
48[a]	86	105	118	130	140	167	195	223	250	276	309	351	381	419	1.0	99.0
49	92	136	143	153	168	198	218	233	250	273	307	350	390	420	1.5	97.0
50	90	111	117	121	131	151	174	200	229	259	293	341	375	426	1.0	99.0
51[a]	99	116	122	127	131	141	150	172	222	254	285	330	361	409	1.0	99.0
52[a]	91	109	119	128	138	146	181	208	235	264	300	325	362	420	1.0	99.0
53	95	113	120	125	130	139	150	177	228	260	293	337	365	412	1.0	99.0
54	87	108	120	130	140	161	187	215	243	275	307	346	381	426	1.0	98.0
55	86	117	130	139	150	168	188	219	244	271	310	357	397	427	1.5	97.0
56[b]																
57	94	115	128	140	150	171	193	218	240	268	304	355	390	426	1.0	98.5
58	86	110	121	130	138	156	177	197	228	260	301	350	382	424	1.5	98.5
59	94	114	121	128	134	144	155	206	238	266	302	352	384	421	1.5	98.5
60	102	122	127	133	137	146	158	187	229	266	302	345	374	414	1.0	99.0
61	84	106	118	129	144	167	196	221	250	279	318	372	414	425	1.5	97.0
62	87	110	120	130	140	163	192	237	243	270	308	362	404	424	1.5	97.5
63	89	112	122	130	138	158	179	206	234	265	300	337	363	423	1.0	99.0
64	91	124	136	148	160	187	214	239	262	288	311	354	392	437	1.0	99.0
65	90	114	126	135	145	165	190	214	247	279	315	365	399	430	1.5	97.5
66	84	113	120	126	131	141	151	181	225	254	293	347	379	420	1.0	99.0
67	91	111	124	136	149	180	208	235	261	288	318	367	403	430	1.5	97.5
68	91	108	117	123	131	144	153	189	234	265	299	343	372	420	1.5	98.5
69	90	104	113	118	123	133	144	154	208	248	288	336	374	406	1.5	98.0
70	98	115	122	129	132	145	155	210	244	274	309	362	406	425	1.5	98.0
71	90	109	118	126	132	145	155	199	238	260	300	347	383	420	1.0	99.0
72	96	111	117	124	130	144	156	208	219	264	298	343	381	403	1.5	98.0
73	97	122	134	145	156	178	203	230	257	284	318	358	394	434	1.5	98.0
74	89	112	121	130	139	158	182	207	236	264	295	330	366	410	1.0	99.0
75[a]	96	117	130	140	143	157	180	207	236	264	298	332	364	417	1.0	99.0

[a]Instrument #2
[b]No data

Table 7. Distillation Data from Philadelphia Fuel Samples

Sample Number	Temperature, °F at % Evaporated														Residue (%)	Recovered (%)
	IBP	5%	10%	15%	20%	30%	40%	50%	60%	70%	80%	90%	95%	EP		
	National															
76	89	107	120	130	141	164	188	206	232	259	289	326	356	399	1.5	98.0
77	91	121	132	141	149	155	175	201	223	246	275	321	356	408	1.5	98.5
78[a]	90	108	116	125	135	156	180	208	238	258	307	345	370	419	1.0	99.0
79	90	109	120	130	141	162	190	218	238	257	290	336	357	403	1.0	99.0
80	88	110	119	126	137	154	179	206	241	277	310	353	386	425	1.0	99.0
81[a]	90	114	121	130	140	162	186	212	240	270	308	355	387	416	1.5	98.0
82	92	110	120	128	135	149	160	182	208	241	276	315	346	402	1.0	98.5
	Regional															
83[a]	86	108	122	132	140	154	175	200	222	246	278	318	351	389	1.0	98.0
84[a]	85	100	111	121	130	149	169	190	219	250	286	330	357	384	1.5	98.0
85	90	120	131	140	149	167	183	207	226	251	283	313	351	399	1.5	98.5
86[a]	84	119	140	157	175	201	217	232	245	267	300	340	388	398	1.5	96.5
87[a]	87	101	113	123	131	150	172	197	225	256	292	334	362	400	1.5	98.0
88	86	114	126	136	146	164	185	195	221	248	281	314	344	402	1.0	99.0
89	90	115	126	135	145	160	181	205	234	253	299	339	369	414	1.0	99.0
90[a]	85	107	117	128	137	160	184	207	236	264	297	340	372	412	1.5	98.0
91[a]	90	114	129	139	148	162	190	220	248	277	315	360	394	421	1.5	97.5
92[b]																
93[b]																
94[a]	94	132	144	155	170	195	214	228	241	260	288	317	344	399	1.0	99.0
95[a]	86	109	120	130	140	160	180	203	226	250	280	316	343	406	0.5	99.5
96[a]	88	108	120	128	137	158	181	208	236	266	297	334	362	405	1.0	99.0
97	92	107	118	127	136	156	180	207	236	264	301	340	370	411	1.0	98.5
98[a]	93	111	122	131	141	163	192	218	238	256	280	330	368	408	1.5	97.5
99[a]	90	110	122	132	140	160	181	198	228	260	297	338	370	401	1.5	97.5
100[a]	87	103	115	124	134	154	175	206	242	276	311	353	387	421	1.5	97.5
101	92	121	131	136	143	164	182	206	235	265	297	337	360	405	1.0	99.0
102[a]	84	106	120	134	145	172	197	219	236	254	278	330	372	412	1.5	98.0
103	88	112	120	128	137	152	154	199	227	258	294	333	364	405	1.0	98.0
104	90	111	125	136	144	148	162	188	214	242	276	314	343	394	1.0	98.5
105	94	114	122	130	137	156	178	203	238	260	295	336	372	406	1.5	98.0
106	83	137	153	166	177	184	211	227	241	260	290	328	368	406	1.5	97.0
107[a]	86	105	118	127	137	158	176	200	222	244	278	318	348	393	1.5	98.5
108	91	112	123	131	141	160	181	210	235	264	296	332	359	408	1.0	99.0
109	85	112	124	133	140	157	177	195	217	246	278	320	353	399	1.5	98.5
110	90	116	130	140	150	170	183	201	234	254	280	314	346	404	1.0	99.0
111[a]	85	108	120	131	140	160	182	204	226	250	283	316	356	407	1.5	98.0
112[a]	93	100	111	119	128	148	172	204	242	282	311	353	384	421	1.0	99.0
	Oxinol															
113	88	102	109	117	123	136	157	177	210	246	284	315	358	410	1.0	99.0
114	92	106	113	117	122	135	156	178	208	242	280	314	358	401	1.5	98.5
115	92	106	111	117	122	134	156	181	212	247	280	319	357	404	1.0	99.0
116	91	107	113	117	123	136	157	183	209	244	279	318	358	401	1.5	98.5
117[a]	90	111	120	125	133	158	186	217	246	268	294	334	358	400	1.5	97.5
118[a]	89	101	110	115	121	134	156	182	211	244	281	323	346	401	1.0	98.5
119[a]	90	104	110	115	121	134	155	130	208	245	280	323	343	406	1.5	98.5
120[a]	90	103	110	116	121	133	154	179	206	241	281	321	357	399	1.5	98.5
121	95	111	118	122	129	144	171	196	226	259	293	331	371	408	1.5	98.0
122	91	111	117	121	126	142	163	191	218	248	284	325	358	400	1.0	99.0
123	86	101	110	115	120	133	157	183	212	245	279	315	343	406	1.0	99.0

[a]Instrument #2
[b]No data

Table 8. Evaporative Index (EI) of Fuel Samples[a]

Baltimore		Detroit		Philadelphia	
Sample	EI	Sample	EI	Sample	EI
1	14.9	40	14.7	76	16.8
2	15.4	41	15.2	77	16.5
3	14.8	42	17.7[c]	78	15.7
4	14.7	43	14.9	79	14.3
5	16.7	44	14.9	80	15.9
6	15.1	45	14.6	81	15.7
7	15.2	46	12.7	82	18.0
8	16.1	47	15.2	83	16.4
9	15.6	48	15.2	84	16.2
10	15.4	49	13.5	85	16.9
11	15.5	50	16.5	86	14.1
12	14.2	51	16.9[c]	87	15.7
13	14.6	52	15.1	88	15.8
14	14.8	53	17.6[c]	89	15.1
15	14.8	54	15.3	90	15.8
16	14.4	55	15.7	91	15.1
17	15.5	56[b]	----	92[b]	----
18	15.1	57	16.3	93[b]	----
19[b]	----	58	16.4	94	12.6
20[b]	----	59	17.6[c]	95	16.2
21	14.1	60	16.9[c]	96	15.4
22	14.5	61	14.8	97	15.1
23	15.1	62	16.0	98	15.4
24	14.7	63	15.7	99	15.9
25	16.1	64	14.3	100	15.5
26	16.2	65	16.3	101	15.7
27	15.0	66	17.6[c]	102	14.8
28	15.4	67	14.7	103	16.2
29	16.8	68	17.1[c]	104	17.9
30	14.9	69	18.3[c]	105	16.4
31	14.7	70	17.7[c]	106	15.3
32[b]	----	71	16.7[c]	107	16.3
33	15.4	72	16.5[c]	108	15.5
34	15.9	73	15.0	109	17.1
35	14.0	74	15.9	110	15.8
36	14.1	75	15.2	111	15.9
37	15.7	Avg	15.8	112	15.4
38	15.2	Std dev	1.3	113[d]	18.0
39	14.2			114[d]	18.7
Avg	15.1			115[d]	18.4
Std dev	0.7			116[d]	18.5
				117[d]	16.1
				118[d]	17.5
				119[d]	18.3
				120[d]	18.6
				121[d]	17.5
				122[d]	18.0
				123[d]	17.5
				Avg	16.3
				Std dev	1.3

a EI = 0.85 x RVP - 0.32 x (% Evap @100°F) + 0.14 x (% Evap @200°F)

b No data

c Gasohol fuels (approximately 10% ethanol)

d Oxinol fuels

MIDPOINT	DETROIT GASOHOL	DETROIT GASOLINE	BALTIMORE GASOLINE	PHILADELPHIA GASOLINE	PHILADELPHIA OXINOL
12.6	+	+X	+	+X	+
13.0	+	+	+	+	+
13.4	+	+X	+	+	+
13.8	+	+	+	+	+
14.2	+	+X	+XXXXX	+XX	+
14.6	+	+XXX	+XXXXXX	+	+
15.0	+	+XXXXX	+XXXXXXXXX	+XXXX	+
15.4	+	+XXXXX	+XXXXXXXX	+XXXXXX	+
15.8	+	+XXX	+XXX	+XXXXXXXXXX	+
16.2	+	+XXX	+XXX	+XXXX	+X
16.6	+XX	+XX	+X	+XXX	+
17.0	+XXX	+	+X	+XXX	+
17.4	+	+	+	+	+XXX
17.8	+XXXX	+X	+	+X	+
18.2	+X	+	+	+X	+XXX
18.6	+	+	+	+	+XXXX
19.0	+	+	+	+	+

Figure 2. Distributions of Evaporative Index

IV. QUALITY ASSURANCE ASSESSMENT

Six refernce and two control fuels were subjected to several initial analyses. Descriptions of these fuels are listed below. Reference fuel 4 was replaced with Reference fuel 6, which has 500 ppm (0.05 weight percent) of added water. Reference fuel 4 was spiked with 100 ppm (0.01 weight percent) water, which appeared to be at the detectability limits of the water analysis method for use with gasoline-alcohol blends.

Fuel Sample	Description
Reference 1	2,2-dimethylbutane, 9.9 psi at 100°F (for RVP analysis)
Reference 2	5% methanol, 5% TBA in unleaded Indolene (by volume)
Reference 3	10% ethanol in unleaded Indolene (by volume)
Reference 5	Two lead samples provided by the EPA: 5a = 0.717 g/gal, 5b = 0.0166 mg/gal
Reference 6	0.05 weight percent (500 ppm) added water in Reference 2
Control 1	Unleaded Indolene
Control 2	Same fuel batch as Reference 2

The samples were analyzed according to the schedule shown in Table 9, and the results are given in Table 10. Detailed listings of distillation data for Reference 2 (also called Control 2) and Control 1 are presented in Appendix D. With one exception, the reported values fell within the precision, accuracy, and confidence limits specified in the quality assurance plan (Table 11). An exception occurred with Reference 1, in which one of the RVP values using the ASTM D323 method was outside the limit specified in the QA plan by 0.1 psi. The ASTM D323 method appears to give a somewhat wider dispersion of values than initially anticipated. After discussion with the EPA Project Officer, it was decided to accept the RVP values and SwRI was authorized to proceed with sample analyses.

Analysis of an initial Reference 1 sample was considerably outside reasonable limits, indicating some apparent problem with that sample. Therefore, that sample was discarded and another Reference 1 sample was used.

In addition to the initial analyses of reference and control fuels, the two control samples were analyzed in duplicate between batches of samples. The results of the Reid vapor pressure analyses of Controls 1 and 2 are given in Table 12. The average Control 1 RVP for both the automatic and the bomb methods was 8.9 psi. The average Control 2 RVP using the

automatic method was 10.5 psi, and for the bomb method it was 10.4 psi. All but one set of controls fell within the quality assurance guidelines. The controls analyzed between sample batches 4 and 5 were slightly outside the reproducibility specifications of only one value in 20, differing by more than 0.6 psi. A fresh set of controls was analyzed and several samples within batch 5 were re-analyzed. The new control values agreed within the allowed limits, and the re-analyzed samples of batch 5 agreed within two percent of the original values.

Alcohol analyses of Control 1 showed less than 0.1 percent methanol, ethanol, and TBA for all analyses. The results of analyses of Control 2 for alcohols are presented in Table 13. The average measured methanol level in the standards was 5.0, percent and the average measured level of TBA was 4.7 percent. Ethanol was not detected in any of the samples (detectability limit is 0.1 percent). The measurement of methanol fell within the range given in the Quality Assurance Plan, however, several TBA measurements were out of the range given for TBA. Some measured TBA values were up to ten percent lower than the concentrations to which the corresponding controls were prepared. One possible explanation is that samples giving low TBA values may have been drawn from a fuel can which was lower in TBA than other cans. It is also possible that the variability in the procedure for measuring TBA is on the order of ten percent rather than five percent.

Water analysis results for the control samples are given in Table 14. The average water content was about 0.1 weight percent for Control 2 and about 0.02 weight percent for Control 1. Considerable variation in measured water levels occurred. The reason for the variation is not known. However, since the water content of the initial samples was about half of the latter values, it can be speculated that the controls absorbed water from the atmosphere over time. Repeatabilities have not been previously established for water analysis of gasoline-methanol blends, or even for gasolines not containing alcohols. Analysis of the control fuels for lead yielded lead values less than the detection limit of the method, 0.001 g/gal of lead.

The two specified control samples and an additional fuel sample, a regular unleaded gasoline on which distillation data were available, were analyzed for distillation temperature curve. Due to stringent time constraints, two instruments were utilized to analyze the controls and samples. The second instrument, however, was not available until over half the total analyses had been completed.

This situation came about as a result of several factors. The samples were collected in a previous project in late summer of 1984, with the understanding that analyses would be conducted in the fall of 1984 in the same manner as was applied in the analyses given in Report EPA 460/3-84-009. In that study, a reasonable number of data checks were applied to those analyses considered to be of primary importance to the intended usage of the data. The laboratory at SwRI that was scheduled to conduct the fuels analyses has a relatively relaxed schedule in the fall and spring, and a very hectic schedule in the winter and summer.

Authorization to proceed with the analyses was not received until well into the spring of 1985. With the incorporation of numerous quality assurance requirements to be conducted prior to beginning analyses of the fuel samples, it was not possible to begin these analyses before the beginning of the already busy summer schedule. The laboratory at the time, thought it was still possible to conduct the analyses, but it eventually became evident that the distillation analyses could not be completed before the September 30, 1985 deadline. Therefore, an effort was made to locate another fuel analysis laboratory, and one was located in San Antonio. With the verbal approval of the EPA Project Officer, the fuels were delivered to that laboratory for distillation analyses on a rush basis. A question has become evident on the reproducibility of the two instruments used, relative to one of the control fuels. Due to the September 30 deadline, however, it was not possible to incorporate any additional evaluations in an attempt to resolve the question. It also should be pointed out that the ASTM is reviewing the precision for ASTM D86, and that it is not clear how to specifically apply the given precisions to the data generated.

The results from the analyses of control and the additional fuel sample (SwRI Fuel EM-616-F) are given in Appendix D, and are summarized in Tables 15 and 16. The repeatability between duplicate injections for Control fuels 1 and 2 were within the guidelines in the Quality Assurance Plan for 19 out of 20 analyses (95 percent). Duplicate distillation analyses were not performed on fuel EM-616-F. The reproducibilities of distillation temperatures for Controls 1 and 2 on each instrument separately were also within the quality assurance guidelines. Reproducibility between the two instruments for Control fuel 1 and EM-616 were outside the 95% guidelines given by ASTM. Again, however, it should be noted that the precision for ASTM D86 is under review, and that specific applications of the precision values given by ASTM are not defined.

Table 9. Schedule for Initial Analysis of Reference and Control Samples

Sample Number	Number of Evaluations					
	RVP Automatic	RVP, ASTM D323(bomb)	Distillation	Alcohols[a]	Water	Lead
Reference 1	2[b]	2	0	0	0	0
Reference 2 (Control 2)	2	2	2	2	2	2
Reference 3	0	0	0	2	0	0
Reference 5a	0	0	0	0	0	2
Reference 5b	0	0	0	0	0	2
Reference 6	0	0	0	0	2	0
Control 1	2	2	2	2	2	2

[a]Methanol, ethanol, TBA
[b]Two repetitive analyses

Table 10. Results of Initial Analyses of Reference and Control Sample

Sample Number	RVP, psi Automatic	RVP, psi ASTM D323(bomb)	Distillation, °F at % Evap. 10%	50%	90%	Alcohols, % by vol. Methanol	Ethanol	TBA	Water, wt %	Lead, g/gal
Reference 1	10.1[a]	9.7,9.2,9.3	--[b]	--	--	--	--	--	--	--
Reference 2 (Control 2)	10.6,10.7	10.3,10.6	--	--	--	5.21,5.16	< 0.1, < 0.1	5.08,5.01	0.037,0.039	< 0.001, < 0.001
Reference 3	--	--	--	--	--	<0.1, <0.1	10.1,10.1	<0.1, < 0.1	--	--
Reference 5a Final analyses	--	--	--	--	--	--	--	--	--	0.07,0.07
Reference 5b Final analyses	--	--	--	--	--	--	--	--	--	0.015,0.015
Reference 6[c]	--	--	--	--	--	--	--	--	0.0899,0.0830	--
Control 1	8.8,9.1	9.0,9.1	--	--	--	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	0.011,0.009	<0.001, <0.001

[a]Repeat analysis to be run.
[b]Not measured
[c]Reference 6 was prepared by adding 0.050 weight percent water to Reference 2. The average water weight percent difference between Reference 6 and Reference 2 is 0.0485.

Table 11. Objectives for Precision, Accuracy, and Completeness

Analytical Procedure	Reference	Experimental Conditions	Precision[a] Repeat-ability	Precision[a] Reproduc-ibility	Accuracy	Complete-ness[j]
Alcohol Content	FID Chroma-tography (SwRI)	Fuel Sample	2.5%[b,c]	5%[b,c]	d	>95%
Distillation	ASTM D86	Fuel Sample	c,e	c,e	f	>95%
Lead Content	ASTM D3237	Fuel Sample	0.005g/gal[c]	0.01g/gal[c]	d	>95%
RVP	ASTM D323	Fuel Sample	0.25 psi[c,g]	0.55 psi[c,g]	d	>95%
RVP	Automatic RVP Instrument Method	Fuel Sample	0.25 psi[c,h]	0.55 psi[c,g]	d	>95%
Water Content	ASTM D-1744	Fuel Sample	i	i	k	>95%

[a] The ASTM defines precision in terms of repeatability and reproducibility.
[b] The percents given are percents of the measured alcohols content.
[c] Based on 95% confidence limits (i.e., 19 out of 20 measurements should be within the limits given).
[d] The measured concentration for the blended standard solution should be within five percent of the concentration to which it was blended.
[e] Repeatability and reproducibility are given in Fig. 2 and Fig. 3 in ASTM D86; these criteria can not be reduced to only a few numerical values.
[f] Accuracy is obtained through procedural operating requirements (i.e., by following the procedure).
[g] For samples having an RVP of 0 to 15 psi.
[h] The Automatic RVP Instrument Method is designed to be an efficient replacement to the ASTM D323 method and has the same precision given for ASTM D323.
[i] The precision has not been determined for use with gasoline samples.
[j] Unless stated otherwise in a specific work plan, the objective for completeness will be 95%, or better.
[k] To be determined.

Reproduced from section 3E of Quality Assurance Project Plan for this contract.

Table 12. RVP of Control Fuel Samples as Measured by two Methods

	Control 1--Unleaded Indolene						Control 2--Indolene-Alcohol Blend[a]					
	Auto., psi			Bomb, psi			Auto, psi			Bomb, psi		
	1	2	Avg.	1	2	Avg.	1	2	Avg.	1	2	Avg.
Initial - first set	8.8	9.1	9.0	9.0	9.1	9.1	10.9	10.9	10.9	10.6	10.8	10.7
- repeat							10.6	10.7	10.6	10.3	10.6	10.4
Later repeat	9.1		9.1	9.4		9.4	10.5		10.5	10.5		10.5
Between batches 1 and 2	8.9	8.9	8.9	8.9	9.0	9.0	10.6	10.5	10.6	10.5	10.5	10.5
Between batches 2 and 3	9.0	8.8	8.9	9.0	8.9	9.0	10.5	10.4	10.4	10.4	10.4	10.4
Between batches 3 and 4	8.7	8.9	8.8	8.9	8.8	8.9	10.5	10.3	10.4	10.4	10.4	10.4
Between batches 4 and 5	8.4[b]	8.4[b]	8.4	8.3[b]	8.1[b]	8.2[b]	10.2[b]	10.3	10.3	10.0[b]	10.1[b]	10.1
Between batches 5 and 6	8.9	9.2	9.0	8.9	9.0	9.0	10.6	10.6	10.6	10.5	10.5	10.5
Between batches 6 and 7	8.9	8.9	8.9	8.8	9.0	8.9	10.6	10.5	10.6	10.5	10.5	10.5
Between batch 7 and reruns from batch 5[c]	8.9	9.0	9.0	8.9		8.9	10.6	10.6	10.6			10.4
Avg.			8.9			8.9			10.5			10.4

[a]Five percent methanol and five percent TBA (by volume) added to unleaded indolene
[b]These RVP values were outside the reproducibility specification of 0.6 psi. The two cans of fuel samples were discarded and fresh samples were analyzed for the remaining analyses.
[c]Every fifth sample of the fifth batch was reanalyzed with the fresh standard

Table 13. Alcohol Content of Control Sample 2[a]

	Alcohol Content in Percent by Volume							
	Methanol			Ethanol		TBA		
	1	2	Avg.	1	2	1	2	Avg.
Initial								
First set	5.21	5.16	5.2	0.0	0.0	5.08	5.01	5.0
Later repeat	4.86		4.9	0.0		4.68		4.7
Between batches 1 and 2	4.95	4.96		0.0	0.0	4.73	4.74	
Repeat	4.86		4.9	0.0		4.65		4.7
Between batches 2 and 3	4.85	4.85		0.0	0.0	4.68	4.65	
Repeat	5.13		4.9	0.0		4.89		4.7
Between batches 3 and 4	5.08	5.11		0.0	0.0	4.87	4.88	
Repeat	4.95		5.0	0.0		4.78		4.8
Between batches 4 and 5	4.93	4.92	4.9	0.0	0.0	4.76	4.76	4.8
Between batches 5 and 6	4.87	4.87	4.9	0.0	0.0	4.53	4.51	4.5
Between batches 6 and 7	4.89	4.91	4.9	0.0	0.0	4.54	4.55	4.6
After batch 7	5.02	5.05		0.0	0.0	4.66	4.68	
Repeat	5.01	5.02	5.0	0.0	0.0	4.65	4.64	4.7
Later repeat	4.90	4.85		0.0	0.0	4.84	4.77	
	4.86	5.01		0.0	0.0	4.77	4.88	
	4.98	4.89		0.0	0.0	4.85	4.80	
	4.98	4.86		0.0	0.0	4.88	4.83	
	4.93	5.01		0.0		4.87	4.87	
	4.86		4.9			4.75		4.8
		Avg.	5.0				Avg.	4.7

[a]Control sample 2 is unleaded Indolene with 5 percent methanol and 5 percent TBA added (by volume)

[b]About 40 percent of the values varied over 0.25 volume percent from the five volume percent TBA that was added. See text for pertinent discussion

[c]0.0 means < 0.1%

Table 14. Water Content of Control Fuel Samples

	Water Content in Weight Percent					
	Control 1 Unleaded Indolene			Control 2 Unleaded Indolene +5% Methanol +5% TBA		
	1	2	Avg.	1	2	Avg.
Initial						
First set	0.011	0.009	0.010	0.037	0.039	0.038
Later repeat	0.007	0.009	0.008	0.087	0.093	0.090
Between batches 1 and 2	0.025	0.024	0.024	0.107	0.121	
Repeat				0.120		0.116
Between batches 2 and 3	0.009		0.009	0.142	0.132	
Repeat	0.029	0.030	0.030	0.139		0.138
Between batches 3 and 4	0.039	0.031	0.035	0.103	0.103	0.103
Repeat	0.032		0.032			
Between batches 4 and 5	0.025	0.032		0.108	0.126	
Repeat	0.030		0.031	0.117		0.113
Between batches 5 and 6	0.028	0.024	0.026	0.104	0.108	0.106
Between batches 6 and 7	0.033	0.030	0.032	0.125	0.127	0.126
After batch 7	0.034	0.034	0.034	0.152	0.149	0.150
		Avg.	0.02		Avg.	0.1

Table 15. Distillation Temperature Repeatability of Control Fuels

Control Fuel	Instrument	Temperature Difference at Percent Evaporated, °F														Number of Values Above Guidlines	
		IBP	5%	10%	15%	20%	30%	40%	50%	60%	70%	80%	90%	95%	EP	Observed	Acceptance Basis[a, d]
Guidelines in ASTM D86[a]		5	4	3	3	3	3	3	3	3	3	3	4	5	5	--	--
1	1	4	3	3	3	1	3	2	2	2	2	3	3	8[c]	2	1	3
2	1	3	3	3	2	1	2	3	1	2	3	3	1	3	2	0	3 to 4
1	2	3	4	4[b]	3	3	3	3	3	3	4[b]	3	1	2	8[c,d]	2	1 to 2
2	2	5	2	1	2	2	1	1	1	2	2	4[b]	3	3	6[b,d]	2	1 to 2

[a]Precision for ASTM D86 is under review.
Indications are that precision for IBP and EP may be indeterminate.
[b]One °F above values given in guidelines
[c]Two or more °F above values given in guidelines
[d]ASTM D86 bases the repeatability guidelines on 95% probability and makes the statement given in the preceeding note [a].

Table 16. Distillation Temperature Reproducibility of Control Fuels

Control Fuel	Instrument	Temperature Difference at Percent Evaporated, °F														Number of Values Above Guidlines	
		IBP	5%	10%	15%	20%	30%	40%	50%	60%	70%	80%	90%	95%	EP	Observed	Acceptance Basis[a, d]
Guidelines in ASTM D86[a]		12	10	7	6	6	6	6	6	6	6	7	10	13	10	--	--
1	1	7	6	6	7[b]	6	7	4	4	4	6	9[c]	6	14[b]	12[c]	0	5 to 6
2	1	4	5	5	3	3	4	3	2	4	5	4	5	5	3	4	7
1	2	7	6	8[b]	4	3	3	4	3	3	4	3	1	2	8	1	3
2	2	5	6	4	3	3	3	4	5	6	7[b]	8[c]	4	5	6	2	3
1	1 & 2	12	18[c]	18[c]	13[c]	9[c]	7[b]	5	6	6	10[c]	11[c]	9	14[b]	28[c]	30	8 to 9
2	1 & 2	5	6	6	4	3	4	4	5	6	7[b]	8[b]	7	7	7	2	12
616	1 & 2	3	9	10[c]	8[c]	10[c]	10[c]	2	5	6	3	7	13[c]	9	16[c]	7	5 to 6

[a]Precision for ASTM D86 is under review.
Indications are that precision for IBP and EP may be indeterminate.
[b]One °F above values given in guidelines
[c]Two or more °F above values given in guidelines
[d]ASTM D86 bases the repeatability guidelines on 95% probability and makes the statement given in the preceeding note [a].

V. COMPARISON WITH MVMA SURVEY DATA

ASTM guidelines indicate that the samples from Baltimore should be class C in September while those from Detroit and Philadelphia may be either class C or D. There are some samples of Oxinol which were collected from ARCO stations in Philadelphia which are examined separately here. The data are further stratified by the type of petroleum company, that is whether it is a regional (e.g., small or independent) or national company as listed in the report.

MVMA does not take samples in September, so direct comparisons with MVMA data for the same month and city are not possible. However, it is possible to compare the results in this study with the data in the MVMA national survey for fuels with the same ASTM class. The distributions of the RVP, lead, methanol, ethanol, and butyl alcohol within the groups of data were compared to MVMA survey data from June and December of 1984. The MVMA data used for the comparison to the Philadelphia and Detroit distributions include all fuels taken from class C or D areas/seasons. The data from the two classes are simply combined for all of the parameters except RVP. RVP is the parameter most likely to be affected by the ASTM class. The comparison between the RVP data taken in this program and that of the MVMA survey is shown by the histograms in figure 3. The data used for the comparison to the Baltimore samples include only fuels from class C areas/seasons. These analyses show that the distributions of measurements from the national companies were distributed roughly equally to those of the regional companies, except as noted.

RVP

The Baltimore samples have RVP's which were slightly higher than those of the class C fuels in the MVMA surveys. Ninety percent of the Baltimore samples fall in the range of 10.4 - 12.6 psi; ninety percent of the MVMA class C fuels fall in the range of 9.5 - 12.0 psi. The RVP distributions of the Detroit and Philadelphia samples (not including the Oxinol samples which were taken in Philadelphia) fell between the distributions for class C and class D, but they were closer to that of class D. The ninety percent range for these two cities is 10.6 - 13.4 psi. The Oxinol samples had higher RVP's, ranging from 12.7 - 13.7.

Lead

The lead levels found in the samples taken by SwRI are close to but slightly higher than those found in the MVMA survey.

Figure 3. Histograms of RVP

Baltimore

MIDPOINT	Sample Distribution: National Brands	Sample Distribution: Regional Brands	MVMA Reference Distributions: Class C	MVMA Reference Distributions: Class D
8.8000	0 +	0 +	2 +XX	
9.2000	0 +	0 +	3 +XXX	
9.6000	0 +	0 +	14 +XXXXXXXXXXXXXX	
10.000	0 +	0 +	16 +XXXXXXXXXXXXXXXX	
10.400	1 +X	6 +XXXXXX	21 +XXXXXXXXXXXXXXXXXXXXX	
10.800	0 +	11 +XXXXXXXXXXX	27 +XXXXXXXXXXXXXXXXXXXXXXXXXXX	
11.200	7 +XXXXXXX	2 +XX	40 +XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX	
11.600	0 +	6 +XXXXXX	38 +XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX	
12.000	1 +X	1 +X	12 +XXXXXXXXXXXX	
12.400	1 +X	1 +X	4 +XXXX	
12.800	0 +	2 +XX	1 +X	
13.200	0 +	0 +	1 +X	
13.600	0 +	0 +	1 +X	
14.000	0 +	0 +	0 +	
14.400	0 +	0 +	0 +	
14.800	0 +	0 +	0 +	

Detroit

MIDPOINT	Sample Distribution: National Brands	Sample Distribution: Regional Brands	MVMA Reference Distributions: Class C	MVMA Reference Distributions: Class D
8.8000	0 +	0 +	2 +XX	0 +
9.2000	0 +	0 +	3 +XXX	0 +
9.6000	0 +	0 +	14 +XXXXXXXXXXXXXX	0 +
10.000	0 +	0 +	16 +XXXXXXXXXXXXXXXX	0 +
10.400	1 +X	1 +X	21 +XXXXXXXXXXXXXXXXXXXXX	1 +X
10.800	0 +	1 +X	27 +XXXXXXXXXXXXXXXXXXXXXXXXXXX	2 +XX
11.200	4 +XXXX	2 +XX	40 +XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX	2 +XX
11.600	0 +	4 +XXXX	38 +XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX	5 +XXXXX
12.000	1 +X	8 +XXXXXXXX	12 +XXXXXXXXXXXX	16 +XXXXXXXXXXXXXXXX
12.400	0 +	6 +XXXXXX	4 +XXXX	26 +XXXXXXXXXXXXXXXXXXXXXXXXXX
12.800	1 +X	2 +XX	1 +X	24 +XXXXXXXXXXXXXXXXXXXXXXXX
13.200	0 +	5 +XXXXX	1 +X	23 +XXXXXXXXXXXXXXXXXXXXXXX
13.600	0 +	0 +	1 +X	12 +XXXXXXXXXXXX
14.000	0 +	0 +	0 +	0 +
14.400	0 +	0 +	0 +	1 +X
14.800	0 +	0 +	0 +	1 +X
15.200			0 +	1 +X

Philadelphia (Oxinol Excluded)

MIDPOINT	Sample Distribution: National Brands	Sample Distribution: Regional Brands	MVMA Reference Distributions: Class C	MVMA Reference Distributions: Class D
8.8000	0 +	0 +	2 +XX	0 +
9.2000	0 +	0 +	3 +XXX	0 +
9.6000	0 +	1 +X	14 +XXXXXXXXXXXXXX	0 +
10.000	0 +	0 +	16 +XXXXXXXXXXXXXXXX	0 +
10.400	0 +	1 +X	21 +XXXXXXXXXXXXXXXXXXXXX	1 +X
10.800	1 +X	1 +X	27 +XXXXXXXXXXXXXXXXXXXXXXXXXXX	2 +XX
11.200	0 +	4 +XXXX	40 +XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX	2 +XX
11.600	2 +XX	4 +XXXX	38 +XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX	5 +XXXXX
12.000	2 +XX	9 +XXXXXXXXX	12 +XXXXXXXXXXXX	16 +XXXXXXXXXXXXXXXX
12.400	0 +	6 +XXXXXX	4 +XXXX	26 +XXXXXXXXXXXXXXXXXXXXXXXXXX
12.800	1 +X	2 +XX	1 +X	24 +XXXXXXXXXXXXXXXXXXXXXXXX
13.200	1 +X	2 +XX	1 +X	23 +XXXXXXXXXXXXXXXXXXXXXXX
13.600	0 +	0 +	1 +X	12 +XXXXXXXXXXXX
14.000	0 +	0 +	0 +	0 +
14.400	0 +	0 +	0 +	1 +X
14.800	0 +	0 +	0 +	1 +X
15.200			0 +	1 +X

Methanol

Less than 0.25% methanol is found at the ninety fifth percentile in all of the groups except the Oxinol. The Oxinol samples have roughly four percent methanol.

Ethanol

One of the seven national samples taken in Detroit had 7.7% ethanol. Eleven of the twenty nine regional samples had approximately 9% ethanol. None of the other samples contained significant amounts of ethanol. The MVMA survey shows only small amounts of ethanol (0.1%) at the ninety-fifth percentile.

Butyl Alcohol

Small amounts of butyl alcohol (up to 0.6%) are present in many of the samples measured by SwRI. One of the national brand samples from Philadelphia contains 2.1% butyl alcohol, and one of the regional brand samples from Philadelphia contains 1.6%. The samples of Oxinol have roughly 3.7% butyl alcohol. The rest have levels below 1%. The MVMA survey reports no more than 0.1% butyl alcohol at the ninety-fifth percentile.

APPENDIX A

Work Plan

SOUTHWEST RESEARCH INSTITUTE

POST OFFICE DRAWER 28510 • 6220 CULEBRA ROAD • SAN ANTONIO, TEXAS, USA 78284 • (512) 684-5111 • TELEX 76-7357

ENGINES, EMISSIONS AND VEHICLE RESEARCH DIVISION
TWX: 910-871-1084

March 19, 1985

TO: Mr. Albert W. Ahlquist, Contracting Officer
Contracts Management Division
Contracts Branch A
Environmental Protection Agency
Cincinnati, OH 45268

FROM: Charles M. Urban and Charles T. Hare
Department of Emissions Research
Southwest Research Institute
6220 Culebra Road
San Antonio, TX 78284

SUBJECT: Revision B to the Work Plan in response to Work Assignment No. 8 of Contract 68-03-3192, received by SwRI on December 20, 1984 and revised by verbal technical directives in February and March 1985; SwRI Project 03-7774.

Contract Title: "Pollution Control Assessment for the Emission Control Technology Division, Ann Arbor, Michigan"

Assignment 8 Title: "Analysis of Fuel Samples" (Analysis of In-Use Gasolines and Gasoline/Methanol Blends)

I. INTRODUCTION

Southwest Research Institute will comply with the revised technical and quality assurance (Q/A) type requirements of Work Assignment Number 8, and will put forth efforts to do so within the 1985 fiscal year. It will be necessary, however, to coordinate this effort with analyses of fuel samples from MVMA and other currently scheduled fuel surveys. The initial Scope of Work for Work Assignment Number 8 is attached as an Appendix for information purposes.

II. STATEMENT OF TECHNICAL APPROACH

This Work Plan describes the manner in which our understanding of the requirements will be met. Should there be a necessity for changes in the Work Plan which are within the level of effort proposed, they can be documented in a letter or a monthly progress report.

A. Gasoline and Blend Analysis

The following analyses will be performed on each of the one hundred thirty (130) gasoline samples collected from three cities under

Work Assignment No. 14 of Contract 68-03-3162, and on selected reference and control samples:

1. RVP - Automatic RVP Instrument Method. The Automatic RVP instrument developed at SwRI is used to analyze all MVMA survey samples.

2. Distillation - ASTM D-86.

3. Methanol, Ethanol, and Tertiary Butyl Alcohol (Volume Percent) - Water Extraction/Gas Chromatography. This SwRI-developed analytical procedure is based on extraction of the gasoline with 2 volumes of water and gas chromatography of the extract using a flame ionization detector.

4. Water (Weight Percent) - ASTM D-1744, Karl Fischer Titration.

5. Lead Content (Weight %) - ASTM D-3237, Atomic Absorption Spectrometry.

6. FEVI and EI volatility indices - In accord with the Statement of Work, no calculations of indices have been included in this Work Plan.

The procedures described are the same as were previously used in the fuel analyses conducted under Work Assignment No. 14 of EPA Contract No. 68-03-3162. They were reported in the final report EPA 460/3-84-009.

B. Discussion of the Procedures and Q/A

The ASTM maintains system accuracy by equipment calibration and/or by internal standards as appropriate to the specific analyses. This approach is essentially the same as used in the Code of Federal Regulations for emissions measurements. The quality assurance guidelines given in QAMS-005/80 and in referenced handbooks and manuals are specific only for environmental measurements. A major difficulty relative to this Work Assignment has been that definitive guidelines for applying EPA QA requirements to fuel analyses were not available.

The ASTM incorporates quality control into its procedures, to the maximum extent they consider to be practical for widespread use. When attempting to apply Section 5.11 of QAMS-005/80 to a project, several questions arise:

- What specific level of control is essential?
- Who is to determine level of control applied?
- Is the same level of control to be applied to all analyses?
- What degree of quality assurance is to be applied to the reference standards used?

The initial approach taken in developing this Work Plan was to attempt to provide an adequate response without having definition of the specific requirements. This revision incorporates the specific requests from the EPA Project Officer.

C. Test Plan - Including Quality Control and Assurance Provisions

As has been decided, several specific quality control and assurance efforts have been incorporated into this Work Assignment. The revised test plan incorporating those provisions is as follows:

1. Obtain or develop reference fuel samples (to determine procedural accuracy and repeatability):

   - RVP - Fuel R1 - pure grade 2,2-dimethybutane (Neohexane), 9,9 psi at 100°F

   - Distillation - none (D86 provides empirical results)

   - Alcohols - Fuel R2 - 5% pure grade methanol and 5% pure grade TBA in unleaded Indolene

     Fuel R3 - 10% pure grade ethanol in unleaded Indolene

   - Water content - Fuel R4 - Fuel R2 plus 0.100 weight percent water

   - Lead content - Fuel R5 - Reference samples from the EPA

2. Develop control fuel samples (run periodically for repeatability and reproducibility):

   - Fuel C1 - unleaded Indolene

   - Fuel C2 - same fuel batch as Reference Fuel R2

3. Conduct Reference and Control Fuel analyses:

   - RVP (automatic and ASTM D323) - Two repetitive evaluations of the following fuel set - R1, C1, C2

   - Distillation - Two repetitive evaluations of the following fuels - C1, C2

   - Alcohols - Two repetitive evaluations of the following fuel set - R3, C1, C2

   - Water Content - Two repetitive evaluations of the following fuel set - R4, C1, C2

   - Lead Content - Two repetitive evaluations of the following fuels - R5, C1, C2

NOTE: A third evaluation will be run for any result falling outside the Q/A repeatability objectives.

4. After accuracy and repeatability have been established, evaluate the fuel samples. To the extent possible, conduct the evaluation in sets per city sampled (control fuels to be used are Indolene, C1, and Indolene + 5% M&TBA, C2):

BALTIMORE (≈40 fuels)

a. Check time elapsed since last analyses of control samples*

b. Analyze 20 fuel samples (without ASTM D323)

c. Replicate tests of control fuels (with ASTM D323)

d. Repeat b and c

* If over one week, run single test of control fuels (with ASTM D323)

DETROIT (≈40 fuels)

Same sequence as for BALTIMORE

PHILADELPHIA (≈40 majors & minors)

Same sequence as for BALTIMORE

PHILADELPHIA (≈10 Oxinol samples)

Steps a, b (except only 10 fuel samples), and c of the sequence used for BALTIMORE

NOTE: Run a repeat of any control sample result falling outside the Q/A reproducibility objectives. If the repeat result is outside the Q/A objectives for reproducibility, determine the reason and resolve the cause for being outside the control limits.

D. Reporting

Data will be reported in the monthly progress reports in the form of a complete set of all data for each of the cities in which fuel samples were taken. All data generated under this Work Assignment, along with a Q/A assessment, will be provided as a Submittal of Test Results at the end of the project. The format for this submittal will be similar to that used in Work Assignment No. 18 under EPA Contract 68-03-3162. This submittal will provide a brief description of what was done and will report all the data generated. It is planned to report the data separately for each of the three cities using the formats previously used in Tables 1

through 3 in the Final Report EPA 460/3-84-009. In accord with the Statement of Work, no provisions are included in this Work Plan for any analyses of other than the Q/A results.

III. SCHEDULE OF COMPLETION

The Statement of Work for Assignment Number 8 requests a technical effort period of performance of 3 months. We project that obtaining the reference standards, blending the control fuels, verifying accuracy and repeatability, and conducting the analyses of the gasoline and control samples, will require five months.

IV. STAFF ASSIGNMENTS

The Task Leader and principal investigator of the Division 08 effort called for in Work Assignment No. 8 will be Kathleen M. Olson. Project Manager is Charles T. Hare of the Department of Emissions Research, and the Division 03 Task Leader will be Charles M. Urban.

V. PROJECTED LABOR HOURS BY CATEGORY AND OTHER DIRECT COSTS

Based on our understanding of the requirements of the Work Assignment, we project the following breakdown of employee utilization by category:

Labor Category	Div. 03 Employee Hours Projected
Professional Level 4	6
Professional Level 3	12
Professional Level 2	40
Professional Level 1	16
Senior Technical	16
Technical	16
Clerical	32
Laboratory Assistant	8
Total	146

We also project the following other elements of direct cost, not including fee:

Direct Cost Elements	Cost, Exclusive of Fee
Fuel Analyses (Div 08)	$36,456
Purchased parts and supplies	650
Photography, report services, and communications	140
Total	$37,106

VI. SUMMARY

Southwest Research Institute has replied in accord with our understanding of Work Assignment No. 8, as revised verbally, Contract No. 68-03-3192, in a full and complete manner. Should any technical questions arise, please contact Mr. Hare at Area Code 512, 684-5111, extension 2646, or Mr. Urban at exntesion 2644. If cost questions arise, please contact Gerald R. Krisch at extension 2236.

Submitted by:

Charles M. Urban
Senior Research Engineer
Department of Emissions Research
Engines, Emissions and Vehicle
Research Division

Charles T. Hare
Manager, Advanced Technology
Department of Emissions Research
Engines, Emissions and Vehicle
Research Division

APPENDIX B

ANALYTICAL PROCEDURES

B-1 Alcohol Content of Unleaded Gasoline

APPENDIX B-1
ALCOHOL CONTENT IN UNLEADED GASOLINE

% Methanol, Ethanol, and TBA in Gasoline

Scope

An internal standard, isopropanol, is added in known concentrations, along with a pre-determined volume of gasoline sample, to distilled water. The alcohols present in the gasoline are extracted with the distilled water and the extract is introduced into a gas chromatography column. The eluted alcohols are detected by a flame ionization detector and peak areas are measured with an integrator. The peak areas are applied to the appropriate calibration curve, from which the volume percent is obtained.

Method

1. Insert the column for alcohols in side "A" of G.C. - Column-SS Porapak QS 80-100 mesh.
2. Set instrument on FID.
3. Carrier gas is helium - Auxiliary gases are hydrogen and air to light the detector.

Conditions

He -	Carrier gas	25 cc/min at 60 psi
	Hydrogen	30 cc/min at 13.5 psi
	Air	250 cc/min at 28 psi

Temperature

Oven 175°C
Injection Port 200°C
Detector 250°C

Integrator

Delay - off
Stop - 5 min.
Area reject - 100 - (10^2)
Chart Speed - 1 cm/min
Slope Sens. - 1.00
Attenuation - 64

FID

Range - 10
Single Channel
Atten. set on integrator
Zero - as needed for baseline
A & B side (not Diff.)

Sample Size

0.75 μℓ

1. Light detector and wait 15 min for instrument to stabilize. During this period make up standard and extract the sample and standards.

Standard Preparation

Stock Standards - all of the standards must be extracted before being injected.

Std. Conc.	MeOH, ETOH, & TBA
0.0%	--
0.1%	25 μℓ
0.5%	125 μℓ
1.0%	250 μℓ
3.0%	750 μℓ
5.0%	1250 μℓ
7.0%	1750 μℓ
10.0%	2500 μℓ
12.0%	3000 μℓ

Dilute to 25 mℓ with Indolene.

Extraction of Alcohol - for Std. & Samples

10 mℓ of deionized H_2O, along with 5 mℓ of sample or std. and 50 μℓ of isopropyl alcohol are added to a 1 oz. jar. The mixture is shaken for 10 min. on a mechanical shaker and then allowed to stand for 30 min. to assure separation into layers. Part of the lower water layer is then removed for injection into the G.C.

All standards and samples are run, recording the peak areas for MeOH, ETOH, TBA, and isopropyl alcohol (Int. Std.)

Calculation

Divide the area of the MeOH peak by the area of the Int. Std. to get a ratio. Do this for the other two alcohols. The ratio is the number used for calculating percent alcohol.

Run a linear regression on the standard curve for each of the three alcohols. There will be three answers for each sample - % MeOH, % ETOH, and % TBA.

Notes

Do not use acetone to clean the syringe between samples - use the next sample to be injected and rinse the syringe 4-5 times before injecting the sample.

APPENDIX B-2
AUTOMATIC RVP INSTRUMENT METHOD

(Excerpts from the Maintenance and Operating Instructions)

DESCRIPTION

The Reid Vapor Pressure Instrument operates automatically - after sample loading - to determine the Reid Vapor Pressure of gasolines and other hydrocarbons. The instrument reproduces manual ASTM test data.*

CALIBRATION PROCEDURES, FULL RANGE

This instrument measures the vapor pressure in psia of hydrocarbons at 100°F, expanded to five times its liquid volume. An equation relating absolute pressure to Reid Vapor Pressure has been developed by computer analysis of instrument data versus ASTM D-323 data for a large number of hydrocarbon samples. The instrument zero and span controls have been adjusted to convert absolute pressure signals from the pressure transducer to equivalent RVP values for the direct display of RVP on the meter.

OPERATION

Sample handling, including filling the sample cup, follows the ASTM D-323 procedure - except the cup is kept dry. (No water can be permitted in the sample or sample system, and the sample need not be air-saturated).

The cup containing the sample is coupled to the instrument inlet fitting, and a push-button "start" switch is momentarily depressed. The start light will illuminate. At the end of 4 minutes, this light will go out, indicating completion of the analysis. The RVP value for the sample will be locked on the digital panel meter and may be read and recorded anytime before starting the next test.

Depression of the "start" switch provides the impulse to start a 4-minute cycle. The timer operates to produce the required analysis program.

*ASTM Method D-323, "Test for Reid Vapor Pressure of Petroleum," Part 23 of ASTM Book of Standards.

APPENDIX C

Fuel Sample Identification

TABLE C-1. FUEL SAMPLE IDENTIFICATION

Baltimore

MAJORS

Sample Number	Fuel Type	Fuel Brand	Gas Station Address
1	R	Amoco	Gallagar's Amoco 5931 Balto National Pike
2	R	ARCO	Reedy Interprise 7001 Liberty Rd.
3	R	BP	Corbin Auto Repair 18830 York Rd.
4	P	Exxon	Eastern Ave. & Kane Exxon 6408 Eastern Ave.
5	R	Getty	Rockdale Getty 8201 Liberty Rd.
6	R	Gulf	Highland Gulf 400 N. Highland Ave.
7	R	Mobil	Vern's Lutherville Mobil 1545 York Rd.
8	P	Shell	Frankford Shell Service Auto Care 5330 Frankford Ave.
9	R	Sunoco	John's Triangle Sunoco 6401 Kenwood Ave.
10	R	Texaco	Hollenshade's Texaco 1501 Joppa Rd.
			MINORS
11	R	Merit	Harford Merit 2102 Harford Rd.
12	P	Merit	Merit Patapsio 3205 Washington Blvd.
13	R	Crown	Serverna Pk. Crown Ritchie Hwy. - Annapolis Blvd.

TABLE C-1 (CONT'D). FUEL SAMPLE IDENTIFICATION

Baltimore

MINORS

Sample Number	Fuel Type	Fuel Brand	Gas Station Address
14	R	Crown	Hillendale Crown 6819 Lock Raven Blvd.
15	R	Crown	Orleans Crown 1920 Orleans St.
16	P	Crown	Perry Hall Crown 8644 Belair Rd.
17	R	Citgo	Marco Citgo 9301 Liberty Rd.
18	R	Merit	Merit Reisterstown 5128 Reisterstown Rd.
19	R	Crown	Charring Cross Crown 5217 Balto National Pike
20	R	Hess	Ken's Hess 9715 York Rd.
21	P	Crown	Catonsville Crown 500 Frederick Rd.
22	R	Crown	Ed's Crown 4500 W. Northern Pkwy.
23	R	Crown	Merritt Crown 1521 Merritt Blvd.
24	R	Crown	Towson Crown 935 York Rd.
25	P	Merit	Charles St. Merit 1801 N. Charles
26	R	BP	Calvert's BP Station 8716 Liberty Rd.
27	R	Crown	Rodgers Forge Crown 7210 York Rd.

TABLE C-1 (CONT'D). FUEL SAMPLE IDENTIFICATION

Baltimore

MINORS

Sample Number	Fuel Type	Fuel Brand	Gas Station Address
28	R	Merit	Merit Franklintown 510 Franklintown Rd.
29	R	Citgo	Whiz Milford Car Wash & Citgo 8120 Liberty Rd.
30	R	Citgo	Whiz Dolfield Car Wash & Citgo 3321 W. Colespring La
31	R	Citgo	Fell Pt. Auto Repair 1500 Eastern Avenue
32	R	BP	Jimen Enterprises 8913 Belair Rd.
33	R	No Brand	Racetrac 8235 Eastern Ave.
34	R	Big Red	Big Red Compass 1 Compass Rd.
35	R	Crown	Tony's Crown 8623 Lock Raven Blvd.
36	P	BP	Weddmon BP Gas & Go 6861 Lock Raven Blvd.
37	R	Seven-Eleven	7-11 2701 W. Franklin St.
38	R	Merit	Merit Eastern 5802 Eastern Ave.
39	P	Crown	Danny's Crown 7601 Eastern Aven.

TABLE C-2. FUEL SAMPLE IDENTIFICATION

Detroit

MAJORS

Sample Number	Fuel Type	Fuel Brand	Gas Station Address
40	R	Boron	Gas and Go Harper at Metro Pkway
41	R	Shell	Richard Aronki Shell 4000 N. Woodward, Royal Oak
42	R	Union 76	Dallas 10350 Woodward at Harmon
43	R	Sunoco	Aranki Service 2931 E. Six Mile
44	R	Union 76	Pat's Service 1102 Nine Mile, Hazel Park
45	P	Amoco	Auto Elec. Center 4399 Highland Rd, Pontiac
46	P	Mobil	Tillard's Mobil Adams at Maple, Birmingham
			MINORS
47	R	Total	Total 14900 Gratiot
48	R	No Brand	Frank's Full Service 26701 Gratiot, Roseville
49	P	Speedway	Speedway 31015 Hoover & 13 Mi. Warren
50	R	Martin	Blue Island Mini-Mart 5938 Michigan (at Joe St.)
51	R	No Brand	You Save - Rubin Service 6641 Michigan Ave. At Clippert
52	R	Total	Total #1187 Plymouth at Southfield

TABLE C-2 (CONT'D). FUEL SAMPLE IDENTIFICATION

Detroit

MAJORS

Sample Number	Fuel Type	Fuel Brand	Gas Station Address
53	P	Total	#11601 Wyoming at Plymouth
54	R	Total	Total 19018 Woodward at 7 Mile
55	R	Speedway	#2268 22000 Lahser Rd.
56	P	Total	Total 27360 Grand River
57	R	Clark	Clark 27480 W. Seven Mile, Livonia
58	R	Citgo	Phil's Auto Service 29835 W. 8 mi. at Louise
59	R	Tulsa	Tulsa 3640 Six Mile, McNichols
60	P	Total	Total 15 Mi. & Kelly, Fraser
61	R	Speedway	Speedway Service 34977 Groesbeck, Fraser
62	R	Clark	Clark 30990 Utica Rd., Roseville
63	R	Total	Total 12 mi & Utica
64	R	Pennzoil	Pennzoil DeQuindre at Greig
65	R	Clark	Clark Super 100 6800 Highland, Pontiac
66	R	No Brand	K & C 3910 Grand River, Avery

TABLE C-2 (CONT'D). FUEL SAMPLE IDENTIFICATION

Detroit

MAJORS

Sample Number	Fuel Type	Fuel Brand	Gas Station Address
67	R	Gas & Go	Gas & Go 3200 W. Warren
68	P	Host	Dearborn Wheels 6425 Telegraph, Dearborn Hgts.
69	R	Citgo	Citgo Enterprises Telephone Rd.
70	R	Martin	Martin 26050 Ford Rd.
72	P	Hi-Fy	Hi-Fy 34010 Ford
73	R	Clark	Clark Super 100 111 Middlebelt, Garden City
74	R	Total	Total Cherry Hill and Venoy
75	R	Total	Total N. Mill and Wilcox, Plymouth

TABLE A-3. FUEL SAMPLE IDENTIFICATION

Philadelphia

MAJORS

Sample Number	Fuel Type	Fuel Brand	Gas Station Address
76	R	BP Oil	BP Oil #6896 Delaware Ave & Springgarden St.
77	R	Gulf	#00429548 48th & Spruce
78	R	Amoco	E.K. Dowski 154 Girard Ave.
79	P	Exxon	Al Coyle Exxon Washington LA & Old York Rd., Jenkintown
80	R	Sunoco	#642-0010-1709-S Township Line & Cadwalder Ave., Elkins Pk.
81	R	Mobil	Geo Stayton's Mobil 1025 Standbridge & W. Steriglre
82	R	Texaco	Quaker City Texaco Chew St. and Washington LA

MINORS

83	R	Citgo	Paoli Citgo Quik Mart Lincoln Hwy. & Leopard Rd., Paoli
84	R	Hess	#38277 254 Easton Rd.
85	R	BP Oil	#6930 8005 Ogontz Ave.
86	P	Alert	Alert Oil Co. Broad St. & Godfrey
87	R	Merit	Merit Self-Serve Cheltenham Ave. & 15th St.
88	R	Hess	#38284 Lincoln Hwy & Lakeside Rd., Berwyn (Rt. 30)

TABLE C-3 (CONT'D). FUEL SAMPLE IDENTIFICATION

Philadelphia

MINORS

Sample Number	Fuel Type	Fuel Brand	Gas Station Address
89	R	Hess	#38214 Rt. 202 & 422, Norristown
90	P	Citgo	Norristown Citgo Markley St. & Spruce, Norristown
91	R	Golden	Cinelli's Garage 2501 W. Main St. (Ridge Pk), Norristown
92	R	BP Oil	6870 BP Oil Inc. Rt. 309 & Broad St., Colmar (Lansdale)
93	R	Seven-Eleven	(7-11) - #20435 Bethlehem Pk. and Butler, Ambler
94	P	BP Oil	#6912 Bethlehem Pk. & Penn Ave., Ft. Washington
95	R	Citgo	Citgo Quick-Mart Easton Rd. and Keswick, Glenside
96	R	Merit	Merit Self-Serve Broad St. & Godfrey Ave.
97	R	Merit	Merit Bainbridge Broad St. & Bainbridge
98	P	Hess	#38211 Torresdale Ave. & Harbison Ave.
99	R	Merit	Lehigh Merit Lehigh & 5th St.
100	R	T.F.C.O.	T.F.C.O. Fuel Co. 4201 Aramingo
101	R	Merit	Merit Self-Serve Frankford & Tyson
102	P	Hess	#38229 Rt. 1 Feasterville & Trevose, PA.

TABLE C-3 (CONT'D). FUEL SAMPLE IDENTIFICATION

Philadelphia

MINORS

Sample Number	Fuel Type	Fuel Brand	Gas Station Address
103	R	Hess	#38216 Rt. 132 & 513, Bensalem
104	R	BP Oil	#6902 7999 Newfalls Rd., Levittown
105	R	Hess	#38275 Rd. 1 & Woodbourne, Langhorne
106	P	BP Oil	#6915 St. Rd. & Central Ave., Feasterville
107	R	Citgo	Quik Mart #15-0710 2nd St. Pk, Madison Ave. & Rozel, Southampton
108	R	Merit	#3794 52nd St. & City Line Ave.
109	R	Alert	Alert Oil Company Rt. 291 & Jansen, Essington
110	P	Merit	Merit Township Township Line Rd.& State Rd., Drexel Hill
111	R	Citgo	Quik-Mart #16-0692 Township Line Rd. & Fairway, Drexel Hill
112	R	Wm. Penn	Otto's BP MacDade & Spruce St., Holmes
			OXINOL
113	R	ARCO	A.M.-P.M. Mini-Market - Ramsue Chestnut & Farragut Ave.
114	R	ARCO	PSI #470 A.M.-P.M. Mini-Market 2101 S. 17th St.
115	R	ARCO	Steve's ARCO St. Rd. & 2nd St. Pike, Southampton

TABLE C-3 (CONT'D). FUEL SAMPLE IDENTIFICATION

Philadelphia

OXINOL

Sample Number	Fuel Type	Fuel Brand	Gas Station Address
116	R	ARCO	A.M.-P.M. Mini-Market Broad St. & Lehigh Ave.
117	P	ARCO	Blvd. ARCO Rt. 1 Festrvl Trevose
118	R	ARCO	Paul Lopresti A.M.-P.M. Mini-Market Passyunk Ave. & 28th St.
119	R	ARCO	A.M.-P.M. Mini-Market 1311 Bethlehem Pike
120	R	ARCO	Roxy Mini-Mart 6201 Ridge Ave., Phil.
121	P	ARCO	------ W. Wood St. & Markley St., Norristown
122	R	ARCO	Warks Arco Fayette St. & Northlane, Conshohocken
123	R	ARCO	A.M.-P.M. Mini-Market Broad St. & Oxford St.

APPENDIX D

Distillation Data

TABLE D-1. DISTILLATION TEMPERATURES OF CONTROL

IBP	5%	10%	15%	20%	30%	40%	50%	60%	70%	80%	90%	95%	FBP	Residue (%)	Recovered (%)
Instrument 1															
98	128	144	156	168	194	212	226	239	254	279	322	349	396	1.5	98.5
95	125	142	153	167	196	214	227	239	254	267	322	350	394	1.5	98.0
97	131	146	160	172	194	211	223	235	248	275	317	343	385	1.0	99.0
98	131	148	160	172	192	212	224	235	250	274	319	343	384	1.0	99.0
95	130	146	160	171	194	211	223	238	250	273	318	340	385	1.0	99.0
91	129	143	158	170	191	210	225	236	248	270	316	337	386	1.0	99.0
92	131	146	160	173	195	212	225	237	250	278	321	351	386	1.0	98.0
92	129	146	160	172	198	214	227	238	251	276	318	343	388	1.0	99.0
Instrument 2															
86	116	133	150	166	196	213	224	236	248	270	314	338	376	1.0	98.5
88	113	130	147	163	193	210	221	233	244	267	314	338	368	1.0	99.0
93	119	138	152	166	193	209	221	234	246	270	314	338	374	1.0	98.0
90	115	134	151	166	194	210	222	233	246	268	313	336	372	1.0	99.0

TABLE D-2. DISTILLATION TEMPERATURES OF CONTROL 2

IBP	5%	10%	15%	20%	30%	40%	50%	60%	70%	80%	90%	95%	EP	Residue (%)	Recovered (%)
Instrument 1															
99	118	124	132	140	163	195	216	230	243	264	306	335	379	1	99
96	115	123	132	140	161	195	217	230	244	265	307	333	380	1	99
98	120	128	134	141	165	193	216	232	246	268	311	335	379	1	99
95	117	125	132	140	165	196	217	230	244	266	310	338	378	1	99
95	117	124	132	139	163	195	217	230	242	264	311	337	379	1	99
96	115	123	131	138	163	195	218	231	245	267	310	335	381	1	99
97	117	124	131	138	161	195	217	234	246	268	310	337	380	1	99
97	117	124	132	138	163	196	218	233	247	268	311	338	379	1	99
97	117	124	131	139	163	196	217	231	245	267	310	337	380	1	99
97	117	124	131	139	163	196	218	231	245	266	310	337	380	1	99
Instrument 2															
100	118	126	133	141	165	196	218	233	247	270	313	340	--[a]	1.5	98.5
100	116	125	131	139	165	197	219	234	248	269	312	338	376	1	99
95	112	122	130	138	163	193	214	228	241	262	309	335	374	1	99
100	114	122	131	138	162	194	215	230	243	266	312	338	380	1	99

[a] No data

TABLE D-3. DISTILLATION TEMPERATURES OF FUEL EM-616-F

IBP	5%	10%	15%	20%	30%	40%	50%	60%	70%	80%	90%	95%	EP	Residue (%)	Recovered (%)
Instrument 1															
88	114	127	136	147	165	186	209	236	263	289	324	350	406	1	99
90	115	127	135	146	164	188	210	238	264	291	326	352	398	1.5	98
90	118	130	138	150	172	--[a]	207	236	264	296	334	--[a]	414	1	99
90	114	128	137	148	168	186	208	237	263	295	327	355	409	1	99
Instrument 2															
90	111	124	132	144	164	186	210	237	262	289	321	346	408	1	99
91	112	125	133	144	165	188	212	237	264	290	328	348	401	1.5	98
89	110	123	133	143	164	187	210	236	263	296	332	354	405	1	98
91	109	120	130	140	162	186	207	232	261	291	327	350	404	1	99

[a] No data