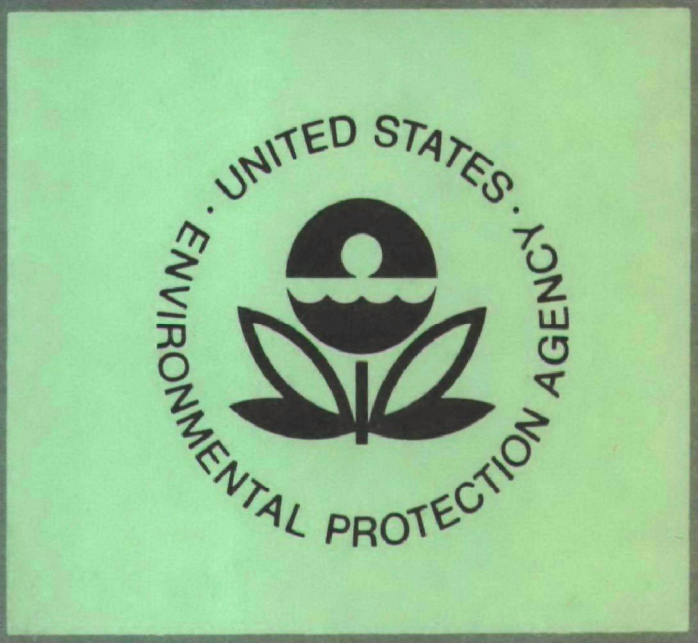
EPA-600/3-75-010c
September 1975

Ecological Research Series

ANNUAL CATALYST RESEARCH PROGRAM REPORT APPENDICES Volume II



Health Effects Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ECOLOGICAL RESEARCH series. This series describes research on the effects of pollution on humans, plant and animal species, and materials. Problems are assessed for their long- and short-term influences. Investigations include formation, transport, and pathway studies to determine the fate of pollutants and their effects. This work provides the technical basis for setting standards to minimize undesirable changes in living organisms in the aquatic, terrestrial and atmospheric environments.

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September 1975

ANNUAL CATALYST RESEARCH PROGRAM REPORT APPENDICES
Volume II

by

Criteria and Special Studies Office
Health Effects Research Laboratory
Research Triangle Park, North Carolina 27711

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
HEALTH EFFECTS RESEARCH LABORATORY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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Appendix B1.1

Fuel Surveillance and Analysis

A national fuel and fuel additive sample collection network has been established. Commercial samples of fuels, consumer-purchased additive packages, and crankcase lubricants are collected at the retail outlets. These samples are shipped to NERC-RTP for detailed analysis. This program, of necessity, has devoted considerable effort toward development of advanced analytical procedures and standardized reference materials which will assure an appropriate and accurate analytical data base. Analysis has focused on lead, phosphorus, sulfur, trace metals, and fuel distillations.

It is the intent of this activity to provide actual commercial product analysis for comparison with registration information. In the case of lead and phosphorus analysis, such information provides a basis for assessing compliance with the two EPA regulations regarding the special fuel for catalyst vehicles (FR, January 10, 1973) and the lead phase-down regulations (RF, Dec. 6, 1973).

In addition, the data gathered through this network and from other sources, regarding the sulfur levels in the unleaded fuel required for catalyst vehicles permits a more realistic estimate of the impact of catalyst generated sulfuric acid on human exposures. This, of course, is due to the fact that the sulfur content of the fuel is a determinant of the sulfuric acid emission rate.

Analysis of gasolines collected in Los Angeles and San Francisco areas, consumer purchased additive packages, motor vehicle crankcase lubricants, and distillate fuel oils are shown on the following pages. Gasoline sulfur levels, by grade, are summarized from the EPA Surveillance Network and U.S. Bureau of Mines Survey in the final table.

Gasoline Analysis

Los Angeles Metropolitan Area

Sample No.	Grade	Sulfur %	Lead gm/gal	Distillation °F IBP	10%	50%	90%
F73-000-504	No Lead	0.005	0.015	107	152	230	300
F73-000-505	No Lead	0.006	0.011	103	144	228	305
F73-000-517	No Lead	0.071	0.019	105	140	218	318
F73-000-519	No Lead	0.073	0.019	98	135	217	323
F73-000-523	No Lead	0.070	0.015	108	144	217	321
F73-000-501	Low Lead	0.025	0.462	96	132	238	328
F73-000-506	Low Lead	0.078	0.385	100	133	228	350
F73-000-508	Low Lead	0.075	0.418	101	132	229	349
F73-000-515	Low Lead	0.051	0.451	93	122	204	311
F73-000-419*	Low Lead	0.062	0.836	92	128	230	364
F73-000-518	Low Lead	0.068	0.473	92	124	218	320
F73-000-509	Regular	0.073	0.92	89	129	241	350
F73-000-511	Regular	0.100	1.17	95	128	227	361
F73-000-514	Regular	0.090	1.53	95	128	207	367
F73-000-522	Regular	0.021	3.72**	102	148	215	277
F73-000-502	Premium	0.020	2.86	98	131	237	339
F73-000-507	Premium	0.070	2.09	99	126	219	344
F73-000-510	Premium	0.021	2.50	94	126	223	339
F73-000-513	Premium	0.023	1.79	92	130	231	333
F73-000-516	Premium	0.041	2.86	90	117	245	323
F73-000-520	Premium	0.026	2.04	101	170	246	337
F73-000-521	Premium	0.017	1.87	106	170	263	335

* Sample taken in San Diego, Ca.
** Run in duplicate.

Gasoline Analysis

San Francisco Metropolitan Area

Sample No.	Grade	Sulfur %	Lead gm/gal	Distillation °F IBP	10%	50%	90%
F73-000-414	No Lead	0.007	0.015	100	137	216	324
F73-000-423	No Lead	0.007	0.013	106	140	217	328
F73-000-401	Low Lead	0.012	0.484	47	134	205	312
F73-000-405	Low Lead	0.005	0.462	100	132	207	325
F73-000-407	Low Lead	0.009	0.561	98	134	209	331
F73-000-408	Low Lead	0.029	0.594	103	138	228	330
F73-000-411	Low Lead	0.030	0.539	102	137	230	333
F73-000-412	Low Lead	0.021	0.550	105	133	202	325
F73-000-415	Low Lead	0.008	0.495	100	130	201	320
F73-000-402	Regular	0.019	2.19	98	136	238	355
F73-000-406	Regular	0.012	1.53	102	135	220	326
F73-000-410	Regular	0.077	1.53	103	132	213	345
F73-000-416	Regular	0.004	1.38	98	136	229	326
F73-000-417	Regular	0.005	0.816	104	138	230	323
F73-000-422	Regular	0.013	2.04	91	128	228	355
F73-000-421	Blend	0.028	1.53	100	139	229	325
F73-000-403	Premium	0.004	1.68	100	140	225	320
F73-000-404	Premium	0.004	2.50	100	129	206	339
F73-000-409	Premium	0.027	2.75	100	136	233	343
F73-000-413	Premium	0.010	2.75	105	132	193	310
F73-000-418	Premium	0.006	0.969	104	145	255	329
F73-000-420	Premium	0.005	1.79	97	143	234	340

ADDITIVE IDENTIFICATION
RTP, N. C. AREA

Sample	Description
F73-000-006	Wynns Engine Tune Up
F73-000-013	Prestone Carb Tune Up
F73-000-016	Dupont Gas Booster
F73-000-477	Preston Carburetor and Fuel System Cleaner
F73-000-478	Marvel Mystery Oil
F73-000-479	STP Oil Treatment
F73-000-480	Rislone Engine Treatment
F73-000-481	Prestone Prime Gas Dryer
F73-000-482	STP Double Power Gas Treatment
F73-000-483	Wynn's Engine Tune Up
F73-000-484	Wynn's Concentrated Supreme Oil Supplement
F73-000-485	Wynn's Gasoline Treatment
F73-000-486	Wynn's Carburetor Cleaner
F73-000-487	Gumout Carburetor Cleaner
F73-000-488	Alemite CD-2 Oil Detergent
F73-000-489	Dupont Oil Treatment
F73-000-490	Dupont Gas Guard
F73-000-491	Casite Motor Honey
F73-000-492	Casite Tune-Up

EPA FUEL ADDITIVES+

SAMPLE NO.	Mg	Mn	Na	Ni	Rb	Sb	Sc	Se	Sm	Sn	Sr	Ta	Tb	Th	V	Zn	DENSITY g/mℓ
F-73-000-006	<20	<0.01	<0.09	<0.09	<0.009	<0.0009	<0.0001	<0.009	<0.0002	<0.4	<0.3	<0.0009	<0.0007	<0.0007	<0.01	0.14 ± 0.02	0.873
" -006*		<0.003	0.024	<0.02	<0.003	<0.0001	<0.00001	<0.002	<0.0002	<0.07	<0.06	<0.0001	<0.0001	<0.0002	<0.003	0.35	
" -013	<20	2.60	7.4	<0.7	<0.2	<0.003	<0.0004	<0.03	<0.0005	110	<1	<0.004	<0.0008	<0.002	0.036 ± 0.010	4.1	0.828
" -013*		2.71	10	<0.1	<0.04	0.002	<0.00005	<0.003	<0.0004	140	<0.2	<0.0005	<0.0003	<0.0004	0.016 ± 0.004	4.2	
" -016	<20	<0.01	0.26	<0.2	<0.04	0.006 ± 0.002	<0.0002	<0.02	<0.0003	<0.8	<0.7	<0.0008	<0.0008	<0.002	<0.01	11	0.838
" -016*		0.012 ± 0.002	0.32	<0.2	<0.04	0.003	<0.0001	<0.007	<0.0002	<0.4	<0.4	<0.0004	<0.0005	<0.0008	<0.01	15	
" -477	<20	0.016 ± 0.004	0.15	<0.3	<0.04	<0.0009	<0.0002	<0.04	<0.0008	<2	<1	<0.002	<0.003	<0.003	<0.01	2.5	0.887
" -478	<60	<0.03	0.79	<0.2	<0.04	<0.0009	<0.0002	<0.04	<0.0003	<2	<1	<0.002	<0.003	<0.003	<0.03	8.8	0.848
" -479	<20	<0.01	0.82	<4	<0.4	<0.009	<0.003	<0.09	<0.0007	<8	<8	<0.009	<0.007	<0.007	<0.01	3170	0.878
" -480	<500	<0.5	<0.09	<0.09	<0.01	<0.0009	<0.0001	<0.009	<0.0004	<0.6	<0.4	<0.0009	<0.0009	<0.0009	<2	0.24	0.898
" -481	<20	<0.1	0.54	<0.8	<0.01	<0.0008	<0.0001	<0.004	<0.0002	12	<0.1	<0.0008	<0.0002	<0.0003	<0.01	0.17	0.775
" -482	<20	0.052 ± 0.008	0.27	<0.3	<0.03	<0.0009	<0.0002	<0.004	<0.0002	1.7 ± 0.3	<0.4	<0.0008	<0.0007	<0.0003	<0.01	2.4	0.859
" -483	<20	<0.01	0.40	<0.2	<0.03	<0.002	<0.0001	<0.02	0.0018 ± 0.0005	<0.9	<0.5	<0.0009	<0.002	<0.0009	<0.01	0.19	0.887
" -484	4740	<0.01	17	<9	2.8 ± 1.7	0.06 ± 0.02	<0.006	<0.2	<0.002	<14	<14	<0.02	<0.02	<0.02	<0.05	6390	0.906
" -485	<20	0.039 ± 0.006	0.59	<0.2	<0.03	<0.002	<0.0001	<0.02	<0.0002	<0.8	<0.6	<0.002	<0.0008	<0.0008	<0.01	3.8	0.802
" -486	<20	<0.01	0.19	<0.2	<0.03	<0.002	<0.0001	<0.004	<0.0002	<0.4	<0.4	<0.0008	<0.0008	<0.0003	<0.01	2.6	0.845
" -487	<20	<0.01	0.05	<0.2	<0.03	<0.002	<0.0001	<0.004	<0.0002	<0.8	<0.5	<0.0009	<0.0009	<0.0004	<0.01	4.9	0.878
" -488	<20	0.086	3.5	<5	0.7 ± 0.7	0.035 ± 0.009	<0.006	<0.2	<0.002	<14	<14	<0.02	<0.02	<0.02	<0.01	4050	0.925
" -489	<20	<0.01	0.21	<0.2	<0.03	<0.002	<0.0001	<0.004	<0.0002	<0.4	<0.3	<0.0008	<0.0008	<0.0008	0.19	0.34	0.853
" -490	<20	0.19	0.65	<0.2	<0.05	0.013	<0.002	<0.02	<0.0002	<0.8	<0.5	<0.002	<0.0008	<0.0008	<0.01	0.85	0.776
" -491	<20	<0.01	0.02	<0.4	0.12	<0.002	0.0004	<0.02	<0.0002	<2	<0.9	<0.002	<0.0009	<0.0009	<0.01	23	0.860
" -492	<20	<0.01	0.45	<0.4	<0.06	0.099	<0.0002	0.60	<0.0002	<2	<0.9	<0.002	<0.0009	<0.0009	<0.01	13	0.900

* DUPLICATES - PREVIOUSLY REPORTED

+ CONCENTRATIONS IN µg/mℓ

EPA FUEL ADDITIVES+

	SAMPLE NO.	Ag	Al	As	Au	Br	Cd	Cl	Co	Cr	Cs	Cu	Eu	Fe	Hf	Hg	In	K	La
	F-73-000-006	<0.004	<2	<0.001	<0.0003	<0.002	<0.03	<2	<0.0004	<0.009	<0.0004	<1	<0.0001	<0.9	<0.0009	<0.004	<0.002	<4	<0.0007
	" -006*	<0.0004	<0.01	<0.001	<0.0003	0.008	<0.02	1±0.2	<0.0001	0.006	<0.0001		<0.00001	<0.04	0.001	<0.0007		<0.7	<0.0003
	" -013	<0.02	2.1	<0.001	<0.002	1.2	<0.1	150	0.031	0.05±0.02	<0.003	<1	<0.0004	535	<0.004	<0.009	<0.002	<8	0.004±0.002
**	" -013*	<0.002	2.0±0.2	<0.007	<0.001	1.6	<0.09	149	0.036	0.10	<0.0004		<0.00003	560	<0.0005	<0.001		<5	<0.001
**	" -016	<0.007	1.3	0.18	<0.0009	0.27	<0.06	110	<0.0006	<0.02	<0.0009	<1	<0.0001	<0.8	<0.002	<0.009	<0.002	<4	<0.0007
	" -016*	<0.004	0.96±0.1	0.23	<0.0005	0.30	<0.04	109	<0.0002	<0.01	<0.0007		<0.00005	<0.2	<0.001	<0.003		<1	<0.0003
	" -477	<0.02	6.1	<0.004	<0.0009	0.004±0.003	<0.1	10	<0.0006	<0.04	<0.0009	<1	<0.0001	<0.9	<0.005	<0.009	<0.002	<4	<0.0007
**	" -478	<0.02	<6	<0.005	<0.0008	0.51	<0.06	590	<0.0004	<0.02	<0.0009	<3	<0.0001	<0.8	<0.005	<0.009	<0.006	<4	<0.0007
**	" -479	<0.08	3.7±0.4	0.018±0.011	<0.0009	<0.03	<0.2	8±1	<0.005	<0.09	<0.02	<1	<0.002	<3	<0.02	<0.03	<0.002	<9	<0.0007
	" -480	<0.004	<400	<0.02	0.0036±0.0022	7.8	<0.2	5890	<0.0004	<0.009	<0.0004	<40	<0.0001	<0.9	<0.002	<0.004	<0.05	<9	<0.0007
	" -481	<0.004	<2	<0.004	<0.0008	<0.006	<0.03	1±0.5	<0.0005	<0.004	<0.0004	<1	<0.0004	<0.8	<0.003	<0.001	<0.002	<4	<0.0006
	" -482	<0.007	<2	<0.02	<0.0009	0.11	<0.06	30	0.016±0.006	<0.009	<0.0009	1.3±0.5	<0.0004	<0.9	<0.0009	<0.001	<0.002	<4	<0.0007
	" -483	<0.006	<2	<0.002	<0.0004	0.018±0.003	<0.04	10	<0.0004	<0.02	<0.0006	<1	<0.0003	<0.4	<0.002	<0.007	<0.002	<4	<0.0007
**	" -484	<0.2	8.3	<0.06	<0.007	0.99	<0.5	20	0.025±0.010	<0.3	<0.04	<6	<0.003	31.6	<0.04	<0.09	0.024±0.006	<36	0.028±0.004
	" -485	<0.007	<2	<0.008	<0.0001	0.27	<0.05	100	<0.0004	<0.02	<0.0008	<1	<0.0003	6.6	<0.002	<0.006	<0.002	<4	<0.0006
	" -486	<0.006	<2	<0.003	<0.0001	0.004±0.003	<0.06	6±1	<0.0004	<0.008	<0.0006	<1	<0.0003	<0.8	<0.0008	<0.001	<0.002	<4	<0.0007
	" -487	<0.007	<2	<0.005	<0.0001	0.003±0.001	<0.06	92	<0.0004	<0.009	<0.0006	<1	<0.0003	<0.9	<0.002	<0.001	<0.002	<4	<0.0007
	" -488	<0.2	5.5	<0.05	<0.005	0.79	<0.3	230	0.015±0.004	<0.3	<0.04	<1	<0.003	15.3	<0.04	<0.09	0.042	24±12	<0.003
**	" -489	<0.006	<2	<0.003	<0.0001	0.04	<0.06	4±1	0.013	<0.009	<0.006	<1	<0.0003	<0.8	<0.0008	<0.001	<0.002	<4	<0.0007
	" -490	<0.007	4.4	<0.001	<0.0001	0.005±0.002	<0.05	<2	0.003±0.001	<0.02	<0.0008	<1	<0.0003	85	<0.002	<0.006	<0.002	<8	<0.0006
	" -491	<0.001	<2	<0.001	<0.0001	0.009	<0.05	7±1	<0.0003	<0.02	<0.002	<1	<0.0003	2±0.4	<0.004	<0.006	<0.002	<4	<0.0007
**	" -492	<0.001	<2	<0.005	<0.0001	0.08	<0.06	20	0.001±0.001	<0.02	<0.002	<1	<0.0003	1±0.6	<0.004	~~0.11~~ <0.0003	<0.002	<4	<0.0007

** sent to JFP Lambert
For Mahon Mar 12 '74

MOTOR OIL IDENTIFICATION

Sample No	Description	Region
F73-000-255	Gulf, SAE 10-20-40	3
F73-000-258	Texaco, SAE 10W-40	3
F73-000-374	Shell, SAE 10W-40	7
F73-000-375	Standard, SAE 10W-40	7
F72-009-572	Gulf, 10W 20W-40	1
F72-009-573	Texaco, 10W-40	1
F72-009-574	Mobil, 10W-40	1
F72-009-620	Texaco, 10W-40	3
F72-009-660	Mobil, 10W-40	4
F72-009-665	Exxon, 10W-40	4
F72-009-707	Texaco, 10W-40	5
F72-009-712	Enco, 10W-40	5
F72-009-752	Mobil, 10W-40	6
F72-009-767	Gulf, 10W-40	6
F72-009-848	Standard, 10W-40	7
F72-009-850	Texaco, 10W-40	7
F72-009-864	Exxon, 10W-40	8
F72-009-870	Texaco, 10W-40	8
F72-009-920	Enco, 10W-20W-40	9
F72-009-922	Gulf, 10W-40	9

Sample Number	Region	Identification
72-009-609	III	Gulf, 10W-40
72-009-658	IV	Texaco, 10W-40
72-009-722	V	Gulf, 10W-40
72-009-751	VI	ENCO, 10W-40
72-009-768	VI	Texaco, 10W-40
72-009-847	VII	Gulf, 10W-40
72-009-858	VIII	Mobil, 10W-40
72-009-878	VIII	Gulf, 10W-40
72-009-921	IX	Texaco, 10W-40
72-009-923	IX	Mobil, 10W-40
72-009-953	X	Texaco, 10W-40
72-009-961	X	Shell, 10W-40
72-009-964	X	Mobil, 10W-40
72-009-971	X	Gulf, 10W-40
72-009-994	X	Texaco, 10W-40
73-000-320	V	Gulf, 10W-40
73-000-323	V	Texaco, 10W-40
73-000-391	VIII	Gulf, 10W-40
73-000-392	VIII	Texaco, 10W-40
73-000-424	IX	Gulf, 10W-40
73-000-425	IX	Texaco, 10W-40
73-000-464	I	Texaco, 10W-40
73-000-465	I	Gulf, 10W-40

EPA MOTOR OILS[+]

SAMPLE NO.	Ag	Al	As	Au	Br	Cd	Cl	Co	Cr	Cs	Cu	Eu	Fe	Hf	Hg	In	K	La
F-73-000-255	<0.07	<2	0.086	<0.0008	0.06	<0.09	4±1	<0.003	<0.2	<0.02	<1	<0.0008	<3	<0.02	<0.04	0.116	<0.6	0.0008±0.0008
" -258	<0.08	3.6±0.5	0.26	<0.0008	0.06	<0.09	14	<0.009	<0.1	<0.009	<1	<0.0009	<3	<0.02	<0.04	0.062	<0.6	0.0034±0.0010
" -374	<0.06	2.7±0.5	0.24	<0.002	0.13	<0.2	160	0.0017±0.0017	<0.09	<0.009	<1	<0.0008	<3	<0.009	<0.03	0.006	<9	0.014
" -375	<0.08	2.3	0.043	<0.0008	0.052±0.008	<0.09	7±1	<0.003	<0.2	<0.02	<1	<0.0005	7.9±2.0	<0.02	<0.04	0.003	<0.5	<0.0009
F-72-009-572	<0.06	<2	0.096	<0.0009	0.052±0.008	<0.09	6±1	<0.002	<0.09	<0.009	<1	<0.0009	<3	<0.009	<0.03	0.060	<0.7	0.0026±0.0008
" -573	<0.06	3.5	0.16	<0.002	0.026±0.009	<0.2	13	0.0026±0.0018	<0.09	<0.009	<1	<0.0006	<3	<0.009	<0.03	0.051	<0.6	0.0035±0.0010
" -574	<0.05	<2	<0.004	<0.0009	0.39	<0.09	93	0.0034±0.0017	0.051±0.036	<0.009	<1	<0.0006	<5	<0.009	<0.02	0.009	7.7	0.0026±0.0008
" -574*	<0.03	2.9±0.6	0.05	<0.003	0.70	<0.2	83	0.0017	0.28	<0.006	<0.2	<0.0004	4.8	<0.006	<0.01	0.011	14	<0.004
" -620	<0.06	3.7	0.29	<0.0009	0.043±0.009	<0.09	9	0.0026±0.0018	<0.08	<0.009	<1	<0.0006	3.4±1.7	<0.009	<0.03	0.063	<0.6	0.0034±0.0010
" -660	<0.06	2.8±0.5	0.017±0.004	<0.002	0.28	<0.2	91	<0.002	<0.08	<0.02	<1	<0.0006	5.2±1.3	<0.009	<0.03	0.010	<4	0.0035±0.0010
" -665	<0.05	2.6±0.5	<0.02	<0.002	0.24	<0.2	42	0.0068±0.0014	<0.07	<0.009	<3	<0.0006	<5	<0.009	<0.03	<0.006	<7	<0.0009
" -707	<0.06	3.6±0.5	0.21	<0.0009	0.017±0.004	<0.09	11	0.0026±0.0013	<0.09	<0.009	<1	<0.0006	3.8±1.5	<0.009	<0.03	0.034	<0.6	0.0034±0.0010
" -712	<0.06	2.4±0.5	0.034±0.007	<0.002	0.27	<0.2	33	0.0043±0.0015	<0.09	<0.02	<3	<0.0006	4.6±1.4	<0.009	<0.03	<0.006	<4	0.0026±0.0008
" -712*	<0.02	1.9±0.4	0.025	<0.002	0.30	<0.2	34	0.0029	<0.07	<0.003	<0.2	0.00036	4.1	<0.005	<0.01	<0.001	<2	<0.002
" -752	<0.05	<2	<0.02	<0.002	0.26	<0.2	93	<0.002	<0.06	<0.009	<1	<0.0006	<5	<0.009	<0.02	0.011	<7	0.0026±0.0008
" -767	<0.06	1.7	0.009±0.003	<0.0009	0.08	<0.09	17	0.0026±0.0008	<0.09	<0.009	<1	<0.0006	2.4±1.2	<0.009	<0.03	0.006	<0.6	0.0017±0.0017
" -767*	<0.02	1.4	0.017	<0.002	0.09	0.42	15	<0.0004	<0.08	<0.003	<0.2	<0.0001	<0.5	<0.006	<0.01	0.012	<2	<0.002
" -848	<0.07	2.5±0.5	0.030±0.005	<0.002	0.06	<0.2	7±1	<0.003	<0.09	<0.02	<1	<0.0009	<3	<0.02	<0.03	0.002	<4	<0.009
" -850	<0.05	3.3	0.22	<0.002	0.009±0.009	<0.2	11	0.0043±0.0015	<0.06	<0.009	<1	<0.0006	<2	<0.009	<0.02	0.037	<7	0.0043±0.0009
" -864	<0.06	<2	0.035±0.010	<0.002	1.3	<0.2	45	0.0061±0.0012	<0.09	<0.009	<1	<0.0006	7.3±1.5	<0.009	<0.03	<0.002	<10	0.0043±0.0009
" -870	<0.04	3.8	0.16	<0.002	0.026±0.009	<0.2	14	0.0043±0.0015	0.18±0.05	<0.002	<1	<0.0006	3.5±1.4	<0.009	<0.02	0.056	<4	0.0017±0.0005
" -920	<0.06	<2	<0.2	<0.002	0.23	<0.2	47	0.0052±0.0010	<0.09	<0.009	<1	<0.0006	4.6±1.4	<0.009	<0.03	<0.002	<9	0.009±0.009
" -922	<0.04	1.5	0.04	<0.002	0.06	<0.2	6±1	0.0043±0.0015	<0.06	<0.02	<1	<0.0005	3.1±1.6	<0.009	<0.02	<0.002	<4	0.0017±0.0005

EPA MOTOR OILS +

SAMPLE NO.	Mg	Mn	Na	Ni	Rb	Sb	Sc	Se	Sm	Sn	Sr	Ta	Tb	Th	V	Zn	DENSITY g/mL
F-73-000-255	460	0.18	3.3	<4	0.56 ± 0.34	0.26	<0.003	<0.05	0.007 ± 0.003	<6	<8	<0.005	<0.007	<0.009	<0.01	1360	0.855
" -258	<20	0.23	8.6	<4	<0.5	0.16	<0.003	<0.05	0.019 ± 0.003	<6	<8	<0.007	<0.007	<0.009	<0.01	1310	0.852
" -374	<20	0.25	15	<3	<0.4	0.021 ± 0.003	<0.002	<0.05	0.011 ± 0.004	<4	<7	<0.006	<0.006	<0.009	<0.01	1700	0.859
" -375	1160	0.10 ± 0.03	1.7	<4	<0.6	<0.007	<0.003	<0.05	<0.0003	<6	<9	<0.006	<0.007	<0.009	<0.01	1880	0.859
F-72-009-572	410	0.14 ± 0.02	2.6	<3	1.1 ± 0.4	0.25	<0.002	<0.07	0.005 ± 0.002	<4	<7	<0.006	<0.006	<0.007	<0.01	1450	0.872
" -573	<20	0.22	4.8	<3	<0.3	0.084	<0.002	<0.05	0.010 ± 0.004	<4	<7	<0.006	<0.006	<0.009	<0.01	1290	0.863
" -574	16 ± 10	0.21	8.0	<3	<0.3	0.009 ± 0.003	0.0019	<0.05	0.016 ± 0.005	<3	<4	<0.004	<0.004	<0.005	<0.01	1040	0.856
" -574*	20 ± 7	0.19	13	<1	<0.3	0.016	<0.0008	<0.03	0.034	<2	<11	<0.002	<0.002	<0.007	<0.01	1700	
" -620	<20	0.30	6.6	<3	<0.3	0.022 ± 0.003	<0.002	<0.05	0.008 ± 0.003	<4	<5	<0.006	<0.005	<0.006	<0.01	1240	0.860
" -660	50 ± 10	0.22	8.2	<4	<0.5	0.009 ± 0.003	0.0014	<0.05	0.010 ± 0.004	<4	<4	<0.005	<0.006	<0.007	<0.01	1500	0.865
" -665	<60	0.08 ± 0.03	4.3	<2	<0.3	0.005 ± 0.002	<0.002	<0.05	<0.0007	<3	<4	<0.006	<0.006	<0.006	0.04 ± 0.02	1120	0.854
" -707	<20	0.16	4.0	<3	<0.3	0.064	<0.002	<0.05	0.014 ± 0.004	<4	<7	<0.006	<0.006	<0.006	0.04 ± 0.02	1310	0.856
" -712	<60	0.08 ± 0.02	2.6	<3	<0.4	0.005 ± 0.002	0.0021	<0.05	<0.0007	<4	<4	<0.005	<0.006	<0.009	<0.03	1090	0.858
" -712*	8 ± 4	0.10	3.2	<1	<0.3	0.005	<0.0005	<0.02	<0.0007	<1	<7	<0.001	<0.002	<0.007	<0.01	1100	
" -752	40 ± 10	0.19	7.2	<3	0.37 ± 0.19	0.013 ± 0.005	<0.002	<0.05	0.019 ± 0.003	<3	<4	<0.004	<0.004	<0.005	<0.01	1200	0.866
" -767	670	0.10 ± 0.02	3.8	<3	0.21 ± 0.11	0.008 ± 0.003	<0.002	<0.05	0.002 ± 0.002	<4	<7	<0.006	<0.006	<0.006	<0.01	1110	0.852
" -767*	770	<0.04	5.9	<1	<0.4	0.007	<0.0006	<0.02	<0.0004	<1	<7	<0.001	<0.002	<0.008	0.006 ± 0.01 ?	1300	
" -848	1170	0.21	1.5	<3	<0.6	0.006 ± 0.002	<0.003	<0.09	<0.0007	<6	<7	<0.006	<0.007	<0.009	<0.01	1990	0.855
" -850	<20	0.16	4.6	<3	<0.3	0.043	<0.002	<0.05	0.013 ± 0.006	<3	<4	<0.006	<0.005	<0.006	0.016 ± 0.008	1230	0.866
" -864	<20	0.08 ± 0.02	2.1	<3	<0.3	<0.005	<0.002	<0.05	<0.0007	<4	<7	<0.006	<0.006	<0.009	<0.01	1240	0.869
" -870	<20	0.30	4.7	<2	<0.3	0.066	<0.002	<0.04	0.014 ± 0.004	<3	<3	<0.005	<0.004	<0.005	<0.01	1280	0.866
" -920	<20	0.04 ± 0.02	2.9	<3	<0.3	0.008 ± 0.003	<0.002	<0.05	<0.0007	<4	<7	<0.006	<0.006	<0.009	<0.01	1180	0.868
" -922	390	0.17	2.5	<2	<0.3	0.017 ± 0.003	<0.002	<0.04	0.007 ± 0.003	<3	<3	<0.005	<0.004	<0.005	<0.01	1140	0.863

* DUPLICATES - PREVIOUSLY REPORTED

+ CONCENTRATIONS in µg/ml

ELEMENTAL ANALYSIS OF E.P.A. MOTOR OILS µg/ml

SAMPLE #	Ag	Al	As	Au	Ba	Br	Ca	Cd	Cl	Co	Cr	Cs	Cu
72-C09-609	<0.02	1.5±0.5	<0.02	<0.002	12	0.029	570	0.24	7	<0.0007	<0.03	<0.006	<2
72-C09-653	<0.02	4.7	<0.02	<0.002	<1	0.021	1300	0.54	16	<0.0006	<0.03	<0.005	<1
72-C09-722	<0.02	1.8±0.5	<0.01	<0.002	<1	0.069	<80	<0.2	20	<0.0004	<0.03	<0.006	<1
72-C09-751	<0.02	2.4	<0.02	<0.003	3200	0.36	1100	<0.3	48	<0.0006	<0.05	<0.007	<1
72-C09-768	<0.02	3.5±0.5	0.14	<0.003	<2	<0.03	2000	0.46	15	<0.0007	<0.04	<0.007	<1
72-C09-847	<0.02	1.8	<0.01	<0.002	9.4	0.091	<100	<0.2	20	<0.0005	<0.04	<0.006	<1
72-C09-853	<0.02	<7	<0.02	<0.002	5.1	0.20	3200	<0.2	83	<0.0005	<0.04	<0.006	<1
72-C09-878	<0.02	1.5	<0.01	<0.002	<2	0.056	<90	<0.2	16	<0.0005	0.053	<0.006	<0.3
72-C09-921	<0.02	6.1	<0.01	<0.002	<2	<0.02	1500	1.1	10	0.0020	<0.04	<0.005	<1
72-C09-923	<0.02	2.4	<0.01	<0.002	<2	0.17	2900	<0.2	96	<0.0005	<0.04	<0.005	<1
72-C09-953	<0.02	3.2±0.5	0.14	<0.002	<9	0.096	2800	0.67	20	0.0031	<0.06	<0.005	<2
72-C09-961	<0.02	1.2±0.3	<0.02	<0.003	<4	0.094	2000	<0.2	160	<0.0007	<0.05	<0.005	<1
72-C09-964	<0.02	<8	<0.02	<0.002	<10	0.20	3200	<0.2	99	0.0018	<0.07	<0.005	<3
72-C09-971	<0.02	1.4	0.037	<0.002	<0.9	0.026	770	1.9	5	0.0012	<0.02	<0.004	<0.3
72-C09-994	<0.02	<4	<0.008	<0.002	3600	0.19	1300	<0.2	41	0.0015	<0.06	<0.004	<2
73-C00-320	<0.02	1.7	<0.02	<0.003	<3	0.10	<80	<0.2	16	<0.0006	<0.05	<0.007	<0.5
73-C00-323	<0.03	4.6±1.5	0.095	<0.003	<4	<0.04	2200	1.1	14	<0.0008	<0.06	<0.008	<2
73-C00-391	<0.02	1.5	<0.02	<0.003	<4	0.077	<100	<0.2	16	<0.0006	<0.05	<0.007	<0.5
73-C00-392	<0.02	2.5	0.15	<0.003	<4	<0.04	2100	<0.2	11	<0.0007	<0.05	<0.007	<1
73-C00-424	<0.02	1.6	<0.02	<0.003	<4	<0.04	700	3.1	4	<0.0006	<0.05	<0.007	<0.5
73-C00-425	<0.02	3.7±0.6	0.19	<0.003	<5	<0.04	1800	0.89	13	0.0042	<0.06	<0.007	<2
73-C00-464	<0.02	3.1	0.15	<0.003	9.2	0.12	2500	0.85	14	0.0030	<0.06	<0.008	<1
73-C00-465	<0.02	2.0±0.5	<0.02	<0.003	<5	<0.04	730	2.4	3	0.00092	<0.06	<0.007	<1
73-C00-473	<0.003	2.0	<0.02	<0.002	<0.9	1.4	<200	<0.2	170	0.0010	0.060	<0.0053	<1

ELEMENTAL ANALYSIS OF E.P.A. MOTOR OILS µg/ml (cont)

SAMPLE #	Eu	Fe	Hf	Hg	In	K	La	Mg	Mn	Na	Ni	Rb	Sb
72-009-609	<0.0003	<0.5	<0.003	<0.009	0.117	<8	<0.001	420	0.16	1.2	<0.7	<0.08	0.13
72-009-658	<0.0003	1.1	<0.003	<0.01	0.113	<10	<0.002	<20	0.20	3.1	<0.7	<0.09	0.090
72-009-722	<0.0002	<0.4	<0.003	<0.009	0.003	<6	<0.0009	800	0.10±0.05	2.0	<0.7	<0.1	0.0051
72-009-751	<0.0002	3.2	<0.005	<0.01	<0.004	<8	<0.002	<20	0.10	1.9	<0.8	<0.1	0.0036
72-009-763	<0.0002	1.8	<0.004	<0.01	0.035	<20	<0.002	<20	0.25	3.1	<0.9	<0.1	0.024
72-009-847	<0.0002	<0.4	<0.004	<0.01	0.008	<10	<0.002	730	0.23±0.03	2.7	<0.8	<0.1	0.0066
72-009-858	<0.0002	2.0	<0.004	<0.01	0.019	<20	<0.002	20±10	0.14	5.8	<0.8	<0.1	0.0032
72-009-878	<0.0002	3.2	<0.004	<0.01	0.007	<10	<0.001	740	<0.06	2.9	<0.8	<0.1	0.0055
72-009-921	<0.0002	2.1	<0.003	<0.01	0.030	<10	<0.001	<20	0.28	2.6	<0.7	<0.1	0.026
72-009-923	<0.0002	1.9	<0.004	<0.01	0.012	<10	<0.002	30±10	0.18	4.2	<0.7	<0.1	0.0057
72-009-953	<0.0002	3.4	<0.005	<0.01	0.032	<20	<0.002	<20	0.45	9.9	<1	<0.3	0.012
72-009-961	<0.0003	<0.7	<0.005	<0.01	0.011	<20	0.0092	30±10	0.25	11	<1	<0.2	0.021
72-009-964	<0.0002	<0.8	<0.006	<0.02	0.008	<10	<0.002	<30	0.14	5.8	<1	<0.3	0.0098
72-009-971	<0.0001	<0.3	<0.003	<0.008	0.002±0.001	<4	<0.001	360	0.08±0.04	3.2	<0.6	<0.06	0.0028
72-009-994	0.00029	3.7	<0.005	<0.01	<0.003	<4	<0.001	<30	0.09±0.04	2.3	<0.8	<0.2	0.0024
73-000-320	<0.0002	<0.6	<0.005	<0.01	0.021	<10	<0.001	820	<0.05	2.3	<1	<0.2	0.0062
73-000-323	<0.0003	<0.8	<0.006	<0.02	0.005	<20	<0.002	<20	0.43	5.1	<1	<0.2	0.011
73-000-391	<0.0002	<0.6	<0.005	<0.01	0.011	<10	<0.002	690	<0.06	3.3	<0.9	<0.2	0.0064
73-000-392	<0.0003	<0.7	<0.005	<0.01	0.020	<20	<0.002	<20	0.25	5.4	<1	<0.2	0.017
73-000-424	<0.0002	<0.6	<0.005	<0.01	0.005	<10	<0.002	410	0.13±0.04	1.9	<0.9	<0.2	0.0096
73-000-425	<0.0003	4.2	<0.005	<0.02	0.062	<20	<0.002	<20	0.26	3.8	<1	<0.2	0.078
73-000-464	<0.0003	2.2	<0.006	<0.02	0.037	<20	<0.002	<20	0.26	4.2	<1	<0.2	0.049
73-000-465	<0.0003	1.8	<0.005	<0.01	0.065	<20	<0.002	390	0.16±0.03	2.6	<1	<0.2	0.080
73-000-476	<0.00009	6.2	<0.001	<0.01	<0.002	<20	<0.002	<20	0.049±0.008	2.2	<0.1	<0.03	0.0017

ELEMENTAL ANALYSIS OF E.P.A. MOTOR OILS µg/ml (cont)

SAMPLE #	Sc	Se	Sm	Sn	Sr	Ta	Tb	Th	V	Zn	DENSITY g/ml
72-C09-609	<0.0004	<0.02	<0.0008	<1	<2	<0.0005	<0.001	<0.003	<0.02	570	0.86
72-C09-658	<0.0004	<0.03	<0.001	<1	<2	<0.0005	<0.001	<0.004	0.010±0.005	600	0.86
72-C09-722	<0.0004	<0.02	<0.0009	<1	<2	<0.0004	<0.001	<0.004	<0.02	540	0.85
72-C09-751	<0.0005	<0.03	<0.002	<2	<2	<0.0006	<0.002	<0.006	<0.02	690	0.88
72-C09-768	<0.0006	<0.03	<0.001	<2	<3	<0.0006	<0.002	<0.005	<0.03	850	0.83
72-C09-847	<0.0005	<0.02	<0.0008	<1	<2	<0.0005	<0.001	<0.004	<0.01	700	0.86
72-C09-858	<0.0005	<0.03	<0.0009	<1	<2	<0.0005	<0.001	<0.005	<0.08	830	0.90
72-C09-878	<0.0005	<0.02	<0.0008	<1	<2	<0.0004	<0.001	<0.004	0.075±0.005	630	0.87
72-C09-921	<0.0004	<0.02	<0.0009	<1	<2	<0.0004	<0.001	<0.004	<0.03	600	0.88
72-C09-923	<0.0004	<0.02	0.0017	<1	<2	<0.0004	<0.001	<0.004	0.024±0.005	690	0.87
72-C09-953	<0.0006	<0.03	<0.001	<1	<2	<0.0006	<0.002	<0.008	<0.04	860	0.85
72-C09-961	<0.0006	<0.03	<0.001	<2	<3	<0.0007	<0.002	<0.007	<0.03	1100	0.88
72-C09-964	<0.0007	<0.03	<0.0009	<2	<3	<0.0006	<0.002	<0.009	<0.09	830	0.86
72-C09-971	<0.0004	<0.02	<0.0005	<1	<1	<0.0004	<0.001	<0.003	0.12±0.004	790	0.85
72-C09-994	<0.0005	<0.02	<0.0009	<1	<2	<0.0005	<0.002	<0.007	<0.06	660	0.87
73-C00-320	<0.0006	<0.03	<0.001	<2	<3	<0.0007	<0.002	<0.006	<0.01	1000	0.85
73-C00-323	<0.0007	<0.04	<0.001	<2	<3	<0.0009	<0.002	<0.007	<0.03	1400	0.86
73-C00-391	<0.0006	<0.03	<0.001	<1	<3	<0.0006	<0.002	<0.006	0.010±0.005	950	0.85
73-C00-392	<0.0006	<0.03	<0.001	<2	<3	<0.0007	<0.002	<0.006	<0.02	1200	0.87
73-C00-424	<0.0006	<0.03	<0.001	<1	<2	<0.0006	<0.002	<0.006	<0.01	1000	0.86
73-C00-425	<0.0006	<0.03	<0.001	<2	<3	<0.0007	<0.002	<0.007	<0.02	1100	0.85
73-C00-434	<0.0007	<0.03	<0.001	<2	<3	<0.0007	<0.002	<0.007	0.015±0.005	1100	0.89
73-C00-465	<0.0006	<0.03	<0.001	<2	<3	<0.0007	<0.002	<0.007	<0.02	1000	0.86
~~73-C00-473~~	~~<0.00007~~	~~<0.009~~	~~<0.001~~	~~11~~	~~<0.4~~	~~<0.0003~~	~~<0.0005~~	~~<0.002~~	~~<0.01~~	~~8.0~~	~~0.83~~

FUEL OIL ANALYSIS

Sample Number	Region	Brand Identification
72-009-622	III	Texaco, No. 2
72-009-623	III	Shell, No. 2
72-009-726	V	ARCO, No. 2
72-009-727	V	Texaco, No. 2
72-009-735	V	Mobil, No. 2
72-009-746	V	ARCO, No. 6
72-009-747	V	Hartney Oil Co. No. 6
72-009-748	V	Allied Oil, No. 6
72-009-749	V	Allied Oil, No. 6
72-009-750	V	Apex Oil
72-009-790	VI	Fort Worth Refinery, No. 5
72-009-791	VI	Fort Worth Refinery, No. 5
72-009-792	VI	Fort Worth Refinery, No. 5
72-009-833	VII	Phillips, No. 2
72-009-938	IX	Navy Fuel Depot
72-009-972	X	Pacific, Mixture
72-009-979	X	Shell, No. 2

ELEMENTAL ANALYSIS OF E.P.A. DISTILLATE FUEL OILS µg/ml

SAMPLE #	Ag	Al	As	Au	Ba	Br	Ca	Cd	Cl	Co	Cr	Cs	Cu
72-C09-622	<0.0005	<0.1	<0.003	<0.0004	<0.1	0.16	<30	<0.03	0.7±0.2	<0.00008	<0.002	<0.00003	<0.2
72-C09-623	<0.0005	<0.2	<0.001	<0.0002	<0.05	0.016	<20	<0.02	<0.5	0.00017	<0.002	<0.0003	<0.4
72-C09-726	<0.0004	<0.1	0.017	<0.0004	<0.2	0.14	<30	<0.03	3.4±0.4	0.00031	<0.003	<0.00007	<0.3
72-C09-727	<0.0005	<0.2	<0.002	<0.0002	<0.04	0.019	<10	<0.02	<0.5	<0.00008	<0.002	<0.00007	<0.4
72-C09-735	<0.0004	<0.1	<0.0006	<0.0001	<0.02	<0.001	<10	<0.007	1.5±0.5	<0.00007	<0.0003	<0.00009	<0.3
72-C09-746	0.0013	60	0.15	<0.002	2.8	0.32	<500	<0.1	16	0.36	0.96	0.0013	<7
72-C09-747	0.0023	13	0.17	<0.001	<1	0.24	<300	<0.09	63	0.86	0.80	0.00044	<7
72-C09-748	0.0014	24	0.33	<0.002	8.3	0.43	<400	<0.1	169	0.64	0.92	0.0012	<7
72-C09-749	0.0017	4.3	0.15	<0.001	2.0	0.12	<200	<0.09	42	1.3	0.80	0.00035	<4
72-C09-750	0.00022	<3	0.11	<0.0009	<1	0.17	<200	<0.07	25	0.16	0.077	0.00067	<8
72-C09-790	0.00024	0.8±0.2	0.20	<0.0007	<0.4	0.21	<100	<0.06	5	0.010	0.037	0.00025	<8
72-C09-791	<0.001	<1	0.21	<0.0006	0.54	0.23	<100	<0.05	7	0.012	0.035	0.00040	<2
72-C09-792	<0.001	0.8±0.2	0.13	<0.0007	<0.3	0.16	<100	<0.05	7	0.0072	0.030	0.00023	<2
72-C09-833	<0.0003	<0.2	<0.001	<0.0003	<0.05	0.006±0.003	<10	<0.02	<0.5	0.000091	<0.003	<0.0001	<0.5
72-C09-938	0.00019	<0.1	0.0037	<0.0003	<0.03	0.021	<10	<0.03	<0.5	0.00015	<0.003	0.00011	<0.2
72-C09-972	<0.0005	<0.1	<0.002	<0.0002	<0.05	0.039	<20	<0.02	<0.5	0.00027	<0.002	<0.00009	<0.5
72-C09-979	0.0017	<0.1	<0.001	<0.0002	<0.1	0.016	<10	<0.02	<0.5	0.000054	<0.003	<0.0003	<0.2

ELEMENTAL ANALYSIS OF E.P.A. DISTILLATE FUEL OILS µg/ml (cont)

SAMPLE #	Eu	Fe	Hf	Hg	In	K	La	Mg	Mn	Na	Ni	Rb	Sb
72-009-622	<0.00003	<0.03	<0.0002	<0.0008	<0.0004	<3	<0.0004	<4	<0.005	<0.02	<0.02	<0.005	<0.0002
72-009-623	<0.00004	<0.07	<0.0002	<0.001	<0.0003	<3	<0.0003	<4	<0.004	<0.01	<0.01	<0.002	<0.0002
72-009-726	<0.00003	<0.09	<0.0002	<0.0009	<0.0003	<4	<0.0003	<4	<0.005	<0.02	<0.01	<0.007	<0.0002
72-009-727	<0.00003	<0.06	<0.0001	<0.0008	<0.0004	<2	<0.0003	<5	<0.004	0.18	<0.01	<0.002	<0.0001
72-009-735	<0.00003	<0.05	<0.00008	<0.0003	<0.01	<2	<0.0003	<4	<0.004	<0.01	<0.01	<0.002	<0.0001
72-009-746	0.0069	20	0.0015	<0.002	<0.005	<50	4.3	<80	0.24	35	11	<0.05	0.0031
72-009-747	0.0024	18	<0.001	<0.003	<0.005	<30	0.47	<100	0.14±0.04	72	16	<0.1	0.0074
72-009-748	0.0018	35	0.0012	<0.003	<0.006	<60	0.81	<70	0.20	210	14	<0.06	0.0070
72-009-749	0.0034	15	<0.001	<0.004	<0.004	<30	0.18	<60	0.18	43	12	<0.1	0.0035
72-009-750	<0.00009	13	<0.0007	<0.003	<0.006	<20	<0.003	<100	<0.07	34	13	<0.06	0.0015
72-009-790	<0.00006	12	<0.0005	<0.002	<0.004	<10	0.020	<50	0.05±0.02	4.9	4.6	<0.02	0.0016
72-009-791	<0.00005	14	<0.0004	<0.002	<0.002	<9	0.021	<30	0.08±0.04	4.9	6.0	<0.01	0.0016
72-009-792	<0.00007	8.8	<0.0004	<0.002	<0.004	<10	0.014	<50	<0.05	3.0	4.0	<0.02	0.0011
72-009-933	<0.00003	<0.05	<0.0002	<0.001	<0.0003	<2	<0.0002	<5	<0.003	<0.01	<0.02	<0.002	<0.0001
72-009-938	<0.00003	<0.07	<0.0002	<0.001	<0.0004	<2	<0.0002	<4	<0.004	<0.02	<0.02	<0.003	<0.0001
72-009-972	<0.00003	<0.07	<0.0001	<0.0007	<0.0003	<2	<0.0003	<5	<0.004	0.18	<0.01	<0.003	<0.0001
72-009-979	<0.00003	<0.06	<0.0003	<0.001	<0.0003	<0.7	<0.0002	<5	<0.004	<0.007	<0.04	<0.005	<0.002

ELEMENTAL ANALYSIS OF E.P.A. DISTILLATE FUEL OILS µg/ml (cont)

SAMPLE #	Sc	Se	Sm	Sn	Sr	Ta	Tb	Th	V	Zn	DENSITY g/ml
72-009-622	<0.000008	0.0034	<0.0001	<0.06	<0.06	<0.00009	<0.00009	<0.0003	<0.001	0.089	0.83
72-009-623	<0.000006	<0.003	<0.0002	<0.09	<0.07	<0.00008	<0.0001	<0.0003	<0.003	0.044	0.86
72-009-726	0.000029	0.012	<0.0002	<0.06	<0.06	<0.00009	<0.00009	<0.0004	<0.003	0.11	0.84
72-009-727	<0.000006	0.023	<0.0001	<0.07	<0.06	<0.00006	<0.0001	<0.0002	<0.003	0.075	0.84
72-009-735	<0.000009	<0.0009	<0.0001	<0.04	<0.05	<0.00005	<0.00005	<0.0001	<0.002	0.56	0.81
72-009-746	0.0037	0.11	0.15	<0.2	<0.3	<0.0004	0.0071	0.015	24.2	3.4	0.99
72-009-747	0.0030	0.14	0.021	<0.3	<0.4	<0.0006	0.0022	0.0059	21.3	1.7	0.95
72-009-748	0.0015	0.15	0.021	<0.2	<0.3	<0.0005	0.00096	0.0068	10.2	3.0	0.97
72-009-749	0.0049	0.15	0.016	<0.4	<0.5	<0.0009	0.0036	0.0077	9.5	1.8	0.95
72-009-750	0.00040	0.11	<0.0004	<0.2	<0.3	<0.0004	<0.0003	<0.001	38.1	1.0	0.93
72-009-790	0.00023	0.034	0.00092	<0.1	<0.2	<0.0002	<0.0002	<0.0007	5.9	0.31	0.94
72-009-791	0.00024	0.092	0.0011	<0.1	<0.1	<0.0001	<0.0002	<0.0006	6.6	0.83	0.93
72-009-792	0.00015	0.058	<0.0004	<0.1	<0.2	<0.0002	<0.0002	<0.0006	5.9	0.21	0.94
72-009-833	<0.00001	<0.004	<0.0002	<0.1	<0.08	<0.00007	<0.0002	<0.0004	<0.003	0.11	0.84
72-009-938	0.000014	0.045	<0.0002	<0.1	<0.09	<0.00007	<0.0002	<0.0004	0.004±0.002	0.23	0.85
72-009-972	<0.000009	0.0037	<0.0001	<0.06	<0.06	<0.00006	<0.0001	<0.0002	<0.003	0.28	0.83
72-009-979	<0.00003	<0.003	<0.0001	<0.1	<0.1	<0.00007	<0.0001	<0.0004	<0.003	4.1	0.84

GASOLINE SULFUR CONTENT*

A. NATIONWIDE FIGURES	WT. % SULFUR AVG	WT. % SULFUR MAX	WT. % SULFUR*** AVG	WT. % SULFUR*** MAX
1. REGULAR	0.038	0.069	.034	.119
2. PREMIUM	0.023	0.045	.015	.067
3. NON-LEADED	0.023	0.060	.035	.133
B. SOUTHERN CALIFORNIA				
1. REGULAR	0.069	0.116		
2. PREMIUM	0.042	0.056		
3. NON-LEADED**	0.023	0.037		

*SOURCE - U. S. BUREAU OF MINES MINERAL INDUSTRY SURVEY 200, JUNE 1973

**ONLY 19 SAMPLES WERE TESTED

***EPA FUEL SURVEILLANCE NETWORK - 120 COMMERCIAL GASOLINE SAMPLES

Appendix B1.2

The EPA National Fuels Surveillance Network
I. Trace Constituents in Gasoline and Commercial Gasoline Fuel Additives

by

Robert H. Jungers

Robert E. Lee, Jr.

and

Darryl J. von Lehmden

Environmental Protection Agency
National Environmental Research Center
Research Triangle Park, North Carolina 27711

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Sulfur Results on Regional Gasoline Samples
(Results Reported in Percents)

Total Samples - 111
34 Premium w/avg of 0.019 %S
40 Regular w/avg of 0.032 %S
37 Low Lead w/avg of 0.021 %S

REGION I (Boston)

Premium	Hi	Lo	Average
6	0.037	0.011	0.016
Regular	**Hi**	**Lo**	**Average**
5	0.033	0.007	0.022
Low Lead	**Hi**	**Lo**	**Average**
8	0.057	0.007	0.040

REGION III (Charlottesville, Va.)

Premium	Hi	Lo	Average
6	0.025	0.011	0.017
Regular	**Hi**	**Lo**	**Average**
7	0.049	0.023	0.040
Low Lead	**Hi**	**Lo**	**Average**
5	0.042	0.007	0.027

REGION IV (Atlanta)

Premium	Hi	Lo	Average
2	0.035	0.024	0.030
Regular	**Hi**	**Lo**	**Average**
4	0.028	0.039	0.033
Low Lead	**Hi**	**Lo**	**Average**
5	0.10	0.055	0.018

ABSTRACT

A National Fuels Surveillance Network has been established to collect gasoline and other fuels through the 10 Regional Offices of the Environmental Protection Agency. Physical, chemical, and trace element analytical determinations are made on the collected fuel samples to detect components which may present an air pollution hazard or poison exhaust catalytic control devices now under development.

A summary of trace elemental constituents in over 50 gasoline samples and 18 commercially marketed consumer purchased gasoline additives is presented. Quantities of Mn, Ni, Cr, Zn, Cu, Fe, Sb, B, Mg, Pb and S were found in most regular and premium gasoline. Environmental implications of trace constituents in gasoline are discussed.

INTRODUCTION

The combustion of petroleum based fuel in motor vehicles represents an important emission source of both particulate and gaseous pollutants to the environment. The potential health hazard associated with the combustion products from fuels and fuel additives was recognized in the Clean Air Act as amended in 1970, Section 211, which empowers the Environmental Protection Agency (EPA) to require manufacturers of fuels and fuel additives to register their products. As an integral part of this program, EPA established a National Fuels Surveillance Network (NFSN) in 1972 for the collection and analysis of fuels and fuel additives throughout the country.

In addition to providing data for validating information provided by fuel and fuel additive manufacturers, the NFSN should also serve as a source of information for a variety of other uses including: (a) the detection of constituents in motor vehicle fuel which could poison exhaust catalytic control systems now under development to meet statutory standards, (b) detection of toxic components in fuel, especially heavy metal contaminants introduced during transport and storage processes, (c) the development of accurate emission factors for assessing the contribution of trace metals and other fuel components to the atmosphere, (d) the enforcement of federal regulations on fuel additives such as the regulated limits on lead and phosphorus in gasoline (Federal Register, Part II, Jan. 10, 1973), and (e) the design of studies to identify emission constituents.

This is the first in a series of reports on the NFSN, and is limited to a description of the network operation, chemical analytical methods used, and a summary of results of trace constituents in gasoline and commercially marketed consumer purchased gasoline additives.

EXPERIMENTAL

The Operation of the National Fuels Surveillance Network

Fuel samples are generally collected by the ten EPA regional offices in accordance with specific requests from EPA's National Environmental Research Center (NERC) located in Research Triangle Park, North Carolina. NFSN was established in 1972 during which 200 gasoline samples were collected. It is anticipated that approximately 1000 samples will be collected annually thereafter and sent to the NERC for in-depth chemical and physical analysis. During the early phases of the network, the collection of gasoline and consumer purchased gasoline fuel additives was emphasized, however, proportionately larger quantities of other fuels will be collected in subsequent years to include aviation gasoline, jet fuel, diesel fuel, distillate and residual fuel oil, and motor oil samples.

Generally, fuel samples are collected at the last point in the distribution system, i.e., the retail outlet such as service stations and heating oil distributors, although selected samples from refineries and pipelines will also be collected. Samples are collected in a metal-jacketed 500 ml Wheaton* hard-glass container (Wheaton Glass Co.) with a

*Mention of commercial products does not constitute endorsement by the EPA.

teflon*-lined cap. The Wheaton bottle is cleaned by soaking 24 hours in 1:1 nitric acid, rinsing with distilled water and soaking for an additional 24 hours in distilled water. This procedure has been found to remove detectable levels of trace metal contaminants from the container.

In sampling gasoline, at least one gallon is discarded from the pump before filling the container completely, discarding the gasoline, refilling the container to the shoulder, capping tightly, and marking the level on the bottle. The collected sample is placed inside another metal can which is filled with an absorbant, sealed, labeled and sent to the NERC Fuels Laboratory by ground transportation in accordance with Title 49, Code of Federal Regulations (Code of Federal Regulations, 1968). In the laboratory, the samples are ordinarily stored at room temperature in subdued light although refrigeration is suggested for long term storage.

CHEMICAL ANALYSIS

Procedures outlined by the American Society for Testing and Materials (ASTM) are followed from gasoline, diesel fuel, distillate and residual fuel oil, crankcase oil and consumer purchased fuel additives to determine ash content (ASTM, D-482, 1971), viscosity (ASTM, D-445, 1971), thermal value (ASTM, D-240, 1971), API gravity (ASTM, D-287, 1971), and saturates non aromatic olefins and aromatics (ASTM, D-1319, 1971). Ordinarily these determinations are made only on selected samples and are not part of the routine analysis carried out.

Sulfur is determined by combustion in an oxygen enriched atmosphere or by burning in an artificial atmosphere of 70% carbon dioxide and 30%

*Mention of commercial products does not constitute endorsement by the EPA.

oxygen (ASTM, D-1266 and D-129, 1971); phosphorus in gasoline by ignition with zinc oxide, dissolution in sulfuric acid followed by spectrophotometric analysis using ammonium molybdate-hydrazine sulfate; and carbon, hydrogen, and nitrogen by pyrolysis at 975° C over platinized carbon utilizing a Perkin-Elmer 240 elemental analyzer in accordance with the manufacturer's instructions.

Lead in gasoline in the range of 0.01 to 0.10 gm/gal. is determined by atomic absorption (ASTM, 1973). The lead in the sample is extracted into methyl isobutyl ketone with a quaternary ammonium salt (tricapyl methyl ammonium chloride) after the organic lead has been converted to inorganic lead with iodine. The lead content of the sample is determined by atomic absorption flame spectrometry at 2833 Å using standards prepared from reagent grade lead chloride. By the use of this treatment, all alkyl lead compounds give identical response.

Two multi-element techniques that were intensively investigated for obtaining elemental data on gasoline and other fuels in the trace concentration (ppm-ppb) range were neutron activation analysis and spark source mass spectrometry. Studies to evaluate the accuracy and precision of these methods are reported elsewhere. (vonLehmden, Jungers and Lee, 1973) Neutron activation analysis was limited for the analysis of gasoline because of the possible explosion of the volatile sample in the nuclear reactor and the masking effect of bromine which swamps the radioactive signal of elements having similar half-lifes.

On the other hand, spark source mass spectrometry was applicable for the analysis of over 20 elements in gasoline including Be, Cd, As, V, Mn,

Ni, Sb, Cr, Zn, Cu, Se, B, Ag, Al, Fe, Mg, Cl, P, Pb, and Ca. A gasoline sample is oxidized with bromine followed by freeze drying to remove the liquid and final drying to remove the odor of gasoline. The remaining residue, including the trace elements, is mixed with graphite until homogenous and is pressed into an electrode for analysis with an AEI MS 702R spark source mass spectrometer equipped with photograph plate output (Carter, 1973).

In the study reported here, over 40 gasoline samples were collected for trace element analysis which included at least two regular grades in each of the following cities: Boston, New York, Philadelphia, Atlanta, Chicago, Kansas City, Denver, Dallas, San Francisco, and Seattle. In addition, a total of 6 no-lead or low-lead gasoline samples were collected in Seattle, Boston, Philadelphia and, Kansas City. Six oil companies were represented in the study including Texaco, Mobil, Shell, American, Exxon, and Gulf.

Eighteen samples of commercially available consumer purchased gasoline additives were purchased at retail outlets in the Raleigh-Durham, North Carolina area and analyzed by neutron activation. The brands sampled included: STP Gas Treatment; Gumout, Fuel Mix Tune Up; Wynn's Engine Tune up: Wynn's Spitfire Gas Power Booster; K-Mart Gas Treatment; Zerex Gasoline Antifreeze; Prestone Carb Tune up; Dupont Gas Booster; and Max S-E-T Gas Booster.

RESULTS AND DISCUSSION

Trace Elements in Gasoline

Table I presents a summary of the concentration range of trace constituents in 50 gasoline samples collected for the NFSN. Except for

Pb and S, all determinations were made by spark source mass spectrometry (Carter, 1973). In premium grade gasoline measureable concentrations of Cd, As, V, Mn, Ni, Sb, Cr, Zn, Cu, B, Ca, Ag, Al, Fe, Mg, Cl, P as well as Pb and S were found. Trace amounts of the same elements were also found in regular grade gasoline except for Cd, V, Ag, Al and P. In low lead or no lead gasoline, trace amounts of Mn, Ni, Cr, Zn, Cu, Fe, Cl, Ca, Pb and S were detected.

No association was apparent in the levels of trace constituent found in gasoline and the sampling location. It seems, therefore, that the elements detected were (a) native to the crude oil before refining, (b) introducted as a fuel additive or as a contaminant of a fuel additive, or (c) extracted during the transfer and storage process, e.g., pipelines and service station tanks. In both imported and domestic crude oils, Se, As, Ni, S, and V are known to be present (Anderson, 1973), however, it is likely that the levels of these elements are reduced or even removed in the gasoline fractions during the refining process. On the other hand, B, Ca, Cu, Mn, Zn, P, Pb, Cl and S are known to be components in some organic fuel additives reported to EPA (Bridbord, 1972) although not all are necessarily associated with an individual fuel manufacturer.

It appears that a portion of the trace constituents found in gasoline is introduced in fuel additives or is extracted from the transport and storage system. Hydrocarbon soluble metal compounds can form by reaction of phenols, mercaptans and other acidic materials in gasoline with metals in contact with the gasoline between the refinery and the automobile.

(Polss, 1973). Metals can deteriorate antioxidant addivites such as phenylenediamines and hindered phenols which prevent gum formation. To reduce oxidative deterioration in gasoline, a metal deactivator such as N, N'-disalicylidene-1,2-propanediamine is used to chelate Cu and other metals. Although metal deactivators are effective suppressors of oxidative deterioration, the chelated metal contaminants will be combusted thereby acting as potential poisons of exhaust catalytic devices now under development or the metals may be emitted into the air as pollutants. Indeed, most of these elements have been identified in auto exhaust particulate (Moran, Baldwin, Manary and Valenta, 1972).

Table II presents concentration ranges of lead and phosphorus for 197 premium, regular and low lead gasoline samples collected during 1972 in ten designated cities. A review of this table shows that the lead concentration range in New York is well below 2.0 grams Pb/gallon as required by NYC regulations. The Federal standard for lead and phosphorus as published in the Federal Register (Part II, 1973) defines "lead free" gasoline as containing not more than 0.05 g/gal. and "phosphorus free" as containing not more than 0.005 g/gal. This 91 minimum octane gasoline must be made available after July 1, 1974 in a substantial percentage of gasoline retail stations to provide a fuel which can be used with exhaust catalytic system. Of further interest the proposed standard (Federal Regulation, Part III, 1973) specifies a decreasing amount of lead which will be allowed in all gasoline dispensed by either the refiner, distributor or retailer. This decrease is January 1, 1975 - 2.0g Pb/gal; January 1, 1976 - 1.7g Pb/gal.; January 1, 1977 - 1.5g Pb/gal.;

January 1, 1978 - 1.25g Pb/gas. In non-lead manufacturing areas, the reduction in lead should result in a definite decrease in atmospheric lead.

Trace Constituents in Commercial Consumer Purchased Fuel Additives

Eighteen commercially marketed gasoline additives were analyzed by neutron activation analysis (Rancitelli, 1973). Results, summarized in Table III show that measureable levels of Hg, As, V, Mn, Sb, Cr, Zn, Co, Se, Sn, Ag, Al, Fe, and Sr were found. Additives of this type are multi-functional acting as antioxidants, metal deactivators, corrosion inhibitors, anti-icers, and carburetor and valve deposit detergents. Ordinarily, these additives are used to supplement the additives already present in fuel and may not necessarily be representative of additives blended at the refinery.

Examination of Table III reveals the presence of comparative high levels of Sn (up to 140 μg/ml). Apparently the predominant source of the Sn and possible other elements such as Fe in the fuel additives may have been the metal packaging container, especially from the soldered connection. Intensive use of commercially-marketed additives can add to the environmental trace metal burden and increase the potential for poisoning exhaust catalytic control devices.

Environmental Implications

The presence of metallic elements in gasoline, especially those which have suspected biological toxicity such as Cd, As, V, Ni, and Cr

is of concern to environmentalists because of the potential widespread dissemination of these constituents, most in the respirable range, at ground level. Several studies of the particle size of trace metal components in ambient air have shown that Pb, V, and Zn are associated with particles predominantly of a submicron aerodynamic size (Lee, Goranson, Enrione, and Morgan, 1972; Lee, Patterson, and Wagman, 1968). Particles in this size range can remain suspended in air for long periods of time and can penetrate deep into the human respiratory system (Morrow, 1964). Furthermore, many of the metals found in gasoline, notably Fe and Pb (Urone, Lutsep, Noyes, and Parcher, 1968) can act as catalysts in the transformation of primary atmospheric pollutants to secondary pollutants, e.g. SO_2 to SO_4. Although gasoline combustion may not necessarily be the major source of these constituents, the fact that over 100 billion gallons are consumed annually indicates that gasoline combustion should be considered in estimates of environmental emissions of these metals.

Another environmental concern, mentioned earlier is the presence of constituents such as S, which may poison exhaust catalytic devices now under development thereby reducing their effective operating life. Coupled with this concern is the distinct possibility that fine metal particles may be produced from the exhaust catalysts themselves as recently reported by Balgord (1963). It becomes important, therefore to characterize the trace constituents in the fuel in order to assess the amount of trace metals emitted by exhaust catalytic devices. The widespread use of consumer purchased gasoline additives which contain trace elements that can effect catalytic performance also presents a serious problem.

As more information becomes available through the National Fuels Surveillance Network, it may be necessary to institute some type of control at the refinery or distributor outlet to remove trace contaminants from fuel before it is combusted in the motor vehicle.

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Table I

Trace Elements in Gasoline (μg/ml)*

Element	Premium (22 Samples) Range	Avg	Regular (22 Samples) Range	Avg	Low Lead (6 Samples) Range	Avg
Be	<0.001		<0.001		<0.001	
Cd	<0.001 - 0.03		<0.08		<0.04	
As	<0.001 - 0.002		<0.004 - 0.009		<0.1	
V	0.001 - 0.002		<0.007		<0.003	
Mn	0.002 - 0.03	0.013	.0.001 - 0.011	0.006	<0.002 - 0.03	
Ni	0.003 - 1.5	0.086	0.001 - 0.07	0.02	0.03 - 2.00	0.12
Sb	<0.003 - 0.05		<0.007 - 0.5		<0.10	
Cr	<0.001 - 0.34		<0.003 - 0.03		<0.005 - 0.016	
Zn	0.004 - 2.00	0.16	0.010 - 2.00	0.06	0.20 - 0.50	0.35
Cu	0.011 - 0.25	0.14	0.010 - 0.40	0.08	0.06 - 0.20	0.13
Se	<0.06		<0.05		<0.04	
B	0.001 - 0.210	0.021	0.004 - 0.08	0.02	Not analyzed	
Ag	<0.002 - 0.03		<0.54		<0.1	
Al	<0.001 - 0.02		<0.007		Not analyzed	
Fe	0.07 - 6.00	1.07	0.07 - 3.80	0.91	0.3 - 13.0	6.7
Mg	<0.002 - 0.004		<0.002 - 0.01		Not analyzed	
Cl	0.02 - 0.80	0.19	0.05 - 1.10		<0.007 - 0.90	
P	<0.001 - 0.30		<0.001 - 2.0		<0.02	
Pb**	238 - 763	600	190 - 750	494	132 - 135	134
S***	10 - 360	81	10 - 640	177	4 - 720	200
Ca	0.06 - 0.26	0.24	<0.06 - 3.0		<0.2 - 0.7	

*Determined by spark source mass spectrometry (Carter, 1973) except as noted.
**200 samples by atomic absorption spectrometry
***103 samples by ASTM D-1266 (1971).

Table II

Concentration Ranges of Lead and Phosphorus in Gasoline Samples Collected during 1972 in Ten EPA Regions

City (Metropolitan)	Lead (grams/U.S. Gallon)			Phosphorus (grams/U.S. Gallon)		
	Premium	Regular	Low Lead	Premium	Regular	Low Lead
[illegible]ston	(9)* 1.49-2.85	(5) 1.23-2.84	(11) 0.009-0.68	(9)<0.0001-0.006	(5)<0.0001-0.004	(11)<0.0001-0.00
[illegible] York	(9) 0.85-1.31	(11)0.72-1.08	(5) 0.018 - 0.29	(9)<0.0001-0.0002	(11)<0.0001-0.0001	(5)<0.0001-0.00
[illegible]delphia	(8) 1.31 -2.77	(9) 1.19-2.70	(8) 0.010 - 0.60	(8)<0.0001-0.0003	(9)<0.0001-0.0001	(8)<0.0001-0.00
[illegible]lanta	(6) 1.78 -2.50	(7) 0.90-2.36	(6) 0.016 - 0.48	(6)<0.0001-0.004	(7)<0.0001-0.0001	(5)<0.0001-0.01
[illegible]ego	(11)1.09 - 2.72	(7) 0.98-2.43	(7) 0.003 - 1.70	(11)<0.0001-0.0003	(7)all <0.0001	(7)<0.0001-0.00
[illegible]as	(5) 2.10 - 2.89	(5) 1.39-2.72	(5) 0.032 - 0.44	(5)<0.0001-0.0002	(5)<0.0001-0.0001	(5)<0.0001-0.00
[illegible]s City	(5) 1.21 - 2.65	(5) 1.42-2.20	(5) 0.011 - 1.46	(5)<0.0001-0.0001	(5)all <0.0001	(5)<0.0001-0.00
[illegible]	(5) 1.84 - 2.72	(5) 1.14-1.94	(4) 0.022 - 1.20	(5)<0.0001-0.0001	(5)all<0.0001	(4)<0.0001-0.0
[illegible] Francisco	(9) 1.48 - 3.52	(5) 1.28-2.32	(6) 0.037 - 0.63	(9)all <0.0001	(5)all <0.0001	(6)<0.0001-0.00
[illegible]ttle	(4) 1.80 - 2.65	(7) 1.62-3.40	(3) 0.020 - 0.50	(4)<0.0001-0.0001	(7)<0.0001-0.0001	(3)<0.0001-0.00

*Number in parenthesis represents the number of samples specified for that concentration range.

Table III

Trace Elements in Consumer Purchased Fuel Additives*

Element	Concentration Range (µg/ml)	Avg (µg/ml)
Hg	<0.0002 - 0.002	
Cd	<0.02 - 0.20	
As	<0.001 - 0.23	
V	<0.001 - 0.031	
Mn	0.007 - 2.71	0.16
Ni	<0.013 - <0.340	
Sb	<0.0005 - 0.0041	
Cr	<0.002 - 0.095	
Zn	0.032 - 38.0	8.8
Co	<0.0002 - 0.0360	
Se	<0.001 - 0.032	
Sn	<0.07 - 140	
Ag	<0.0003 - 0.0035	
Al	<0.01 - 2.30	
Fe	<0.03 - 560	
Sr	<0.033 - 37	
Br	<0.014 - 10	
Cl	0.5 - 18200	1334
Na	<0.01 - 99	
Ba	<0.02 - 4.2	
Ca	<17 - 1900	
K	<0.7 - 63	

*18 samples analyzed by neutron activation (Rancitelli, 1973).

United States Environmental Protection Agency

FEB 22 1974

SUBJECT Status of NBS-EPA Certification Program for Trace Elements in Coal Fly Ash, Residual Fuel Oil and Gasoline

DATE February 19, 1974

FROM Darryl J. von Lehmden, Chief, IOS, QCB/QAEML

TO See Below

The status of the EPA-NBS funded program for the certification of 13 trace elements (Hg, Be, Pb, Cd, V, Mn, Ni, Cr, As, Se, Zn, S, P, F, and U) in coal, fly ash, fuel oil, and gasoline is as follows:

A. Coal and fly ash will be issued by March 1, 1974.
B. Residual fuel oil will be issued by June 30, 1974, for selected elements.
C. Gasoline certification is under way with no set date for issuance.

The following information is required to order the NBS-SRM:

Coal, SRM # 1632. Cost - $73.00 (75 gm)
Fly ash, SRM # 1633. Cost - $73.00 (75 gm)
Fuel oil, SRM # 1634. Cost - $75.00 (100 ml)

Attached is a copy of the latest report on the certification progress. One item is of particular significance in the report. The lead content in gasoline decreases during storage when the gasoline is exposed to direct light. It has been found that storage in the darkness will prevent lead decomposition and that samples stored for 18 months at ambient temperature in darkness show no signs of decomposition.

The implication of this finding to the enforcement program for unleaded gasoline is that all samples collected by mobile van operators which become chain of custody samples by nature of being a violation or a border line case, and all samples used as quality control test samples must be stored in such a manner to prevent exposure to light.

Attachment

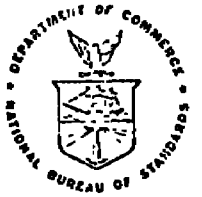
Addresses:
OD/QAEML (D. Shearer, T. Hauser)
RB/CSL (C. Craig, J. Dorsey)
DEB/CSL (R. Rangebrauck, K. Janes)
FIB/ISED (C. Freed, J. Sakofosky)
ACB/QAEML (R. Thompson, R. Jungers)
QAD (C. Plost)
QCB/QAEML (S. Hochheiser, T. Clark, S. Bromberg)

EPA Form 1320-6 (11-71)

File Number
NBS-EPA-IAG-015

CHARACTERIZATION OF STANDARD REFERENCE MATERIALS FOR DETERMINATION OF TRACE ELEMENTS IN FUELS

Division of Atmospheric Surveillance
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, N.C.



U.S. Department of Commerce
National Bureau of Standards
Washington, D.C. 20234

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

Date: February 1, 1974

To James R. McNesby, Manager
Measures for Air Quality
Through: Philip D. LaFleur, Acting Chief
Analytical Chemistry Division
Via: John K. Taylor, Manager
Environmental Analysis Program, Division 310

From Donald A. Becker, Acting Chief
Activation Analysis Section

Subject First Half FY 1974 Progress Report on the Determination of Trace Elements in Fuel Oil and Gasoline

Progress has been made in several areas in the determination of trace elements in fuel oil and gasoline. These specific areas include storage conditions, sample handling techniques, and analytical methodology. Both standards are currently undergoing analysis, and the present status of each is discussed separately below.

Trace Elements in Gasoline

Initial testing of the gasoline stability with time on the open shelf indicated definite decomposition was occurring, most likely of the lead tetraethyl. This was obvious through the deposition of a coating on the glass surface, a scum on the top of the gasoline still inside the original bottle, and a definite increase in particulate matter in the liquid itself. Thus, much of the work on this material was held up until definitive storage conditions could be determined. It has now been established that storage in the dark will prevent this decomposition, and samples stored for 18 months at ambient temperatures in the dark show no signs of decomposition. Therefore, work on the sample-handling and analysis of of gasoline is being continued.

Sampling handling aspects of the gasoline are very difficult, since considerable evaporation occurs during sampling and analysis causing significant decreases in analytical precision and accuracy. A number of methods of sampling and sample handling are being evaluated, including direct evaporation techniques, direct solvent extraction techniques, and direct aspiration of the gasoline into a flame type atomic absorption spectrometer. The determination of some elements may also be possible using non-destructive neutron activation analysis, however the high bromine content of the gasoline will make this analysis difficult.

In order to determine what trace elements are actually present in the gasoline in measurable quantities, a general scan using optical emission spectroscopy was made. Due to sample handling problems, this technique cannot be quantitative for gasoline, but detectable quantities of Pb, Si, P, Mg, Sn, Fe, Al, Cu, Ag, Zn, Ti, Ba, Ca, Sc and Cr were seen. The methods used included slow evaporation of 100 ml of gasoline down to ∿30 mg of tar-like material. This procedure probably loses some of the trace elements, especially ones like Ni (probably present as the carbonyl), but is valuable for obtaining a "more than" figure for quantitative evaluation by other analytical techniques.

Trace Elements in Fuel Oil

Significant progress has been made in the analysis of trace elements in the fuel oil. The present status is shown in Table 1, and reveals that four elements (Ni, Pb, V, Fe) have been determined by two or more methods which agree, and can be certified when necessary. One element (Zn), has been determined by two methods which disagree (NAA and ATA), so additional work is necessary to resolve this discrepancy.

Three more elements (Hg, Mn, Se) have been determined by one method, and have a second method in process or being examined for feasibility. Another three elements (Cr, Cd, Be) are currently undergoing analysis, two of which (Cr, Cd) should be feasible by at least two methods. Arsenic and beryllium can be determined by only one analytical method at present, with arsenic already determined and beryllium currently undergoing analysis. The fuel oil used was originally certified for sulfur

content, but is undergoing reanalysis by NAA in order to verify that the sulfur content is still the same as previously. Finally, two elements (U, Th) have been determined by IDMS and found to be extremely low. A second method is probably possible (NAA) but is not felt to be justified for this material.

Thus, it is apparent that the analysis of the fuel oils is progressing satisfactorily, and most of the stated elements of interest (arsenic through zinc in Table 1) should be able to be certified by the end of FY 1974.

Table 1. Trace Elements in Fuel Oil Standard

Element	Method 1	Method 2
Arsenic	NAA - Determined	
Beryllium	SPEC - In process	
Cadmium	NAA - In process	POL - In process
Chromium	NAA - In process	ATA or IDSSMA - Feasible
Mercury	NAA - Determined	ATA - Feasible
Manganese	NAA - Determined	SPEC - Feasible
Nickel*	IDMS - Determined	POL and ATA - Determined
Lead*	IDMS - Determined	POL - Determined
Sulfur	Previously certified	NAA - In process
Selenium	NAA - Determined	IDSSMS - Feasible
Vanadium*	NAA - Determined	ATA - Determined
Zinc**	NAA - Determined**	ATA - Determined**
Iron*	POL - Determined	ATA - Determined
Thorium	IDMS - Determined	
Uranium	IDMS - Determined	

*Have two methods which agree
**Methods disagree

IDMS = Isotope Dilution Mass Spectrometry; IDSSMS = ID Spark Source MS; POL = Polarography; SPEC = Spectrophotometry; ATA = Atomic Absorption; NAA = Neutron Activation Analysis; MICRO = Microcalorimetry (Bomb.)

Appendix B2.1

EMISSIONS CHARACTERIZATION
SUMMARY

The major effort in the ORD Fuel and Fuel Additive, Catalyst, and Mobile Source Emissions Research Programs has involved detailed characterization of non-regulated emissions from mobile sources and the effect fuel additives and control devices might have on such emissions. Past efforts focused upon characterization of particulate emissions and the related development of a particulate measurement method (Appendix B3). This has been an extremely difficult and complex task but is reflective of the problems involved in the characterization and subsequent development of new measurement and analytical technology. This broad and advanced capability within the ORD research staff, specific to mobile source particulate measurement methodology has been a positive critical factor in our ability to ascertain the magnitude of sulfuric acid emissions from both catalyst- and non-catalyst-equipped vehicles.

Detailed analysis of gaseous emissions products have also been conducted within the control of these programs.

The effects sought in this research are really twofold: (1) determination of the change in relative ratios of identified non-regulated gaseous and particulate emission species as a result of fuel, fuel additive, or control device changes, and (2) determination of new exhaust species which may result from fuel, fuel additives, or control device changes. Once an emission product of concern or interest has been identified, the program emphasis shifts to one of development of a detailed, specific measurement methodology. Measurement methodology development is covered in detail in the following Appendix B3.

Contained within this Appendix are those ORD programs which focus upon the characterization of non-regulated gaseous and particulate exhaust products from both catalyst and non-catalyst-equipped motor vehicles.

SULFATE EMISSIONS FROM CATALYST AND NON-CATALYST EQUIPPED AUTOMOBILES

Chemistry and Physics Laboratory
NERC-RTP

INTRODUCTION

Recent observation of unusually high particulate emissions from catalyst-equipped automobiles has revived interest in sulfate, platinum and other condensed phase substances which may be present in the exhaust of catalyst-equipped automobiles (1). Since full-scale production of such cars is in progress, it is extremely important to assess the impact of such substances on the roadway air quality. Recent calculations from roadway dispersion models suggest that automotive sulfate accumulation could cause localized problems if the emission rate is as high as 0.05 grams/mile (3).

In the past several months abundant data has emerged to show that sulfate emission rates at least that high can be expected with either pelleted or monolithic catalysts (4-10). Additionally, some estimates of non-catalyst automobile emission rates have been made, this latter with considerable attendent controversy over experimental methods. A number of EPA and industrial investigators, using filtration or condensation procedures, contend that sulfate emissions from conventional non-catalyst cars is minimal (4-8). Other groups, using a bubbler collection method, feel there is substantial sulfate emission from non-catalyst cars (9,10). It seems possible that at least some of this bubbler-found sulfate could be

an artifact of the chemical reaction with some of the many reactive compounds present in exhaust (6,7).

The purpose of this paper is to present additional data on this topic, to compare the sulfate emissions values from other groups, and to suggest avenues for future research. Recognition of a new environmental problem associated with catalyst-equipped automobiles in the months immediately preceding their production by the millions points as clearly as any event of recent years to the continuing need for high quality scientific research into the overall economic, environmental, and energy conservation consequences of automotive technology.

EXPERIMENTAL

All automotive testing was carried out on a water-brake chassis dynamometer, qualified and calibrated according to the Federal Register procedures. Exhaust gas sampling was also carried out, using Constant Volume Sampling equipment and procedures as prescribed in the 1975 Federal Test Procedure (11), i.e. a six-bag CVS gas handling system.

Filter samples of condensed phase substances occurring in the exhaust were obtained, using a 5 meter-long, 0.5 meter diameter cylindrical stainless steel tunnel, interposed between the dilution air box and the CVS. Auto exhaust was injected into the center of this tube through a 5 cm. O.D. downstream facing tube terminating in the plane of a baffle-plate orifice which restricts the dilution air flow to a diameter of 25 cm. The tunnel design is similar to that used by Moran and Manary (12) and by Habibi (13), except for its greatly reduced length. A diagram of the apparatus is shown in Figure 1, and photographs of both floor- and over-mounted installations are shown in Figures 2 and 3. By placing the CVS system toward the front of the automobile and the floow mounted tunnel along side, a fairly compact chassis dynamometer test stand can be achieved. While the bulk of the dilution tunnel system is ungainly, a reasonably satisfactory particulate handling system can be achieved without undue cost of impact on auto exhaust gas analysis facilities.

Under the conditions of the experiments reported herein, the combined exhaust-dilution air flow rate was the maximum rate available with the 4 speed CVS, 11.5 m^3/min. (406.9 SCFM),

corresponding to a linear flow rate of approximately 1 meter/sec. (3.2 ft/sec) and a Reynolds number of about 60,000. The baffle-orifice plate functions as a mixing device, forcing the gas to high center-tube velocities and intense mixing with minimal wall contact. While no studies of recirculation patterns in the mixing zone have as yet been made, rather extensive flow and aerosol concentration profiles have been determined and wall and sampling system loss experiments have been made. Results of these experiments are being presented in detail in other publications (14); the results to date indicate the flow profile to be uniform within $\pm$ 10% and the aerosol concentration to be uniform with $\pm$ 15%. Aerosol loss experiments were conducted by operating several 1975 Federal test procedures with a catalyst-equipped automobile after thorough steam and solvent cleaning of the tunnel. Following the vehicle experiments, the tunnel was then disassembled and thoroughly washed with a measured volume of distilled water. Measurement of sulfate in the washings indicated less than 1% of the sulfate handled by the tunnel was lost to the walls. A similar experiment with non-catalyst cars indicated about 3% of the organic aerosol handled was recovered in the methylene chloride wall washings.

Samples of particulate matter were obtained through a rake of four 2.5 cm (1 in.) stainless steel probes at the isokinetic flow rate of 28 liters/min (1CFM). The probe centerlines are located on the corners of a 15 cm. diameter square, the center of which is located on the tunnel centerline. Aerosol is ducted through tubing and filter holders to 47mm, 0.45 micron fluorocarbon filters. The sample handling and filtering system was designed and constructed with smooth continuous walls, long radius bends, no restrictions and only gradual (20°) increases in diameter in the filter holder. Experiments with both organic and sulfate aerosols indicate that insignificant aerosol handling losses were incurred with this apparatus (14).

Automobiles used in these studies included two full size sedans, one equipped with a 400 CID V-8 engine, air-pump and monolithic platinum catalyst and the other with a 455 CID V-8 engine with pelleted catalyst and no air pump. For the monolithic catalyst car, the oxygen content was approximately 4% in the pre-catalyst gases and the overall engine air-fuel ratio was approximately 16/1 (4). For the pelleted-catalyst equipped car, the exhaust oxygen content was about 2 vol.%. Both cars

were conditioned and tested according to the provisions of the 1975 Federal Test Procedure, except that the heat-build and evaporative loss sections of the test were omitted. Some recent experiments have been carried out with the Highway Fuel Economy test. Base fuel used for all the tests was the same reference gasoline being used throughout the EPA contract fuel additive programs. It has been described previously (4).

Methods of analysis for sulfate (15), SO_2 (16), and individual hydrocarbons (17) have also been described previously. Sulfate is analyzed by an automated colorimetric procedure involving barium chloranilate as the colorimetric reagent. SO_2 is determined by an adaptation of the method of West and Gaeke, and detailed hydrocarbons by an automated gas chromatographic procedure. Bubbler samples for SO2 determination were obtained using a gas handling manifold, equipped with solenoid valves which switch the bubbler vacuum. Valve operation is controlled by relays switched by the CVS logic. The CVS bag samples and bubblers, in turn, are switched by a clock-timer sequencing mechanism initiated by the cycle driver at his station. No special sequencing of filter samples was used and, consequently, the gas volume sampled was integrated equally

over the entire 31 minute active portion of the test. This resulted in equal weighting of the cold and hot start tests, but decreased the number of samples handled by a factor of three. This single sample integrating technique was necessary, however, to provide sufficient sample for further analysis. All gas samples were properly sequenced, however, and conform to the Federal Register procedure, except that an additional 5 second of sampling time is provided for on each bag to allow for sample residence time in the tunnel.

With these methods additional studies of sulfate formation was begun.

RESULTS AND DISCUSSION

Fairly extensive discussion of chemical reactions which produce sulfuric acid (for it is this species which accounts for the sulfate) in the exhaust of catalyst-equipped cars and the thermodynamics of those processes have been recently presented (6,7). Those discussions have shown that, if thermodynamic equilibrium is achieved, sulfate formation will vary linearly with exhaust SO_2

concentration (hence fuel sulfur) and with the square root of oxygen concentration (7). Increasing catalyst temperature from 480° C (900°F) to 580° C (1080°F) decreased equilibrium sulfate yield from about 90% to 70% of the fuel sulfur. Further increase to 680° C (1260° F) decreases equilibrium sulfate to 40% of the fuel sulfur converted (7). Actual conversion data is far below these figures, however, probably because of storage of sulfate as aluminum sulfate on the catalyst surfaces (4-10). Some evidence has been presented to the effect that some of the sulfate stored at low temperatures on the catalyst is re-equilibrated at the higher release temperatures (e.g. at high speed cruise) and is in part released as SO_2 (5). Thus, it appears that an overall catalyst conversion of fuel sulfur to sulfate is from about 55% to about 10% for monolithic catalysts, depending on driving conditions. For pelleted catalysts the extent of sulfate storage is much greater and the conversion varies from about 2% (4,5,6) under 1975 FTP conditions to about 40% (7) under high speed cruise with air injection. Since most pelleted catalyst models will not use air pumps, the in-use maximum for the upcoming model year GM non-air injection products will be about 25% if operated long enough to achieve equilibrium (4,6). However, pelleted catalysts are capable of emitting much of the stored sulfate in

the first ten minutes or so of high speed driving. Thus, apparant fuel conversions of greater than 100% are possible under very real conditions (4,6,7). Because of the great difficulty in sorting out storage and formation phenomena, the monolithic catalyst-air pump combination was used as a model for further studies. However, even in this case, our data have been none too reproducible.

Table 1 presents a series of 1975 FTP runs with the base fuel of 0.0124 wt.% sulfur and that same fuel doped to sulfur levels of 0.025, 0.05, 0.075 and 0.1 wt.% with thiophene. Conditioning runs on fuel change consisted of a 1975 FTP, 2 hours of 15mph cruise, a second FTP, followed by the dataaFTP. Data obtained at 0.025% sulfur was fairly consistent except for an unexplained shift upwards of about 20% in the sulfate emissions level for two runs and a shift downward of 15% in one run. In short, our data was nowhere near as consistent as that of Esso (6)with this catalyst. Table 1 also shows the CO and hydrocarbon emissions levels and indicates that these were not materially influenced by fuel sulfur level. Thus, the extent of conversion decreases with increasing fuel sulfur and this effect does not appear to be especially tied to

catalytic activity for hydrocarbon or CO oxidation. Since the conversion rate is below that predicted by thermodynamic equilibrium, it it possible that diffusion to active catalyst sites may control the process.

Table 2 compares the present results with those of Esso and General Motors on this system. Our data is significantly lower than that obtained by either GM or Esso. It is not clear whether the automobile, catalyst, or experimental techniques account for the differences.

Table 3 presents the results of steady state tests at idle to 60 mph. Similar Esso and GM results are shown for comparison. Clearly the lower speed tests yield higher conversions. A similar result has been obtained by EPA-Ann Arbor (9). Ford-Battelle experiments indicate conversions of 40% or better at steady state. This results is contrasted with the results from a pelleted catalyst-equipped car, shown in Table 4. Again GM and Esso data are shown for comparison. Clearly the fact of decreasing catalyst storage with increasing temperature accounts for these results.

Table 5 presents a summary of data obtained with non-catalyst cars under FTP and steady state conditions. A total of sevel vehicles were investigated, ranging from '72, '73, and '74 model year conventional vehicles. A '74 rotary engine vehicle and light duty diesel powered car have also redently been tested. None of these emitted detectable water soluble sulfate. X-ray analysis of the diesel particulate samples indicated substantial amounts of sulfur present, however, about 4 wt.% of the particulate. The form of this material is currently under investigation. Both organically bound sulfur and SO_2 absorbed strongly on soot may account for the sulfur found. General Motors has reported very low sulfate emissions $.10^3$ grams/mile for both rotary and diesel powered cars.

Table 6 presents a comparison of hydrocarbon distributions found with the two catalyst systems under FTP and Fuel Economy cycles. The individual hydrocarbons are similar for the two catalysts for FTP conditions, surprisingly there were no substantial shift in the hydrocarbon distribution for the highway Fuel Economy test. Unfortunately, the pelleted catalyst car was not available for these runs. In summary, the milder, higher

speed Highway Fuel Economy test yields a surprisingly high hydrocarbon output, mainly unreactive hydrocarbons, however.

CONCLUSIONS

1. In those cruise portions of the passenger car operating envelop most likely to influence atmospheric sulfate on an isolated roadway, sulfate emissions from various catalyst cars appear to be nearly the same, i.e., about 0.05 gram/mile. Apparently, it is the isolated roadway which is likely to be location of any automotive sulfates problem. Variance among experimental groups is great, however.

2. Beaded catalysts appear to give substantially lower emissions rates in urban driving patterns than do monolithic catalysts. However, sulfate emissions from passenger cars are not likely to influence the urban sulfates burden.

3. Fuel sulfur level influences catalyst sulfates emissions, but not in a linear fashion. Lower SO_2 exhausts are somewhat more efficiently converted to sulfate than are exhausts from higher sulfur fuels.

4. Hydrocarbon emissions patterns are similar for the various catalysts under a variety of driving patterns, including both urban and highway driving cycles.

FUTURE WORK

Since shortages of petroleum-based fuels seem inevitable for the foreseeable future, both the automotive and energy industries must certainly seriously consider and eventually adopt new production technologies to remain healthy. It will fall to research groups to thoroughly investigate the environmental and energy conservation consequences of new power plants, new fuels, or of substantial modifications of present fuel, power plants, and control systems.

For the present, study of the sulfate emissions from various catalyst systems under both FTP and steady-state conditions is underway. Parametric studies of sulfate formation under various catalyst operating conditions of light duty diesel, stratified charge, and rotary engine emissions, and on sulfate trap feasibility are either planned for initiation within the next few months or have recently begun under EPA

sponsorship by both the Office of Research and Development and the Office of Air and Water programs. Differences in test results and the wide scatter thus far reported must be reconciled. More work on methods of test is needed and planned.

Further studies of the detailed emissions patterns of any significant pollutants emitted from advanced power plants or fuels are planned for the next few years.

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TABLE 1

Sulfate Results - Monolithic Platinum Catalyst

1975 FTP

Fuel S, ppm	No. of runs	grams/mile						
		HC	CO	NO_x	Particulates	SO_4	Fuel S as SO_4	% S converted
124	10	0.254	4.34	2.55	0.0310	0.00962	0.0924	10.4
250	11	0.215	5.33	2.60	0.0400	0.0139	0.191	7.3
500	9	0.187	5.28	2.49	0.0574	0.0187	0.378	4.9
750	10	0.211	4.90	2.63	0.0563	0.0225	0.568	4.0
1000	10	0.258	4.32	2.80	0.0828	0.0290	0.757	3.8

TABLE 2

Comparison of Cold Start FTP Sulfate Emissions Data

Monolithic Catalysts

Fuel S, ppm	Experimenter	Particulate g/mile	SO_4 g/mile	Conversion of S to SO_4, %
40	ESSO	0.036	0.014	35
124	EPA/ORD	0.031	0.0096	10.4
250	EPA/ORD	0.040	0.014	7.3
200	GM	--	0.028	13.3
300	GM	--	0.019	7.8
320	ESSO	0.183	0.061	23
500	EPA/ORD	0.057	0.019	4.9
650	GM	--	0.143	27
670	ESSO	0.249	0.134	23
750	EPA/ORD	0.056	0.022	4.0
1000	EPA/ORD	0.083	0.029	3.8

TABLE 3

Steady State Sulfate Emissions

0.05%S - Monolithic Catalyst

Run Condition	Grams/Mile Particulate	SO_4
Idle	0.050	0.029
15 mph	0.068	0.037
30 mph	0.043	0.025
45 mph	0.048	0.021
60 mph	0.033	0.019
HWFET	0.072	0.031
Esso Data 0.067% S fuel		
40 mph	0.210	0.090
GM Data 0.065% s fuel.		
30 mph		0.134
40 mph		0.164
60 mph		0.105

TABLE 4

Steady State Sulfate Emissions

0.1% S fuel - pelleted catalyst

Run condition	Grams/Mile Particulate	SO_4
Idle	0.0022	0.0005
15 mph	0.027	0.013
45 mph	0.111	0.069
60 mph	0.045	0.020
60 mph	0.186	0.121

TABLE 5

Particulate Emissions Non-Catalyst Cars

1975 FTP

0.1% Sulfur Fuel

Car	Particulate g/mile	SO_4 g/mile
1974 Chevelle	0.0323	N.D.
1973 Chevelle	0.0717	N.D.
1972 Impala	0.0121	0.0008
1971 Ford (Catalyst Car Without Catalyst)	0.0232	0.00112

N.D. - None Detected

Table 6

Individual Hydrocarbon Analysis

	Pelleted Catalyst-LA-4 no air pump-Bag 1	Monolithic Catalyst LA-4 Bag 1	Monolithic Catalyst Highway Fuel Economy Test
Hydrocarbons, ppmc	81	31	28
	% of total (ppmc/ppmc total)		
Methane	7.5	17.2	19.6
Ethylene	8.8	9.0	8.5
Acetylene	1.7	3.5	2.1
Butane	8.2	6.5	7.5
Isopentane	5.2	6.1	8.0
N-pentane	3.7	5.0	7.0
Isooctane	6.7	6.4	5.2
Benzene	5.1	3.3	6.5
Toluene	13.4	9.1	9.1

Appendix B2.3

Status Report
ROAP 21BCE
Task 02

Characterize Particulate Emissions - Prototype Catalyst Cars

Concept:

The sulfate and abraded catalyst particle emissions have not been systematically measured from a variety of catalysts under consistent conditions. A contract program was instituted to study a wide variety of catalyst compositions (15 in all) representative of current and future production types. Particulate composition and emission rate will be determined with three different gasolines under FTP, high and moderate speed steady states, and at idle. Vibration tests will be carried out in later stages of the program to study relative abrasion classes of catalyst material and potential noble metal emissions. It is expected that this program will suggest the feasibility of emissions control by modification of catalyst composition.

Status:

The contract has been let to Exxon Research and Engineering who have now completed non-catalyst gasoline testing. Catalyst testing with the first five catalysts is in progress and completed data on the first one or two is expected by this fall. Completion of the first eight catalyst determinations including all production catalysts for 75 model year cars is expected by November 15.

THE CHARACTERIZATION OF PARTICULATE EMISSIONS FROM PROTOTYPE CATALYST VEHICLES

MONTHLY PROGRESS REPORT NO. 1
FOR PERIOD JUNE 1 TO JUNE 30, 1974
PREPARED BY MORTON BELTZER

CONTRACT NO. 68-02-1279

Prepared by

Exxon Products Research Division
Exxon Research and Engineering Company
Linden, New Jersey

for

Environmental Protection Agency
Research Triangle Park, North Carolina 27711

July 1974

Section I

Purpose and Scope of Work

Exxon Research and Engineering Company, under contract with the Environmental Protection Agency, is engaged in a research program designed to measure and characterize the exhaust particulate emissions from a variety of catalyst systems, both commercial and prototype, that are candidates for use in automotive emissions control. Due to such mechanisms as mechanical and thermal shock, and possible chemical conversion of catalyst material to a mobile condensed material, particulate emissions from catalyst equipped vehicles could differ markedly from that of conventional vehicles. Furthermore, catalytic conversion of gaseous exhaust components to particulate exhaust matter introduces exhaust components that are not now present in the exhaust from conventional vehicles. A case in point is the catalytic oxidation of exhaust sulfur dioxide to the trioxide which is then emitted as sulfate aerosol.

In order to separate vehicle and catalyst effects on total particulate emissions, it will be necessary to measure and characterize particulate emissions from the vehicles in their conventional configuration before they are equipped with catalysts.

Eight catalyst systems (three monolithic oxidation catalysts, two beaded oxidation catalysts, and three reduction catalysts will be tested with three fuels.

The three fuels that will be tested are:

(1) an EPA furnished reference fuel.

(2) the EPA fuel treated with an additive package consisting of thiophene and t-butyl sulfide to a fuel sulfur level of 0.1 wt.% sulfur, and TEL as motor mix to a level of 0.05 gms Pb/gal.

(3) A high aromatic content fuel similarly treated.

Both treated fuels shall also contain an additive package comprised of Lubrizol 596 (0.27 g/gal) and Paradyne 502 (0.45 g/gal). The former functions as detergent, corrosion inhibitor, anti-stall, and anti-icing agent and contains about 2.25 - 2.75 wt.% nitrogen. Paradyne 502 contains 0.75 wt.% nitrogen and functions as a detergent, anti-rust agent, and deposit modifier.

This fuel selection should allow exhaust particulate characterization as follows:

(1) level of composition of exhaust particulate resulting from the use of an additive-free fuel in conventional and catalyst equipped vehicles.

(2) effect of fuel additives on particulate emissions from conventional and catalyst equipped vehicles.

(3) effect of a high aromatic fuel containing additives on particulate emissions from conventional and catalyst equipped vehicles.

Due to its introductory nature and the range of areas covered, the following sections of this Monthly Technical Progress Narrative are somewhat detailed. Future monthly reports will be more brief and informal as desired by EPA.

Section II

A. Work During Period of June 1-30, 1974

The first month of this contract effort was concentrated on alterations and additions to the particulate sampling system, and an evaluation of the analytical scheme for metal particulate and organic exhaust particulate matter. A dry run sequence was also carried out to establish a working procedure and to determine where problems could occur. Each of these will be briefly discussed below. In addition four catalyst systems have been received to date. These systems are being adapted to the vehicle so that they can be readily interchanged between the mileage accumulation vehicle and the test vehicle. Both vehicles have been broken in at this point by a combination of about 2000 miles of commuter type driving, and 2000 miles on the Mileage Accumulation Dynamometers (MADS) using the Federal Mileage Accumulation Schedule.

A.1. Revamping and Testing of Sampling System

Probes sampling at a 15 CFM rate instead of the 10 CFM rate were installed in order to obtain larger samples of particulate for analysis. In addition, an Anderson Impactor was reactivated to obtain particle size distributions. It was necessary to check out the internal agreement between the two probes, and between the Impactor and the two probes.

A series of runs with a catalyst equipped vehicle was carried out using these new probes. Agreement between the two sampling probes was excellent, both for total particulate, and for sulfuric acid emissions. Several of the test results with an oxidation catalyst equipped vehicle are shown below.

CORRESPONDENCE BETWEEN 15 CFM SAMPLING PROBES

Test	% Fuel Sulfur	Emission Rate, gms/km: Total Particulate, Filter # 1	Total Particulate, Filter # 2	H_2SO_4, Filter # 1	H_2SO_4, Filter # 2
60 mph, 1 hr	0.046	0.101	0.098	0.041	0.039
" "	"	0.098	0.098	0.044	0.042
" "	"	0.106	0.104	0.045	0.045
" "	"	0.108	0.106	0.042	0.042
" "	"	0.111	0.113	0.046	0.051

A.2. Agreement between Impactor and 15 CFM Filters

Several runs were carried out to check the particulate emission rate correspondence between the Anderson Impactor and the 15 CFM sampling probes. The impactor probe samples at 1.5 CFM rate. The impactor as adapted to our needs contains one mil thick stainless steel shim stock collection plates, placed on the particulate collection plates normally used in this impactor.

The shim stock was washed progressively in cyclohexane-toluene mixture, alcohol, acetone, and then cleaned ultrasonically in a detergent-containing solution of water. Extensive testing indicated that weight changes measured on the shim stocks as a result of being used during a run would be a reliable measure of the weight of material of a given particle size range.

Initial tests used all seven impactor stages and the absolute filter. This filter is from the same batch as the 15 CFM filters (Gelman Type A glass fiber filter). A PTX oxidation catalyst equipped vehicle was run at 40 mph for one hour and 60 mph for two hours on a 0.046% sulfur fuel. The results for each run are shown below .

COMPARISON OF IMPACTOR AND 15 CFM SAMPLING PROBES

40 MPH, 1 HR. CRUISE

(A) Total Particulate

Anderson Impactor	gms/km	gms/km 15 CFM Filters #1	#2
Sum of shims (1 to 7)	0.009		
Absolute filter	0.071		
Shims + filter	0.080	0.087	0.087

(B) Sulfuric Acid Emissions

System	gms/km
Absolute filter	0.034
#1, 15 CFM filter	0.034
#2, 15 CFM filter	0.033

---

60 MPH, 1 HR. CRUISE

(A) Total Particulate

Anderson Impactor	gms/km	gms/km 15 CFM Filters #1	#2
Sum of shims (1 to 7)	0.004		
Absolute filter	0.124		
Shims + filter	0.128	0.130	0.131

(B) Sulfuric Acid Emissions

System	gms/km
Absolute filter	0.060
#1, 15 CFM filter	0.055
#2, 15 CFM filter	0.053

The agreement between the impactor and the large filters with respect to total particulate and sulfuric acid emission rates was within 5%. Over 90% of the particulate and all of the sulfate was less than one micron in diameter. The particulates above one micron were log normally distributed as shown in Figure I.

It was found that the particulate matter on the shim stocks was difficult to remove. Accordingly, new shim stocks will be used for each run.

Preliminary examination of the particulate matter on the shim stock by X-ray energy non-dispersive analysis in the scanning electron microscope indicated that this is composed of silicon, sulfur, possibly aluminum which could be masked by the silicon, and possibly platinum. These results are to be regarded as strictly tentative at this stage.

A.3. Exhaust Splitter

The exhaust particulate sampler was originally designed to sample particulate at 32°C for the 1972 or 1975 Federal Test Procedure, with the minimum dilution rate compatible with that goal. We have found that at a total flow rate of 450 CFM (exhaust + dilution air), temperature control is maintained operating with catalyst-equipped and with conventional vehicles. However, in order to maintain temperature control for a 70 mph cruise test run with a catalyst equipped vehicle, it is necessary to dilute the exhaust by venting an accurately known amount of raw exhaust. To this end, we have designed and tested two types of exhaust splitters.

The initial approach was to split the raw exhaust so that only a portion is injected into the flow development funnel. Linear velocity is maintained in each leg of the splitter. Velocities were to be measured using Pitot tubes and equalized by adjusting the pressure drop in the vent leg using a variable speed pump. However, the pressure drops were small and subject to rapid oscillations, making equalization extremely difficult. Attempts to damp the oscillations were not successful.

An alternative approach utilized hot wire anemometers with the same splitting principle and method of flow balance. This method was shown to work with ambient air but has not been successful to date with raw exhaust. Several anenometer probes have failed during actual vehicle runs due to corrosion of the sensing wires. At present, we do not plan to split the raw exhaust for the 70 mph cruises until we have a workable splitter. Efforts to develop the splitter will continue. This will be discussed in Section III of this letter.

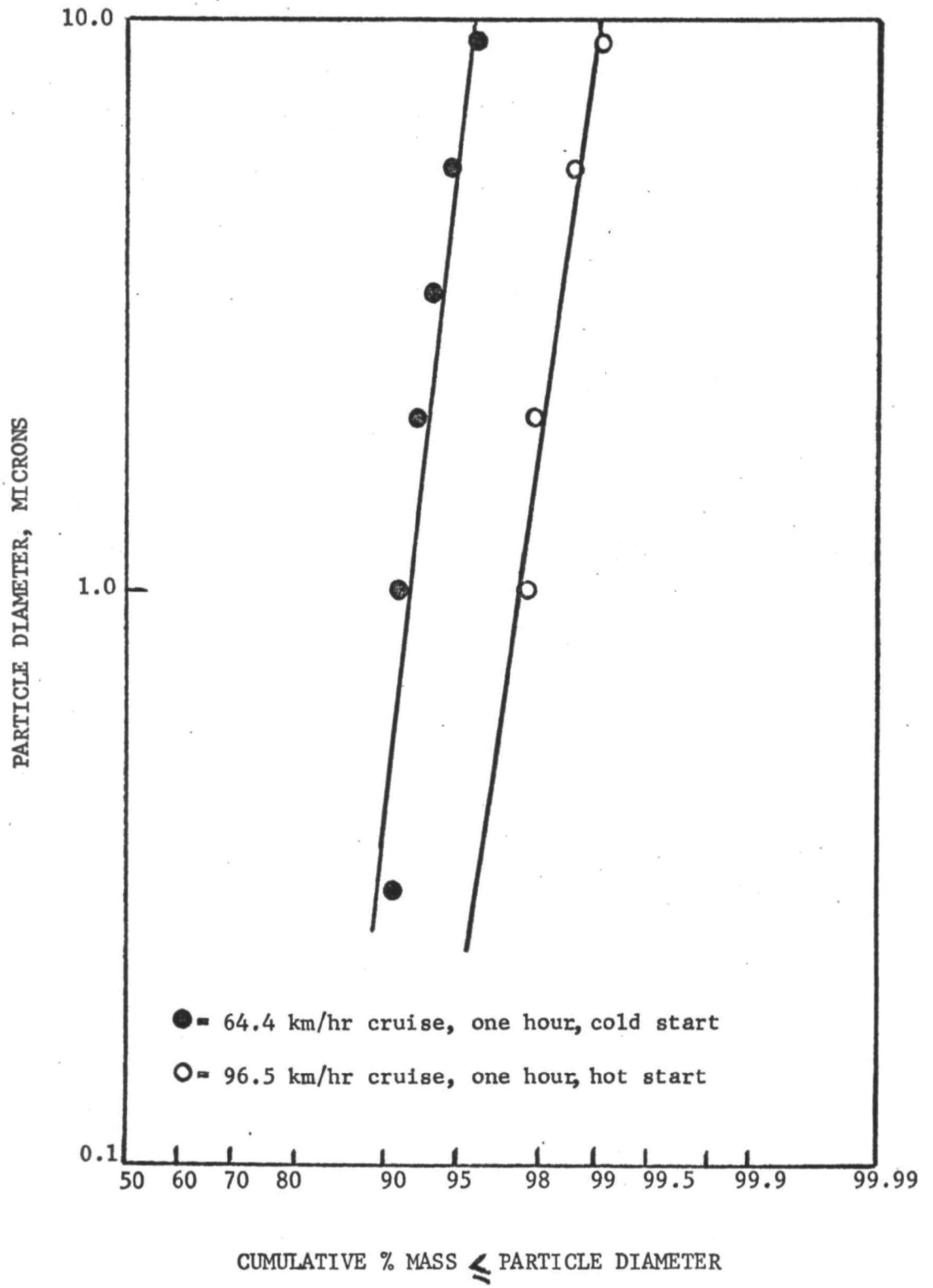
B. Analytical Scheme

Chemical analysis in conjunction with measurements of total particulate emission rates and particle size distributions is required to characterize exhaust particulate emissions. We have devised a scheme for

FIGURE I

OXIDATION CATALYST
EQUIPPED VEHICLE

0.046% S FUEL



quantitative analysis for lead, aluminum, calcium, platinum and other trace elements, nitrogen, and carbon.

Analytical techniques were developed to measure Ca, Al, Pb, Ni, Fe, Cu, Cr, Zn, Pt, and C in particulates collected from automotive exhaust. Emission spectroscopy was used to determine Ca, Al, Ph, Ni, Fe, Cu, Cr, Zn and Pt collected on an organic filter. X-ray fluorescence was also used for Pt, and a semi-micro combustion technique for C.

B.2. Emission Spectroscopy (Ca, Al, Pb, Ni, Fe, Cu, Cr, Zn, Pt

In this procedure, the above metals are collected on a 44 cm^2 Millipore filter. The entire filter is ashed with Mg $(NO_3)_2$ as a carrier, the ash blended with graphite containing cobalt and lithium, and the concentration of each of the metals determined by comparing the quantometer reading of the sample with that of standards. The concentration range covered is equivalent to 0.1 to 4 $\mu gm/cm^2$ of sample, corresponding to an emission rate range for the 1975 FTP of 2.2 X 10^{-5} to 0.87 X 10^{-3} g/km. No interferences were noted, except for I t by Cr.

The results of metal emissions from a test run with an oxidation catalyst equipped vehicle are given below. The vehicle was operated at 60 mph for 2 hours. The metals listed below represented 0.2% of the total particulate emitted during that test run.

EXHAUST PARTICULATE METAL EMISSIONS

Metal	Emission Rate (gms/km)
Ca	0.000039
Pb	0.000071
Cu	0.000017
Al	0.000017
Zn	0.000099
Cr	0.000016
Ni	0.000008

B.2. X-Ray Fluorescence (Pt)

The platinum analysis was performed by exposing circular sections of the glass fiber particulate filter in the X-ray beam of a Phillips Number 1220 X-ray spectrometer. The minimum detectable level of platinum is about 0.35 $\mu gms/cm^2$ corresponding to about 2.6 X 10^{-5} gms/km for a 1975 FTP.

A variation of this technique was attempted in order to increase the sensitivity for platinum. A Millipore filter was used instead of a glass fiber filter. The entire filter was ashed with Mg $(NO_3)_2$, the ash blended with boric acid, pressed into a pellet, and the Pt fluorescence

of the blend measured. Despite the fact that the sample was concentrated prior to analysis, no increase in sensitivity for Pt was obtained.

B.3. Carbon Analysis

Analysis of glass fiber particulate filters from test runs has shown that the semi micro combustion technique for carbon is not sufficiently sensitive for organics from oxidation catalyst equipped vehicles. Type A Gelman glass fiber filters were used. The results show that the organic particulate from a catalyst equipped vehicle is so low that it cannot be distinguished from a blank filter.

ANALYSIS OF ORGANIC PARTICULATE
ON TYPE A GELMAN GLASS FIBER FILTER

No. of Tests	Catalyst	Fuel % S	Test	gms/km Total Particulate	gms/km As Carbon
2	PTX	0.004	75 FTP	0.032	0.004
4	Pelletized	0.004	40 cruise mph	0.004	NIL
3	PTX	0.14	" "	0.263	NIL

B.4. Analytical Techniques for Sulfate

In our previous work we have used a modification of the standard gravimetric procedure for sulfate, ASTM Procedure D1099. Recently we have developed a titrimetric method for sulfate. The leach solution is filtered to remove insoluble material and passed through an ion-exchange column to remove interfering cations. The resulting solution is buffered with Methenamine to a pH $\gtrsim$ 3 and titrated with $Ba(ClO_4)_2$ using Sulfanazo III as an indicator. This method which has been found to be sensitive to levels of 2 μgms $SO_4^=/cm^2$ of filter will be routinely used for sulfate determinations.

C. Preliminary Run

A preliminary run not involving a contract test vehicle, was carried out to evaluate the particulate measurement and analyses procedure over the test modes stipulated in the contract.

(1) 1975 FTP
(2) one hour idle
(3) one hour 40 mph cruise
(4) two hour 70 mph cruise
(5) overnight cool-down
(6) 1975 FTP

No major obstacles were encountered in the above run sequence. The 70 mph, 2 hour cruise will be carried out using the entire auto exhaust until the exhaust splitter is incorporated in the program. Until that time,

temperatures greater than 32°C will be experienced during the 70 mph cruise mode.

Section III Current Problems

As discussed in Section A.3. of this letter, the exhaust splitter has not functioned workably under actual run conditions. Corrosion of the stainless steel anenometer sensing wires upon exposure to hot (>150°C) exhaust containing H_2SO_4 aerosol has been observed. We should shortly be receiving anenometer probes with platinum sensing wires. While more fragile physically (since a thinner Pt wire has to be used to give the same resistance as stainless steel), the platinum anenometers should be more chemically resistant to auto exhaust. Anenometer probes containing tungsten wire will also be tested.

Section IV Work to be Performed July 1-31, 1974

Base case runs on both vehicles on the three test fuels will be carried out. Gaseous and particulate emissions will be measured, and chemical analysis of the particulate matter will be performed.

Thermal conditioning of the catalysts will be initiated. When the additional catalysts are received they will be mounted such that they can be rapidly interchanged between the mileage accumulation and the test vehicle.

THE CHARACTERIZATION OF PARTICULATE EMISSIONS FROM PROTOTYPE CATALYST VEHICLES

MONTHLY PROGRESS REPORT NO. 2
FOR PERIOD JULY 1 TO JULY 31, 1974
PREPARED BY MORTON BELTZER

CONTRACT NO. 68-02-1279

9 AUGUST, 1974

Prepared by

Exxon Products Research Division
Exxon Research and Engineering Company
Linden, New Jersey

for

Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Section I

Purpose and Scope of Work

Exxon Research and Engineering Company, under contract with the Environmental Protection Agency, is engaged in a research program designed to measure and characterize the exhaust particulate emissions from a variety of catalyst systems, both commercial and prototype, that are candidates for use in automotive emissions control. Due to such mechanisms as mechanical and thermal shock, and possible chemical conversion of catalyst material to a mobile condensed material, particulate emissions from catalyst equipped vehicles could differ markedly from that of conventional vehicles. Furthermore, catalytic conversion of gaseous exhaust components to particulate exhaust matter introduces exhaust components that are not now present in the exhaust from conventional vehicles. A case in point is the catalytic oxidation of exhaust sulfur dioxide to the trioxide which is then emitted as sulfate aerosol.

In order to separate vehicle and catalyst effects on total particulate emissions, it will be necessary to measure and characterize particulate emissions from the vehicles in their conventional configuration before they are equipped with catalysts.

Eight catalyst systems (three monolithic oxidation catalysts, two beaded oxidation catalysts, and three reduction catalysts will be tested with three fuels.

The three fuels that will be tested are:

(1) an EPA furnished reference fuel.

(2) the EPA fuel treated with an additive package consisting of thiophene and t-butyl sulfide to a fuel sulfur level of 0.1 wt.% sulfur, and TEL as motor mix to a level of 0.05 gms Pb/gal.

(3) a high aromatic content fuel similarly treated.

Both treated fuels shall also contain an additive package comprised of Lubrizol 596 (0.27 g/gal) and Paradyne 502 (0.45 g/gal). The former functions as detergent, corrosion inhibitor, anti-stall, and anti-icing agent and contains about 2.25 - 2.75 wt.% nitrogen. Paradyne 502 contains 0.75 wt.% nitrogen and functions as a detergent, anti-rust agent, and deposit modifier.

This fuel selection should allow exhaust particulate characterization as follows:

(1) level of composition of exhaust particulate resulting from the use of an additive-free fuel in conventional and and catalyst equipped vehicles.

(2) effect of fuel additives on particulate emissions from conventional and catalyst equipped vehicles.

(3) effect of a high aromatic fuel containing additives on particulate emissions from conventional and catalyst equipped vehicles.

Section II

A. Work During Period of July 1-31, 1974

A.1. Base Case Runs on the Test and Mileage Accumulation Vehicle

Each vehicle was put through the following conditioning and test sequence on each of the three test fuels:

(1) 321.8 km (200 mile) conditioning using the Federal Durability Cycle followed by a 16 hour soak.

(2) 1975 FTP.

(3) one hour idle.

(4) one hour, 64.36 km (40 mile) cruise.

(5) two hour, 112.63 km (70 mile) cruise.

(6) overnight soak.

(7) 1975 FTP.

In all, thirty runs were carried out. Gaseous emissions were measured and particulate samples were obtained in each run. Except for trace metals, particulate analysis has not been started. Analysis will be carried out in August.

The entire exhaust was injected into the dilution tunnel during the 112.63 km (70mph) cruises so that temperature at the particulate filter in these runs exceeded 32°C.

A.2. Catalysts

To date, four catalysts have been received. These systems

have been mounted for interchangeability between the mileage accumulation vehicle and the test vehicle. One catalyst has been conditioned and thermally stressed for 2896.2 km (1800 miles) on the Federal Durability Cycle on an 8 hour on, 8 hour off basis. Conditioning of the other catalysts will be initiated.

The acquisition of the remaining catalysts, with the exception of the Engelhard reduction catalyst, which is unavailable is currently being negotiated.

THE CHARACTERIZATION OF PARTICULATE EMISSIONS FROM PROTOTYPE CATALYST VEHICLES

MONTHLY PROGRESS REPORT NO. 3
FOR PERIOD AUGUST 1 TO AUGUST 31, 1974
PREPARED BY MORTON BELTZER

CONTRACT NO. 68-02-1279

10 SEPTEMBER, 1974

Prepared by

Exxon Products Research Division
Exxon Research and Engineering Company
Linden, New Jersey

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(3) a high aromatic content fuel similarly treated.

Both treated fuels shall also contain an additive package comprised of Lubrizol 596 (0.27 g/gal) and Paradyne 502 (0.45 g/gal). The former functions as detergent, corrosion inhibitor, anti-stall, and anti-icing agent and contains about 2.25 - 2.75 wt.% nitrogen. Paradyne 502 contains 0.75 wt.% nitrogen and functions as a detergent, anti-rust agent, and deposit modifier.

This fuel selection should allow exhaust particulate characterization as follows:

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(2) effect of fuel additives on particulate emissions from conventional and catalyst equipped vehicles.

(3) effect of a high aromatic fuel containing additives on particulate emissions from conventional and catalyst equipped vehicles.

Section II

A. Preliminary Results of Base Case Runs, July 1-31, 1974

Thirty runs were carried out in July in which the particulate and gaseous emissions of the test vehicle and the mileage accumulation vehicle operating on the three fuels were measured. There were inter-vehicle differences with respect to both types of emissions as shown below in Tables I and II.

Table I

Comparison of Total Particulate Emissions
Base Case Runs, Vehicles 116 and 115

Vehicle	Test	Total Particulate, gms/km*		
		Fuel 1	Fuel 2	Fuel 3
116	FTP**	0.043	0.026	0.026
"	Idle	[0.197]	[0.373]	[0.209]
"	40 mph	0.006	0.007	0.005
"	70 mph	0.009	0.012	0.008
115	FTP**	0.017	0.022	0.014
"	Idle	[0.070]	0.094	0.115
"	40 mph	0.002	0.004	0.005
"	70 mph	0.003	0.005	0.004

* Idle emissions, bracketed numbers are in (gms/hr).

** FTP values are averaged values of initial and final tests on each fuel.

Unlike the earlier work, the instrument was calibrated differently by using a SO_2 in N_2 calibration gas. Based on recent work at Exxon and corroborated by the instrument manufacturer, it was shown that SO_2 in air (the diluted exhaust samples are predominantly air) gives a much lower response. The data shown in Appendix II have been corrected using a factor of 1.4 based on recent calibration tests using SO_2 in air and SO_2 in N_2.

In about one-fourth of the base case runs in which SO_2 was measured, agreement between the experimental SO_2 emission rate and the theoretical based on fuel consumption was within 10%. In general, the discrepancies between experimental and expected SO_2 emission rates were about ± 25%. We are planning to investigate the causes for these discrepancies.

A.3. Sulfate Emission Rates

Sulfuric acid emission rates are shown in Appendix III. The sulfate levels while low are somewhat higher than what was obtained in earlier results from tests on conventional vehicles carried out in our laboratory. The sulfate emission rate appears to be independent of fuel sulfur content. For example compare Federal Cycles (numbers 1 and 5 with 6 and 10). The average sulfate emissions for the first pair of 75 FTP's is 0.0022 gms/km, while it is 0.0024 gms/km for the latter although the sulfur content of the fuel used in runs 6 and 10 was six times greater than that used in runs 1 and 5. The percent conversions calculated on the basis of sulfate measured to fuel sulfur consumed consequently are higher the lower the fuel sulfur content. These results indicate that there may be some background level of sulfate which should be backed out of emission rates obtained in each run although it is not clear at this stage what the reason is. As will be shown in Section II, the sulfate emissions of the test vehicle equipped with a catalyst are generally higher than what was obtained in the absence of a catalyst with the vehicle operating on a higher sulfur fuel, and depends markedly on fuel sulfur content.

A.4. Metal Emission Rates

Metal emission rates were obtained in each vehicle test for Ca, Al, Zn, Cr, Fe, Cu, Ni, and Pb. The detailed metals emission data are shown in Appendix IV. The emitted metals constituted a small fraction of the total particulate. The lowest total particulate emission rate obtained was during a 40 mph cruise on vehicle 115 operating on the EPA reference fuel 0.002 gms/km (Appendix I, Test No. 18). Even in this case, the metals constituted at most 9% of the total particulate.

Table III below shows Ca and Al emission rates for each vehicle operating on each of the test fuels.

TABLE III

Ca and Al Emission Rates, (gms/km)*
Vehicle Operating on Indicated Fuels

Vehicle	Test	Fuel 1		Fuel 2		Fuel 3	
		Ca	Al	Ca	Al	Ca	Al
116	75 FTP**	0.00020	<0.00005	0.00015	0.00013	0.00004	≃0.00003‡
"	Idle	[<0.00008]	[<0.00008]	[0.0022]	[0.0015]	[0.0012]	[<0.0004]
"	40	0.00003	<0.00001	0.00004	0.00002	0.00002	$<6 \times 10^{-6}$
"	70	0.00011	6×10^{-6}	0.00001	<0.00001	0.00001	<0.00001
115	75 FTP	0.00005	0.00006	0.00004	≃0.00003‡	0.00004	∿0.00003
"	Idle	0.00004	<0.00004	[<0.0004]	[<0.0004]	[0.0004]	[<0.0004]
"	40	0.00001	$<6 \times 10^{-6}$	0.00002	$<6 \times 10^{-6}$	0.00001	$<6 \times 10^{-6}$
"	70	$<6 \times 10^{-6}$	$<6 \times 10^{-6}$	0.00001	<0.00001	0.00002	0.00002

* Values for the Idle Cruises, brackets are in [gms/hr].

** Averaged values of initial and final 75 FTP runs for vehicle-fuel combination.

‡ ≃ Average of two values, one of which is below the detection limit.

A.5. Carbon Content of Exhaust Particulate

It was previously noted (Monthly Progress Report No. 1, Section B.3) that the semi-microcombustion technique for carbon is not sufficiently sensitive for organics from oxidation catalyst equipped vehicles. The Type A Gelman glass fiber filters used in this program although ostensibly free of organic binder gave high carbon blanks, equivalent to about an emission rate of about 0.014 gms/km for the 1975 FTP, 0.004 gm/km for 40 mph, 1 hour cruise and 0.001 gm/km for the 70 mph, 2 hour cruise. In many of the base case runs, the blank carbon correction exceeds the measured carbon content of the particulate loaded filters. In other cases, the blank carbon correction exceeds the total particulate emission rate. In still other cases, the measured carbon content corrected for the blank exceeds the total particulate.

Carbon analysis was performed on the first thirty base case runs. In 14 cases, the blank carbon correction exceeded the measured carbon values. Table IV below shows those runs in which the measured carbon values exceeded the blank. It can be seen that these cases include those in which the organic particulate (as carbon) exceeds the total particulate.

Table IV

Organic Particulate Emissions
Base Case Runs

Run No.	Run Type	Emission Rate gms/km	
		Total Particulate	As Carbon
1	75 FTP	0.050	0.053
2	Idle (1)	[0.197]	[0.846]
4	70 (2)	0.007	0.017
9	70 (2)	0.012	0.0001
14	70 (2)	0.008	0.0001

In Run No. 1 above, the carbon level is comparable to the total particulate level. It is possible that the relatively high particulate loading obtained in this run is due to the high level of organic particulate.

In general, the semi-microcombustion technique for particulate apparently is only reliable when the organic particulate loadings on the filters are very high. Since a major portion of the program to be carried out involves oxidation catalyst systems which further reduce organic particulate levels, the semi-microcombustion technique appears to be unsuitable. Similar considerations probably apply to those tests in which a NO_x reduction catalyst would be used, since the organic emission output of the program vehicles operating in the conventional mode is quite low.

Section III

A. Work During Period of August 1-31, 1974

A.1. Runs with Catalyst Equipped Test Vehicle

Runs with the test vehicle equipped with catalysts were started. The first catalyst tested was a PTX-IIB monolithic oxidation system. The conditioning and test sequence was identical to that previously used in the first 30 base case runs (Monthly Report No. 2, Section II, A.1).

Unlike the base case runs, problems were encountered during the 112.6 km/hr (70 mph) cruises. In the first high speed cruise, (Run No. 34), misfire and spark plug failure occurred some 20 minutes into the run. This caused a catalyst temperature increase to about 1040°C for about 10 minutes. The test was terminated, new plugs installed, and the vehicle checked out.

A 1975 FTP the next day (Run No. 35) showed that the catalyst was inactive as a result of the temperature excursion the previous day. The CO, HC, and SO_2 emissions were considerably higher than what was obtained on the initial 1975 FTP run with the catalyst (compare Run No. 31 with Run No. 35, Appendix V. The CO, HC, and SO_2 emissions were similar to what was obtained when the vehicle without a catalyst was tested on the same fuel (thus, compare Run No. 35, Appendix V, with Runs No. 16 and 20, Appendix II. Tests with the deactivated catalyst were terminated.

The vehicle was re-equipped with a fresh PTX-IIB catalyst which was subjected to accelerated conditioning prior to testing in order to make up for lost time and closely adhere to the program schedule.

Some 20 runs were carried out in August, but in no case were we able to carry out a high speed cruise for the entire two hours. Tire blowouts were responsible in most cases for the shorter duration high speed cruises. In all the high speed cruise runs, gaseous and particulate samples were obtained and emission rates could be presented on a normalized basis.

Although sulfuric acid analyses for most of the catalyst car runs have not been carried out, the large increase in total particulate emissions with the higher sulfur content fuels is indicative of sulfate formation. Table V shows the average of the initial and final FTP total particulate emissions for the PTX-IIB catalyst on the three fuels.

Table V

Average Total Particulate Emissions
Vehicle 115, 1975 FTP
(gms/km)

Fuel % Sulfur	PTX-IIB Catalyst	No Catalyst
0.019	0.037	0.017
0.110	0.160	0.022
0.091	0.179	0.014

It will be noticed, comparing Appendix V with Appendix III that when the low sulfur fuel was used, there are cases when the total particulate and sulfuric acid emission rates are comparable whether or not the vehicle was equipped with the PTX-IIB catalyst. This may be indicative of sulfate storage occurring. The relative effects of storage would be expected to be greater, the lower the fuel sulfur content.

Section IV

Catalysts

Four catalysts have been conditioned and thermally stressed. We have just received a Matthey-Bishop monolithic oxidation catalyst. This system will be mounted and conditioned for the program test sequence. Delivery of the GEM 68 (Gould NO_x Reduction Catalyst) is expected shortly.

APPENDIX I

TOTAL PARTICULATE EMISSIONS, BASE CASE RUNS

Test No.	Run Type	Fuel	Emission Rate* (gms/km)
1	75 FTP	EPA	0.050
2	Idle (1)	"	[0.197]
3	40 (1)	"	0.006
4	70 (2)	"	0.009
5	75 FTP	"	0.036
6	75 FTP	EPA+	0.029
7	Idle (1)	"	[0.373]
8	40 (1)	"	0.007
9	70 (2)	"	0.012
10	75 FTP	"	0.023
11	75 FTP	HA+	0.030
12	Idle (1)	"	[0.209]
13	40 (1)	"	0.005
14	70 (1)	"	0.008
15	75 FTP	"	0.022
16	75 FTP	EPA	0.015
17	Idle (1)	"	[0.070]
18	40 (1)	"	0.002
19	70 (2)	"	0.003
20	75 FTP	"	0.019
21	75 FTP	EPA+	0.034
22	Idle (1)	"	[0.094]
23	40 (1)	"	0.004
24	70 (2)	"	0.005
25	75 FTP	"	0.010
26	75 FTP	HA+	0.014
27	Idle (1)	"	[0.115]
28	40 (1)	"	0.005
29	70 (2)	"	0.004
30	75 FTP	"	0.014

EPA = EPA furnished reference fuel
EPA+ = EPA reference fuel plus additive package
HA+ = High aromatic fuel plus additive package

75 FTP = 1975 Federal test procedure
Idle (1) = One hour idle
40 (1) = 40 mph (64.36 km/hr) cruise for one hour
70 (2) = 70 mph (112.63 km/hr) cruise for two hours

Runs 1-15 were with Test Vehicle No. 116
Runs 1-16 were with Test Vehicle No. 115
(Idle total particulate emissions, brackets, are in gms/hr)*

APPENDIX II

GASEOUS EMISSIONS, BASE CASE RUNS

Test No.	Run Type	Fuel	Emissions Rate gms/km CO	HC	NO_x	SO_2
1	75 FTP	EPA	8.76	1.23	0.86	---
2	Idle (1)	"	[170.38]	[9.24]	[19.12]	---
3	40 (1)	"	7.54	0.417	0.61	---
4	70 (2)	"	5.90	0.05	1.76	---
5	75 FTP	"	8.58	1.57	0.97	---
6	75 FTP	EPA+	9.09	1.38	1.02	0.239
7	Idle (1)	"	[---]	[---]	[---]	---
8	40 (1)	"	---	---	---	---
9	70 (2)	"	2.63	0.06	0.73	0.181
10	75 FTP	"	8.59	1.21	1.00	0.301
11	75 FTP	HA+	9.49	1.62	1.38	0.363
12	Idle (1)	"	[169.92]	[24.43]	[2.93]	[4.47]
13	40 (1)	"	4.23	2.60	0.34	0.154
14	70 (2)	"	2.62	0.010	0.60	0.154
15	75 FTP	"	8.24	1.80	1.17	0.347
16	75 FTP	EPA	6.33	0.78	0.97	0.048
17	Idle (1)	"	[21.69]	[10.85]	[3.05]	[1.260]
18	40 (1)	"	3.15	0.18	0.28	[0.025]
19	70 (2)	"	2.32	0.04	0.86	[0.035]
20	75 FTP	"	6.84	3.70	0.78	0.076
21	75 FTP	EPA+	6.23	0.71	0.77	0.284
22	Idle (1)	"	[29.4]	[7.06]	[2.20]	[3.262]
23	40 (1)	"	3.09	0.17	0.29	0.202
24	70 (2)	"	1.72	0.05	0.86	0.167
25	75 FTP	"	6.28	0.99	0.85	0.295
26	75 FTP	HA+	7.13	0.75	0.84	0.318
27	Idle (1)	"	[35.14]	[8.56]	[6.30]	[5.26]
28	40 (1)	"	1.92	0.17	0.43	0.160
29	70 (2)	"	0.61	0.05	0.54	0.136
30	75 FTP	"	6.61	0.74	0.84	0.301

EPA = EPA furnished reference fuel
EPA+ = EPA reference fuel plus additive package
HA+ = High aromatic fuel plus additive package

75 FTP = 1975 Federal test procedure
Idle (1) = One hour idle
40 (1) = 40 mph (64.36 km/hr) cruise for one hour
70 (2) = 70 mph (112.63 km/hr) cruise for two hours

Runs 1-15 were with Test Vehicle No. 116
Runs 1-16 were with Test Vehicle No. 115
(Idle gaseous emissions, brackets, are in gms/hr)*

APPENDIX III

SULFURIC ACID EMISSIONS, BASE CASE RUNS

Test No.	Run Type	Fuel	H_2SO_4 Emission Rate (gms/km)*		% of Total Particulate
1	75 FTP	EPA	0.0018	(2.3)	3.6
2	Idle (1)	"	[0.0045]	(---)	[2.3]
3	40 (1)	"	0.0010	(1.8)	16.6
4	70 (2)	"	0.0020	(3.2)	22.2
5	75 FTP	"	0.0027	(3.2)	7.5
6	75 FTP	EPA+	0.0026	(0.55)	9.0
7	Idle (1)	"	[0.0273]	(0.48)	[7.3]
8	40 (1)	"	0.0005	(0.15)	7.1
9	70 (2)	"	0.0048	(1.5)	40.0
10	75 FTP	"	0.0022	(0.45)	7.3
11	75 FTP	HA+	0.0018	(0.41)	6.0
12	Idle (1)	"	[0.0282]	(0.44)	[13.5]
13	40 (1)	"	0.0001	(0.03)	1.3
14	70 (2)	"	0.0032	(1.17)	14.5
15	75 FTP	"	0.0006	(0.14)	2.7
16	75 FTP	EPA	0.0004	(0.50)	2.7
17	Idle (1)	"	[0.0209]	(0.18)	[29.9]
18	40 (1)	"	0.0002	(0.36)	10.0
19	70 (2)	"	0.0011	(2.00)	36.7
20	75 FTP	"	0.0014	(1.64)	7.4
21	75 FTP	EPA+	0.0032	(0.60)	9.4
22	Idle (1)	"	[0.0209]	(0.03)	[22.2]
23	40 (1)	"	0.0005	(0.14)	12.5
24	70 (2)	"	0.0017	(0.51)	34.0
25	75 FTP	"	0.0015	(0.31	15.0
26	75 FTP	HA+	0.0015	(0.36)	10.7
27	Idle (1)	"	[0.0242]	(0.40)	[21.0]
28	40 (1)	"	0.0004	(0.13)	8.0
29	70 (2)	"	0.0017	(0.14)	42.5
30	75 FTP	"	0.0016	(0.39)	11.4

EPA = EPA furnished reference fuel
EPA+ = EPA reference fuel plus additive package
HA+ = High aromatic fuel plus additive package

75 FTP = 1975 Federal test procedure
Idle (1) = One hour idle
40 (1) = 40 mph (64.36 km/hr) cruise for one hour
70 (2) = 70 mph (112.63 km/hr) cruise for two hours

Runs 1-15 were with Test Vehicle No. 116
Runs 1-16 were with Test Vehicle No. 115
(Idle total particulate emissions, brackets, are in gms/hr)*
Numbers in parentheses in column 4 are percent conversions fuel sulfur to sulfate.

APPENDIX IV

METAL EMISSIONS, BASE CASE RUNS

EMISSION RATE (gms/km)*

Test No.	Run Type	Fuel	Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb
1	75 FTP	EPA	0.00025	<0.00005	0.00035	0.00005	0.00134	0.00012	<0.00005	0.00043
2	Idle (1)	"	[<0.0008]	[<0.0008]	[0.0008]	[<0.0008]	[0.00032]	[<0.0008]	[<0.0008]	[0.0008]
3	40 (1)	"	0.00003	<0.00001	0.00010	0.00003	0.00022	0.00002	0.00001	0.00011
4	70 (2)	"	0.00011	6×10^{-6}	0.00009	<0.00001	0.00015	$<6 \times 10^{-6}$	<0.00001	0.00009
5	75 FTP	"	0.00016	0.00006	0.00064	0.00005	0.00080	0.00016	0.00004	0.00042
6	75 FTP	EPA+	0.00014	0.00020	0.00027	0.00007	0.00022	0.00014	0.00005	0.00058
7	Idle (1)	"	[0.0022]	[0.0015]	[0.0035]	[0.0009]	0.0080	[0.0019]	[0.0009]	[0.0063]
8	40 (1)	"	0.00004	0.00002	0.00005	0.00002	0.00022	0.00002	0.00001	0.00014
9	70 (2)	"	0.00001	0.00001	0.00003	<0.00001	0.00012	0.00001	<0.00001	0.00006
10	75 FTP	"	0.00017	0.00006	0.00080	0.00009	0.00132	0.00031	0.00008	0.00006
11	75 FTP	HA+	0.00014	0.00006	0.00027	0.00020	0.00134	0.00027	0.00019	0.00087
12	Idle (1)	"	[0.0012]	[<0.0004]	[0.0006]	[0.0006]	[0.0040]	[<0.0004]	[<0.0004]	[0.0122]
13	40 (1)	"	0.00002	$<6 \times 10^{-6}$	0.00002	$<6 \times 10^{-6}$	0.00003	$<6 \times 10^{-6}$	$<6 \times 10^{-6}$	0.00010
14	70 (2)	"	0.00001	<0.00001	0.00003	$<6 \times 10^{-6}$	0.00008	0.00002	0.00001	0.00006
15	75 FTP	"	0.00009	0.00004	0.00040	0.00005	0.00052	0.00025	0.00005	0.00049
16	75 FTP	EPA	0.00007	0.00007	0.00016	0.00007	0.00121	0.00047	0.00008	0.00070
17	Idle (1)	"	[0.0004]	[<0.0004]	[0.0006]	[<0.0004]	[0.0037]	[0.0009]	[<0.0004]	[0.0024]
18	40 (1)	"	0.00001	$<6 \times 10^{-6}$	0.00001	<0.00001	0.00009	$<6 \times 10^{-6}$	$<6 \times 10^{-6}$	0.00005
19	70 (2)	"	$<6 \times 10^{-6}$	$<6 \times 10^{-6}$	0.00001	$<6 \times 10^{-6}$	0.00006	0.00004	$<6 \times 10^{-6}$	0.00004
20	75 FTP	"	0.00002	<0.00002	<0.00002	<0.00002	0.00004	0.00002	<0.00002	<0.00002
21	75 FTP	EPA+	0.00005	0.00004	0.00007	0.00012	0.00123	0.00040	0.00009	0.00062
22	Idle (1)	"	[<0.0004]	[<0.0004]	[0.0004]	[<0.0004]	[0.0005]	[0.0008]	[<0.0004]	[0.0069]
23	40 (1)	"	0.00002	$<6 \times 10^{-6}$	0.00001	$<6 \times 10^{-6}$	0.00004	0.00002	$<6 \times 10^{-6}$	0.00021
24	70 (2)	"	$<6 \times 10^{-6}$	$<6 \times 10^{-6}$	<0.00001	$<6 \times 10^{-6}$	0.00004	0.00001	<0.00001	0.00010
25	75 FTP	"	0.00004	<0.00002	0.00006	<0.00002	0.00028	0.00037	<0.00002	0.00042
26	75 FTP	HA+	0.00007	0.00004	0.00010	0.00004	0.00091	0.00021	0.00004	0.00059
27	Idle (1)	"	[0.0004]	[<0.0004]	[<0.0004]	[<0.0004]	[0.0018]	[0.0008]	[<0.0004]	[0.0004]
28	40 (1)	"	0.00001	$<6 \times 10^{-6}$	$<6 \times 10^{-6}$	$<6 \times 10^{-6}$	0.00002	0.00002	$<6 \times 10^{-6}$	0.00011
29	70 (2)	"	<0.00001	$<6 \times 10^{-6}$	<0.00001	$<6 \times 10^{-6}$	0.00006	0.00002	$<6 \times 10^{-6}$	0.00009
30	75 FTP	"	0.00002	<0.00002	0.00007	<0.00002	0.00031	0.00039	<0.00002	0.00037

EPA = EPA furnished reference fuel
EPA+ = EPA reference fuel plus additive package
HA+ = High aromatic fuel plus additive package

75 FTP = 1975 federal test procedure
Idle (1) = one hour idle
40 (1) = 40 mph (64.36 km/hr) cruise for one hour
70 (2) = 70 mph (112.63 km/hr) cruise for two hours

Runs 1-15 were with Test Vehicle No. 116
Runs 1-16 were with Test Vehicle No. 115
(Idle metal emissions, brackets, are in gms/hr)*

APPENDIX V

EMISSIONS FROM PTX-IIB EQUIPPED VEHICLE[a] ON EPA REFERENCE FUEL

Test No.	Catalyst	Run Type	Emission Rates, gms/km: Particulate Emissions: Total Particulate	Particulate Emissions: H_2SO_4	Gaseous Emissions: CO	Gaseous Emissions: HC	Gaseous Emissions: NO_x	Gaseous Emissions: SO_2
31	PTXIIB	75 FTP	0.032	0.013 (15.0)	0.77	0.70	1.66	0.035
32	"	Idle (1)	[0.104]	[0.068] (5.7)	[6.11]	[2.08]	[6.98]	[1.54]
33	"	40 (1)	0.018	0.009 (13.7)	0.22	0.050	0.38	0.045
34	"*	70 (2)	0.114	0.045 (32.1)	0.15	0.010	0.18	0.003
35	"	75 FTP	0.139	0.007 (5.0)	4.84	0.92	1.11	0.057
36	PTXIIB**	75 FTP	0.031	0.002 (1.5)	3.26‡‡	0.29	0.91	‡0.0
37	"	Idle (1)	[0.294]	[0.103] (4.7)	[7.70]	[4.45]	[8.66]	[0]
38	"	40 (1)	0.018	0.012 (12.8)	0.05	0.04	0.148	0.0
39	"	70 (2)	---	---	0.06	0.23	5.54	0.0
40	"	75 FTP	0.043	0.004 (2.7)	1.18	0.63	0.74	0.0

(a) Vehicle No. 115

EPA = EPA furnished reference fuel
EPA+ = EPA reference fuel plus additive package
HA+ = High aromatic fuel plus additive package

75 FTP = 1975 Federal Test Procedure
Idle (1) = One hour idle
40 (1) = 40 mph (64.36 km/hr) cruise for one hour
70 (2) = 70 mph (112.63 km/hr) cruise for two hours

Numbers in parentheses, Column 5, are % conversions, fuel sulfur to SO_4^{-2}.

* = Temperature excursion due to misfire
** = New catalyst system
‡ = Below limit of detection of SO_2 instrument
‡‡ = Defective vacuum breaker

THE CHARACTERIZATION OF PARTICULATE EMISSIONS FROM PROTOTYPE CATALYST VEHICLES

MONTHLY PROGRESS REPORT NO. 4
FOR PERIOD SEPTEMBER 1 TO SEPTEMBER 30, 1974
PREPARED BY MORTON BELTZER

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Prepared by

Exxon Products Research Division
Exxon Research and Engineering Company
Linden, New Jersey

for

Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Section I

Purpose and Scope of Work

Exxon Research and Engineering Company, under contract with the Environmental Protection Agency, is engaged in a research program designed to measure and characterize the exhaust particulate emissions from a variety of catalyst systems, both commercial and prototype, that are candidates for use in automotive emissions control. Due to such mechanisms as mechanical and thermal shock, and possible chemical conversion of catalyst material to a mobile condensed material, particulate emissions from catalyst equipped vehicles could differ markedly from that of conventional vehicles. Furthermore, catalytic conversion of gaseous exhaust components to particulate exhaust matter introduces exhaust components that are not now present in the exhaust from conventional vehicles. A case in point is the catalytic oxidation of exhaust sulfur dioxide to the trioxide which is then emitted as sulfate aerosol.

In order to separate vehicle and catalyst effects on total particulate emissions, it will be necessary to measure and characterize particulate emissions from the vehicles in their conventional configuration before they are equipped with catalysts.

Eight catalyst systems (three monolithic oxidation catalysts, two beaded oxidation catalysts, and three reduction catalysts will be tested with three fuels.

The three fuels that will be tested are:

(1) an EPA furnished reference fuel.

(2) the EPA fuel treated with an additive package consisting of thiophene and t-butyl sulfide to a fuel sulfur level of 0.1 wt.% sulfur, and TEL as motor mix to a level of 0.05 gms Pb/gal.

(3) a high aromatic content fuel similarly treated.

Both treated fuels shall also contain an additive package comprised of Lubrizol 596 (0.27 g/gal) and Paradyne 502 (0.45 g/gal). The former functions as detergent, corrosion inhibitor, anti-stall, and anti-icing agent and contains about 2.25 - 2.75 wt.% nitrogen. Paradyne 502 contains 0.75 wt.% nitrogen and functions as a detergent, anti-rust agent, and deposit modifier.

This fuel selection should allow exhaust particulate characterization as follows:

(1) level and composition of exhaust particulate resulting from the use of an additive-free fuel in conventional and catalyst equipped vehicles.

(2) effect of fuel additives on particulate emissions from conventional and catalyst equipped vehicles.

(3) effect of a high aromatic fuel containing additives on particulate emissions from conventional and catalyst equipped vehicles.

Section II

A. Work During Period of September 1-30, 1974

The test sequences (Monthly Report No. 2, Section II, A.1) were carried out with three more catalyst systems. These included two monolithic oxidation catalysts and a pelletized oxidation catalyst. Monolithic catalysts tested were a Universal Oil Products (UOP) system and a Matthey Bishop system, hereinafter referred to as MONO (2) and MONO (3) respectively. The Engelhard PTX-IIB discussed in the previous monthly is hereinafter referred to as MONO (1).

The pelletized oxidation catalyst was an Engelhard system, hereinafter referred to as Pellet (1).

Total particulate, sulfuric acid, gaseous and metal emission rates were measured. Metal analyses have not been completed for the MONO (3) runs.

A.1 Total Particulate Emission Rates

Table I shows the average of the initial and final FTP total particulate emissions for each of the catalysts on the three fuels. The results obtained with the PTX-IIB catalyst, MONO (1) reported in the previous monthly are also shown in order to compare the four oxidation catalysts tested thus far in this program.

TABLE I

Average Total Particulate Emission Rate
(1975 FTP, Vehicle 115 Equipped with Indicated Catalyst Systems)

Fuel % Sulfur	gms/km			
	MONO (1)	PELLET (1)	MONO (2)	MONO (3)
0.019	0.037	0.049	0.032	0.025
0.110	0.160	0.071	0.097	0.068
0.091	0.179	0.063	0.088	0.055

The detailed total particulate emission results are given in Appendices I to IV.

A.2 Sulfuric Acid Emission Rates

Table II shows the sulfuric acid emission rates corresponding to the runs presented in Table I. Also shown in Table II are the percent conversions (numbers in parentheses), based on fuel consumption and measured sulfate particulate.

Both the sulfuric acid emission rates and percent conversions are generally lower than what had been obtained in earlier work (1, 2) using this particulate sampling system.

TABLE II

Average Sulfuric Acid Emission Rate
(1975 FTP, Vehicle 115 equipped with oxidation catalyst systems)

gms/km*

Fuel % Sulfur	MONO (1)	Pellet (1)	MONO (2)	MONO (3)
0.019	0.003(2.1)	0.003(2.6)	0.002(1.9)	0.003(3.1)
0.110	0.057(10.4)	0.018(2.1)	0.025(4.6)	0.024(4.3)
0.091	0.069(15)	0.011(2.2)	0.020(4.2)	0.020(7.7)

(* Numbers in parenthesis are averaged % conversions)

Several factors could be responsible for the differences between the above results and the results of the earlier work. In the present work, the test sequence is different from any previous sequence we have used. In addition, the catalysts used in this program are essentially fresh catalysts in terms of exposure to sulfur-containing fuels. Similar considerations apply to the exhaust systems used in the test vehicle systems.

By contrast, the percent conversions obtained on the 64.36 km/hr (40 mph) cruises are generally somewhat higher than what was previously obtained, inducating that the test sequence may be the most dominant parameter affecting sulfate emissions. The cruise results are shown in Table III below.

(1) M. Beltzer, R. J. Campion, and W. L. Petersen, "Measurement of Vehicle Particulate Emissions," SAE Paper 740286, February, 1974.
(2) Esso Research and Engineering Company, Submission to EPA, Data on Automotive Sulfate Emissions, May, 1974.

TABLE III

Sulfuric Acid Emission Rates for 40 mph, 1 hour Cruise Conditions
(Vehicle 115 Equipped with Oxidation Catalyst Systems)

Fuel % Sulfur	gms/km* MONO (1)	Pellet (1)	MONO (2)	MONO (3)
0.019	0.012(12.8)	0.001(1.5)	0.013(20.3)	0.006(9.4)
0.110	0.101(30.1)	0.104(27.2)	0.183(47.8)	0.055(15.3)
0.091	0.076(25.7)	0.078(22.4)	0.165(52.1)	0.043(13.1)

(* Numbers in parentheses are % conversions)

Appendices I to IV show the detailed sulfuric acid emission results. The data for MONO (1), the PTX-IIB of the third monthly are also included in this report to allow rapid comparison of the emission characteristics of the four catalyst systems tested to date.

A.3 Gaseous Emission Rates

Appendices I to IV also show the detailed gaseous emission results for CO, HC, NO_x, and SO_2.

A.4 Metal Emission Rates

Emission rates of Ca, Al, Zn, Cr, Fe, Cu, Ni, Pb, and Pt were obtained in each test run when vehicle 115 was equipped with a catalyst. The analysis for Pt has not yet been completed, nor has the remaining metal analysis been completed for the MONO (3) catalyst tests (Runs 81-95). Appendices V to VII show the detailed metal emission rates when vehicle 115 was equipped with MONO (1) and (2) and Pellet (1) catalyst systems.

No detectable quantities of platinum have been found on the filters analyzed to date (Runs 31 to 45). The minimum detectable level of Pt by our X-ray fluorescence analysis procedure is 0.35 $\mu gms/cm^2$. Consequently, the maximum emission rates for platinum based on negative results, the accumulated test mileage and the minimum detection level is 5.6×10^{-5} gms/km for the 1975 FTP, 1.55×10^{-5} gms/km for the 40 mph one hour cruise, and 4.43×10^{-6} for the 70 mph two hour cruise. For the idle cruise, the corresponding maximum emission rate in gms/hr is 1×10^{-3}. The platinum emission results obtained to date are given in Appendix V. It will be noticed that the platinum emission rates for the 70 mph cruises differ from the 4.43×10^{-6} gms/km cited above. This is because Runs 34, 39 and 44 were terminated due to misfire or blown tires before the full 225.26 km (140 miles) could be accumulated. Consequently, the

platinum emission rates for these runs are based on the mileage accumulated prior to run termination. Similar considerations apply to the emission rates of total particulates, H_2SO_4, the other metals, and to the gaseous exhaust components as well.

To make an initial assessment of the effect of the catalysts on metal emissions rates, the emission rates for six metals obtained on the Federal Cycles for vehicle 115 were plotted, Figures I to VIII. The abscissa (test number) are cardinal numbers only with respect to the Federal Test Cycles. These figures consequently are not intended to depict metal emission rates under consecutive continuous testing since three other tests or a conditioning procedure occur between successive Federal Test Procedures. Nevertheless, using this approach, it is possible to draw some tentative conclusions.

Figure I shows that the aluminum emission rate increases sharply when the vehicle is equipped with the various oxidation catalysts. It should be noted that if aluminum is used as a platinum surrogate, even at the highest aluminum FTP emission rate (about 0.001 gms/km), the platinum could be as much as 5.6% of the aluminum content and still be below our detection limits. Since the platinum content of the catalyst is well below 1 wt % of the substrate, it is not surprising that no platinum has been detected in the samples analyzed to date.

Iron emission rates for the 75 Federal Test Procedures are shown in Figure II. While there is an increase in iron emissions when the vehicle is equipped with a catalyst, the relative increase is considerably lower than that for aluminum emissions. A possible reason for the increased iron levels above that obtained when the vehicle was operated in the conventional mode may be due to reaction of parts of the exhaust train with catalytically produced H_2SO_4 aerosol. This could result in increased iron emissions above that due to normal attrition.

A test of this hypothesis will come when the vehicle is equipped with a NO_x reduction catalyst. It would be expected that iron emissions would decrease to the base case levels in this case.

Figure III depicts the lead emission rates. There is a small increase in the lead emission rate when the vehicle is equipped with catalysts. This, however, may be due to the vehicle becoming conditioned to fuels containing lead at about the 0.05 gms/gal level. The vehicle is operated on lead sterile fuel until a 200 mile conditioning procedure prior to the first test sequence. It is probable therefore that if this is taken into consideration, the lead emission rates are independent of whether or not the vehicle is equipped with a catalyst.

Figure IV shows the zinc emission rates increase when the vehicle is equipped with the oxidation catalysts. It is not certain what the source of the zinc is. We plan to analyze a standard 1974 GM muffler to determine if there is any zinc on its internal surfaces. The increased zinc emissions in the case of a catalyst equipped vehicle could be ascribed to corrosion as a result of contact with H_2SO_4.

Figures V and VI show the nickel and calcium emission rates respectively. The emission rates of both these metals is considerably lower than the rates for lead, zinc, and iron. Here too, the emission rates with a catalyst equipped vehicle are greater than when the vehicle is in the conventional mode. Nickel may be due to corrosion by the H_2SO_4 of stainless steel (sampling system) or cold rolled steel (exhaust system). The calcium may be a low level impurity in the catalyst substrate that is attriting.

Figures VII and VIII show the FTP emission rates for chromium and copper respectively, the pattern also being an approximate sawtooth.

The sawtooth emission pattern shown in the figures may in part be due to deposits being built up on the mileage accumulation and emitted on the first run of the test sequence, that is the first FTP. The higher metal emission rates on many of the first FTP's of the run sequence would tend to substantiate the above hypothesis. However, there are cases where the metal emissions on successive FTP's are comparable and do not show the sawtooth pattern. This could be due to re-entrainment of deposited material from the inner surfaces of the exhaust system. Since re-entrainment of deposited material into the exhaust stream occurs on a seemingly erratic basis, this phenomenon could account for the gaps in the approximate periodicity of the sawtooth emission pattern.

In addition the periodicity does not match for all the metals. This can be seen by comparing the iron and copper emission rates. What is a crest in the emission rate of one metal corresponds to a trough in the emission rate of the other, on the same FTP. This indicates that different mechanisms for metal emissions may be operative. For example accumulation of one metal may be occurring while another is being depleted through emission.

Section III

Catalysts

The Grace NO_x reduction catalyst has been mounted, and conditioned for the test program. The GEM 68 (Gould NO_x reduction catalyst) has been received. This catalyst has been mounted and is undergoing conditioning.

The last two catalyst systems (both oxidation catalysts) are expected shortly. These in turn will be mounted, conditioned, and tested as the previous systems.

FIGURE I

ALUMINUM EMISSION RATES
ON FEDERAL TEST CYCLES

CATALYST SYSTEM

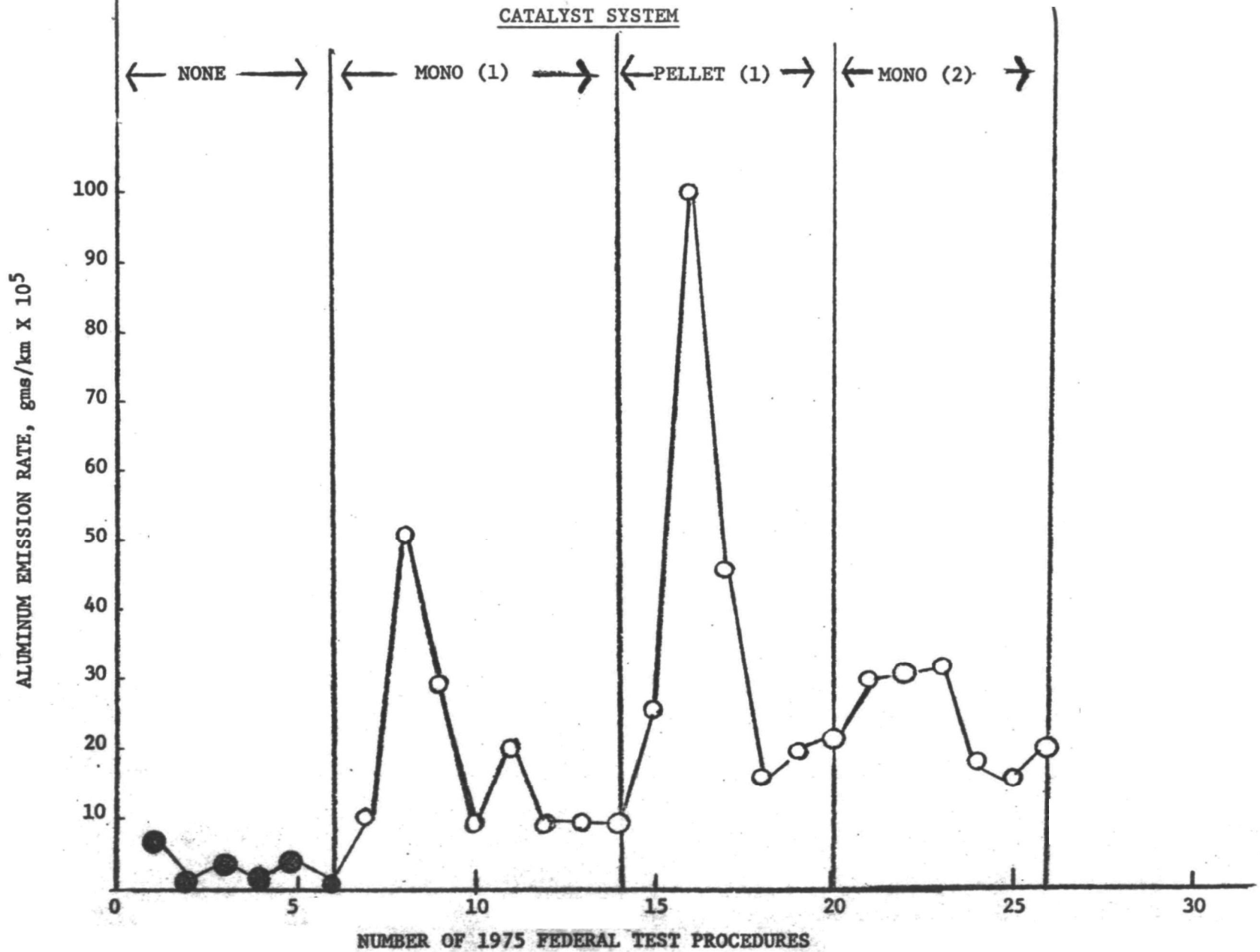


FIGURE II

IRON EMISSION RATES
ON FEDERAL TEST CYCLES

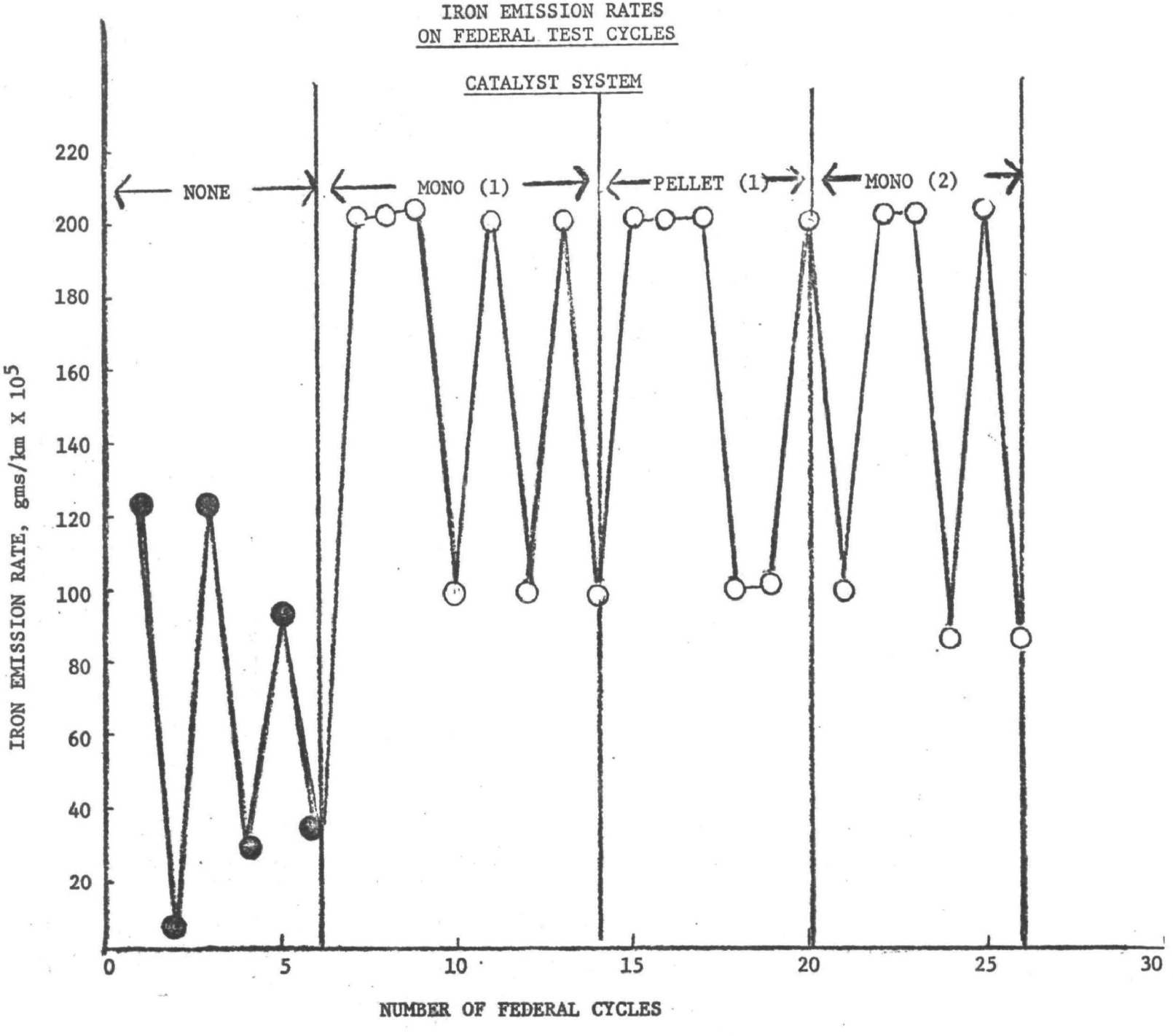


FIGURE III

LEAD EMISSION RATES ON
FEDERAL TEST CYCLES

CATALYST SYSTEM

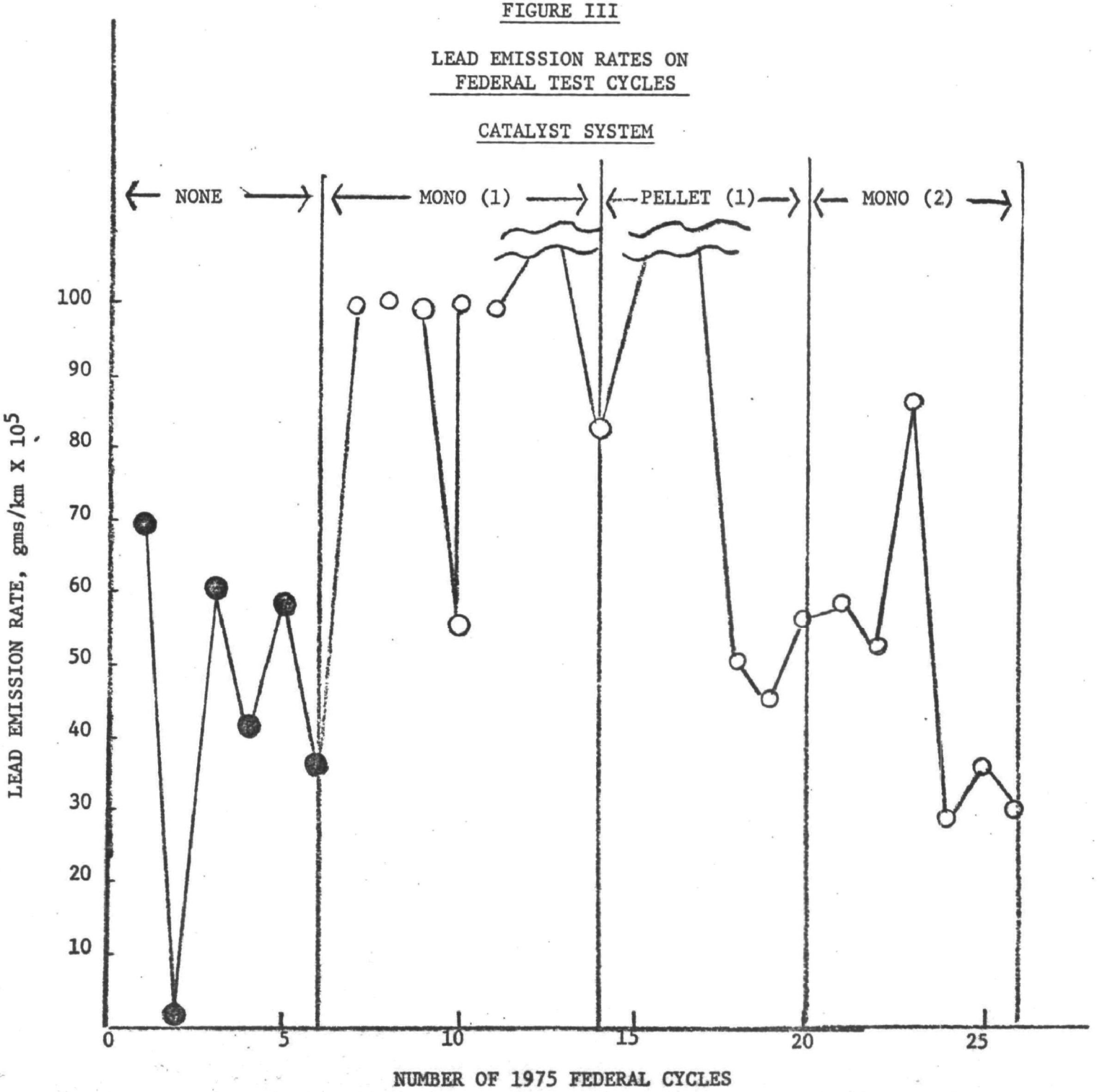


FIGURE IV

ZINC EMISSION RATES
ON FEDERAL TEST CYCLES

CATALYST SYSTEM

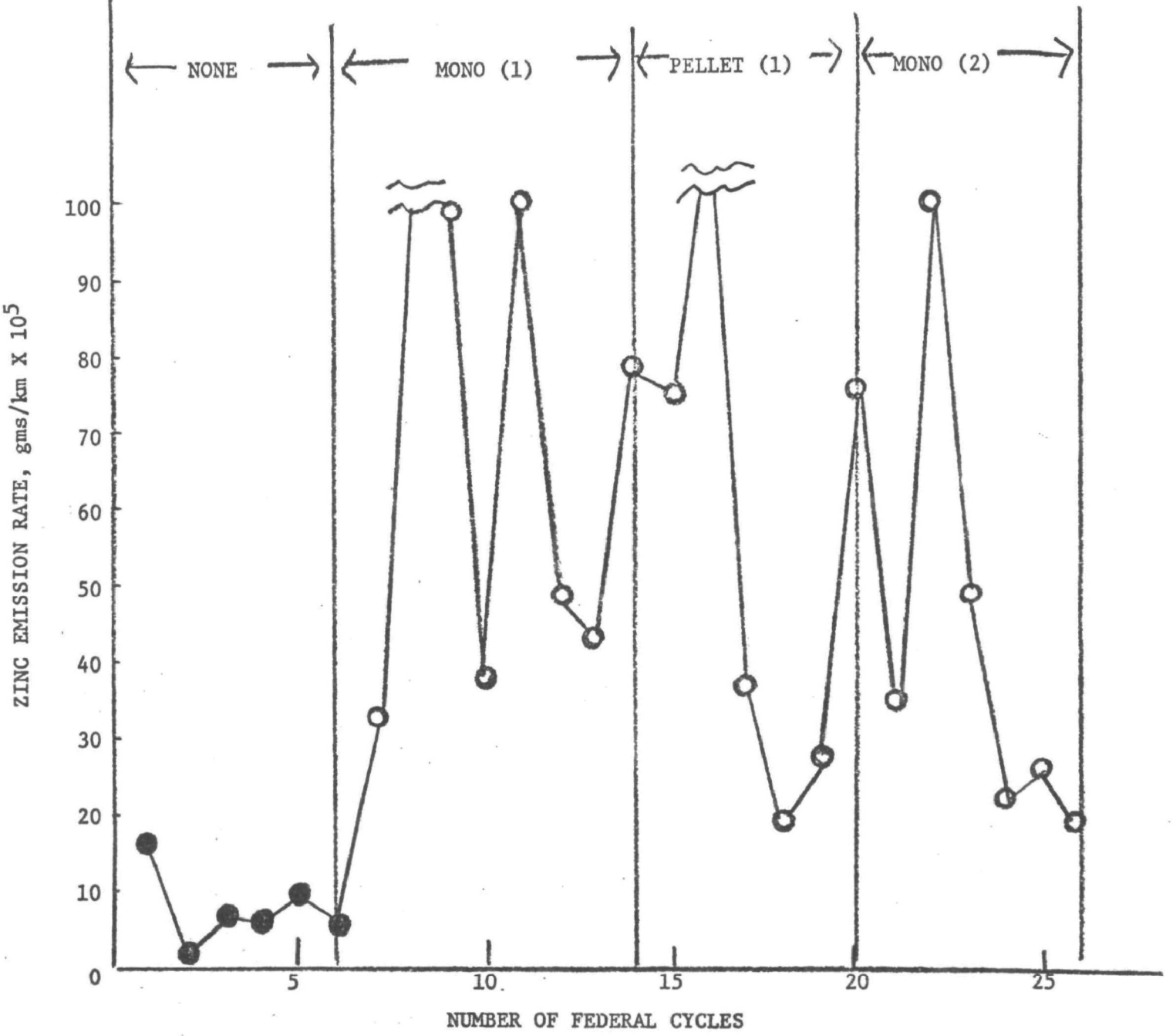
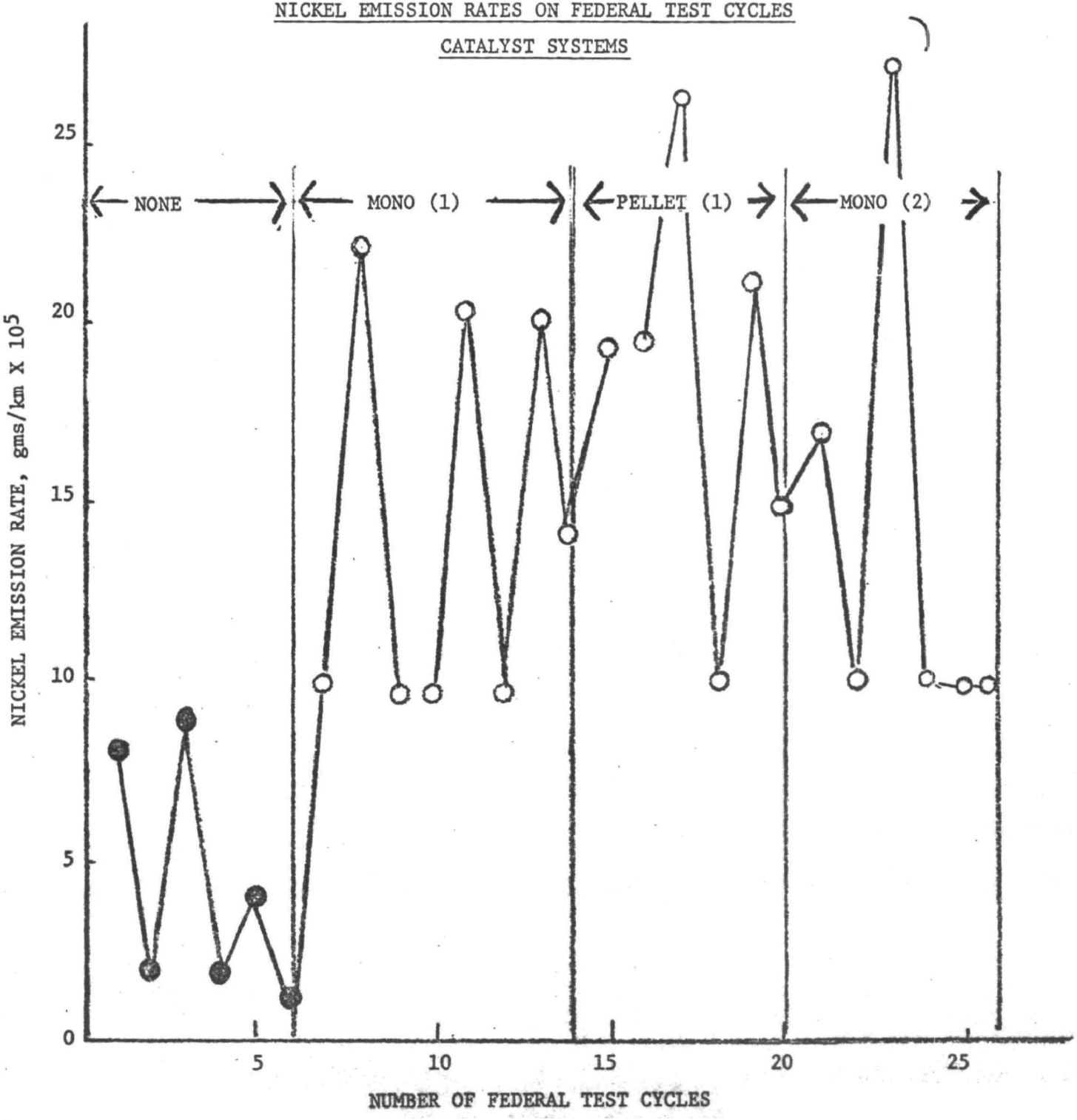


FIGURE V

NICKEL EMISSION RATES ON FEDERAL TEST CYCLES

CATALYST SYSTEMS



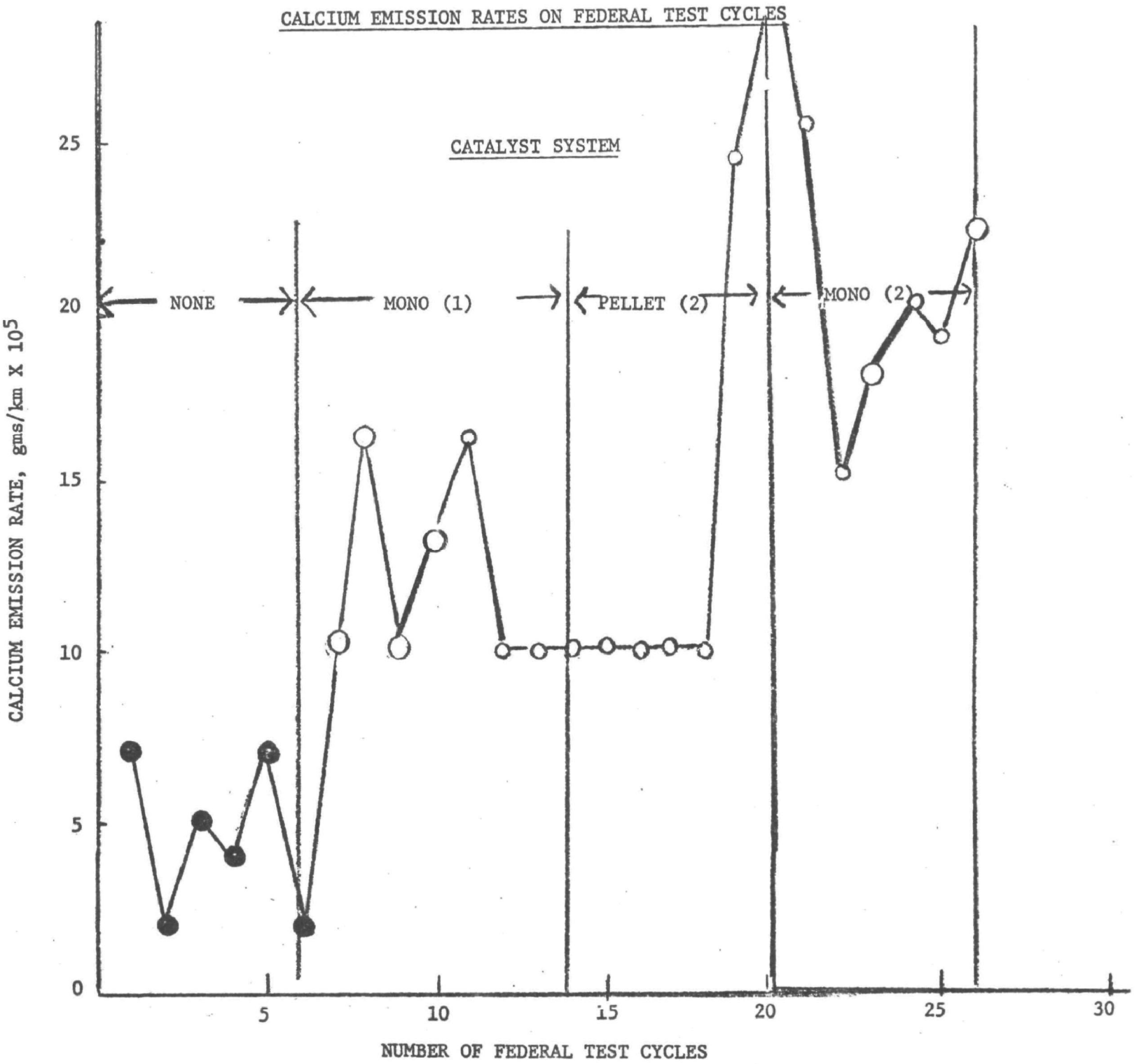

CALCIUM EMISSION RATES ON FEDERAL TEST CYCLES
CATALYST SYSTEM
NONE
MONO (1)
PELLET (2)
MONO (2)
CALCIUM EMISSION RATE, gms/km X 10^5
0
5
10
15
20
25
5
10
15
20
25
30
NUMBER OF FEDERAL TEST CYCLES

FIGURE VII

CHROMIUM EMISSION RATES
ON FEDERAL TEST CYCLES

CATALYST SYSTEM

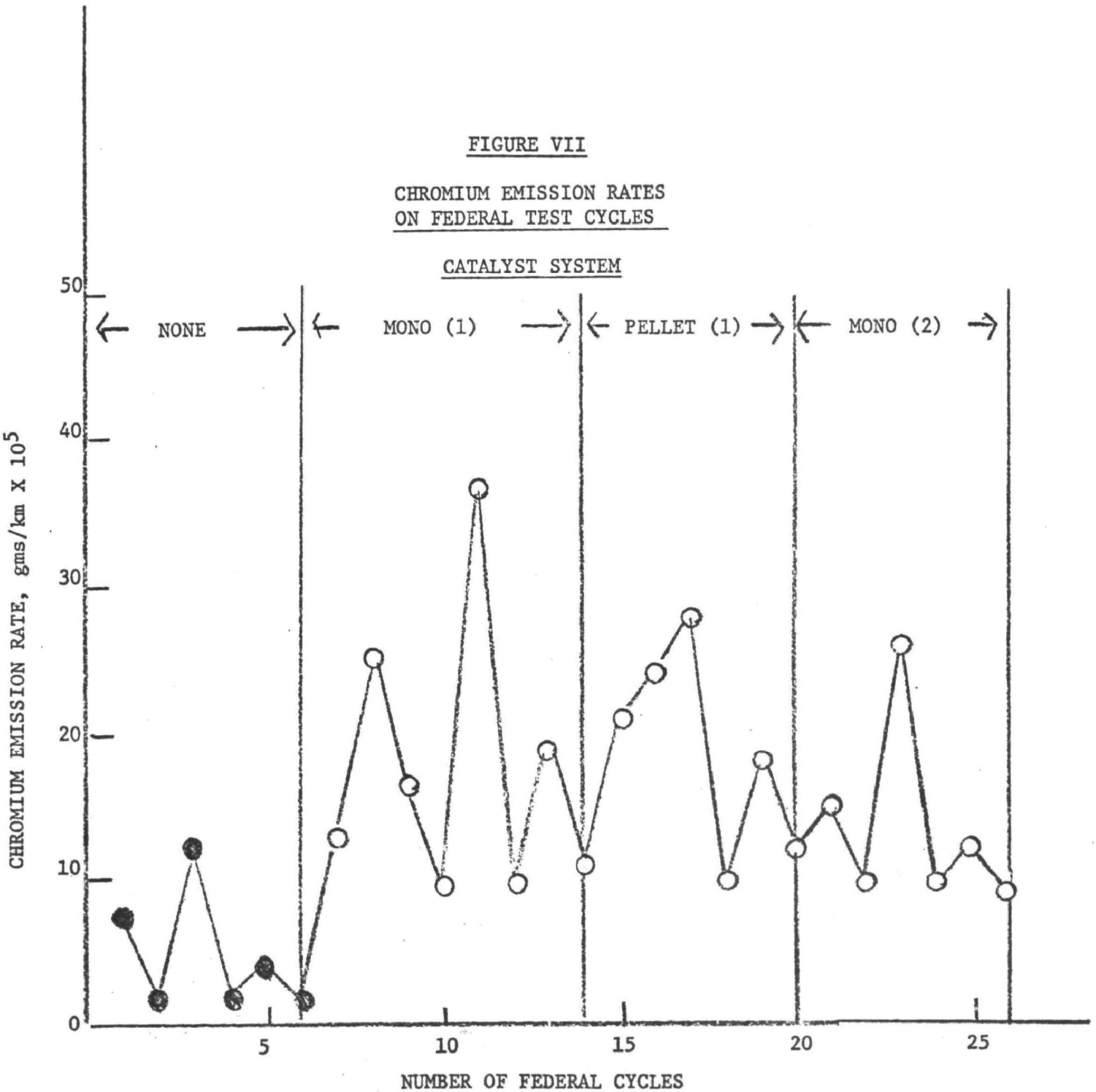
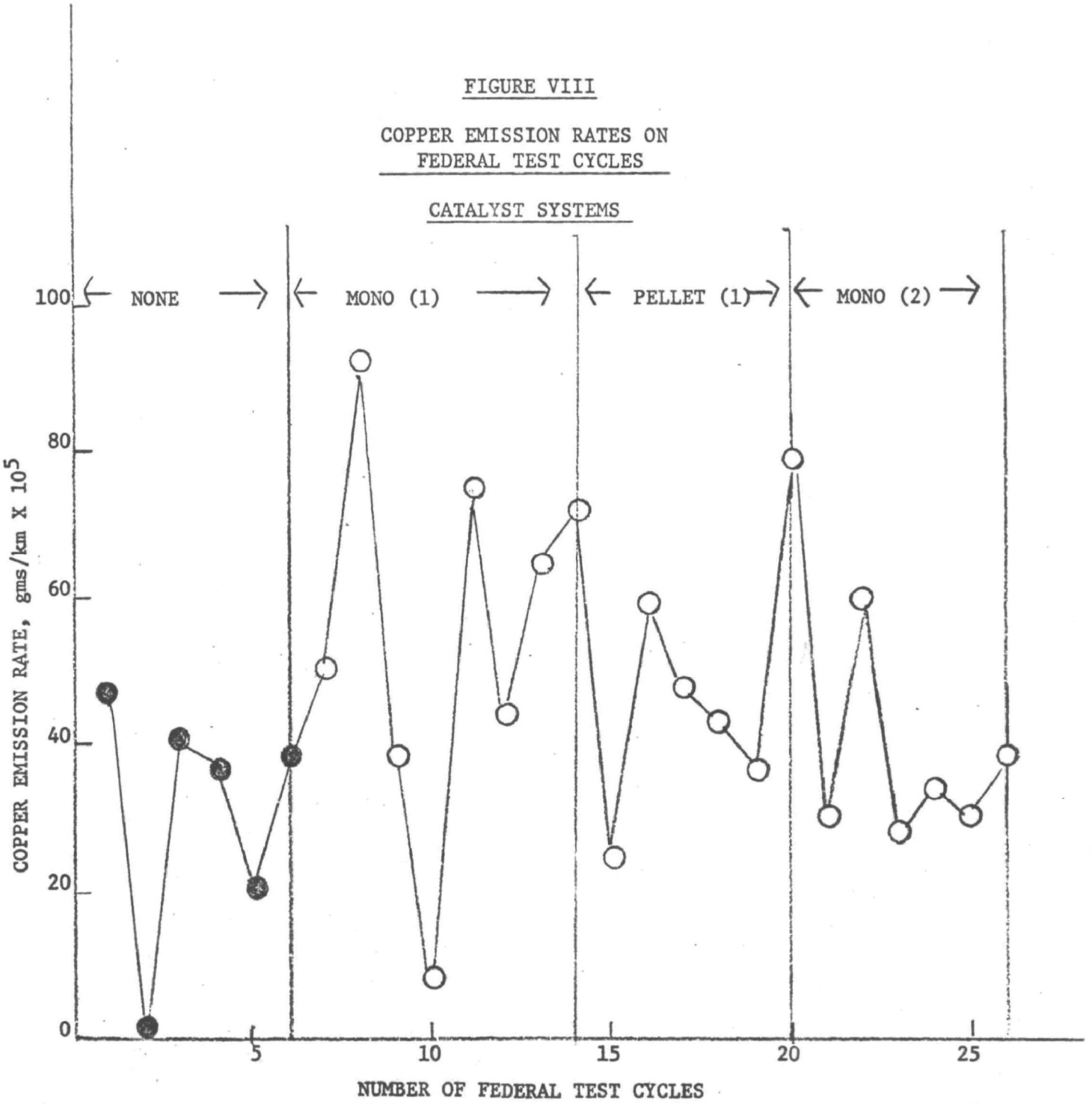


FIGURE VIII

COPPER EMISSION RATES ON
FEDERAL TEST CYCLES

CATALYST SYSTEMS



APPENDIX I

MONO (1) EQUIPPED CHEVROLET 115

Test No.	% Fuel Sulfur	Catalyst Type	Run Type	Emission Rates, gms/km: Particulate Emissions: Total Particulate	Particulate Emissions: H_2SO_4*	Gaseous Emissions: CO	Gaseous Emissions: HC	Gaseous Emissions: NO_x	Gaseous Emissions: SO_2
36	0.019	PTX-IIB	75 FTP	0.031	0.002 (1.5)	3.26	0.29	0.91	~0
37	"	"	Idle (1)	[0.294]	[0.103] (4.7)	[7.70]	[4.45]	[8.66]	0
38	"	"	40 (1)	0.018	0.012 (12.8)	0.05	0.04	0.15	0
39	"	"	70 (2)	0.039	0.010 (13.2)	---	---	---	0
40	"	"	75 FTP	0.043	0.004 (2.7)	1.18	0.63	0.74	0
41	0.110	"	75 FTP	0.169	0.060 (11.1)	1.45	0.80	1.20	0.134
42	"	"	Idle (1)	[0.106]	[0.048] (7.0)	[5.32]	[5.62]	[3.91]	[2.55]
43	"	"	40 (1)	0.262	0.101 (30.1)	0.20	0.08	0.52	0.057
44	"	"	70 (2)	0.150	0.055 (12.2)	0.024	0.003	0.19	0.009
45	"	"	75 FTP	0.150	0.053 (9.7)	2.03	0.42	0.88	0.139
46	0.091	"	75 FTP	0.226	0.087 (19.2)	1.40	0.28	1.33	0.080
47	"	"	Idle (1)	[0.100]	[0.028] (0.5)	[7.26]	[6.10]	[3.91]	[2.14]
48	"	"	40 (1)	0.192	0.076 (25.7)	0.28	0.08	1.04	0.050
49	"	"	70 (2)	0.146	0.057 (15.7)	---	---	---	---
50	"	"	75 FTP	0.131	0.050 (10.7)	2.01	0.28	1.31	0.098

* Numbers in Parentheses are % Conversions Based on Emitted Sulfate
Bracketed Numbers are Emission Rates in gms/hr
0.019% S = EPA Reference Fuel
0.110% S = EPA+
0.091% S = HA+

APPENDIX II

PELLET (1) EQUIPPED CHEVROLET 115

Test No.	% Fuel Sulfur	Run Type	Emission Rates, gms/km					
			Particulate Emissions		Gaseous Emissions			
			Total* Particulate	H_2SO_4**	CO	HC	NO_x	SO_2
51	0.019	75 FTP	0.061	0.003 (3.19)	2.528	0.217	1.370	0.015
52	"	Idle (1)	[0.130]	[0.022] (1.76)	[0.81]	[1.458]	[0.54]	[0.0]
53	"	40 (1)	0.009	0.001 (1.52)	0.019	0.016	0.008	0.0
54	"	70 (2)	0.115	0.027 (36.00)	---	---	---	---
55	"	75 FTP	0.036	0.002 (2.08)	2.501	0.224	1.318	0.093
56	0.110	75 FTP	0.059	0.008 (1.42)	1.528	0.349	1.229	0.043
57	"	Idle (1)	[0.099]	[0.052] (1.01)	[7.506]	[3.964]	[8.73]	[0.544]
58	"	40 (1)	0.246	0.104 (27.15)	0.154	0.075	0.601	0.0
59	"	70 (2)	0.287	0.103 (25.31)	0.086	0.029	1.581	0.0
60	"	75 FTP	0.083	0.029 (5.02)	1.327	0.176	1.013	0.058
61	0.091	75 FTP	0.062	0.016 (3.16)	2.162	0.324	1.194	0.061
62	"	Idle (1)	[0.062]	[0.0] (0.0)	[4.676]	[2.333]	[8.932]	0.0
63	"	40 (1)	0.201	0.078 (22.41)	0 218	0.089	0.740	0.022
64	"	70 (2)	0.117	0.046 (5.71)	0.044	0.008	3.111	0.129
65	"	75 FTP	0.064	0.006 (1.17)	2.808	0.219	1.171	0.066

* Bracketed numbers are emission rates in gms/hour for the idle cruises.

** Numbers in parentheses, Column 4, are % conversions, $SO_2 \longrightarrow H_2SO_4$ based on fuel consumption and particulate sulfate measured.

APPENDIX III

MONO (2) EQUIPPED CHEVROLET 115

Test No.	% Fuel Sulfur	Run Type	Emission Rates, gms/km					
			Particulate Emissions		Gaseous Emissions			
			Total* Particulate	H_2SO_4**	CO	HC	NO_x	SO_2
66	0.019	75 FTP	0.029	0.003 (2.88)	2.652	0.274	1.091	0.061
67	"	Idle (1)	[0.064]	[0.021] (1.71)	[22.766]	[11.416]	[6.728]	[0.0]
68	"	40 (1)	0.037	0.013 (20.31)	0.129	0.042	0.694	0.0
69	"	70 (2)	0.031	0.011 (7.43)	0.174	0.018	1.955	0.031
70	"	75 FTP	0.035	0.001 (0.99)	1.770	0.191	0.927	0.029
71	0.110	75 FTP	0.104	0.022 (3.93)	1.742	0.250	1.079	0.190
72	"	Idle (1)	[0.073]	[0.011] (0.16)	[4.946]	[4.277]	[5.098]	[0.0]
73	"	40 (1)	0.490	0.183 (47.78)	0.119	0.048	0.505	0.031
74	"	70 (2)	0.168	0.065 (8.05)	0.121	0.014	0.118	0.117
75	"	75 FTP	0.090	0.027 (5.29)	2.124	0.264	0.622	0.186
76	0.091	75 FTP	0.134	0.033 (6.78)	1.800	0.191	1.277	0.074
77	"	Idle (1)	[0.142]	[0.034] (0.56)	[4.136]	[4.158]	[6.836]	[0.0]
78	"	40 (1)	0.462	0.165 (52.05)	0.132	0.033	0.706	0.043
79	"	70 (2)	0.138	0.061 (7.79)	0.147	0.013	3.570	0.107
80	"	75 FTP	0.042	0.008 (1.57)	1.863	0.150	1.305	0.004

* Bracketed numbers are emission rates in gms/hour for the idle cruises.

** Numbers in parentheses, Column 4, are % conversions, $SO_2 \longrightarrow H_2SO_4$, based on fuel consumption and particulate sulfate measured.

APPENDIX IV

MONO (3) EQUIPPED CHEVROLET 115

Test No.	% Fuel Sulfur	Run Type	Emission Rates, gms/km†					
			Particulate Emissions		Gaseous Emissions			
			Total* Particulate	H_2SO_4	CO	HC	NO_x	SO_2*
81	0.019	75 FTP	0.028	0.003 (3.15)	1.373	0.232	1.083	0.031
82	"	Idle (1)	[0.185]	[0.0] (0.0)	[8.834]	[5.584]	[11.524]	[0.961]
83	"	40 (1)	0.014	0.006 (9.38)	0.200	0.047	0.598	0.037
84	"	60 (2)**	0.025	0.010 (7.19)	0.427	0.033	2.208	0.022
85	"	75 FTP	0.021	0.003 (3.09)	0.959	0.146	0.578	0.023
86	0.110	75 FTP	0.086	0.032 (5.66)	1.035	0.241	1.116	0.245
87	"	Idle (1)	[0.068]	[0.0] (0.0)	[8.067]	[6.361]	[7.020]	[3.694]
88	"	40 (1)	0.118	0.055 (15.32)	0.267	0.058	0.648	0.197
89	"	60 (2)	0.141	0.068 (16.71)	0.555	0.033	2.430	0.213
90	"	75 FTP	0.050	0.016 (2.9)	2.663	0.323	1.136	0.275
91	0.091	75 FTP	0.069	0.024 (5.07)	1.040	0.244	1.313	0.233
92	"	Idle (1)	[0.101]	[0.0] (0.0)	[5.430]	[4.061]	[8.381]	[2.960]
93	"	40 (1)	0.087	0.043 (13.1)	0.288	0.049	30.890	0.160
94	"	60 (2)	0.097	0.058 (15.8)	0.549	0.030	2.938	0.194
95	"	75 FTP	0.040	0.015 (10.3)	2.087	0.253	2.112	0.388

† Idle emission rate, bracketed numbers are in gms/hour

* SO_2 calibrated from SO_2 in air calibration curve (no correction factor was used)

** 60 mph (96.54 km/hr) supplants the former 70 mph cruise test runs

gm/mi = gm/km x 1.61

APPENDIX V

METAL EMISSIONS, CHEVROLET 115 EQUIPPED WITH MONO (1) CATALYST
Emission Rate (gms/km)*

Test No.	Run Type	% Fuel Sulfur	Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb	Pt
31	75 FTP	0.019	0.00010	>0.00010	>0.00033	0.00013	0.00202	0.00051	0.00010	0.00100	<0.00006
32	Idle (1)	"	[<0.00180]	[0.00180]	[0.00180]	[0.00180]	[0.03600]	[0.00920]	[0.00180]	[0.0180]	[<0.00100]
33	40 (1)	"	0.00004	<0.00003	<0.00003	<0.00003	0.00010	<0.00003	<0.00003	0.00011	<0.00001
34	70 (2)	"	0.00021	0.00079	0.00204	0.00031	0.00440	0.00115	0.00021	0.00440	<0.00002
35	75 FTP	"	0.00016	0.00051	0.00202	0.00025	0.00202	0.00092	0.00022	0.00101	<0.00006
36	75 FTP	0.019	0.00010	0.00029	>0.00100	0.00016	>0.00200	0.00038	<0.00010	>0.00100	<0.00006
37	Idle (1)	"	[0.00180]	[0.00400]	[0.01440]	[<0.00180]	[>0.0018]	[<0.00180]	[<0.0018]	[0.00680]	[<0.00100]
38	40 (1)	"	<0.00003	0.00005	0.00011	<0.00003	0.00021	<0.00003	<0.00003	0.00015	<0.00001
39	70 (2)	"	0.00009	0.00016	0.00027	<0.00058	>0.00058	0.00008	<0.00058	0.00046	<0.00003
40	75 FTP	"	0.00013	<0.00010	0.00039	<0.00010	>0.00100	<0.00010	<0.00010	0.00056	<0.00006
41	75 FTP	0.110	0.00016	0.00021	0.00100	0.00037	>0.00202	0.00075	0.00020	0.00101	<0.00006
42	Idle (1)	"	[0.00160]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00320]	[<0.00180]	[<0.00180]	[0.00320]	[<0.00100]
43	40 (1)	"	0.00003	0.00004	0.00016	0.00003	>0.00028	0.00005	0.00004	0.00024	<0.00001
44	70 (2)	"	<0.00002	0.00003	0.00015	0.00004	>0.00020	0.00006	0.00004	>0.00020	<0.00001
45	75 FTP	"	<0.00010	<0.00010	0.00048	<0.00010	>0.00100	0.00045	<0.00010	>0.00100	<0.00006
46	75 FTP	0.091	<0.00010	<0.00010	0.00043	0.00019	>0.00100	0.00065	0.00020	0.00100	---
47	Idle (1)	"	[<0.00180]	[<0.00180]	[0.00220]	[<0.00180]	[0.00240]	[<0.00180]	[<0.00180]	[0.00400]	---
48	40 (1)	"	<0.00003	<0.00003	0.00003	<0.00003	0.00006	<0.00003	<0.00003	0.00004	---
49	70 (2)	"	<0.00001	<0.00001	>0.00024	0.00001	>0.00012	0.00003	<0.00001	>0.00012	---
50	75 FTP	"	<0.00010	<0.00010	0.00079	0.00011	>0.00100	0.00072	0.00015	0.00085	---

* Bracketed numbers are idle emission rates of metals in gms/hour.

** Replacement PTX-IIB (Runs 36-50) after first PTX-IIB deactivated (Run 34) due to excessive temperature rise resulting from misfire.

APPENDIX VI

METAL EMISSIONS, CHEVROLET 115 EQUIPPED WITH PELLET (1) CATALYST
Emission Rate (gms/km)*

Test No.	Run Type	% Fuel Sulfur	Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb
51	75 FTP	0.019	0.00010	0.00026	0.00076	0.00021	>0.00202	0.00025	0.00019	>0.00100
52	Idle (1)	"	[<0.00180]	[<0.00180]	[0.00260]	[<0.01800]	[>0.01800]	[<0.01800]	[<0.00180]	[0.00860]
53	40 (1)	"	0.00003	<0.00003	0.00004	<0.00003	0.00028	0.00004	0.00003	0.00016
54	70 (2)	"	0.00004	>0.00028	>0.00057	>0.00026	>0.00057	>0.00028	0.00026	>0.00057
55	75 FTP	"	<0.00010	>0.00100	>0.00200	0.00024	>0.00200	0.00059	0.00019	>0.00100
56	75 FTP	0.110	<0.00010	0.00046	0.00037	0.00028	>0.00202	0.00048	0.00026	>0.00202
57	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00760]	[<0.00180]	[<0.00180]	[0.00480]
58	40 (1)	'	<0.00003	<0.00003	0.00005	<0.00003	0.00018	<0.00003	<0.00003	0.00015
59	70 (2)	"	<0.00004	0.00006	0.00012	0.00005	0.00073	0.00010	0.00006	>0.00036
60	75 FTP	"	<0.00010	0.00016	0.00019	<0.00010	>0.00100	0.00043	<0.00010	0.00050
61	75 FTP	0.091	0.00024	0.00020	0.00027	0.00018	>0.00101	0.00037	0.00021	0.00076
62	Idle (1)	"	[0.00380]	[0.00200]	[<0.00180]	[<0.00180]	[0.00720]	[<0.00180]	[<0.00180]	0.00200
63	40 (1)	"	0.00006	<0.00003	<0.00003	<0.00003	0.00023	<0.00003	<0.00003	0.00007
64	70 (2)	"	0.00002	0.00001	0.00002	<0.00001	>0.00010	0.00001	<0.00001	0.00003
65	75 FTP	"	0.00029	0.00022	0.00075	0.00012	>0.00202	0.00078	0.00015	0.00057

* Bracketed numbers are idle emission rates in gms/hour.

APPENDIX VII

METAL EMISSIONS, CHEVROLET 115 EQUIPPED WITH MONO (2) CATALYST
Emission Rate (gms/km)*

Test No.	Run Type	% Fuel Sulfur	Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb
66	75 FTP	0.019	0.00025	0.00030	0.00035	0.00015	>0.00101	0.00030	0.00017	0.00059
67	Idle (1)	"	[0.00240]	[0.00180]	[<0.00180]	[<0.00180]	[0.00740]	[<0.00180]	[<0.00180]	[<0.00180]
68	40 (1)	"	0.00005	<0.00003	<0.00003	<0.00003	0.00010	<0.00003	<0.00003	0.00004
69	70 (2)	"	0.00002	0.00002	0.00008	0.00002	0.00016	0.00003	<0.00001	0.00008
70	75 FTP	"	0.00015	0.00031	0.00100	<0.00010	>0.00202	0.00060	<0.00010	0.00053
71	75 FTP	0.110	0.00018	0.00032	0.00048	0.00026	>0.00202	0.00028	0.00027	0.00087
72	Idle (1)	"	[0.00440]	[0.00640]	[0.00280]	[0.00240]	[>0.01800]	[0.00260]	[0.00260]	[0.00780]
73	40 (1)	"	0.00005	0.00003	0.00004	<0.00003	0.00021	<0.00003	<0.00003	0.00007
74	70 (2)	"	<0.00010	0.00001	0.00001	<0.00001	>0.00008	<0.00001	<0.00001	0.00002
75	75 FTP	"	0.00020	0.00018	0.00022	<0.00010	0.00087	0.00034	<0.00010	0.00029
76	75 FTP	0.091	0.00019	0.00016	0.00025	0.00012	0.00202	0.00030	0.00010	0.00037
77	Idle (1)	"	[0.00380]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00280]	[0.00180]	[<0.00180]	[0.00200]
78	40 (1)	"	0.00006	<0.00003	<0.00003	<0.00003	0.00016	<0.00003	<0.00003	0.00014
79	70 (2)	"	0.00007	0.00007	0.00016	0.00008	0.00016	0.00008	0.00008	>0.00008
80	75 FTP	"	0.00022	0.00021	0.00018	<0.00010	0.00085	0.00038	<0.00010	0.00039

* Bracketed numbers are idle emission rates in gms/hour.

THE CHARACTERIZATION OF PARTICULATE EMISSIONS FROM PROTOTYPE CATALYST VEHICLES

MONTHLY PROGRESS REPORT NO. 5
FOR PERIOD OCTOBER 1 TO OCTOBER 31, 1974
PREPARED BY MORTON BELTZER

CONTRACT NO. 68-02-1279

10 NOVEMBER, 1974

Prepared by

Exxon Products Research Division
Exxon Research and Engineering Company
Linden, New Jersey

for

Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Section I

Purpose and Scope of Work

Exxon Research and Engineering Company, under contract with the Environmental Protection Agency, is engaged in a research program designed to measure and characterize the exhaust particulate emissions from a variety of catalyst systems, both commercial and prototype, that are candidates for use in automotive emissions control. Due to such mechanisms as mechanical and thermal shock, and possible chemical conversion of catalyst material to a mobile condensed material, particulate emissions from catalyst equipped vehicles could differ markedly from that of conventional vehicles. Furthermore, catalytic conversion of gaseous exhaust components to particulate exhaust matter introduces exhaust components that are not now present in the exhaust from conventional vehicles. A case in point is the catalytic oxidation of exhaust sulfur dioxide to the trioxide which is then emitted as sulfate aerosol.

In order to separate vehicle and catalyst effects on total particulate emissions, it will be necessary to measure and characterize particulate emissions from the vehicles in their conventional configuration before they are equipped with catalysts.

Eight catalyst systems (three monolithic oxidation catalysts, two beaded oxidation catalysts, and three reduction catalysts will be tested with three fuels.

The three fuels that will be tested are:

(1) an EPA furnished reference fuel.

(2) the EPA fuel treated with an additive package consisting of thiophene and t-butyl sulfide to a fuel sulfur level of 0.1 wt.% sulfur, and TEL as motor mix to a level of 0.05 gms Pb/gal.

(3) a high aromatic content fuel similarly treated.

Both treated fuels shall also contain an additive package comprised of Lubrizol 596 (0.27 g/gal) and Paradyne 502 (0.45 g/gal). The former functions as detergent, corrosion inhibitor, anti-stall, and anti-icing agent and contains about 2.25 - 2.75 wt.% nitrogen. Paradyne 502 contains 0.75 wt.% nitrogen and functions as a detergent, anti-rust agent, and deposit modifier.

This fuel selection should allow exhaust particulate characterization as follows:

(1) level of composition of exhaust particulate resulting from the use of an additive-free fuel in conventional and and catalyst equipped vehicles.

(2) effect of fuel additives on particulate emissions from conventional and catalyst equipped vehicles.

(3) effect of a high aromatic fuel containing additives on particulate emissions from conventional and catalyst equipped vehicles.

Section II

A. Work During Period of October 1-31, 1974

The test sequences (Monthly Report No. 2, Section II, A.1) were carried out with two NO_x reduction catalysts. These catalytic systems supplied by W. R. Grace and Gould Incorporated are hereinafter referred to as REDN (1) and REDN (2) respectively. In order to assess the NO_x reduction capabilities of these systems, the exhaust gas recycle EGR was disconnected. The air pumps from the mileage accumulation vehicle and the test vehicle were disconnected to minimize the occurrence of lean operating conditions over the catalysts during mileage accumulation or testing. Carburetion was not modified for either vehicle. Analysis of the raw exhaust upstream to the catalysts at about 16, 32, 48, 64, and 96 km/hour showed that the catalysts are exposed to a net rich exhaust in these cases except for slightly lean operation at 64 km/hour. The REDN (2) catalyst package contains an oxygen control system called a "Getter" upstream to the reduction catalyst which functions by scavenging the residual oxygen in raw exhaust.

Total particulate, sulfuric acid, gaseous and metal emission rates were measured. Metal analyses have been completed for the REDN (1) runs; partial analyses are available for the REDN (2) runs.

A.1. Total Particulate Emission Rates

Table I shows the average of the initial and final FTP total particulate emission rates for both NO_x reduction catalysts on the three test fuels.

Table I

Average Total Particulate Emission Rate
(1975 FTP, Vehicle 115 Equipped with Indicated Catalyst Systems)
gms/km

Fuel % Sulfur	REDN (1)	REDN (2)
0.019	0.012	0.027
0.110	0.017	0.020
0.091	0.030	0.025

The fuel sulfur content does not appear to have a marked influence on the total particulate emission rate as in the cases where the vehicle was equipped with oxidation catalysts. This is readily evident if one compares the above Table with the results in Table I, Fourth Monthly Report. In fact the lack of dependence of particulate emission rates on fuel sulfur content is similar to what was exhibited in the base case runs, Table I, Third Monthly Report. The detailed total particulate emission rates for these catalyst systems are given in Appendices I and II.

A.2 Sulfuric Acid Emission Rates

Table II shows the sulfuric acid emission rates corresponding to the runs in Table I. Also shown in Table II are the percent conversions (numbers in parentheses) based on fuel consumption and measured sulfate particulate.

Table II

Average Sulfuric Acid Emission Rate
(1975 FTP, Vehicle 115 Equipped with Reduction Catalysts)
gms/km

Fuel % Sulfur	REDN (1)	REDN (2)
0.019	0.001 (1.7)	~0.001 (1.7)
0.110	0.004 (0.87)	0.002 (0.33)
0.091	≈0.001 (0.22)	<0.001 (0.11)

The low levels of sulfuric acid emissions, independent of fuel sulfur content, are consistent with the results shown in Table I, which indicate the lack of dependence of total particulate emissions on fuel sulfur content.

Although sulfuric acid emissions were low under cyclic test conditions and negligible on the idle cruises, readily detectable quantities of sulfate were detected on the steady state cruises. The levels were generally well below the sulfate levels obtained when the vehicle was equipped with oxidation catalysts. Table III shows the sulfate emissions for the two reduction catalyst systems at 40 and 60 mph cruises.

Table III

Sulfuric Acid Emission Rates
at 40 and 60 mph Cruises with
Reduction Catalyst Equipped Vehicle

% Fuel Sulfur	Run Type	gms/km, H_2SO_4 with Indicated Catalyst REDN (1)	REDN (2)
0.019	40 (1)	0.002 (3.45)	0.002 (3.70)
"	60 (2)	0.001 (1.52)	0.006 (9.68)
0.110	40 (1)	0.065 (18.1)	0.044 (13.10)
"	60 (2)	0.027 (6.91)	0.039 (9.97)
0.091	40 (1)	0.043 (14.01)	0.034 (11.85)
"	60 (2)	0.024 (7.19)	0.040 (15.04)

A.3 Gaseous Emission Rates

Emission rates for CO, HC, NO_x, and SO_2 are also shown in Appendices I and II.

The NO_x emissions from both catalyst systems was comparable to what was obtained with the vehicle equipped solely with EGR. Steady state cruise A/F ratio measurements prior to actual vehicle tests indicated net rich operating conditions. However, A/F ratio measurements during the transient portions of the test cycle indicate that the reduction catalysts have been exposed to a net lean environment during a major portion of both the test procedures and the conditioning sequence prior to testing. Thus, both reduction catalysts were not operated at conditions recommended by the catalyst manufacturer. Consequently the results obtained with these catalysts under our test conditions are not to be considered as representative of the true NO_x reducing capabilities of these catalysts.

A.4 Metal Emission Rates

Metal analyses for the MONO (3) catalyst test runs (Runs 81-95) have been completed. The MONO (3) metal emission rates are shown in Appendix III. Platinum analyses have not yet been completed for the MONO (3) runs.

Metal emission rates REDN (1) and REDN (2) are shown in Appendices IV and V.

In the Fourth Monthly Report, the metal emission rates measured on the 1975 Federal Test Cycles were plotted to make an initial assessment of the effect of catalysts. In this report, these plots are carried out for nickel and iron only, Figures I and II respectively. It can be seen from Figure I that the nickel emission rate increases sharply when

the vehicle is equipped with the REDN (2) reduction catalyst. Presently, it is not known if the increased nickel emission rates observed with the REDN (2) catalyst are also the result of generally lean or near stoichiometric operating conditions. Nickel emissions on the idle cruise tests were readily detectable when the vehicle was equipped with REDN (2) system, despite the net rich operating mode of the vehicle. However, the nickel emissions from the REDN (2) catalyst system may be due to its lean pre-history. Consequently, at this stage of testing, the nickel emission rates should not be considered as being typical of this catalyst system.

Figure II shows the iron emission rates during the 75 FTP's. Not all samples were available for plotting. FTP Nos. 28 and 29 corresponding to Runs 85 and 86 were sent to EPA for Pt analysis and have not yet been returned for our metals analysis, and the results of the 42nd and 43rd FTP are not yet available. However, based on the limited data available, there does seem to be a decrease in the iron emission rate when the reduction catalysts are on the vehicle. With the exception of one high value (FTP Number 34), the iron emission rates resemble those of the unequipped vehicle (FTP Runs Nos. 1 to 6). This lends support to the theory that the increased iron emission rates obtained when the vehicle is equipped with an oxidation catalyst may be due to reaction of the exhaust system with the sulfuric acid aerosol.

In many cases, the iron emission rates have exceeded our original upper calibration limits. We have extended this limit and will rework those samples which exceeded the original calibration limits. The upper calibration limits for lead and zinc will also be extended.

The results obtained on the reworked samples will be presented in the final report.

Section III

Catalysts

Another UOP catalyst has been received from Chrysler Corporation. This system has been mounted, conditioned and is currently being tested.

An additional pelleted oxidation catalyst purchased from AC Division of General Motors has been received. This system, a production unit, is manufactured by Air Products for General Motors. This catalyst has been mounted and is undergoing conditioning.

Section IV

Organic Analysis of Exhaust Particulate

The analytical program to characterize the nitrogenous and non-sulfate sulfur components of exhaust particulate has been initiated. The results of this work will be presented in the next monthly progress report.

Error Note

The NO_x emission rate for Run Number 93 in the fourth monthly was erroneously reported as 30.890 gms/km. The correct rate is 0.772 gms/km.

The percent conversion Run Number 95 (Appendix IV of fourth monthly report) was listed as 10.3. The correct value is 3.4%. The average percent conversion on the FTP for this system (Runs 91 and 95 is therefore 4.2, not 7.7%).

FIGURE I

NICKEL EMISSION RATES ON FEDERAL TEST CYCLES
CATALYST SYSTEM

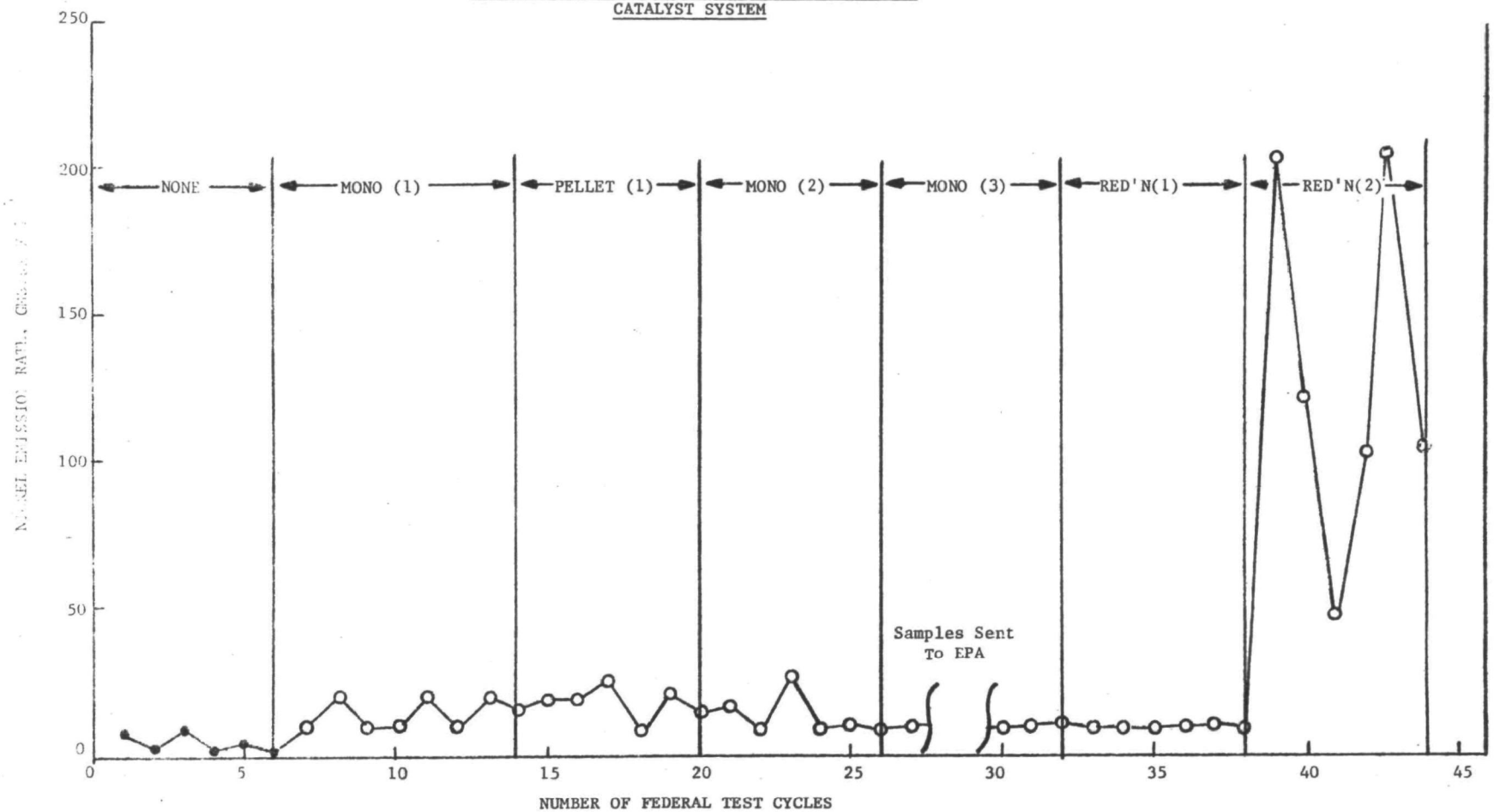
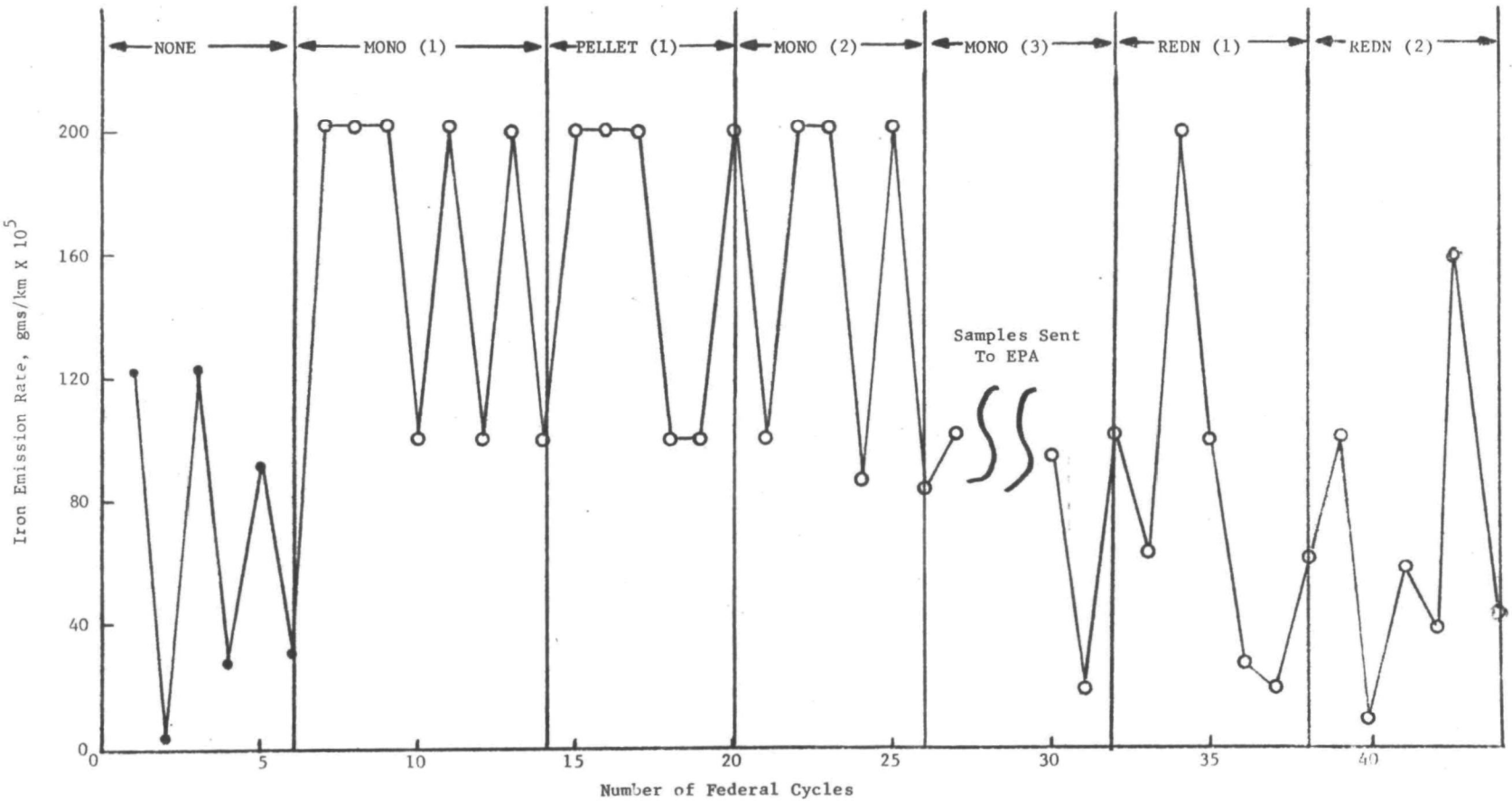


FIGURE II

IRON EMISSION RATES ON FEDERAL TEST CYCLES
CATALYST SYSTEM



APPENDIX I

REDN (1) EQUIPPED CHEVROLET 115*

Test No.	% Fuel Sulfur	Run Type	Emission Rates, gms/km**					
			Particulate Emissions		Gaseous Emissions			
			Total Particulate	H_2SO_4***	CO	HC	NO_x	SO_2
96	0.019	75 FTP	0.007	0.002 (2.15)	10.177	0.375	2.006	0.142
97	"	Idle (1)	[0.001]	0.000 (0.00)	[42.206]	[4.19]	[8.906]	[0.972]
98	"	40 (1)	0.005	0.002 (3.45)	0.350	0.055	1.469	0.027
99	"	60 (2)	0.005	0.001 (1.52)	1.913	0.057	3.175	0.040
100	"	75 FTP	0.017	0.001 (1.14)	7.298	0.498	1.907	0.031
101	0.110	75 FTP	0.016	0.004 (0.76)	10.657	0.446	2.138	0.339
102	"	Idle (1)	[---]†	[0.000] (0.00)	[98.550]	[11.804]	[10.530]	[4.892]
103	"	40 (1)	0.133	0.065 (18.1)	0.603	0.099	1.976	0.137
104	"	60 (2)	0.076	0.027 (6.91)	0.208	0.024	1.682	0.084
105	"	75 FTP	0.019	0.005 (0.97)	10.439	0.455	1.860	0.333
106	0.091	75 FTP	0.020	0.001 (0.22)	10.828	0.454	2.529	0.321
107	"	Idle (1)	[0.175]	[0.000] (0.00)	[41.926]	[13.640]	[7.873]	[7.495]
108	"	40 (1)	0.118	0.043 (14.01)	0.474	0.077	1.842	0.131
109	"	60 (2)	0.066	0.024 (7.19)	0.350	0.057	4.783	0.202
110	"	75 FTP	0.041	<0.001 (<0.22)	14.262	0.531	2.705	0.346

* Exhaust Gas Recycle and Air Pump Disconnected

** Numbers in Brackets are Emission Rates in gms/hour

*** Numbers in Parentheses are % Conversions Based on Emitted Sulfate

† Filters Too Fragmented to Obtain Accurate Weighings

APPENDIX II

REDN (2)* EQUIPPED CHEVROLET 115

Test No.	% Fuel Sulfur	Run Type	Emission Rates, gms/km: Particulate Emissions: Total Particulate	Particulate Emissions: H_2SO_4	Gaseous Emissions: CO	Gaseous Emissions: HC	Gaseous Emissions: NO_x	Gaseous Emissions: SO_2
111	0.019	75 FTP	0.041	0.002 (2.33)	12.560	0.582	1.515	0.119
112	"	Idle (1)	[0.092]	0.000 (0.00)	[75.589]	[7.247]	[1.205]	[0.035]
113	"	40 (1)	0.005	0.002 (3.70)	0.131	0.055	1.721	0.024
114	"	60 (2)	0.017	0.006 (9.68)	0.006	0.003	0.319	0.004
115	"	75 FTP	0.013	<0.001 (<1.10)	8.102	0.285	1.890	0.053
116	0.110	75 FTP	0.025	<0.001 (<0.18)	11.558	0.430	2.032	0.290
117	"	Idle (1)	[0.169]	0.000 (0.00)	[5.195]	[3.424]	[6.134]	[1.62]
118	"	40 (1)	0.116	0.044 (13.10)	0.180	0.046	2.083	0.139
119	"	60 (2)	0.110	0.039 (9.97)	0.014	0.005	0.503	0.020
120	"	75 FTP	0.016	0.003 (0.57)	6.458	0.297	2.967	0.271
121	0.091	75 FTP	0.031	0.001 (0.22)	6.173	0.452	1.966	0.243
122	"	Idle (1)	[0.081]	[0.000] (0.00)	[9.050]	[4.428]	[6.588]	[1.577]
123	"	40 (1)	0.089	0.034 (11.85)	0.140	0.038	2.249	0.107
124	"	60 (2)	0.114	0.040 (15.04)	0.066	0.023	3.865	0.125
125	"	75 FTP	0.019	0.000 (0.00)	6.466	0.327	2.620	0.242

* Exhaust Gas Recycle and Air Pump Disconnected

** Numbers in Brackets are Emission Rates in gms/hour

*** Numbers in Parentheses are % Conversions Based on Emitted Sulfate

APPENDIX III

METAL EMISSIONS, CHEVROLET 115 EQUIPPED WITH MONO (3) CATALYST
Emission Rate (gms/km)*

Test No	Run Type	% Fuel Sulfur	Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb	Pt
81	75 FTP	0.019	<0.00010	0.00012	0.00024	<0.00010	>0.00101	<0.00010	<0.00010	0.00514	
82	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.01820]	[<0.00180]	[<0.00180]	[0.00300]	
83	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00017	<0.00003	<0.00003	0.00014	
84	60 (2)	"	<0.00001	0.00002	>0.00010	0.00001	>0.00020	0.00004	<0.00001	>0.00010	
85*	75 FTP	"	--	--	--	--	--	--	--	--	
86*	75 FTP	0.110	--	--	--	--	--	--	--	--	
87	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00360]	[<0.00180]	[<0.00180]	[0.00280]	
88	40 (1)	"	0.00003	<0.00003	0.00003	<0.00003	>0.00030	<0.00003	<0.00003	0.00013	
89	60 (2)	"	<0.00001	<0.00001	0.00008	0.00001	>0.00018	0.00002	<0.00001	0.00009	
90	75 FTP	"	<0.00010	<0.00010	0.00018	<0.00010	0.00095	0.00030	<0.00010	0.00034	
91	75 FTP	0.091	<0.00010	<0.00010	0.00013	<0.00010	>0.00020	0.00039	<0.00010	0.00048	
92	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00600]	[<0.00180]	[<0.00180]	[0.00240]	
93	40 (1)	"	<0.00003	<0.00003	0.00007	<0.00003	0.00025	<0.00003	<0.00003	0.00004	
94	60 (2)	"	0.00001	0.00001	>0.00010	<0.00001	>0.00020	0.00003	<0.00001	>0.00010	
95	75 FTP	"	<0.00010	<0.00010	0.00020	<0.00010	>0.00101	0.00037	0.00010	0.00029	

* Samples 85, 86 Submitted to EPA for Platinum Analysis

APPENDIX IV

METAL EMISSIONS, CHEVROLET 115 EQUIPPED WITH REDN (1) CATALYST
Emission Rate (gms/km)*

Test No.	Run Type	% Fuel Sulfur	Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb	Ft
96	75 FTP	0.019	<0.00010	<0.00010	0.00025	<0.00010	0.00064	0.00016	<0.00010	0.00016	
97	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00580]	[<0.00180]	[<0.00180]	[0.00200]	
98	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00014	<0.00003	<0.00003	0.00005	
99	60 (2)	"	<0.00001	<0.00001	0.00008	<0.00001	>0.00009	<0.00001	<0.00001	0.00005	
100	75 FTP	"	<0.00010	<0.00010	0.00045	<0.00010	>0.00200	0.00025	<0.00010	0.00045	
101	75 FTP	0.110	<0.00010	0.00010	0.00021	<0.00010	>0.00100	0.00017	<0.00010	0.00045	
102	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00240]	
103	40 (1)	"	<0.00006	<0.00006	<0.00006	<0.00006	>0.00056	<0.00006	<0.00006	0.00010	
104	60 (2)	"	<0.00001	<0.00001	>0.00010	<0.00001	>0.00009	0.00002	<0.00001	0.00006	
105	75 FTP	"	<0.00010	<0.00010	0.00016	<0.00010	0.00028	0.00021	<0.00010	0.00019	
106	75 FTP	0.091	<0.00010	<0.00010	<0.00010	<0.00010	0.00020	0.00016	<0.00010	0.00025	
107	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00220]	[<0.00180]	[<0.00180]	[0.00300]	
108	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00011	<0.00003	<0.00003	0.00007	
109	60 (2)	"	<0.00001	<0.00001	0.00005	<0.00001	0.00005	0.00001	<0.00001	0.00002	
110	75 FTP	"	<0.00010	<0.00010	0.00027	<0.00010	0.00062	0.00037	<0.00010	0.00036	

* Numbers in Brackets are Emission Rates in gms/hour.

APPENDIX V

METAL EMISSIONS, CHEVROLET 115 EQUIPPED WITH REDN (2) CATALYST
Emission Rate (gms/km)*

Test No.	Run Type	% Fuel Sulfur	Ca	Al	Zn	Cr	Fe	Cu	Ni	Pb
111	75 FTP	0.019	<0.00010	0.00016	0.00012	<0.00010	>0.00100	0.00030	>0.00202	0.00036
112	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00400]	[<0.00180]	[0.01040]	[0.00200]
113	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00006	<0.00003	0.00016	0.00003
114	60 (2)	"	<0.00001	<0.00001	<0.00001	<0.00001	0.00004	<0.00001	0.00008	0.00006
115	75 FTP	"	<0.00010	<0.00010	<0.00010	<0.00010	<0.00010	0.00017	>0.00100	0.00017
116	75 FTP	0.110	<0.00010	<0.00010	0.00016	<0.00010	0.00058	0.00010	0.00047	0.00026
117	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00260]	[<0.00180]
118	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00008	<0.00003	0.00005	0.00002
119	60 (2)	"	<0.00001	0.00002	0.00006	<0.00001	>0.00020	0.00003	0.00010	>0.00010
120	75 FTP	"	<0.00010	<0.00010	0.00010	<0.00010	0.00038	0.00024	0.00103	0.00022
121	75 FTP	0.091	0.00010	<0.00010	0.00022	<0.00010	0.00165	0.00038	>0.00202	0.00043
122	Idle (1)	"	[<0.00180]	[<0.00180]	[<0.00180]	[<0.00180]	[0.00820]	[<0.00180]	[0.00680]	[<0.00180]
123	40 (1)	"	<0.00003	<0.00003	<0.00003	<0.00003	0.00008	<0.00003	0.00008	<0.00003
124	60 (2)	"	<0.00001	<0.00001	0.00002	<0.00001	0.00040	0.00002	>0.00009	0.00002
125	75 FTP	"	<0.00010	<0.00010	0.00020	<0.00010	0.00047	0.00025	>0.00101	0.00054

* Numbers in Brackets are Idle Emission Rates in gms/hour.

Appendix B2.4

Status Report
ROAP 21BCE
Task 044
Characterize Particulate Emissions from
Production Catalyst Cars

Concept:

Aside from the influence of the catalyst itself, the overall engineering system for emissions control involved integrated, EGR, engine modifications, fuel-air ratio modulation and the like. In order to accurately assess the impact of sulfate emissions, it is necessary to survey a significant number of production cars which will be available for the first time in October and November 1974. It is projected that as many as 20 such cars (mainly rental vehicles) will be surveyed during the current fiscal year.

Status:

Purchase plans for several automobiles to be retained for two years as part of the test fleet are being arranged. Surveys of auto manufacturers are being conducted to select cars for testing. New facilities and improvements to the present chassis dynamometer test cell are being constructed to increase that efficiency.

Appendix B2.5

Status Report

ROAP 21BCE

Task 001

Survey Gaseous and Particulate Emissions - California 1975 Model Year Vehicles

This contract program is intended to ascertain the emissions of regulated pollutants (CO, HC, NO_x) and selected non-regulated pollutants (particulates and sulfates) from consumer-owned, operated, and maintained 1975 model year catalyst-equipped light-duty motor vehicles certified to meet the 1975 California Interim Federal Emissions Standards. Vehicles will be repeat-tested during mileage accumulation. The major intent of this effort is to determine two important factors:

1. The ability of catalyst-equipped vehicles when owned, operated, and maintained by the general public to achieve the regulated emissions standards in-use.

2. The "real-world" emission rate of total particulates and sulfates from catalyst-equipped vehicles.

All tests will be run with the vehicles in the "as received" condition utilizing tank fuel which will be analyzed.

The procurement package for this contractual program is being processed at this time. Award is expected in early 1975.

Appendix B2.6

Status Report

ROAP 21BCE
Task 082

Characterization and Measurement of Regulated, Sulfate, and Particulate Emissions from In-Use Catalyst Vehicles - 1975 National Standard

This grant program is a companion to ROAP 21BCE, Task 001, "Survey Gaseous and Particulate Emissions - California 1975 Model Year Vehicles." In-use catalyst-equipped vehicles will be tested during mileage accumulation to ascertain the emissions rate of both regulated pollutants (HC, CO, NO_x) and selected non-regulated pollutants (particulates and sulfates). This particular grant will focus on 1975 vehicles equipped with catalysts, certified to meet the 1975 49-state Interim Federal Emissions Standards, while the above mentioned contract will examine vehicles certified to meet the 1975 Interim Federal Emission Standards for California.

Award of this grant is anticipated in December 1974.

United States Department of the Interior
BUREAU OF MINES
BARTLESVILLE ENERGY RESEARCH CENTER
P. O. BOX 1398
BARTLESVILLE, OKLAHOMA 74003

September 12, 1974 Attachment A to memo dated Sept. 12, 1974

Monthly Progress Report
Work Accomplished Through
August 1974
Project No. 4844

Gaseous Emissions Associated with Gasoline Additives--Reciprocating Engines

Tests were completed using Texaco TFA 318 fuel additive in the Volkswagen (table 1). Tests with the Ford and Chevrolet using the TFA 318 were completed and reported last month. The TFA 318 is a polyisopropylene carrier oil and is primarily an induction system cleaning agent, especially intake valves. The recommended dosage of 220 lbs per 1,000 barrels was used in all vehicles.

Tests were also completed on the Ford, Chevrolet, and Volkswagen using a combination of Lubrizol 8101 and Texaco TFA 318 fuel additive. The Lubrizol 8101 is a succamid and is multifunctional dispersant-type additive for gasoline. The dosage used was 140 lbs of Lubrizol 8101 per 1,000 barrels of fuel plus 220 lbs of Texaco TFA 318 per 1,000 barrels of fuel resulting in a total of 360 lbs of combined additive per 1,000 barrels of gasoline. Emission data for the three vehicles are presented in tables 2-4. Routine exhaust emissions (CO, HC, NO_x, aldehydes) were not satistically affected by change in fuels or additives; however, further examination of the data is necessary before definitive statements may be made pertaining to the additive related materials.

Experimental work on the three vehicles and 6 fuel additives is now complete. Compilation of all experimental data and drafting of the final report is in progress and a rough draft is expected to be available within 30 to 60 days.

TABLE 1. - Exhaust emissions from 1974 Volkswagen with TFA 318 fuel additive

Fuel	Elapsed miles	1975 FTP g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	30.7	2.65	4.45	0.088
Clear + TFA 318..	10	27.9	2.50	4.23	.082
Clear + TFA 318..	20	29.4	2.60	4.42	.082
Clear + TFA 318..	480	26.5	2.36	4.27	.085
Clear + TFA 318..	1,400	32.5	2.42	3.79	.075
High Aromatic + TFA 318.....	1,420	28.5	2.46	3.96	.065

TABLE 2. - Exhaust emissions from 1974 Volkswagen with Lubrizol 8101 + TFA 318 fuel additive

Fuel	Elapsed miles	1975 FTP g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	30.5	2.61	3.95	0.067
Clear + 8101 + 318...	20	29.0	2.45	3.97	.065
Clear + 8101 + 318...	30	30.4	2.58	4.22	.064
Clear + 8101 + 318...	540	28.2	2.65	4.62	.085
Clear + 8101 + 318...	1,580	31.4	2.65	4.60	.074
High Aromatic + 8101 + 318.....	1,600	30.3	2.76	4.71	.048

TABLE 3. - Exhaust emissions from 1974 Chevrolet with Lubrizol 8101 and TFA 318 fuel additves

Fuel	Elapsed miles	1975 FTP g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	38.1	1.09	1.94	0.119
Clear + 8101 + 318..	20	37.4	1.49	1.66	.215
Clear + 8101 + 318..	40	38.3	1.26	1.75	.087
Clear + 8101 + 318..	500	51.1	1.17	1.77	.106
Clear + 8101 + 318..	1,500	41.1	.96	2.57	.102
High Aromatic + 8101 + 318.....	1,540	43.7	1.24	2.01	.112

TABLE 4. - Exhaust emissions from 1974 Ford with Lubrizol 8101 and TFA 318 fuel additves

Fuel	Elapsed miles	1975 FTP g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	35.4	2.64	3.84	0.117
Clear + 8101 + 318..	20	29.4	2.16	3.61	.100
Clear + 8101 + 318..	40	33.6	2.46	3.97	.107
Clear + 8101 + 318..	500	33.5	2.41	4.03	.113
Clear + 8101 + 318..	1,500	32.8	2.37	4.38	.139
High Aromatic + 8101 + 318.....	1,520	32.4	2.30	4.18	.118

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BARTLESVILLE, OKLAHOMA 74003

August 19, 1974 Attachment A to memo dated August 19, 1974

Monthly Progress Report
Work Accomplished Through
July 1974
Project No. 4844

Gaseous Emissions Associated with Gasoline Additives--Reciprocating Engines

Tests were completed using Du Pont DMA-51 fuel additive in the Ford, Chevrolet, and Volkswagen. The DMA-51, a carboxylate, is a multi-functional cleaning additive and was used at a dosage of 15 lbs per 1,000 barrels. Routine emission data are presented in tables 1-3.

In addition, tests were completed on the Ford and Chevrolet using Texaco TFA 318 fuel additive, emission data is presented in tables 4 and 5. The TFA 318 is a polyisopropylene carrier oil and is primarily an induction system cleaning agent, especially for intake valve stems and intake ports. The TFA 318 was used at the recommended dosage of 220 lbs per 1,000 barrels.

The Chevrolet vehicle was involved in a minor accident at about 200 miles into the test using TFA 318. The accident resulted in damage to the front bumper and front fender. Exhaust emissions were not measurably affected, therefore, the test was continued.

TABLE 1. - Exhaust emissions from 1974 Volkswagen with DMA-51 fuel additive

Fuel	Elapsed miles	1975 FTP g/mile			
		CO	HC	NO_x	Aldehydes
Clear.	0	30.6	2.51	4.19	0.093
Clear + DMA-51 .	10.	26.9	2.54	4.64	.105
Clear + DMA-51 .	20	34.6	2.82	4.98	.121
Clear + DMA-51 .	500	29.9	2.66	5.16	.096
Clear + DMA-51 .	1500	30.8	2.48	4.98	.095
High aromatic + DMA-51. . . .	1520	27.8	2.49	4.47	.099

TABLE 2. - Exhaust emissions from 1974 Ford with DMA-51 fuel additive

Fuel	Elapsed miles		1975 FTP g/mile		
		CO	HC	NO_x	Aldehydes
Clear.	0	37.0	2.69	3.76	0.115
Clear + DMA-51 .	20	27.3	2.54	3.10	.147
Clear + DMA-51 .	40	24.8	2.12	4.24	.156
Clear + DMA-51 .	500	24.7	2.41	4.24	.160
Clear + DMA-51 .	1500	26.2	2.68	3.88	.146
High Aromatic + DMA-51. . . .	1520	30.3	2.63	3.75	.150

TABLE 3. - Exhaust emissions from 1974 Chevrolet with DMA-51 fuel additive

Fuel	Elapsed miles		1975 FTP g/mile		
		CO	HC	NO_x	Aldehydes
Clear.	0	47.7	1.27	1.80	0.128
Clear + DMA-51 .	40	31.3	.98	2.02	.112
Clear + DMA-51 .	60	35.2	1.10	2.21	.128
Clear + DMA-51 .	500	41.5	1.23	2.07	.118
Clear + DMA-51 .	1520	37.8	1.21	1.81	.158
High Aromatic + DMA-51. . . .	1530	40.5	1.49	1.92	.114

TABLE 4. - Exhaust emissions from 1974 Chevrolet using Texaco TFA 318 fuel additive

Fuel	Elapsed miles	1975 FTP g/mile			
		CO	HC	NO_x	Aldehydes
Clear.	0	47.5	2.08	1.62	0.125
Clear + TFA 318. .	20	38.5	1.56	2.06	.133
Clear + TFA 318. .	30	35.4	1.25	2.04	.114
Clear + TFA 318. .	550	37.7	1.59	1.42	.117
Clear + TFA 318. .	1490	29.4	1.02	2.01	.119
High Aromatic + TFA 318	1510	35.6	1.02	2.14	.105

TABLE 5. - Exhaust emissions from 1974 Ford using Texaco TFA 318 fuel additive

Fuel	Elapsed miles	1975 FTP g/mile			
		CO	HC	NO_x	Aldehydes
Clear.	0	30.2	2.51	3.22	0.151
Clear + TFA 318. .	20	26.6	2.58	3.25	.159
Clear + TFA 318. .	30	29.9	2.74	3.73	.154
Clear + TFA 318. .	550	24.7	2.27	3.48	.145
Clear + TFA 318. .	1560	26.4	2.15	3.83	.120
High Aromatic + TFA 318	1580	34.6	2.41	4.00	.113

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BARTLESVILLE, OKLAHOMA 74003

June 18, 1974 Attachment A to memo dated June 18, 1974

Monthly Progess Report
Work Accomplished Through
May 1974
Project No. 4844

Gaseous Emissions Associated with Gasoline Additives--Reciprocating Engines

Tests have been completed on all vehicles using amine neutralized alkyl phosphate fuel additive (DMA4) at a concentration of 15 lbs per 1,000 barrels. The emission data are presented in tables 1-3. Tests are in progress on all vehicles using the succinamide fuel additive (Lubrizol 8101) at a concentration of 140 lbs per 1,000 barrels with about 500 miles accumulated to date.

A problem with the Volkswagen was encountered at about 500 miles into the test with the Lubrizol fuel additive when a cylinder misfire was noted. The misfire was caused by a tappet adjusting nut coming loose and resulting in a valve that was not seating and a bent push rod. The push rod was replaced and the valve readjusted. The test was continued rather than repeated from the beginning after an emission check showed the emissions to be normal.

Analytical Procedures

Analytical methods for quantifying hydrogen cyanid and cyanogen are inadequate and are requiring still more analytical development. Tests for nitromethane and nitroethane in vehicular exhaust are continuing with 1 to 5 ppm nitromethane and up to 1 ppm nitroethane present in the raw exhaust, with the rotary engines emitting considerably more than the reciprocating engines. Comparisons are being made to determine if the nitromethane and nitroethane content in the exhaust is also related to additive dosage or engine duty cycle.

TABLE 1. - Exhaust emissions from 1974 Volkswagen with DMA4 fuel additive

Fuel	Elapsed mile	1975 FTP, g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	24.5	2.35	3.88	0.070
Clear + DMA4.....	10	22.1	2.34	3.32	.078
Clear + DMA4.....	20	23.9	2.47	3.25	.064
Clear + DMA4.....	470	28.5	2.68	3.89	.077
Clear + DMA4.....	1,430	21.3	2.53	4.35	.096
High aromatic + DMA4..	1,450	26.4	2.78	4.18	.076

TABLE 2. - Exhaust emissions from 1974 Ford with DMA4 fuel additive

Fuel	Elapsed mile	1975 FTP, g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	24.3	2.19	2.60	0.123
Clear + DMA4.....	10	26.0	2.41	3.40	.150
Clear + DMA4.....	20	27.5	2.38	3.35	.115
Clear + DMA4.....	490	29.9	2.61	4.20	.155
Clear + DMA4.....	1,600	35.0	2.85	3.58	.139
High aromatic + DMA4..	1,610	37.6	2.97	3.94	.093

TABLE 3. - Exhaust emissions from 1974 Chevrolet with DMA4 fuel additive

Fuel	Elapsed mile	1975 FTP, g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	59.7	1.30	2.24	0.086
Clear + DMA4.....	15	41.3	1.42	2.02	.100
Clear + DMA4.....	40	30.4	.86	2.07	.112
Clear + DMA4.....	490	39.7	1.04	1.81	.133
Clear + DMA4.....	1,490	48.6	1.62	1.90	.123
High aromatic + DMA4	1,500	50.9	1.51	1.71	.095

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BARTLESVILLE ENERGY RESEARCH CENTER

P. O. BOX 1398

BARTLESVILLE, OKLAHOMA 74003

July 22, 1974 Attachment A to memo dated July 22, 1974

Monthly Progress Report
Work Accomplished Through
June 1974
Project No. 4844

Gaseous Emissions Associated with Gasoline Additives--Reciprocating Engines

Tests have been completed on all vehicles using succinamide fuel additive (Lubrizol 8101) at a concentration of 140 lb per 1,000 barrels. The emission data are presented in tables 1-3. Tests are in progress using a Du Pont carboxylate (DMA 51) fuel additive at a concentration of 15 lbs per 1,000 barrels. Approximately 800 miles have been completed to date on each vehicle using the DMA 51.

Analytical Procedures

Preliminary analysis of nitrogen compounds produced in automotive exhaust using clear fuel and F-310 additive shows that the rotary engine vehicles produce more nitromethane and nitroethane than the reciprocating engines. The data scatter does not allow distinguishing any fuel additive effect per se. The data presented in table 4 represent averages of the Volkswagen, Ford, and Chevelle while operating on both clear fuel and F-310 fuel additive. Table 5 represents averages of the rotary engine vehicle and stationary engine using the same fuels in the same time span.

TABLE 1. - Exhaust emissions from 1974 Volkswagen with Lubrizol 8101 fuel additive

Fuel	Elapsed miles	1975 FTP, g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	25.9	2.73	3.88	0.084
Clear + 8101...	10	28.2	2.71	3.99	.086
Clear + 8101...	20	24.0	2.59	4.11	.074
Clear + 8101...	560	22.8	2.43	4.03	.086
Clear + 8101...	1,470	33.0	2.79	4.24	.097
High aromatic + 8101.....	1,480	32.7	2.76	3.86	.082

TABLE 2. - Exhaust emissions from 1974 Ford with Lubrizol 8101 fuel additive

Fuel	Elapsed miles	1975 FTP, g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	38.4	2.95	4.56	0.125
Clear + 8101...	20	32.5	2.90	3.50	-
Clear + 8101...	30	36.8	3.33	3.63	.118
Clear + 8101...	460	41.0	2.63	3.57	.124
Clear + 8101...	1,500	37.0	2.60	4.09	.124
High aromatic + 8101.....	1,520	32.6	2.14	2.83	.113

TABLE 3. - Exhaust emissions from 1974 Chevrolet with Lubrizol 8101 fuel additive

Fuel	Elapsed miles	1975 FTP, g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	50.3	1.49	2.00	0.116
Clear + 8101...	20	45.9	1.35	1.99	.119
Clear + 8101...	40	55.6	1.55	1.78	.114
Clear + 8101...	480	38.0	1.11	1.48	.125
Clear + 8101	1,460	44.6	1.19	2.15	.128
High aromatic + 8101.....	1,480	56.4	1.50	1.86	.087

TABLE 4. - Comparison of F-310 fuel additive and clear fuel on nitrogen compounds emitted using reciprocating engines

	Grams/test			Composite, grams/mile
	Bag 1	Bag 2	Bag 3	
CLEAR FUEL				
Hydrogen cyanide...	0.039	0.022	0.045	0.009
Nitromethane.....	.022	.022	.022	.006
Nitroethane.....	.005	T	.004	.001
F-310 FUEL ADDITIVE				
Hydrogen cyanide...	0.054	0.039	0.052	0.012
Nitromethane.....	.016	.023	.019	.006
Nitroethane.....	.005	.004	.005	.001

TABLE 5. - Comparison of F-310 fuel additive and clear fuel on nitrogen compounds emitted using rotary engines

	Grams/test			Composite, grams/mile
	Bag 1	Bag 2	Bag 3	
CLEAR FUEL				
Hydrogen cyanide...	0.044	0.025	0.017	0.007
Nitromethane.....	.061	.020	.093	.013
Nitroethane.....	.013	T	.018	.002
F-310 FUEL ADDITIVE				
Hydrogen cyanide...	0.018	0.011	0.032	0.005
Nitromethane.....	.059	.035	.072	.014
Nitroethane.....	.012	.015	.016	.004

REVIEW COPY

EFFECT OF GASOLINE ADDITIVES ON GASEOUS EMISSIONS

FINAL REPORT

Prepared for
Office of Research and Monitoring
Environmental Protection Agency

by

FUELS COMBUSTION RESEARCH GROUP
BARTLESVILLE ENERGY RESEARCH CENTER
BUREAU OF MINES

under Interagency
agreement number EPA-IAG-097(D)

Review copy--August 197.

FOREWORD

This report presents a summary of work performed by the Fuels Combustion Research Group, Bartlesville Energy Research Center, Bureau of Mines, for the Environmental Protection Agency, (EPA), Office of Research and Monitoring under Interagency agreement number EPA-IAG-097(D).

Mr. John E. Sigsby, Jr., was the Project Officer for EPA. The program at Bartlesville was directed by R. W. Hurn, Research Supervisor; J. R. Allsup, Mechanical Engineer, was the Project Leader; Frank Cox, Research Chemist, was responsible for the analytical development work and was assisted by D. E. Seizinger, Research Chemist, and Dr. James Vogh, Research Chemist. Others who contributed to the experimental work were L. Wilson, D. Thompson, S. Bishop, and L. Nichols, Engineering Technicians. J. M. Clingenpeel, Chemical Engineer, and R. E. Stevens, Mechanical Engineering Technician, assisted in the aldehyde and other routine chemical measurements.

OBJECTIVE

The need to assess the effects of fuel additives upon auto emissions has become increasingly pressing as the number and variety of additive materials have been expanded to meet a growing desire for increased engine life and performance. To be complete, such an assessment must include not only information pertinent to the direct contribution of the additives themselves to the appearance or composition of objectionable pollutants, but also the indirect contribution resulting from the use of these materials.

The primary objective of this study is to provide information which will serve as a basis to establish the methodology essential to standardization of additive effect testing. The experimental objective is to provide data indicating the effect, if any, of each of two fuel additives upon the character and/or composition of pollutants emitted by two test engines and three test vehicles.

The experimental methods described in this study for the production, collection, and analysis of gaseous auto exhaust samples are expected to contribute to the specification of fuel additive related test procedures.

EXPERIMENTAL APPARATUS

A. Engines and Vehicles

Gaseous emissions from three 1972 Chevrolet Impalas and two Chevrolet stationary engines were measured. The vehicles were 1972 models with 350 cubic-inch-displacement (CID) engines, two-barrel carburetors, and automatic transmissions. Mileage on the vehicles at the time of acquisition ranged from 1,500 to

3,000 miles; therefore, no break-in mileage was accumulated. The stationary engines were new, but otherwise equivalent to the vehicle engines. Stationary engine break-in was according to the Environmental Protection Agency (EPA) 28-hour schedule (table 1). For mileage accumulation, the vehicles were put into "typical" user service by assignment of the vehicles to BERC employees whose normal routes consisted of about equal amounts of city and highway driving. Vehicle inspection and refueling were conducted by technicians assigned to the project. The stationary engines were operated repetitively over the LA-4 test schedule.

B. Fuel

Due to delays in receipt of the EPA fuel, the program was begun using Indolene clear as the basic fuel. Approximately 5,200 miles were accumulated on the three vehicles using Indolene fuel. One test cycle with stationary engine B using clear fuel for 5,000 miles and F-310 for 5,000 miles was completed before the change to EPA fuel was made. Inspection data for the Indolene and EPA fuels are given in tables 2 and 3, respectively.

C. Instrumentation

Analyses of exhaust components which were included in the program and are considered to be routine are:

TABLE 1. - New engine break-in procedure (28 hours)

1. Warm up engine to 180° F coolant outlet temperature at 1,000 rpm, no load. Set spark advance and best idle according to manufacturer's specifications.

2. Run 1 hour at 1,500 rpm, no load, automatic spark advance and fuel flow. Shut down, retorque cylinder heads, and drain and change lubricating oil.

3. Run cycle 1:

RPM	Manifold vacuum, inches Hg	Time, hours
1,500	15.0	1.0
2,000	14.0	1.0
2,400	14.0	1.0
2,600	14.0	1.0
2,000	11.0	1.0
		5.0

4. Run cycle 2:

RPM	Manifold vacuum, inches Hg	Time, hours
1,500	7.0	0.2
2,000	7.0	.6
2,500	7.0	1.0
3,000	7.0	1.0
2,000	7.0	.2
		3.0

5. Repeat cycle 2.

6. Run cycle 3:

RPM	Manifold vacuum, inches Hg	Time, hours
2,000	WOT*	1.0
2,500	WOT	1.0
3,000	WOT	1.0
3,500	WOT	.5
2,800	WOT	.5
		4.0 x 4 cycles = 16 hours

* Wide open throttle.

TABLE 2. - Inspection data for Indolene Motor Fuel HO III

	ASTM method	Specification control limit	Sample No. D-18032
API gravity	D287	58.0-61.0	59.1
Distillation, %F:			
Initial boiling point	D86	75-95	94
10% Evap.	D86	120-135	133
50% Evap.	D86	200-230	224
90% Evap.	D86	300-325	323
Maximum	D86	NMT 415	412
10% Slope	D86	NMT 3.2	2.7
Reid Vapor Pressure	D323	8.7-9.2	8.7
Oxidation stability, min.	D525	NLT 600	1440+
Gum, mg/100 ml (after Heptane wash)	D381	NMT 4.0	1.6
TMEL, grm. lead/gal	D526	Nil	0.02
Sulfur weight, %	D1266	NMT 0.10	0.017
Olefin, %	D1319	NMT 10	5.6
Aromatic, %	D1319	NMT 35	32.6
Saturates, %	D1319	Remainder	61.8
Octane Research (Clear)	D2699	96.0-98.5	97.1
Octane Research (3 cc TEL/gal)	D2699	NLT 103.0	104.1
Phosphorus, gms/gal	ACM 21.00	NMT 0.01	0.0
Sensitivity (Clear)		7.0-10.5	10.3
Sensitivity (3 cc TEL/gal)		NMT 9.0	8.3

TABLE 3. - Inspection data for unleaded gasoline blend

	Results	Specification	
		Minimum	Maximum
Research Octane Number	93.2	91.5	93.5
Motor Octane Number	84.7	82	85
Ron-Mon	8.5	8	10
Reid Vapor Pressure, psia	10.2	9.8	10.2
Distillation, ASTM D-86, °F:			
10%	123	-	140
50%	199	-	250
95%	325	320	350
100%	383	-	380
API gravity at 60° F	61.6	-	-
FIA Analysis, %:			
Aromatics	24.0	24	28
Olefins	8.3	7	10
Paraffins	67.7	62	69
ASTM gum, mg/100 ml	0.57	Nonobservable	
Stability, hrs	24+	24+	-
Sulfur, ppm	127 1/	-	100
Phosphorous, ppm	1	-	30
Lead, g/gal	0.00004	-	0.01
Diene Number, meq/liter	0.0	-	1
Fuel Composition, LV % 2/:			
Benzene	0.1	-	4
Toluene	8.1	-	15
n-Butane	8.0	-	12
Isopentane	8.3	-	12
n-pentane	5.4	-	8

NOTE.-Fuel was inhibited with 5 lbs/1000 bbls of Du Pont 22 oxidation inhibitor.

1/ Fails specification, waiver obtained from customer.
2/ Benzene and toluene were determined by infrared analysis by direct calibration techniques.

1. Total hydrocarbon (HC) by flame ionization detection (FID)--Beckman 400.

2. Nitrogen dioxide (NO_2) and oxides of nitrogen (NO_x) by chemiluminescence--Thermo Electron 10A.

3. Carbon monoxide (CO) and carbon dioxide (CO_2) by non-dispersive infrared (NDIR)--Beckman 315.

4. Detailed hydrocarbon by gas-liquid chromatography (GLC) and FID--modified Perkin-Elmer 900 (1-2)

5. Total aldehydes by 3-methyl-2-benzothiazolone hydrozone (MBTH) colorimetry--Spectronic 20 (3)

The samples for total aldehyde analysis were metered directly from the constant volume sampling (CVS) system into the MBTH reagent solution. With this exception, samples for all routine analyses were collected from the CVS system in light-proof Tedlar bags.

Instrumentation prepared for additive specific exhaust components include:

1. F&M 810 chromatograph fitted with FID, alkali flame, and electron capture as optional detectors.

2. F&M 810 chromatograph fitted with FID and alkali flame parallel detectors and two-pen recorder.

3. Perkin-Elmer 900 fitted with a Coulson electrolytic conductivity detector (figure 1).

4. F&M 810 chromatograph oven system fitted with modified Beckman DU spectrophotometer (figure 2).

EXPERIMENTAL PROCEDURES

The methods for analysis of HC, NO_2, NO_x, CO, and CO_2 are well established and will not be discussed in detail.

A. Organic Manganese Analysis--Methodology

Sample collection was accomplished by drawing diluted exhaust from the CVS system with a Metal Bellows pump. The sample was pumped through a 4 in X 3/8 in O.D. stainless steel column packed with Crhomosorb 102 at ice temperature. Sample flow was measured with a rotometer placed downstream from the collection column.

The sample was recovered and analyzed according to the following procedure:

1. To prevent loss of light sensitive manganese compounds, workup should be carried out in semi-darkness.

2. Backflush the Chromosorb 102 collection column with acetone to a total volume of about 5 ml.

3. To the acetone solution, add 0.2 ml of a sec-butylbenzene solution of a known weight of cyclopentadienylmanganesetricarbonyl (CMT-internal standard).

4. Extract the acetone solution three times with 2 ml volumes of pentane.

5. Bubble dry nitrogen through the pentane solution until it is evaporated to about 0.3 ml of organic (upper) phase (water generally seperates from the organic material upon evaporation).

6. Note the exact volume of the organic layer.

7. Inject 20 μl into a chromatograph equipped with a flame photometric detector (modified Beckman DU).

8. Quantitate by peak height relative to that of the CMT internal standard.

Fuel, lube oil, and intake valve deposits were also analyzed for organic manganese content. The fuel was diluted to a specific volume with a benzene solution of CMT and injected into the chromatograph. Methylcyclopentadienylmanganesetricarbonyl (MCMT) content was calculated from relative peak heights. The lube oil was also analyzed in this manner. Weighed samples of deposits from the manifold side of the intake valves were digested in a known volume of benzene containing CMT and chromatographed.

Conditions for the chromatographic determination were:

1. Column: 11-1/2 feet X 1/8 in O.D. stainless steel tubing packed with 4 pct Apiezon L on 90/100 mesh Anachrom ABS.

2. Carrier: helium flowing at 55 c/min

3. Temperature program: 8° C/min from 100° C to 180° C

4. Emission line measured: 403.3 mμ

B. Inorganic Manganese Analysis--Methodology

A Gelman, Type A, glass fiber filter was placed in the sample line as near as possible to the CVS system. As sample was drawn by the sample pump for delivery to the Chromosorb 102

column, exhaust particulates were collected on the filter. Since MCMT has an appreciable vapor pressure, it was assumed that all organic manganese was swept through and only inorganic manganese retained by the filter. The filter was analyzed for inorganic manganese in the following manner.

1. Place the entire glass fiber filter in a Teflon beaker and digest with 3N HCl near 80° C for 15 minutes.

2. Quantitatively transfer beaker contents to a plastic filtering apparatus containing an acid washed cellulose membrane.

3. Thoroughly wash the filtering apparatus and retained solids with 3N HCl.

4. Transfer the filtrate first to a Teflon beaker for heat evaporation to a few milliliters, then to a 25 ml volumetric flask.

5. Dilute to volume with 1.5N HCl and analyze by atomic absorption (flame) spectroscopy.

6. Use 1.5N HCl as an instrument blank and correct data according to the value obtained from parallel analysis of an unused glass fiber filter.

Deposits from the manifold side of the intake valves and combustion chamber deposits were semi-quantitatively analyzed for total manganese content by neutron activation analysis.

C. Analyses for Nitrogen Compounds --Methodology

Sample collection for nitrogen compound analysis is exceptionally difficult due to their wide variety of chemical and physical properties. Several collection methods were attempted but proved to be inadequate. As a result, vapor samples were taken directly from the CVS system (or bag) and injected into the PE-900 chromatograph via a 25cc gas sample loop.

Differences in the properties of the nitrogen compounds made it necessary to analyze with three separate chromatographic columns. Chromatographic conditions for the analysis of ammonia, light aliphatic amines, and pyridine were:

1. Column: 10 feet X 1/8 in O.D. stainless steel tubing packed with 15 pct Carbowax 600 plus 10 pct KOH on 80/100 mesh Gas-Chrom R

2. Carrier: Helium flowing at 48 cc/min

3. Temperature program: Hold at 25° C for 2 minutes, then program at 5° C/min to 120° C

Substances such as acetonitrile, pyrrolidine, and cyclohexylamine can also be analyzed on this column.

Chromatographic conditions for the analysis of all of the preceding nitrogen compounds (but with less resolution), N-nitrosamines, nitroso aromatics, nitro aromatics, aromatic nitriles, and aromatic amines were:

1. Column: 3 feet X 1/8 in O.D. stainless steel tubing packed with 15 pct Carbowax 1540 plus 10 pct KOH on 80/100 mesh GC-22

2. Carrier: helium flowing at 52 cc/min

3. Temperature program: Hold at 35° C for 2 minutes, then program at 6.5° C/min to 180° C

Molecular size for this column is limited to about C_8.

Chromatographic conditions for the analysis of cyanogen, hydrogen cyanide, nitromethane, and acetonitrile were:

1. Column: 2-1/2 feet X 1/8 in O.D. stainless steel tubing packed with Carbopack B treated with 3-4 drops of H_3PO_4

2. Carrier: helium flowing at 42-1/2 cc/min

3. Temperature program: -70° C for 6 minutes then 13° C/min to 180° C

Detection capability for the nitrogen analyses was provided by a Coulson electrolytic conductivity cell. Nickel wire was used as the reduction catalyst, the furnace temperature was 700° C, and the hydrogen flow through the quartz catalyst tube was 17 cc/min. To prevent moisture condensation, the conductivity cell was warmed by heating tape from the furnace exit to the gas-water mixing chamber.

D. Emission Measurement--Methodology

Emissions from three vehicles and two stationary engines were measured. Prior to testing, each vehicle was driven for 10 minutes at 50 mph to purge the charcoal canister (evaporative loss trap), then immediately placed in a soak area at about 75° F and allowed to stand overnight. Stationary engine test preparation consisted of a shutdown period lasting at least five hours. Exhaust was tested as the vehicles and engines were being operated according to the LA-4 test schedule on chassis and stationary engine dynamometers. A single CVS bag sample was collected at a constant rate for the duration of the test. The Roots blower in the CVS pumped a nominal 330 cfm. This sample was analyzed for total HC, NO_2, NO_x, CO, CO_2, and individual hydrocarbon compounds. CO, HC, and NO_x were calculated in accordance with the Federal Register, Vol. 36, No. 128, Friday, July 2, 1971, section 1201.87.

A test cycle for the engine or vehicle, includes a period of mileage accumulation with additive-free fuel (4,000-5,000 miles) to establish baseline emissions and a period of mileage accumulation with the fuel plus additive to establish the effect, if any, of the additive upon emission levels or trends. Four test cycles were completed with the two stationary engines; each engine being tested with AK33X additive at 0.125gMn per gallon fuel and F-310 additive at 14.2 ml additive plus carrier per gallon fuel. Mileage accumulation with additive-containing fuel was 4,000-5,000 miles.

One test cycle was completed with each of three vehicles. After baseline emissions were established (approximately 5,000 miles) one vehicle was switched to fuel containing AK33X, F310 was added to the fuel for the second vehicle, and the third vehicle remained on additive-free fuel. Slightly more than 9,000 miles were accumulated with additive-containing fuel.

As each test cycle was completed, each engine (both stationary and vehicle) was disassembled and photographed. Samples of engine deposits were taken and, when AK33X had been the additive used, the deposits were analyzed for organic manganese. The oil from the engines and vehicle using AK33X was also analyzed for organic manganese.

RESULTS AND DISCUSSION

A. Manganese Determination-Methodology Background

The primary objective of the study is to provide methodology which can be applied to the determination of the effect of gasoline additives upon emissions and the fate of the additive itself. While the method for organic manganese analysis was developed specifically for this program, the method (or modifications of the method) should be applicable to the analysis of other organo-metallic compounds. As for inorganic manganese analyses, atomic absorption methods are well established for this and other metallic ions.

Chromosorb 102 was very effective as a sample collection medium. Retention capability was high and recovery from the column was simple and efficient. A collection efficiency check was made by applying 0.943 μg of CMT to the upstream end of the 4 in X 3/8 in O.D. Chromosorb 102 column. After exposure to 275 liters of CVS exhaust flowing at 12 liters/min, nearly 99 pct (0.932 μg) of the sample was recovered by direct analysis of the acetone wash. A large variety of porous polymers is commercially available. Stability and diverse physical and chemical properties (pore size, surface area, acid-base properties, polarity, etc) make them likely candidates for application to collection of other volatile organo-metallics.

In the early stages of method development, n-tridecane was added to the recovered sample to minimize loss of the MCMT during evaporation. No problems occured with small chromatographic injections, but when the sample size was increased to 20 μl, the n-C_{13} caused MCMT peak spreading. Chromatographic response, in terms of peak height, was then dependent upon sample size as well as concentration. This problem was circumvented by replacing n-C_{13} with sec-butylbenzene. MCMT evaporative loss with sec-butylbenzene was about 5 pct, but addition of the internal standard (CMT) before the extraction process negates work-up losses. One possible improvement to the method might be to remove most of the moisture from the porous polymer column with a dry nitrogen purge prior to recovery, wash the column with acetone (or pentane), add the internal standard, evaporate to a small volume, and inject a portion into the chromatograph.

The detection system (figure 2) for organic manganese analysis consisted of a Beckman DU Spectrophotometer equipped with standard photomultiplier and flame attachments and the Spectral Energy Recording Adapter (SERA) to allow transfer of the photomultiplier signal to a strip chart recorder. The only modification to the system was interchange of the burner oxygen and fuel supply lines. Oxygen and fuel supplied to the burner in this manner produce an exceptionally small flame which, in turn, allows more precise optical focus by limiting the volume in which the sample is oxidized. Chromatographic effluent was ' i to the flame through a heated line connected to the sample capillary of the burner.

Nickel, iron, and chromium trifluoroacetylacetonates have been chromatographed and detected in this laboratory with the manganese instrumentation. The less stable corresponding manganese chelate decomposed within the chromatographic system. One consideration to be given with respect to chromatographic flame emission analysis is that, although the method may (in many instances) be made specific for the desired element, the triple resonance line of manganese is relatively intense. When coupled with the chromatograph as little as 10^{-11} moles of manganese can be detected with each injection. The sensitivity for other elements may limit the usefulness of the method. Trace quantities of some elements, such as phosphorous and lead, are not suited to detection by flame emission.

B. Manganese Determination--Test Results

Figure 3 shows the results of a typical analysis. It is apparent from this chromatogram that; (1) only extremely high concentrations of hydrocarbons are capable of producing interference (and then only if they are eluted from the column with the internal standard or desired compound), (2) peak quality is good, and (3) complete separation of the desired components is achieved. The peaks in the figure represent 1.07×10^{-10} moles CMT (known quantity) and 3.79×10^{-11} moles MCMT (calculated value). The sample was prepared according to the procedure given previously and calculation back to the CVS exhaust concentration gives a value of 5.10×10^{-2} ppb. Thus, the gaseous sample stream concentration that is detectable by the method is less than 2×10^{-2} ppb.

The procedure for manganese determination was developed early in the prgoram; therefore, the data for AK33X additive related materials are complete. Figures 4A, 5A, and 6A show the manganese present in the exhaust when AK33X is a fuel component. The organic manganese (MCMT) maximum exhaust levels varied considerably for the two stationary engines and the vehicle ranging from 1 μg/mile to 5 μg/mile. Expressed in other terms, these values represent CVS exhaust concentrations of 1.40×10^{-2} ppb and 7.45×10^{-2} ppb,respectively. Up to 0.042 percent of the

MCMT consumed was emitted unaltered and no organic fragments of the molecule were detectable in the exhaust. Under similar conditions, Ethyl Corporation has previously reported (4) considerably higher values. Engine characteristics, proportional sampling, trapping methods, or the inability of the Ethyl Corporation method to detect the organic molecule itself may have been factors in the differences in the reported values; but the most likely contributor was the exceptionally high concentration of manganese (1.25 gMn/gal) in the fuel used for the Ethyl Corporation tests.

It is interesting to note, though not unlikely, that comparison of figures 4 with 4A, 5 with 5A, and 6 with 6A show that changes in hydrocarbon emission levels are generally accompanied by corresponding changes in MCMT emission levels. Both hydrocarbon and MCMT emissions were increasing at 4,000-5,000 miles with additive. The stationary engine cycles were terminated at about this point. Continued mileage accumulation with the vehicle shows hydrocarbons and MCMT decreasing somewhat to an apparent stabilization. The hydrocarbon emission trend using AK33X additive is more easily recognizable by direct comparison of the total hydrocarbon emissions to those using clear fuel or F310 additive (figure 11). The values for figure 11 were taken from the detailed hydrocarbon analysis tables contained in Appendix A.

Inorganic manganese emissions from the stationary engines, figures 5A and 6A, tend to increase along with the MCMT emissions. Figure 4A, however, fails to indicate a trend for inorganic manganese emissions from the vehicle. One possible explanation for this is the relatively mild duty cycle of the stationary engines (repetitive Federal test cycles) in comparison to the vehicle (user service). This assumption was given credence by visual comparison of combustion chamber deposits (to be discussed later in this report).

Manganese mass balance was low with an exhaust emission range of 4-30 percent of ingested material. Since the combustion efficiency of MCMT was 99.4 pct or better, this is due largely to engine and exhaust system retention of inorganic manganese. Intake manifold deposits ranged from 4.2 pct to 5.7 pct manganese (only 0.03 pct or less of this was MCMT). From 7.3 pct to 13.1 pct of the combustion chamber deposits was manganese. Non-homogeneity of particulates within the CVS stream and losses within the CVS system could contribute to erroneous values for the inorganic manganese actually emitted, but program emphasis was not placed upon particulate sampling.

Engine lube oil used in conjunction with AK33X additive testing was analyzed for MCMT content and found to range from 0.95 μg/ml to 2.68 μg/ml depending upon mileage accumulation and lube oil

added during the test cycle. Lack of test procedure information prevents quantitation of MCMT bypass, but estimates made from the levels found in the oil indicate approximately 2 μg/mile. This is comparable to the MCMT levels released to the atmosphere through the exhaust system. Insofar as a potential health hazard is concerned, organic manganese in the lube oil should be given special consideration for two reasons: (1) it is retained by solution in a definite volume of liquid as opposed to eventual dilution by diffusion in the atmosphere and (2) lube oil is an efficient U.V. light filter which prevents photochemical decomposition (there was no detectable difference between fresh samples and those exposed to fluorescent lighting for up to five months).

Periodic checks of the fuel confirmed that the manganese concentration was within 15 pct of the desired level.

C. Nitrogen Compound Determination--Methodology Background

Isolation of the proposed nitrogen bearing compounds from exhaust would be an awesome project within itself. Nonspecific detection systems produce complex exhaust chromatograms in which not all components appear individually, especially those present at low concentrations. The development of the chromatographic techniques for analysis of these compounds was undertaken with this in mind.

Four types of detection systems with some degree of specificity were available; electron capture, alkali flame ionization,

microcoulometry, and electrolytic conductivity. Electron capture was considered primarily for confirmation of the presence of aromatic nitro compounds and N-nitrosoamines, the latter to be accomplished by conversion to nitramines with hydrogen peroxide and trifluoroacetic anhydride or trifluoroacetic acid. With careful attention to parameter adjustments, alkali flame ionization can be made to differentiate between most organic nitrogen compounds and hydrocarbons with essentially complete specificity. The response of nitrogen compounds to alkali flame, however, is not solely dependent upon the number of nitrogen atoms, but also the molecular structure. Nitro compound and hydrogen cyanide responses were comparatively small and ammonia failed to respond detectably. The failure of ammonia to respond led to experiments in which ammonia was mixed with the carrier gas to reduce amine tailing. A column packed with Ucon LB550X-KOH on Chromosorb W was being considered at that time for amine separation and the effectiveness of ammonia in the carrier was demonstrated, but detector specificity for nitrogen compounds as compared to hydrocarbons was decreased from complete to about 10:1. Another characteristic of the alkali flame detector which was considered in judging its applicability was its extreme sensitivity to temperature and gas flow fluctuations.

The remaining two detectors are comparable in terms of nitrogen sensitivity and selectivity. The selectivity is good for both, and both respond to any nitrogen compound which is reduced to ammonia when exposed to nickel catalyst in a hydrogen atmosphere at elevated temperatures. The Coulson electrolytic

conductivity detector was chosen over the Dohrmann microcoulometer because of its relative simplicity of operation and maintenance. The electrolytic conductivity cell requires no periodic cleaning, electrode maintenance, or electrolyte preparation; up to the point of bubble formation within the electrode capillary, hydrogen and carrier flows can be varied over a considerable range without significant damage to peak quality or detector response; light coke deposits can easily be removed from the nickel wire catalyst by in situ treatment with oxygen; and the detector functions satisfactorily with background signals up to about 4 mV. The cell water and/or water conditioning resins must be changed periodically when the background signal becomes excessive, but under normal conditions, this occurs only after several weeks of continuous operation.

The variety of nitrogen compounds of interest was considered when selecting materials for chromatographic columns. Liquid phases containing nitrogen compounds were rejected a priori to minimize the probability of excessive background signal and reduced peak signal due to column bleed. The acid-base properties of the compounds to be separated were considered as the principal factor in determining chromatographic behavior. Several column materials and variations were tested before those which performed acceptably for the entire spectrum of compounds to be analyzed. Chromosorb 103 and several variations of Carbowax-KOH combinations were tested for amine analysis. Porapak Q, S, and QS, Carbosieve B, and Carbopack A were tested for hydrogen cyanide analysis. The

neutral compounds were found to give good quality chromatograms when separated by the columns prepared for analysis of the basic or acidic components.

The nitrogen compound classes proposed for study were amines, pyridines, N-nitrosoamines, and nitro compounds. Individual compounds included were hydrogen cyanide and cyanogen. On first analysis, it appears that the basic compounds (amines and pyridines) can be isolated from the remaining compounds via salt formation with hydrochloric acid and extraction of the neutral and acidic compounds. Further examination, however, reveals that the neutral and acidic compounds become sensitized, to various degrees, to hydrolysis upon addition of mineral acid. Furthermore, hydrolysis of compounds containing the -C:N group produces ammonium ion and N-nitrosoamines produce secondary amines; thus interfering with the analysis of the basic compounds. At best, this method of collection and/or isolation is applicable to the basic compounds, and only then if consideration is given to the fact that some of the analyzed components may be hydrolysis products of non-basic nitrogenous compounds.

Not only the wide range of physical properties (vapor pressure, solubility, acid base character, etc.) but also the complex chemistry of these nitrogen compounds is responsible for the difficulty in their collection, recovery, and analysis. Common exhaust products with which these compounds may react under favorable conditions include water, nitrogen oxides (plus water), aldehydes, ketones, phenols, and unsaturates. In addition,

reactions may take place among the nitrogen bearing species. Hydrogen cyanide may polymerize, nitroso compounds may dimerize or react with aromatic amines, and ammonia or amines add to nitriles under favorable conditions. The presence of some nitrogen compounds enhances the reactivity of other nitrogen compounds. For instance, ammonia enters into the addition of hydrogen cyanide to aldehydes or ketones, and alkylamines or pyridines act as condensing agents for nitroparaffins and aldehydes or ketones.

In light of the foregoing discussion, it is evident that (1) reactions may proceed during sample collection and processing and (2) maintenance of sample integrity during this period is likely to be difficult.

Initial efforts concerning sample collection were based on the idea of class separation during sampling. A sample collection train was constructed consisting of a wet cation exchange column, a wet anion exchange column, and a cold trap at dry ice temperature. A methanol scrubber at ice temperature was subsequently installed upstream from the cold trap to prevent plugging by water freeze-out. The ion exchange resins were wetted by water condensed from the sample stream. Hopefully, amines and pyridines would be retained by the cation exchange column, hydrogen cyanide (and possibly nitroparaffins) retained by the anion exchange column, and neutral compounds trapped by the cold solvent. The system was tested by spiking an exhaust stream with the various compounds.

When practical, known quantities were injected; but the purities of hydrogen cyanide, cyanogen, and N-nitrosoamines were not known and only manufacturer estimates were available for the aqueous solutions of light aliphatic amines. Recovery calculations were based on the detector response to pyridine (known purity) and the number of nitrogen atoms per molecule as well as detector response to equivalent amounts of the individual compounds injected directly into the chromatograph. The system was partially successful. Amine and pyridine recoveries from the cation exchange column were in the 50 to 75 percent range with comparable nitrile and N-nitrosoamine recoveries from the cold solvent scrubber. Minimum detection levels were estimated for those compounds recoverable from this system. These levels for undiluted exhaust were:

1. Pyridine - 0.02 ppm
2. Aromatic amines - 0.02 ppm
3. C_1-C_4 aliphatic amines - 0.10 ppm
4. Nitriles - 0.30 ppm
5. C_2-C_4 N-nitrosoamines - 0.15 ppm.

These figures are only estimates since the efficiency of the system and test repeatability were not considered to be adequate. Hydrogen cyanide, cyanogen, and nitroparaffins were, for practical purposes, lost; however, the chromatographic technique for these compounds had not yet been fully developed.

Methanol alone cannot be used as a solvent for scrubbing the sample stream. Chromatograms of a methanol solution of the various nitrogen compounds gave peaks which did not correspond to any of the individual compounds. Some of these unidentified

peaks diminished or grew upon standing, giving evidence of slow, continuing reactions within the solution. Water solutions of formic and acetic acid were also checked for potential as scrubber solutions, but experimentation indicated that the basic nitrogen compounds could not be concentrated by evaporation and recovered in the original form.

All of the previously discussed sample collection techniques failed to establish the presence of nitrogen bearing compounds (other than NO_x) in auto exhaust even with F310 additive present in the fuel. This is not surprising since testing with synthetic samples gave evidence that one of the techniques were sufficiently quantitative or repeatable.

At this point, a different approach was taken in an effort to demonstrate the presence or absence of the nitrogen compounds in exhaust at some detectable limit that could be established with a reasonable degree of confidence. Direct chromatographic injection of the exhaust (discussed in the Experimental Procedures section of this report) provides a means to obtain an exhaust component profile that is least likely to be altered from the true composition. No intermediate sampling or recovery steps are involved with this technique, and the chromatographic response can be related directly back to the exhaust concentration. Even with this simple introduction system, some precautions are essential. Separate, preconditioned syringes and sample loops are necessary for acidic or basic component analysis. For instance, total loss of small amounts of ammonia results from subsequent

injection into the sample loop used for hydrogen cyanide analysis. The Coulson electrolytic conductivity detector was calibrated with known quantities of pyridine and the response found to be very nearly $5X10^{-10}$ moles nitrogen atom per millivolt. Operating at 4 mV full scale the noise level is slightly less than one division (0.04 mV). Considering the detection limit to be twice the noise level, $4X10^{-11}$ moles nitrogen atom becomes the limit. With a 25cc sample loop, this converts to 0.04 ppm nitrogen atom in the diluted (CVS) exhaust. This is up to twenty times less sensitive than the estimated detection limits for the sampling train collection technique, but the reliability of direct, gaseous sampling tends to compensate for this loss. Results of CVS exhaust analyses by direct injection were:

1. HCN - 1.0-1.5 ppm found and confirmed.
2. CH_3NO_2 - 0.2-0.3 ppm found and confirmed.
3. NCCN - trace possible but presence not confirmed.
4. CH_3CN - trace possible but low levels are rapidly destroyed by exhaust.
5. NH_3 - possible exhaust component but interference peak prevented definite identification.

Nitrogen compounds either not present or present at levels below 0.04 ppm include:

1. Aliphatic and aromatic amines.
2. Pyridine.
3. C_3 and larger aliphatic and aromatic nitriles.
4. C_2 and larger aliphatic and aromatic nitro compounds.
5. C_{2-C_4} N-nitrosoamines.

Hydrogen cyanide and nitromethane consistently appear in exhaust chromatograms regardless of the presence of F310 additive in the fuel. Though stable in exhaust, the appearance of cyanogen was intermittent and could be due to sample syringe hold-over from previous analysis of synthetics. This is also true of acetonitrile, but experimental evidence shows this compound to be unstable in exhaust as well. Vapor samples give a chromatographic peak near the retention time of ammonia even in the absence of the compound, thus small quantities could be present and remain hidden. No chromatographic peaks appeared corresp ding to any of the remaining nitrogen compounds, so, if present, their exhaust concentrations were below the detection limit.

Chromatography of the basic nitrogen compounds is illustrated in figures 12 and 13. Amines and pyridine were separated to show peak quality. Approximate locations are indicated for other amines and compounds representative of the neutral classes which are eluted from these columns. Vapor samples injected downstream from the column have shown that the major portion of the tailing effect takes place within the detector rather than the column. Figures 14 and 15 are chromatograms of synthetic and exhaust components, respectively, which are eluted from the carbopack B-H_3PO_4 column. For figure 15A, 25cc of gaseous sample was drawn from the sample line and immediately injected into the chromatograph. Samples for figures 15B, 15C, and 15D were taken from a single CVS cold-start bag after aging 1 hour, 1.5 hours, and 2 hours in the absence of light. Comparison of the exhaust

chromatograms can leave little doubt that there is continuous sample deterioration. With age, hydrogen cyanide decreases and nitromethane decreases and/or is swamped by a growing peak. Peak A diminishes with time and peaks B, C, D, E, and F appear and grow at various times and rates. Little effort was directed toward identification of the lettered peaks, but oxides of nitrogen are eluted in areas A-B and E-F giving responses similar to those of the aged exhaust sample.

Nitrogen Compound Determination--Test Results

The methodology for nitrogen compound analysis was not adequately developed in time to obtain meaningful data pertinent to the effect of F310 additive on nitrogenous emissions.

ENGINE DEPOSITS

Induction System

Carburetor

Carburetor throats and bases were examined for deposit buildup. The deposits were found to be almost equally independent of fuel additive or duty cycle. Deposits on the carburetor bases are,as well as the following items,shown pictorally in appendix B

Intake Manifold Passages

The deposits were generally equal in amount from both additives in the stationary engines. The F310 additive resulted in softer tar-like deposits in the intake passages of the stationary engines compared to more crusty deposits resulting from all other engine and vehicle conditions. The clear fueled vehicle contained more deposits in the intake passages than did the other vehicles or engines. The F310 additive vehicle produced unusually clean intake passages as compared to those of the other two vehicles or the stationary engines even after F310 use. This suggests that the cleaning ability of the additive is dependent upon duty cycle. It is reasonable

Engine Head

Deposits on the engine heads were similar in amounts and composition to deposits on the piston heads just described; the major exception being extremely white deposits on the exhaust valve face of the stationary engines which used F310. This effect was present but much less pronounced with the vehicles than with the engines suggesting a duty effect.

Spark Plugs

Spark plug deposits from the AK33X fuel again showed the characteristic reddish color and, in addition, on one stationary engine the deposits were so great that the spark gap was being bridged. The deposits were still very soft and fine. The vehicle using AK33X did not have nearly so great a quantity of plug deposits as the engine, also the second engine test with the AK33X additive resulted in less plug deposits than the first test. Undoubtedly the duty cycle has a great effect on plug deposits using the AK33X additive. The plug deposits from tests other than those using AK33X were similar in color and composition.

Exhaust Valve Stems

Deposits on all the exhaust valve stems were similar in amounts and composition. The reddish color continued on the exhaust valves using the AK33X, while the valves of the engine using F310 exhibited a pronounced white color. The white color, however, was not present on the valve stems of the vehicle using F310.

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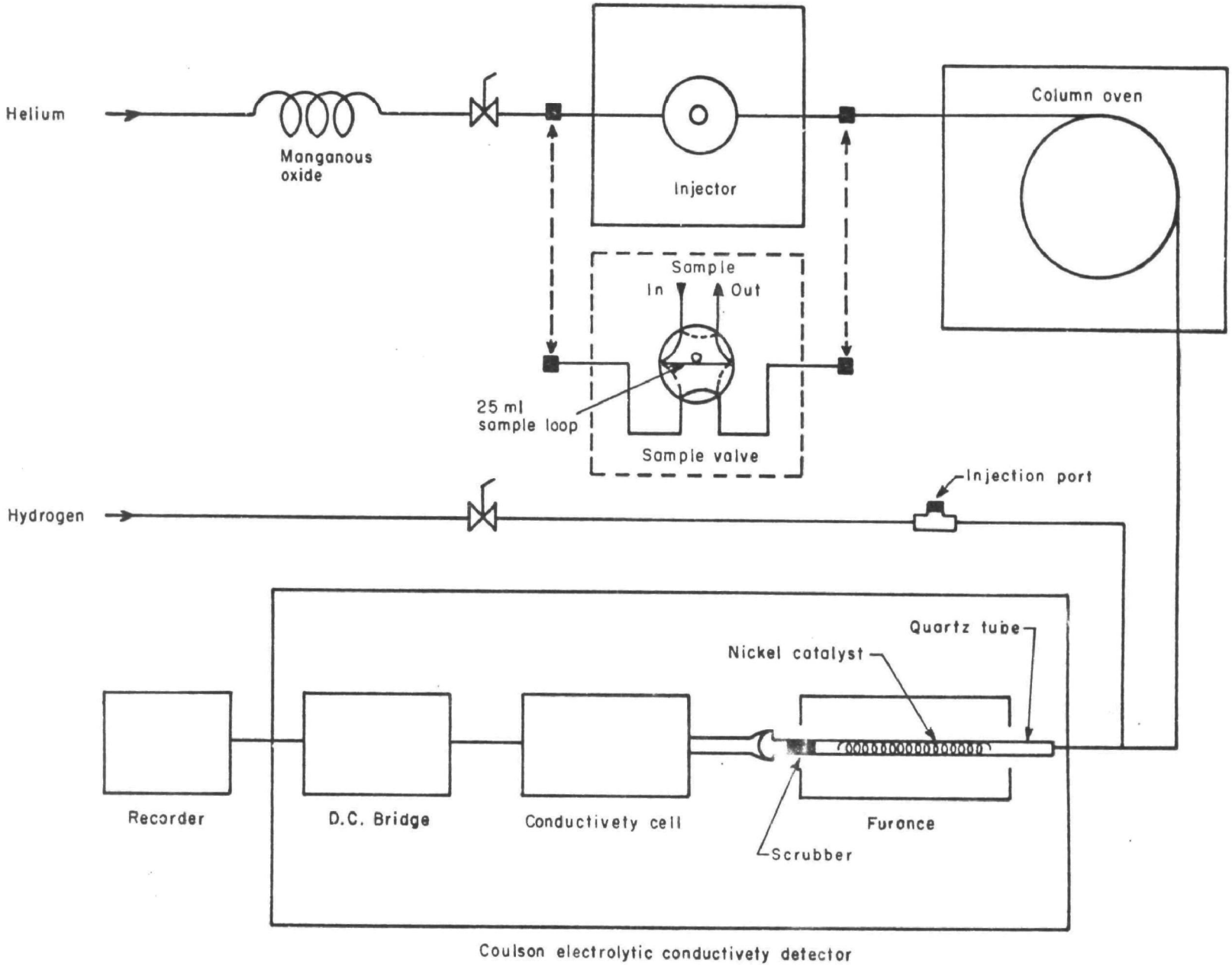


FIGURE 1.-Chromatographic system for analysis of nitrogen compounds.

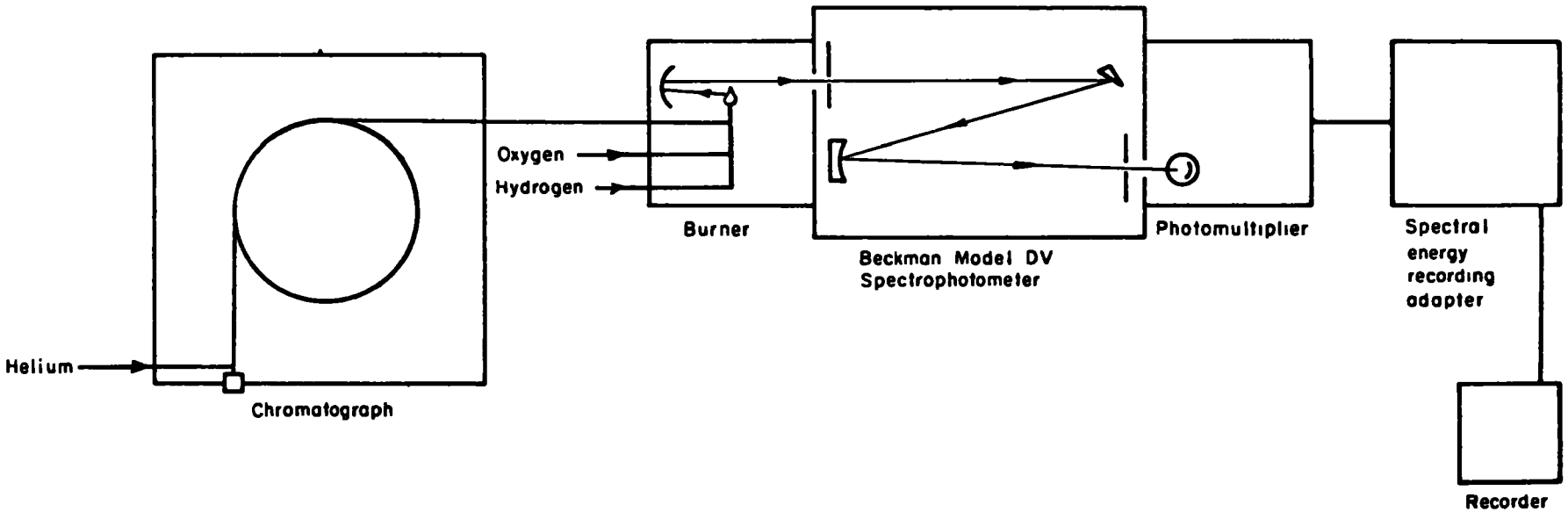


FIGURE 2.-The detection system for organic manganese analysis.

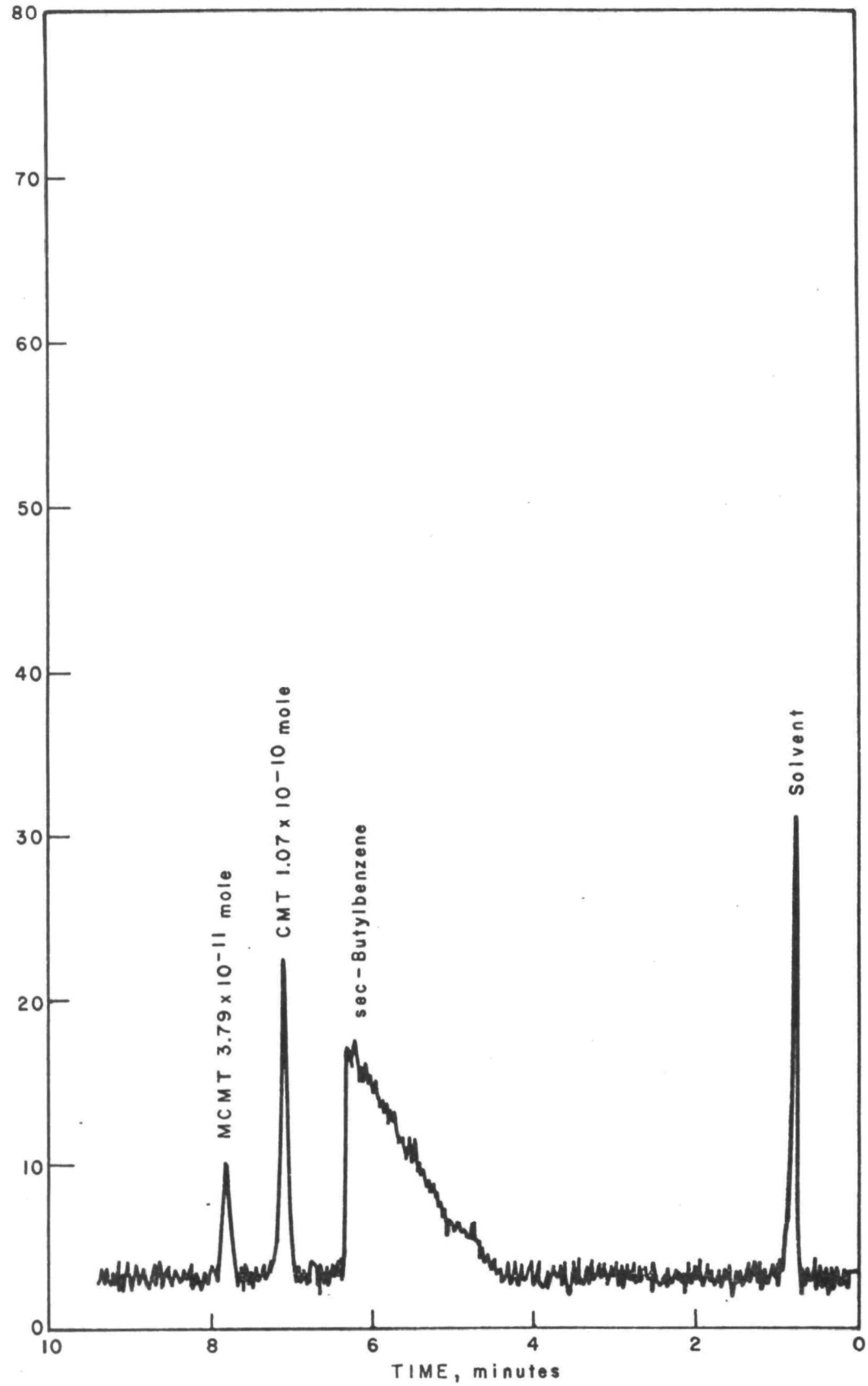


FIGURE 3.- Exhaust analysis for MCMT

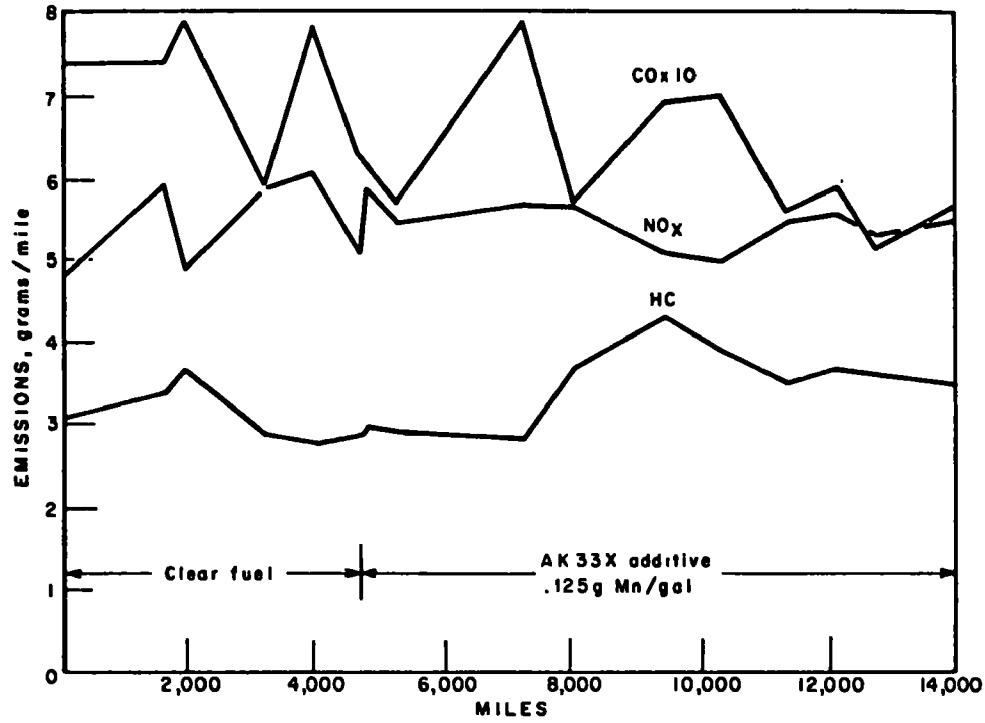


FIGURE 4.-Effect of mileage accumulation on exhaust emissions AK 33X vehicle.

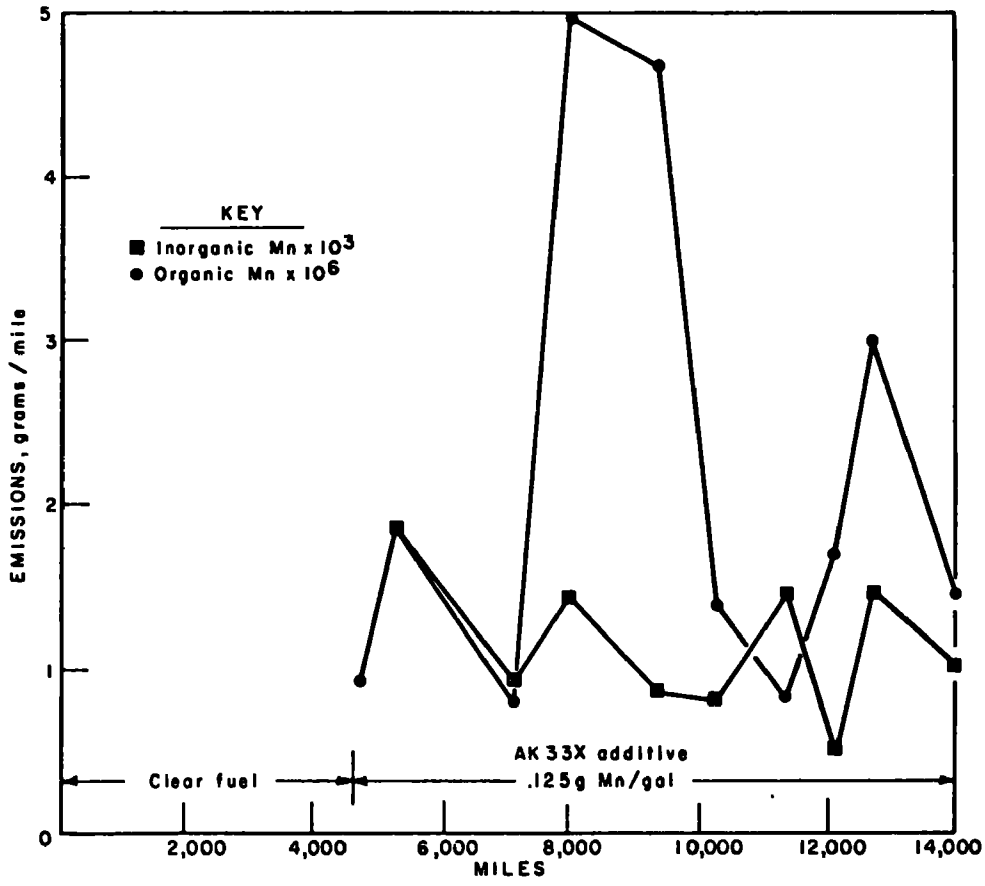


FIGURE 4A -Effect of mileage accumulation on manganese emissions AK 33X vehicle.

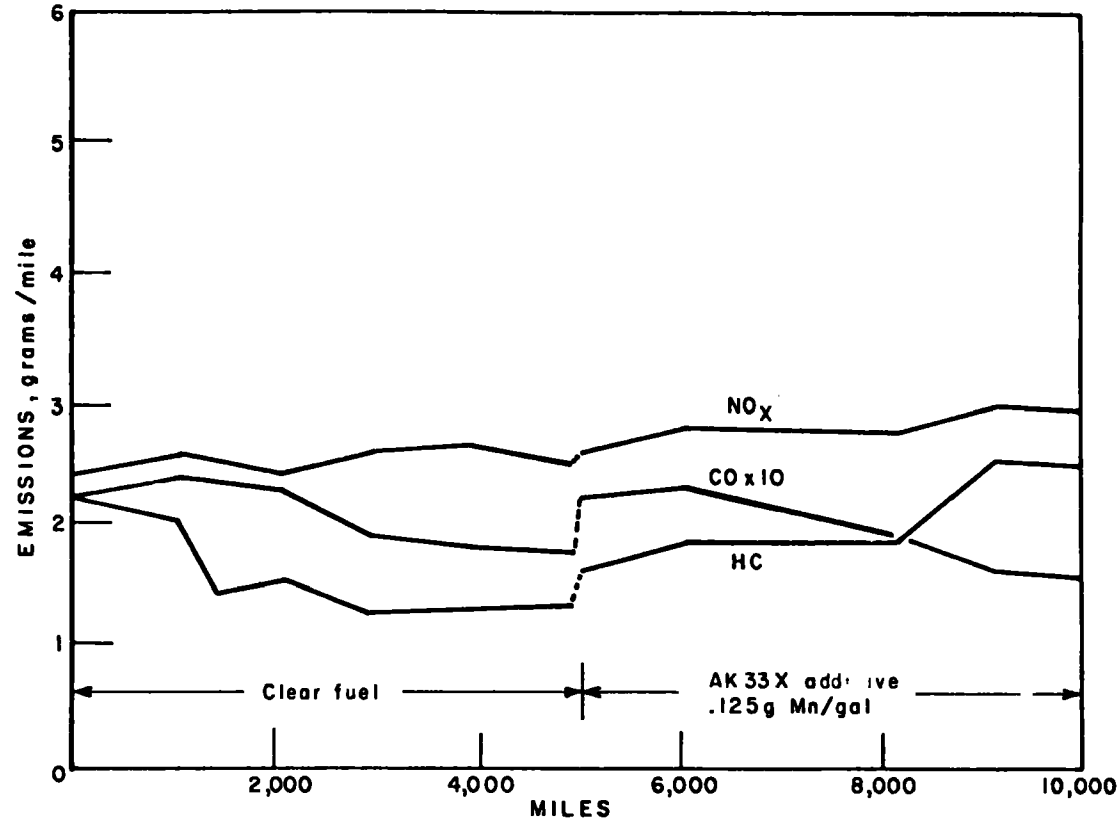


FIGURE 5.-Effect of mileage accumulation on exhaust emissions stationary engine A with AK33X .

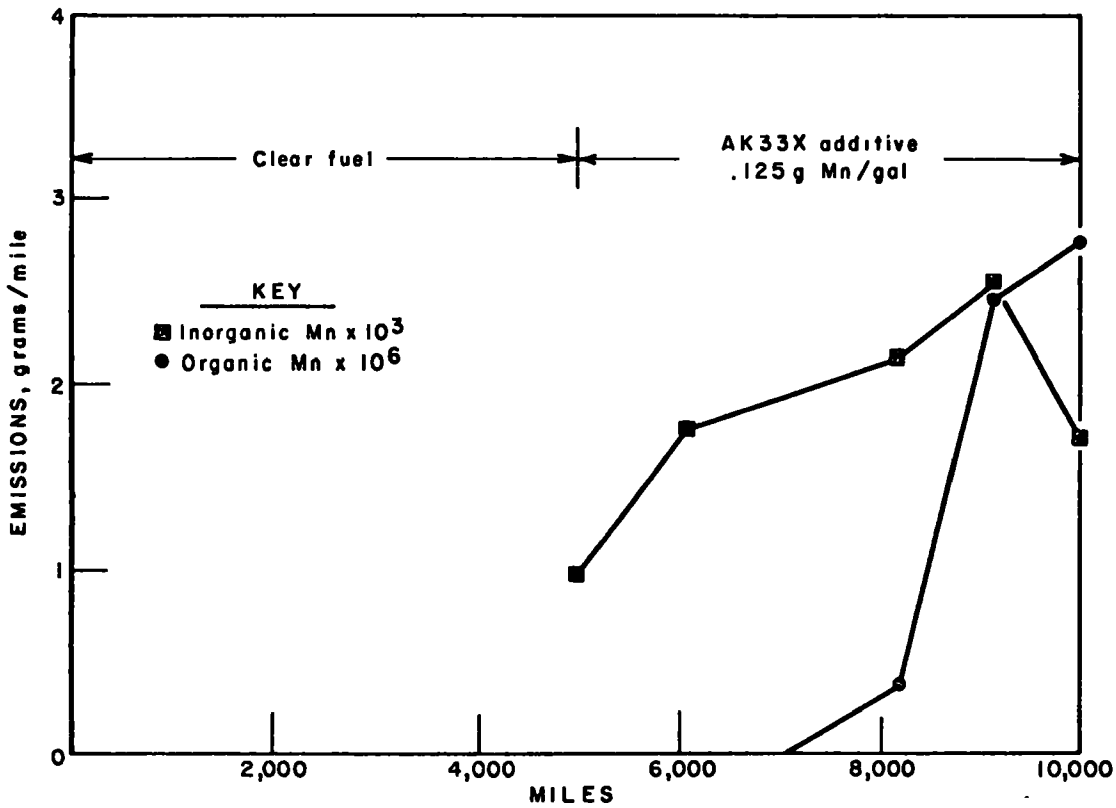


FIGURE 5A.-Effect of mileage accumulation on manganese emissions stationary engine A with AK33X .

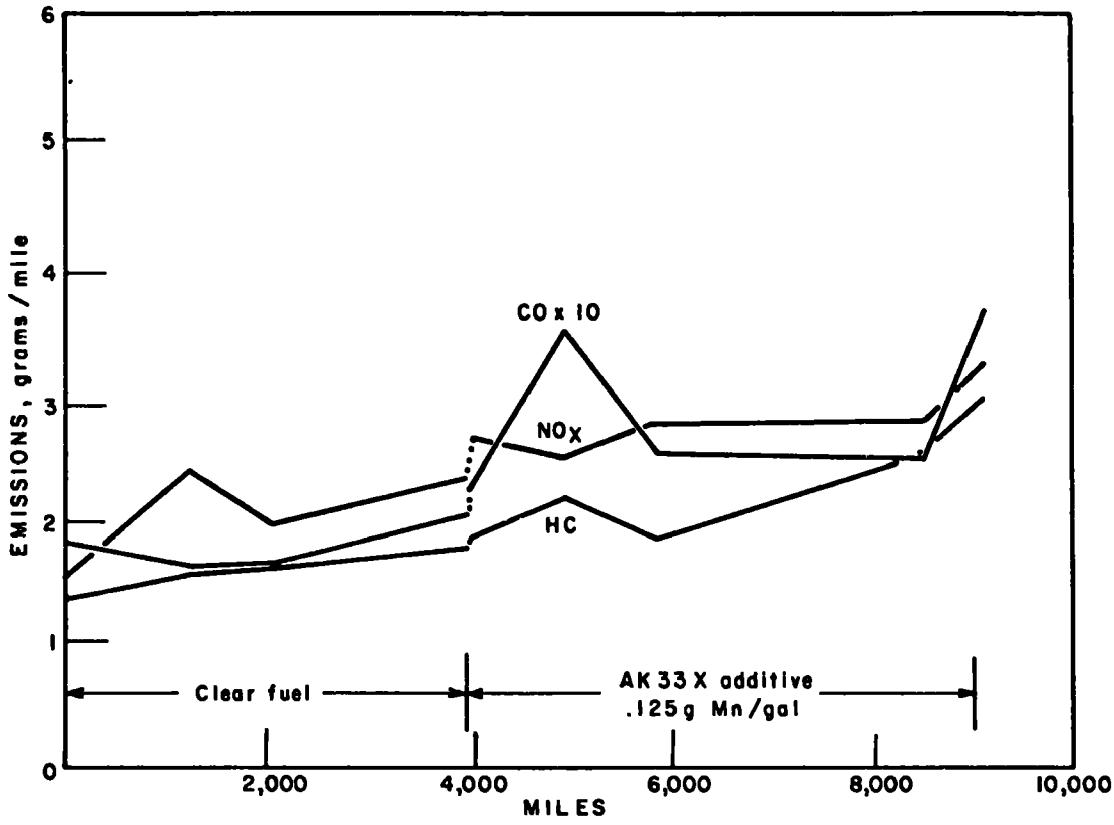


FIGURE 6.- Effect of mileage accumulation on exhaust emissions stationary engine B with AK33X .

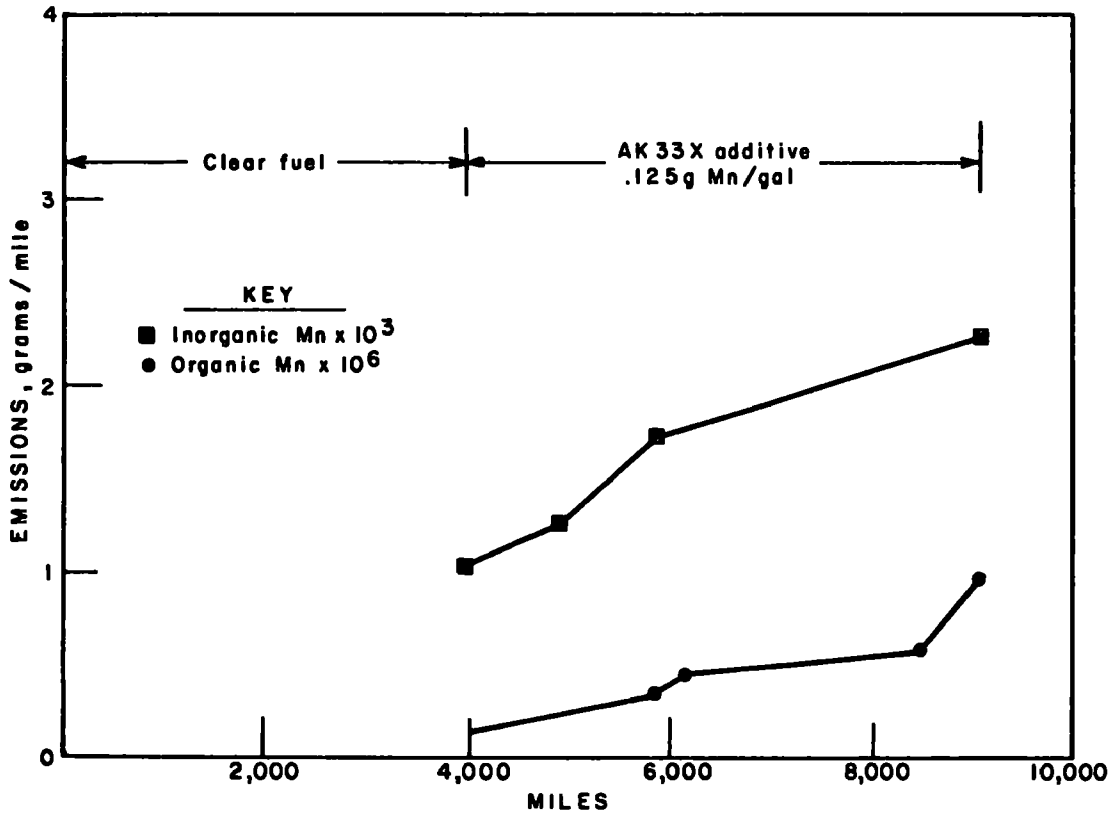


FIGURE 6A.-Effect of mileage accumulation on manganese emissions stationary engine B with AK33X.

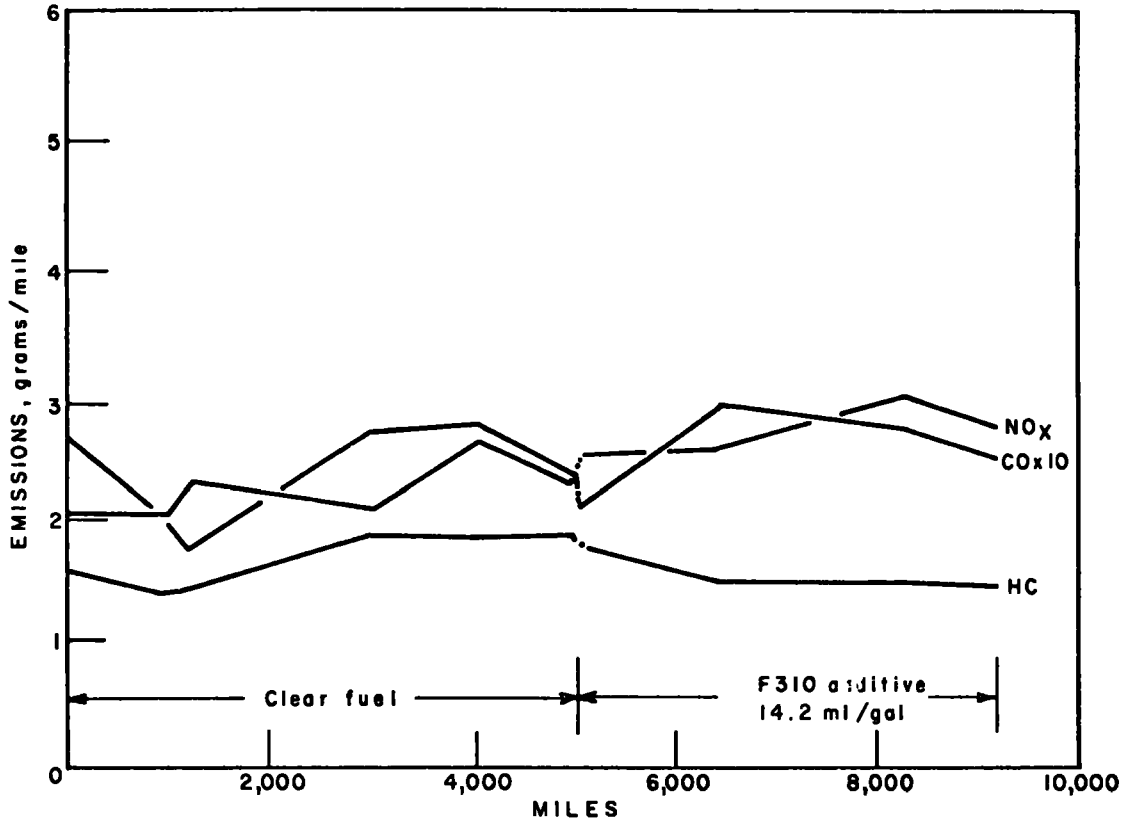


FIGURE 7.- Effect of mileage accumulation on exhaust emissions stationary engine A with F310.

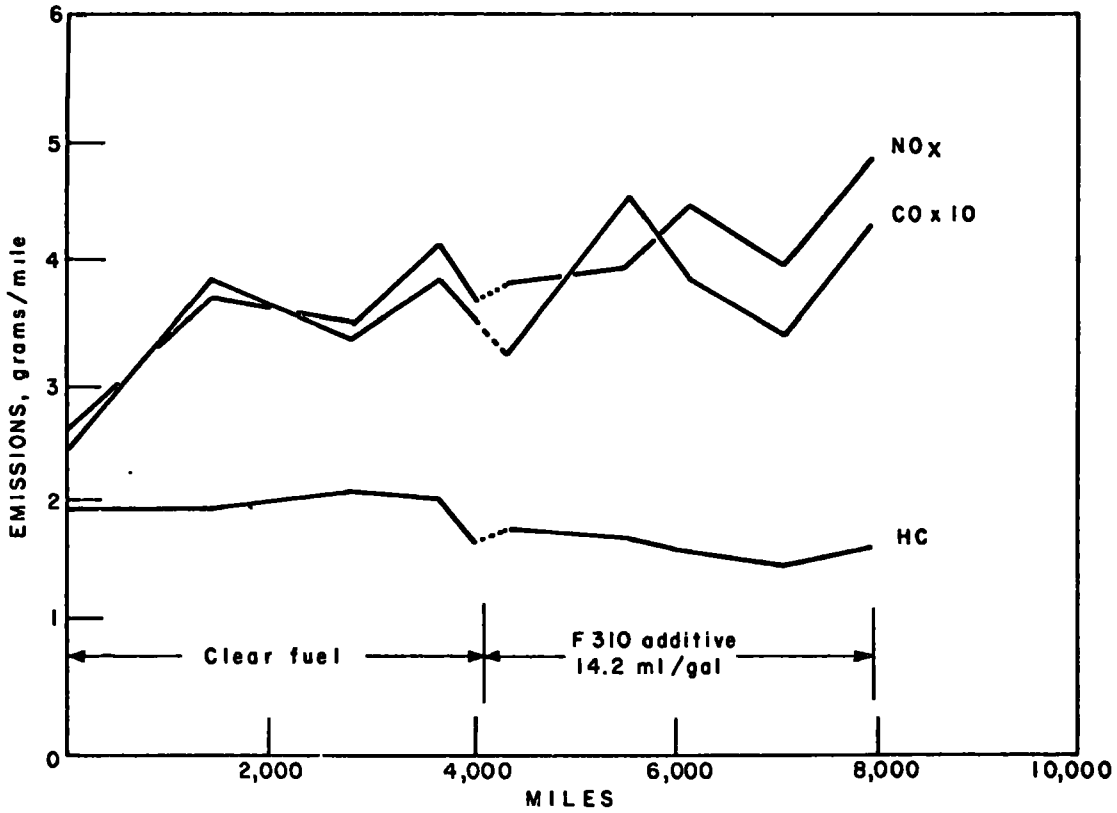


FIGURE 8.-Effect of mileage accumulation on exhaust emissions stationary engine B with F 310.

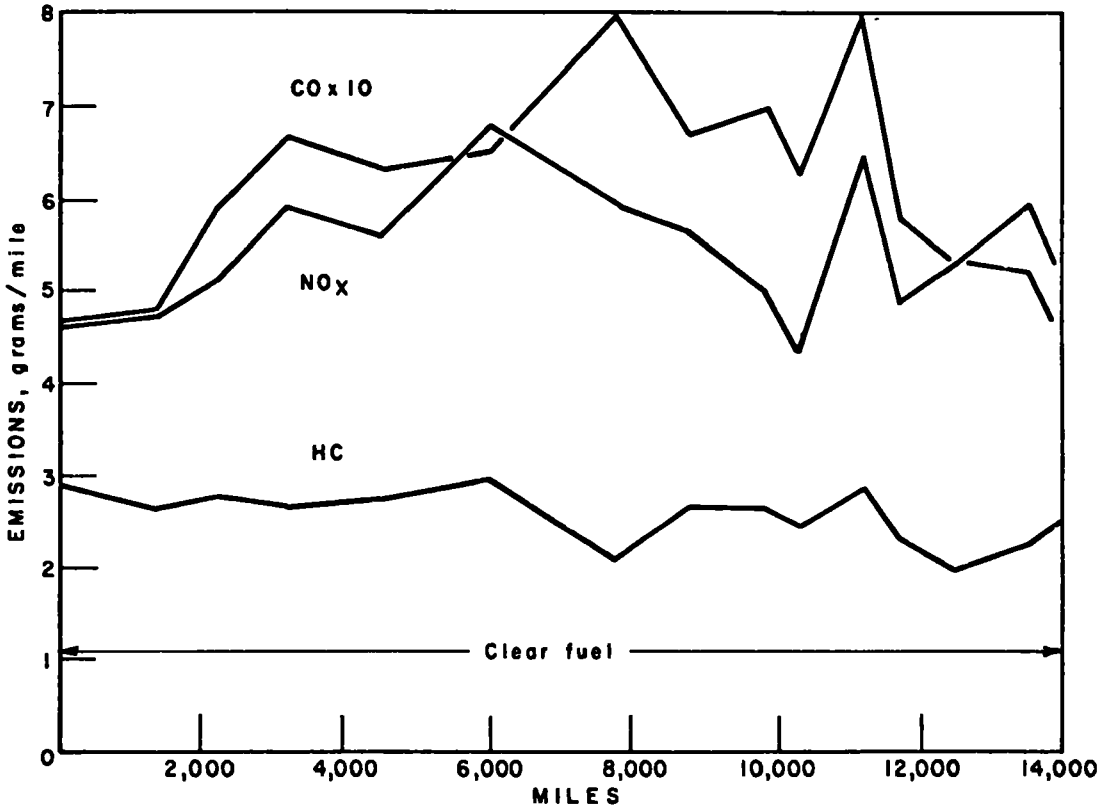


FIGURE 9.-Effect of mileage accumulation on exhaust emissions control vehicle.

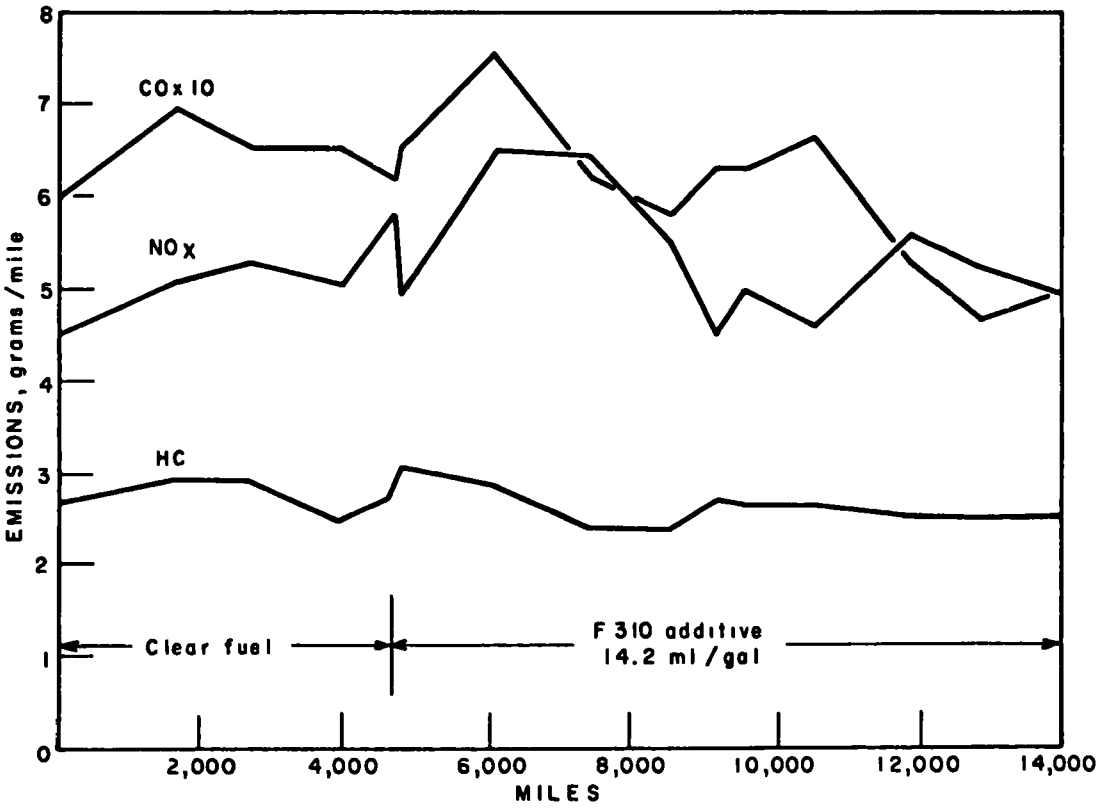


FIGURE 10.-Effect of mileage accumulation on exhaust emissions F 310 vehicle.

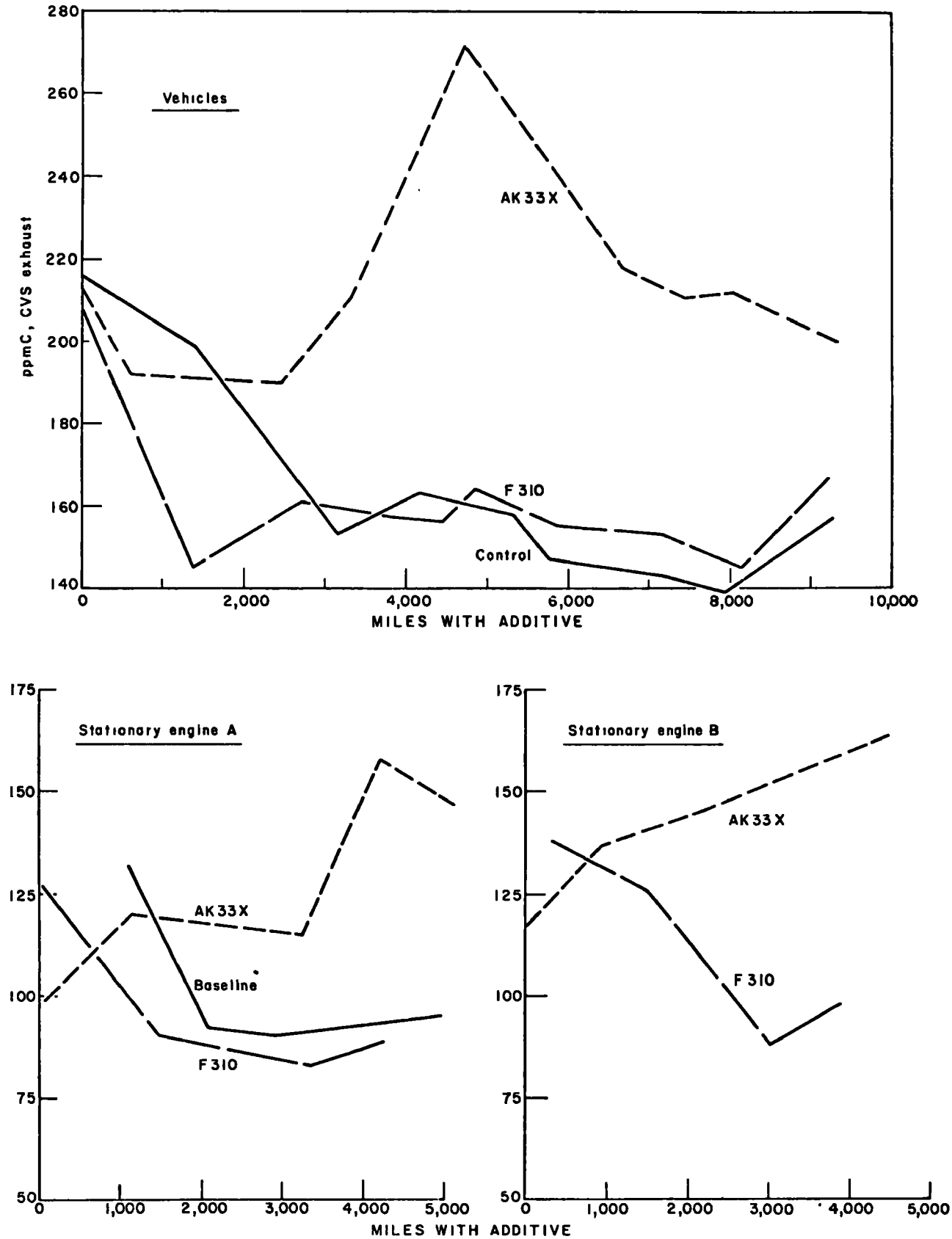


FIGURE 11 - Total CVS exhaust hydrocarbons by GLC.

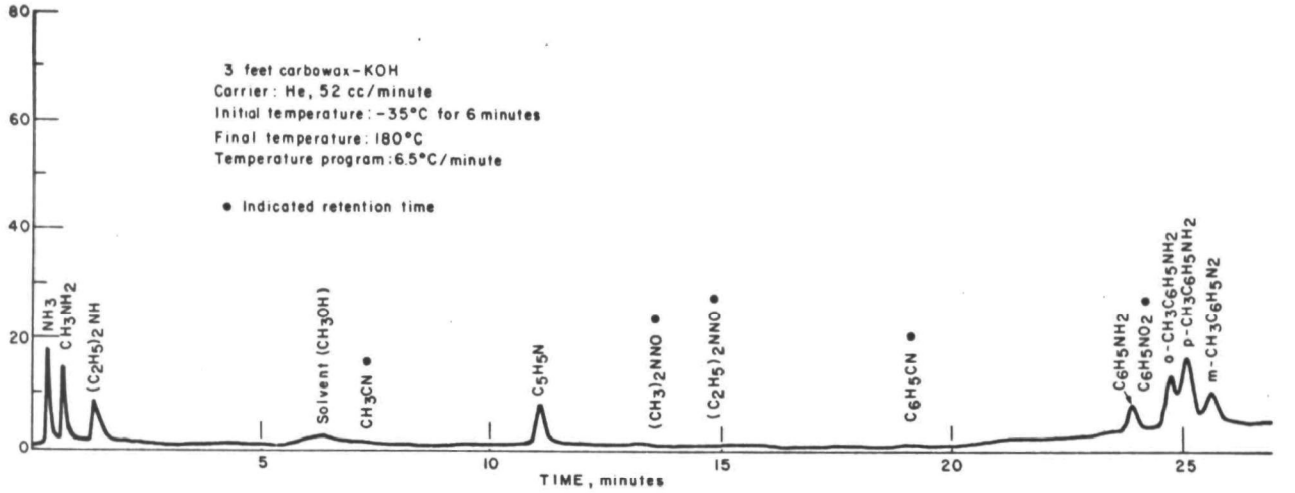


FIGURE 12.-Chromatogram of synthetic amines and pyridine, .08 mV/division.

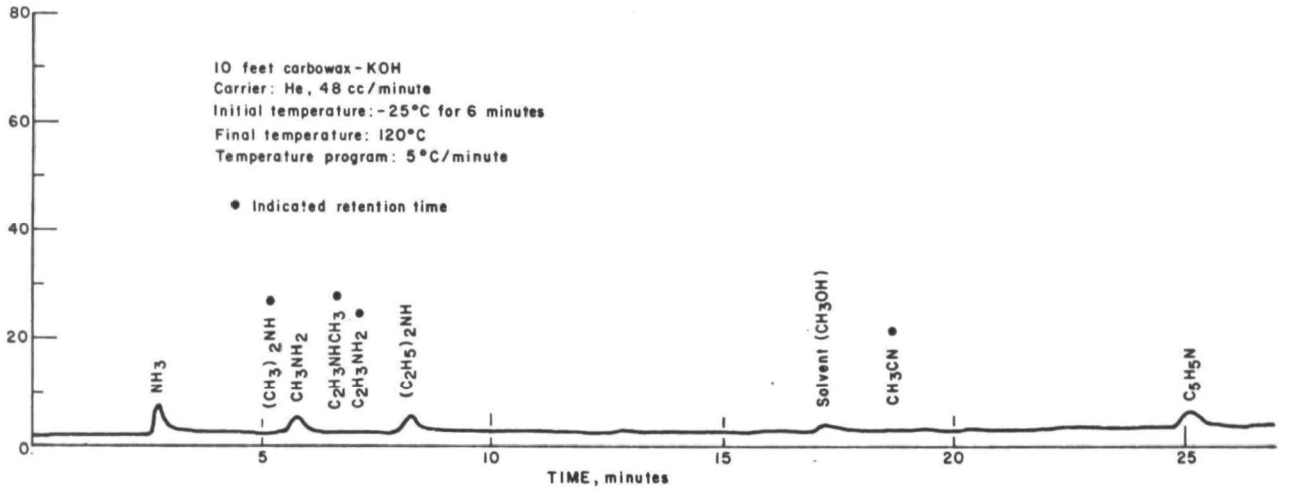


FIGURE 13.-Chromatogram of synthetic amines and pyridine, .08 mV/division.

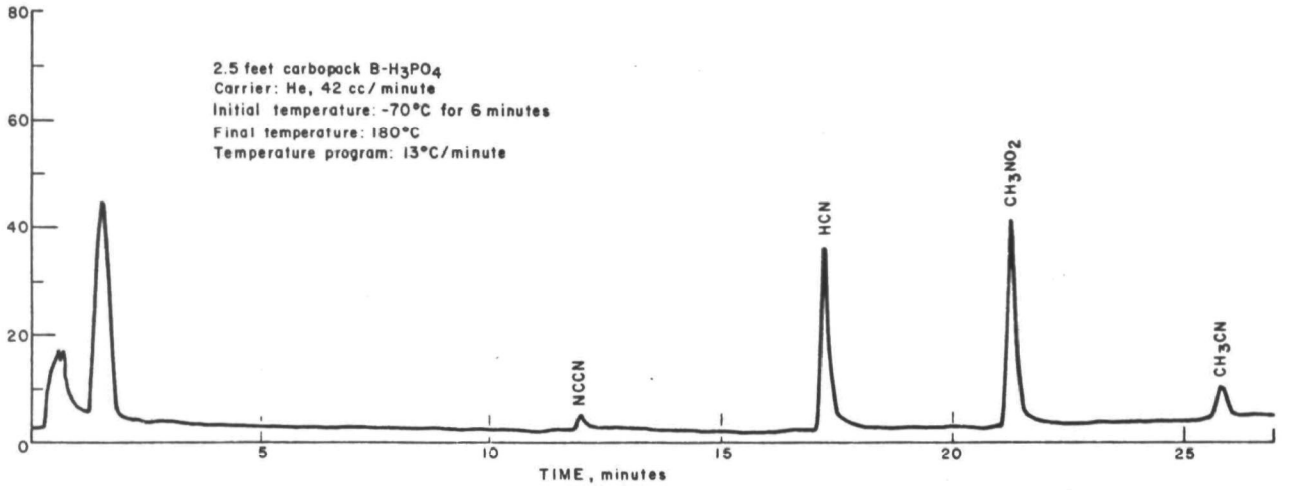


FIGURE 14.-Chromatogram of synthetic acidic and neutral nitrogen compounds, .04 mV/division.

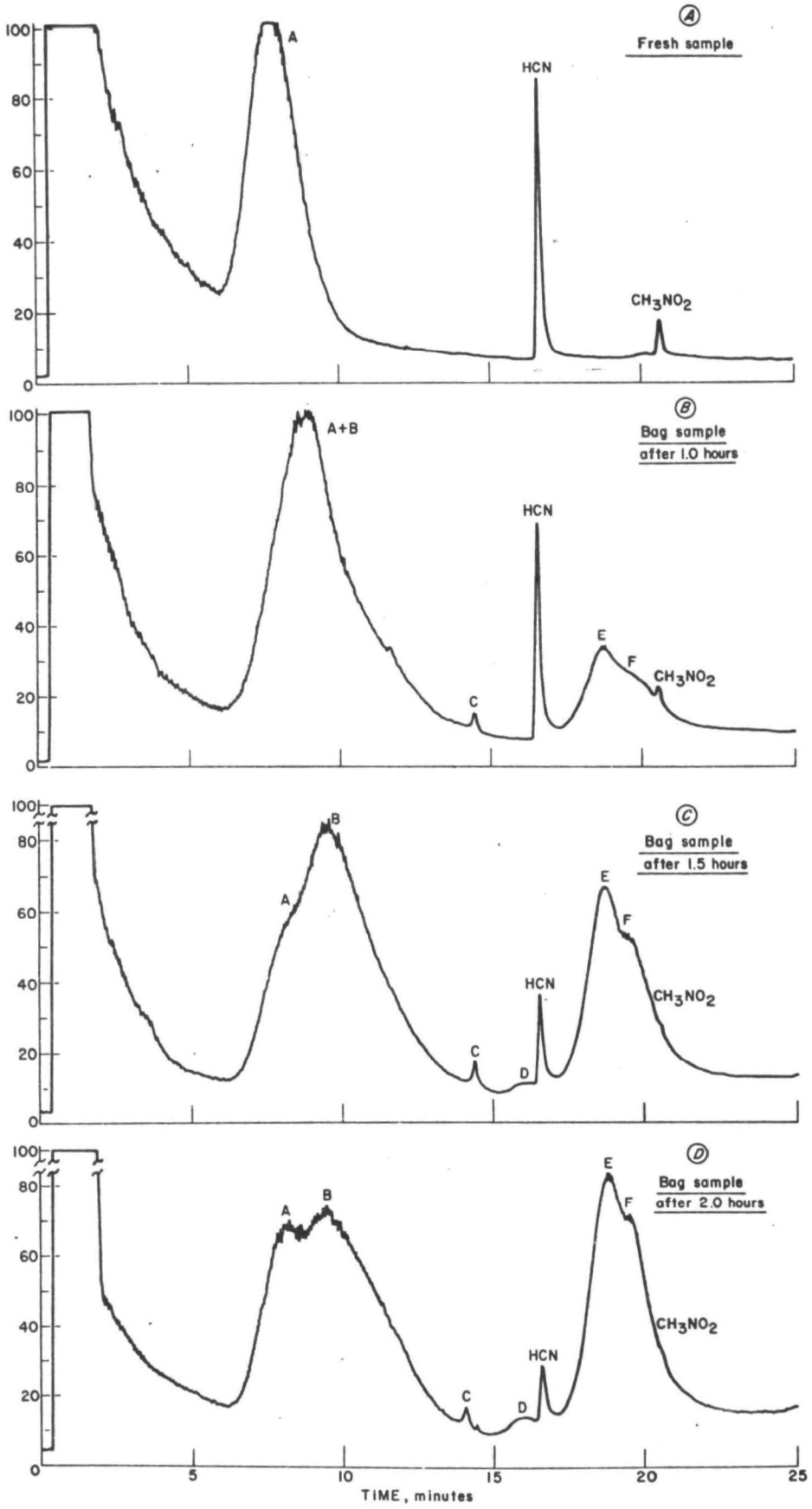


FIGURE 15.- Chromatogram for acidic and neutral nitrogen compounds, CVS exhaust, .04 mV/division.

TABLE A-1. - Detailed Hydrocarbon Analysis
F-310 Vehicle, ppmC

Peak No.	Compound	Accumulated mileage..	4,750		6,070		7,420		8,550		[illegible]	
		Fuel...	Indolene + F-310		Indolene + F-310		EPA + F-310		EPA + F-310		EPA + [illegible]	
			CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	[illegible]
1	Methane		17.39	17.39	16.56	16.56	12.81	12.81	12.95	12.95	12.7[illegible]	[illegible]
2	Ethylene		19.95	-	15.77	-	18.88	-	18.12	-	17.8[illegible]	-
3	Ethane		2.54	2.54	1.94	1.94	1.67	1.67	1.53	1.53	1.59	[illegible]
4	Acetylene		23.45	-	19.96	-	18.24	-	18.11	-	16.70	
5	Propylene, propane		12.46	.11	8.63	.14	9.61	.15	9.20	.07	7.41	[illegible]
6	Isobutane		.81	.21	.29	.10	-	.07	.97	.10	.32	.1[illegible]
7	Butene-1, isobutylene		6.64	-	4.94	-	4.85	-	4.63	-	4.37	-
8	n-Butane, 1,3-butadiene		4.61	2.24	2.67	1.01	3.49	1.81	4.26	2.50	3.81	[illegible]
9	trans-2-Butene		.98	-	.61	-	.79	-	.77	-	.52	-
10	cis-2-Butene		1.20	-	.75	-	.96	-	.93	-	.42	-
11	3-Methyl-1-butene		.28	-	.12	-	.38	-	.34	-	.05	-
12	Isopentane		3.46	3.46	1.77	1.77	2.99	2.99	3.92	3.92	3.54	3.5[illegible]
13	Pentene-1		.16	-	.09	-	.25	-	.25	-	.10	-
14	n-Pentane, 2-methyl-1-butene		1.59	1.08	.89	.53	2.39	2.25	3.12	3.01	2.90	2.7[illegible]
15	trans-2-Pentene		.58	-	.34	-	.34	-	.36	-	.25	-
16	cis-2-Pentene		.24	-	.14	-	.19	-	.20	-	.09	-
17	2-Methyl-2-butene		1.16	-	.73	-	.52	-	.52	-	.36	-
18	Cyclopentane, 3-methyl-1-pentene		.13	.08	.07	.04	4.26	5.08	5.25	5.66	5.76	5.01
19	2,3-Dimethylbutane		1.23	1.23	.62	.62	.44	.44	.51	.51	.40	.40
20	2-Methylpentane, 2,3-dimethyl-1-butene		1.33	1.22	.69	.63	.69	.43	.78	.53	.47	.43
21	3-Methylpentane		.72	.74	.38	.40	.38	.22	.40	.31	.20	.27
22	1-Hexene, 2-ethyl-1-butene		.13	-	.06	-	.40	-	.40	-	.15	-
23	n-Hexane, cis-3-hexene		.69	.67	.35	.36	.26	.15	.26	.21	.16	.23
24	Methylcyclopentane, 3-methyltrans-2-pentene		.70	.53	.39	.27	.37	.15	.39	.17	.26	.18
25	2,4-Dimethylpentane		1.44	1.40	.77	.68	.40	.17	.32	.14	.15	.18
26	Benzene, cyclohexane		9.84	.19	7.78	.15	6.37	.02	5.52	.04	5.38	.04
27	Cyclohexene, 2,3-dimethylpentane, 2-methylhexane		2.94	2.10	1.40	1.06	2.62	2.07	3.15	2.71	3.63	3.23
28	3-Methylhexane		.99	.81	.47	.41	.57	.38	.60	.49	.67	.59
29	Isooctane		7.59	7.44	3.72	3.72	4.57	4.57	5.63	5.63	6.89	6.88
30	n-Heptane		.84	.67	.37	.32	.82	.53	.89	.67	1.31	.87
31	Methylcyclohexane		.44	.34	.19	.17	.44	.25	.48	.34	.57	.44
32	2,4-Dimethylhexane, 2,5-dimethylhexane		2.32	2.38	1.27	1.22	.96	.80	.97	.92	1.23	1.21
33	2,3,4-Trimethylpentane		3.09	3.05	1.45	1.46	.50	.61	.48	.47	.63	.64
34	2,3,3-Trimethylpentane		3.48	3.48	1.63	1.63	.39	.39	.25	.25	.32	.32
35	Toluene, 2,3-dimethylhexane		29.71	1.07	21.25	.51	18.81	.33	19.32	.30	21.49	.39
36	2-Methylheptane		2.28	.62	-	.31	2.16	.92	2.40	.97	2.95	1.30
37	3-Methylheptane		1.21	.52	.68	.26	1.44	.95	1.55	1.01	1.94	1.29
38	2,2,5-Trimethylhexane		1.58	1.24	.85	.63	.36	.24	.20	.07	.23	.10
39	n-Octane		.32	.27	.16	.13	.90	.68	.85	.68	1.10	.97
40	2,3,5-Trimethylhexane		.18	.14	.07	.07	.12	.02	.06	.02	.07	.06
41	2,5-Dimethylheptane, 3,5-dimethylheptane		.13	.12	.04	.08	.31	.16	.20	.19	.27	.20
42	Ethylbenzene		2.46	.06	1.65	.04	1.67	.06	1.46	.10	1.81	.17
43	p-Xylene, m-xylene		5.92	.13	4.29	.08	4.83	.32	4.72	.35	5.20	.40
44	o-Xylene		3.56	.18	2.56	.12	2.72	-	2.35	-	2.56	-
45	n-Propylbenzene		.31	-	.22	-	.24	-	.16	-	.20	-
46	1-Methyl-3-ethylbenzene		1.89	.02	1.40	.01	1.33	.04	1.11	.04	1.26	.05
47	1-Methyl-2-ethylbenzene		.84	.15	.63	.03	.54	.07	.47	.06	.10	.08
48	Mesitylene		.75	.07	.54	.10	.53	-	.43	-	.52	-
49	1,2,4-Trimethylbenzene		3.82	.17	3.63	.11	2.45	-	1.69	-	1.91	03
50	sec-Butylbenzene, n-decane		.42	.14	-	.09	.68	.09	.49	.07	.53	.12
	*Total hydrocarbons by GC.		205.70		144.90		160.65		157.19		156.35	

* Includes exhaust hydrocarbons not reported in detailed analysis.

TABLE A-1. - Detailed Hydrocarbon Analysis
F-310 Vehicle, ppmC--Continued

Peak No.	Compound	Accumulated mileage... Fuel..... 9,550 EPA + F-310 CVS exhaust	9,550 EPA + F-310 CVS exhaust with scrubber	10,550 EPA + F-310 CVS exhaust	10,550 EPA + F-310 CVS exhaust with scrubber	11,880 EPA + F-310 CVS exhaust	11,880 EPA + F-310 CVS exhaust with scrubber	12,840 EPA + F-310 CVS exhaust	12,840 EPA + F-310 CVS exhaust with scrubber	13,940 EPA + F-310 CVS exhaust	13,940 EPA + F-310 CVS exhaust with scrubber
1	Methane.....	12.91	12.91	13.65	13.65	11.85	11.85	9.84	9.84	10.15	10.15
2	Ethylene.....	18.40	-	18.64	-	16.81	-	15.00	-	17.69	-
3	Ethane.....	1.59	1.59	1.57	1.57	1.52	1.52	1.32	1.32	1.59	1.59
4	Acetylene.....	18.27	-	18.90	-	16.99	-	13.67	-	15.84	-
5	Propylene, propane.....	9.57	.20	8.08	.42	7.96	.13	7.73	.19	9.03	.09
6	Isobutane.....	-	.10	--	.40	.67	.10	-	.09	-	.09
7	Butene-1, isobutylene.....	4.86	-	4.87	-	4.20	-	4.06	-	4.76	-
8	n-Butane, 1,3-butadiene.....	3.93	1.88	3.84	1.93	4.29	2.61	3.37	1.93	4.07	2.20
9	trans-2-Butene.....	.75	-	.41	-	.60	-	.39	-	.67	-
10	cis-2-Butene.....	1.05	-	.44	-	.73	-	.75	-	.98	-
11	3-Methyl-1-butene.....	.40	-	.04	-	.14	-	.07	-	.29	-
12	Isopentane.....	3.05	3.05	3.41	3.41	4.10	4.10	3.31	3.31	3.80	3.80
13	Pentene-1.....	.07	-	.10	-	.13	-	.14	-	.17	-
14	n-Pentane, 2-methyl-1-butene	2.71	2.43	2.93	2.89	3.29	3.19	2.92	2.67	3.27	3.06
15	trans-2-Pentene.....	.23	-	.21	-	.26	-	.27	-	.28	-
16	cis-2-Pentene.....	.09	-	.08	-	.12	-	.16	-	.16	-
17	2-Methyl-2-butene.....	.36	-	.35	-	.40	-	.41	-	.47	-
18	Cyclopentane, 3-methyl-1-pentene.....	5.51	4.53	5.58	5.07	6.24	5.57	5.61	5.24	6.33	5.50
19	2,3-Dimethylbutane.....	.36	.36	.32	.32	.43	.43	.37	.37	.47	.47
20	2-Methylpentane, 2,3-dimethyl-1-butene.....	.41	.37	.34	.28	.51	.42	.40	.39	.49	.51
21	3-Methylpentene.....	.17	.21	.15	.16	.23	.22	.26	.18	.34	.33
22	1-Hexene, 2-ethyl-1-butene..	.12	-	.12	-	.17	-	.20	-	.29	-
23	n-Hexane, cis-3-hexene.....	.16	.16	.15	.15	.16	.14	.24	.16	.25	.28
24	Methylcyclopentane, 3-methyltrans-2-pentene...	.25	.14	.20	.11	.20	.14	.29	.17	.34	.22
25	2,4-Dimethylpentane.....	.09	.12	.10	.08	.09	.11	.19	.15	.22	.20
26	Benzene, cyclohexane.....	6.06	.04	6.35	.45	5.15	.04	4.98	.05	5.31	.05
27	Cyclohexene, 2,3-dimethylpentane, 2-methylhexane.....	3.71	3.19	3.15	2.89	3.32	3.09	3.43	3.19	3.76	3.51
28	3-Methylhexane.....	.70	.59	.57	.52	.60	.55	.66	.59	.68	.66
29	Isooctane.....	6.73	6.73	5.96	5.96	6.37	6.37	6.72	6.72	7.18	7.18
30	n-Heptane.....	.98	.84	.82	.69	.87	.78	1.04	.86	1.07	.96
31	Methylcyclohexane.....	.53	.43	.43	.36	.47	.41	.53	.44	.56	.50
32	2,4-Dimethylhexane, 2,5-dimethylhexane.....	1.16	1.16	.99	.95	1.08	1.03	1.19	1.00	1.21	1.17
33	2,3,4-Trimethylpentane.....	.59	.59	.50	.50	.56	.57	.63	.61	.61	.63
34	2,3,3-Trimethylpentane.....	.29	.29	.19	.19	.25	.25	.33	.33	.30	.30
35	Toluene, 2,3-dimethylhexane.	22.54	.36	21.75	.28	20.52	.30	20.73	.42	23.02	.36
36	2-Methylheptane.....	2.55	1.15	2.19	1.09	2.54	1.02	2.02	1.40	2.69	1.14
37	3-Methylheptane.....	1.69	1.20	1.43	1.09	1.67	1.07	1.58	1.37	1.78	1.12
38	2,2,5-Trimethylhexane.....	.19	.09	.31	.11	.16	.07	.15	.10	.19	.09
39	n-Octane.....	.98	.87	.81	.76	.96	.79	.96	.87	1.00	.82
40	2,3,5-Trimethylhexane.....	.06	.04	.01	.01	.04	.03	.07	.04	.06	.03
41	2,5-Dimethylheptane, 3,5-dimethylheptane.....	.23	.29	.15	.19	.21	.26	.29	.28	.25	.25
42	Ethylbenzene.....	1.66	.14	1.60	.09	1.54	1.27	1.66	.13	1.78	.16
43	p-Xylene, m-xylene.....	5.47	.45	5.36	.41	5.51	.44	5.33	.44	5.68	.45
44	o-Xylene.....	2.65	.01	2.58	-	2.52	-	2.52	-	2.76	-
45	n-Propylbenzene.....	.18	-	.11	-	.15	-	.26	-	.23	.04
46	1-Methyl-3-ethylbenzene.....	1.33	.06	1.22	.15	1.46	.19	1.29	.17	1.44	.22
47	1-Methyl-2-ethylbenzene.....	.52	.08	.49	.08	.57	.11	.53	.10	.54	.13
48	Mesitylene.....	.45	-	.41	.07	.48	.11	.55	.11	.46	.15
49	1,2,4-Trimethylbenzene.....	1.76	.02	1.86	-	1.89	-	1.65	-	1.91	-
50	sec-Butylbenzene, n-decane..	.47	.11	.39	.09	.44	.11	.26	.10	.55	.13
	*Total hydrocarbons by GC....	163.61		155.17		153.27		144.90		166.86	

* Includes exhaust hydrocarbons not reported in detailed analysis

TABLE A-2. - Detailed Hydrocarbon Analysis
AK33X Vehicle, ppmC

Peak No.	Compound	Accumulated mileage..	4,740		5,305		7,170		8,030		9,434	
		Fuel.....	Indolene + AK33X		Indolene + AK33X		EPA + AK33X		EPA + AK33X		EPA + AK33X	
			CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber
1	Methane.....		17.49	17.49	17.10	17.10	14.61	14.61	16.01	16.01	18.07	18.07
2	Ethylene.....		19.75	-	19.02	-	23.32	-	24.35	-	28.45	-
3	Ethane.....		2.50	2.50	2.55	2.55	2.27	2.27	2.40	2.40	2.76	2.76
4	Acetylene.....		24.75	-	23.31	-	21.47	-	23.95	-	27.36	-
5	Propylene, propane.....		12.77	.14	12.39	.15	12.32	.18	11.05	.15	14.82	.24
6	Isobutane.....		1.21	.29	1.20	.25	-	.13	-	.13	-	.21
7	Butene-1, isobutylene.....		6.25	-	6.27	-	6.40	-	6.36	-	7.74	-
8	n-Butane, 1,3-butadiene.....		5.26	2.93	4.40	2.10	5.03	2.65	4.78	2.32	7.08	4.19
9	trans-2-Butene.....		1.08	-	1.04	-	.88	-	.68	-	1.07	-
10	cis-2-Butene.....		1.45	-	1.51	-	1.44	-	.68	-	1.67	-
11	3-Methyl-1-butene.....		.36	-	.46	-	.43	-	.07	-	.50	-
12	Isopentane.....		3.98	3.98	2.91	2.91	4.15	4.15	4.50	4.50	6.88	6.88
13	Pentene-1.....		.22	-	.14	-	.32	-	.14	-	.40	-
14	n-Pentane, 2-methyl-1-butene		1.77	1.22	1.40	.95	3.28	2.99	3.69	3.43	5.73	5.50
15	trans-2-Pentene.....		.61	-	.46	-	.45	-	.36	-	.59	-
16	cis-2-Pentene.....		.28	-	.21	-	.27	-	.15	-	.34	-
17	2-Methyl-2-butene.....		1.17	-	1.01	-	.70	-	.58	-	.83	-
18	Cyclopentane, 3-methyl-1-pentene.....		.19	.09	.13	.07	5.29	5.37	6.73	5.88	10.65	10.31
19	2,3-Dimethylbutane.....		1.31	1.31	.98	.98	.60	.60	.63	.63	.85	.85
20	2-Methylpentane, 2,3-dimethyl-1-butene.....		1.48	1.28	1.12	1.01	.60	.59	.69	.63	1.28	.94
21	3-Methylpentane.....		.85	.82	.63	.66	.52	.28	.31	.37	.71	.54
22	1-Hexene, 2-ethyl-1-butene..		.21	-	.14	-	.47	-	.15	-	.59	-
23	n-Hexane, cis-3-hexene.....		.75	.75	.57	.62	.36	.25	.28	.34	.51	.48
24	Methylcyclopentane, 3-methyltrans-2-pentene...		.73	.53	.55	.44	.50	.22	.36	.31	.71	.40
25	2,4-Dimethylpentane.....		1.40	1.32	1.06	1.11	.49	.30	.33	.38	.55	.34
26	Benzene, cyclohexane.....		9.61	.19	8.78	.17	7.46	.05	8.08	.09	8.40	.12
27	Cyclohexene, 2,3-dimethylpentane, 2-methylhexane.....		2.59	1.99	2.00	1.52	3.15	2.43	4.17	3.78	5.92	5.40
28	3-Methylhexane.....		1.04	.78	.68	.60	.64	.50	.84	.77	1.23	1.06
29	Isooctane.....		7.09	7.09	5.56	5.56	5.59	5.59	8.47	8.47	11.08	11.08
30	n-Heptane.....		.76	.62	.56	.54	.74	.67	1.17	1.02	1.70	1.48
31	Methylcyclohexane.....		.38	.30	.28	.27	.37	.31	.60	.50	.90	.74
32	2,4-Dimethylhexane, 2,5-dimethylhexane.....		2.11	2.20	1.66	1.74	1.06	1.03	1.60	1.60	1.94	1.92
33	2,3,4-Trimethylpentane.....		2.87	2.89	2.24	2.16	.67	.64	1.07	1.06	.96	.96
34	2,3,3-Trimethylpentane.....		3.22	3.22	2.48	2.48	.48	.48	.79	.79	.48	.48
35	Toluene, 2,3-dimethylhexane.		28.32	.95	25.18	.78	24.09	.36	29.85	.52	35.69	.59
36	2-Methylheptane.....		2.12	.55	1.63	.46	2.11	.80	3.21	1.24	4.09	1.93
37	3-Methylheptane.....		1.15	.40	.84	.38	1.33	.81	2.03	1.29	2.74	2.06
38	2,2,5-Trimethylhexane.....		1.46	1.04	1.15	.90	.36	.27	.54	.41	.30	.16
39	n-Octane.....		.28	.21	.24	.21	.76	.59	1.12	.93	1.60	1.53
40	2,3,5-Trimethylhexane.....		.14	.13	.13	.11	.06	.02	.07	.05	.10	.09
41	2,5-Dimethylheptane, 3,5-dimethylheptane.....		.08	.11	.10	.09	.19	.15	.25	.25	.40	.49
42	Ethylbenzene.....		2.39	.06	2.30	.05	2.02	.01	2.40	.10	2.93	.39
43	p-Xylene, m-xylene.....		6.06	.13	5.43	.11	5.87	.30	7.42	.46	9.22	.82
44	o-Xylene.....		3.68	.20	3.31	.16	3.20	-	3.77	.01	4.41	.12
45	n-Propylbenzene.....		.37	-	.38	.01	.17	-	.24	-	.33	.10
46	1-Methyl-3-ethylbenzene.....		2.13	.09	2.00	.03	1.48	.04	2.16	.06	2.31	.19
47	1-Methyl-2-ethylbenzene.....		.98	.24	.90	.13	.63	.08	.80	.13	.94	.28
48	Mesitylene.....		.87	.12	.82	.06	.53	-	.76	.01	.84	-
49	1,2,4-Trimethylbenzene.....		4.40	.28	4.18	.13	2.54	.03	2.95	.03	3.21	-
50	sec-Butylbenzene, n-decane..		.50	.22	.57	.11	.60	.12	.64	.13	.80	.26
	Total hydrocarbons by GC....		212.42		191.64		190.29		210.72		271.80	

* Includes exhaust hydrocarbons not reported in detailed analysis.

TABLE A-2. - Detailed Hydrocarbon Analysis
AK33X Vehicle, ppmC--Continued

Peak No.	Compound	Accumulated mileage...	10,353		11,390		12,140		12,740		14,050	
		Fuel.....	EPA + AK33X		EPA + AK33X		EPA + AK33X		EPA + AK33X		EPA + AK33X	
			CVS exhaust	CVS Exhaust with scrubber	CVS exhaust	CVS Exhaust with scrubber	CVS exhaust	CVS Exhaust with scrubber	CVS exhaust	CVS Exhaust with scrubber	CVS exhaust	CVS Exhaust with scrubber
1	Methane.....		15.90	15.90	17.01	17.01	15.85	15.85	14.15	14.15	12.27	12.27
2	Ethylene.....		31.22	-	26.91	-	27.62	-	26.73	-	25.94	-
3	Ethane.....		3.09	3.09	3.02	3.02	2.81	2.81	2.78	2.78	2.65	2.65
4	Acetylene.....		26.87	-	22.25	-	22.31	-	22.12	-	18.80	-
5	Propylene, propane.....		16.05	.53	14.17	.36	14.10	.21	13.98	.13	14.16	.13
6	Isobutane.....		1.46	.48	-	.13	-	.12	-	.12	-	.13
7	Butene-1, isobutylene.....		8.40	-	7.38	-	7.44	-	7.09	-	7.39	-
8	n-Butane, 1,3-butadiene.....		6.70	3.54	5.32	2.13	5.40	2.45	5.82	2.89	5.67	2.62
9	trans-2-Butene.....		1.15	-	.95	-	.77	-	.84	-	1.22	-
10	cis-2-Butene.....		1.66	-	1.47	-	1.87	-	1.05	-	1.60	-
11	3-Methyl-1-butene.....		.30	-	.33	-	.21	-	.09	-	.47	-
12	Isopentane.....		5.45	5.45	3.90	3.90	3.99	3.99	4.76	4.76	4.25	4.25
13	Pentene-1.....		.28	-	.15	-	.18	-	.13	-	.16	-
14	n-Pentane, 2-methyl-1-butene		4.57	4.29	3.70	3.17	3.53	3.15	4.13	3.75	3.62	3.31
15	trans-2-Pentene.....		.47	-	.31	-	.37	-	.30	-	.30	-
16	cis-2-Pentene.....		.23	-	.13	-	.18	-	.11	-	.13	-
17	2-Methyl-2-butene.....		.65	-	.49	-	.51	-	.46	-	.50	-
18	Cyclopentane, 3-methyl-1-pentene.....		8.24	7.72	6.91	6.22	6.30	4.87	7.75	6.23	6.59	5.26
19	2,3-Dimethylbutane.....		.59	.59	.45	.45	.35	.35	.47	.47	.45	.45
20	2-Methylpentane, 2,3-dimethyl-1-butene.....		.78	.64	.56	.51	.41	.37	.48	.47	.51	.47
21	3-Methylpentane.....		.37	.34	.24	.26	.21	.17	.20	.21	.22	.28
22	1-Hexene, 2-ethyl-1-butene..		.27	-	.15	-	.16	-	.14	-	.20	-
23	n-Hexane, cis-3-hexene.....		.29	.30	.25	.24	.23	.15	.21	.17	.18	.20
24	Methylcyclopentane, 3-methyltrans-2-pentene...		.35	.26	.32	.21	.27	.15	.29	.18	.23	.15
25	2,4-Dimethylpentane.....		.17	.21	.14	.14	.14	.11	.13	.14	.10	.12
26	Benzene, cyclohexane.....		9.00	.07	7.92	.08	8.39	.05	7.31	.05	6.52	.03
27	Cyclohexene, 2,3-dimethylpentane, 2-methylhexane.....		4.38	3.96	4.09	3.61	3.21	2.93	4.37	3.85	3.64	3.10
28	3-Methylhexane.....		.87	.78	.85	.72	.64	.57	.83	.72	.69	.59
29	Isooctane.....		8.18	8.18	7.43	7.43	6.20	6.20	8.08	8.08	6.65	6.65
30	n-Heptane.....		1.26	1.11	1.13	1.00	.93	.86	1.79	1.04	.94	.82
31	Methylcyclohexane.....		.65	.58	.59	.51	.48	.43	.67	.51	.54	.42
32	2,4-Dimethylhexane, 2,5-dimethylhexane.....		1.26	1.23	1.17	1.16	1.01	1.02	1.42	1.35	1.14	1.12
33	2,3,4-Trimethylpentane.....		.64	.64	.59	.60	.49	.51	.68	.67	.52	.52
34	2,3,3-Trimethylpentane.....		.30	.30	.28	.28	.20	.20	.32	.32	.22	.22
35	Toluene, 2,3-dimethylhexane.		32.29	.39	29.44	.35	28.57	.31	30.16	.43	26.23	.27
36	2-Methylheptane.....		3.54	1.27	3.12	1.19	2.44	1.08	3.57	1.58	3.38	1.04
37	3-Methylheptane.....		2.25	1.35	2.02	1.28	1.62	1.13	2.32	1.63	2.12	1.09
38	2,2,5-Trimethylhexane.....		.65	.25	.21	.10	.15	.08	.25	.09	.23	.07
39	n-Octane.....		1.27	.94	1.14	.97	.95	.89	1.25	1.15	1.06	.78
40	2,3,5-Trimethylhexane.....		.08	.03	.07	.06	.05	.04	.06	.02	.05	.03
41	2,5-Dimethylheptane, 3,5-dimethylheptane.....		.31	.25	.27	.34	.26	.31	.27	.26	.21	.21
42	Ethylbenzene.....		2.80	.16	2.56	.11	2.55	.20	2.60	.16	2.33	.07
43	p-Xylene, m-xylene.....		8.31	.47	7.55	.53	7.44	.50	7.94	.65	6.65	.37
44	o-Xylene.....		4.25	-	3.87	-	3.76	-	3.89	-	3.39	-
45	n-Propylbenzene.....		.31	-	.25	.01	.29	-	.22	-	.20	-
46	1-Methyl-3-ethylbenzene.....		2.29	.18	2.09	.19	2.07	.20	.22	.24	1.82	.12
47	1-Methyl-2-ethylbenzene.....		.86	.09	.76	.11	.77	.11	.78	.15	.66	.07
48	Mesitylene.....		.77	.10	.65	.11	.68	.11	.71	.15	.60	.06
49	1,2,4-Trimethylbenzene.....		3.52	-	2.79	-	2.64	-	2.73	-	2.96	-
50	sec-Butylbenzene, n-decane..		.81	.10	.67	.12	.64	.11	.56	.14	.83	.07
	*Total hydrocarbons by GC....		247.27		217.74		211.23		212.18		200.46	

* Includes exhaust hydrocarbons not reported in detailed analysis.

TABLE A-3. - Detailed Hydrocarbon Analysis
Control Vehicle, ppmC

Peak No.	Compound	Accumulated mileage..	4,550		5,930		7,700		8,725		9,865	
		Fuel.....	Indolene		Indolene		EPA		EPA		EPA	
			CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber
1	Methane.....		16.86	16.86	17.40	17.40	12.04	12.04	13.77	13.77	13.45	13.45
2	Ethylene.....		17.79	-	17.07	-	17.02	-	18.34	-	17.92	-
3	Ethane.....		2.22	2.22	2.20	2.20	1.48	1.48	1.52	1.52	1.48	1.48
4	Acetylene.....		23.96	-	24.65	-	17.05	-	19.40	-	18.36	-
5	Propylene, propane.....		11.01	.10	10.62	.13	8.48	.13	9.35	.10	7.42	.24
6	Isobutane.....		.98	.27	.70	.16	-	.08	.99	.09	.26	.13
7	Butene-1, isobutylene.....		5.82	-	5.72	-	4.41	-	4.77	-	4.30	-
8	n-Butane, 1,3-butadiene.....		4.93	2.98	3.77	1.92	3.28	1.81	4.20	2.39	4.13	2.56
9	trans-2-Butene.....		.95	-	.83	-	.61	-	.73	-	.50	-
10	cis-2-Butene.....		1.06	-	1.11	-	.95	-	.97	-	.51	-
11	3-Mechyl-1-butene.....		.31	-	.32	-	.34	-	.42	-	.07	-
12	Isopentane.....		4.46	4.46	3.43	3.43	2.93	2.93	3.90	3.90	3.77	3.77
13	Pentene-1.....		.24	-	.19	-	.26	-	.08	-	.12	-
14	n-Pentane, 2-methyl-1-butene		1.95	1.35	1.59	1.07	2.36	2.18	3.30	3.01	3.03	2.90
15	trans-2-Pentene.....		.69	-	.56	-	.35	-	.16	-	.25	-
16	cis-2-Pentene.....		.32	-	.28	-	.23	-	.06	-	.11	-
17	2-Methyl-2-butene.....		1.35	-	1.15	-	.54	-	.34	-	.39	-
18	Cyclopentane, 3-methyl-1-pentene.....		.22	.10	.14	.09	4.04	4.16	6.42	5.22	5.78	4.76
19	2,3-Dimethylbutane.....		1.63	1.63	1.23	1.23	.43	.43	.41	.41	.39	.39
20	2-Methylpentane, 2,3-dimethyl-1-butene.....		1.83	1.62	1.24	1.23	.43	.39	.42	.40	.47	.41
21	3-Methylpentane.....		1.03	.98	.75	.79	.42	.17	.17	.19	.22	.26
22	1-Hexene, 2-ethyl-1-butene..		.26	-	.16	-	.43	-	.10	-	.16	-
23	n-Hexane, cis-3-hexene.....		.92	.91	.68	.72	.26	.16	.16	.15	.16	.23
24	Methylcyclopentane, 3-methyltrans-2-pentene...		.92	.67	.65	.54	.38	.17	.22	.15	.26	.18
25	2,4-Dimethylpentane.....		1.91	1.77	1.35	1.39	.36	.19	.13	.14	.17	.20
26	Benzene, cyclohexane.....		8.70	.24	8.69	.27	5.99	.02	6.04	.07	5.80	.09
27	Cyclohexene, 2,3-dimethylpentane, 2-methylhexane.....		3.33	2.75	2.42	2.01	2.46	2.06	3.72	3.44	3.56	3.12
28	3-Methylhexane.....		1.17	1.04	.83	.76	.55	.39	.71	.62	.66	.57
29	Isooctane.....		9.90	9.57	7.08	7.08	4.53	4.53	7.10	7.10	6.72	6.72
30	n-Heptane.....		1.12	.82	.73	.59	.76	.54	.99	.83	.96	.87
31	Methylcyclohexane.....		.52	.41	.38	.31	.41	.26	.51	.41	.53	.43
32	2,4-Dimethylhexane, 2,5-dimethylhexane.....		2.91	2.93	2.22	2.28	.93	.81	1.20	1.17	1.21	1.21
33	2,3,4-Trimethylpentane.....		3.95	3.99	3.06	3.05	.50	.63	.64	.72	.63	.65
34	2,3,3-Trimethylpentane.....		4.49	4.48	3.46	3.46	.40	.40	.36	.36	.31	.31
35	Toluene, 2,3-dimethylhexane.		29.56	1.29	26.36	1.04	16.77	.38	21.37	.37	21.26	.40
36	2-Methylheptane.....		2.62	.73	1.91	.60	1.71	.94	2.39	1.16	2.53	1.20
37	3-Methylheptane.....		1.42	.57	.96	.49	1.22	.97	1.58	1.20	1.74	1.30
38	2,2,5-Trimethylhexane.....		1.92	1.45	1.50	1.25	.29	.26	.22	.12	.19	.10
39	n-Octane.....		.39	.31	.32	.26	.88	.59	.95	.80	1.15	1.01
40	2,3,5-Trimethylhexane.....		.24	.18	.18	.16	.13	.01	.06	.02	.09	.07
41	2,5-Dimethylheptane, 3,5-dimethylheptane.....		.19	.15	.13	.15	.34	.15	.25	.20	.32	.34
42	Ethylbenzene.....		2.39	.08	2.29	.08	1.62	.01	1.57	.09	1.67	.18
43	p-Xylene, m-xylene.....		5.73	.16	5.62	.16	4.27	.33	5.09	.39	5.57	.51
44	o-Xylene.....		3.35	.22	3.26	.23	2.47	-	2.38	-	2.60	-
45	n-Propylbenzene.....		.42	-	.49	-	.26	-	.13	-	.14	-
46	1-Methyl-3-ethylbenzene.....		2.00	.07	2.15	.05	1.04	.05	1.25	.05	1.30	.06
47	1-Methyl-2-ethylbenzene.....		.92	.26	.99	.21	.50	.09	.48	.09	.49	.10
48	Mesitylene.....		.88	.12	.94	.10	.46	-	.42	-	.42	-
49	1,2,4-Trimethylbenzene.....		3.91	.31	4.12	.24	1.72	.02	1.58	-	1.59	-
50	sec-Butylbenzene, n-decane..		.72	.14	.77	.15	.58	.11	.42	.08	.39	09
	*Total hydrocarbons by GC....		216.16		198.66		153.15		163.42		157.81	

* Includes exhaust hydrocarbons not reported in detailed analysis.

TABLE A-3. - Detailed Hydrocarbon Analysis
Control Vehicle, ppmC--Continued

Peak No.	Compound	Accumulated mileage... Fuel..... 10,320 EPA CVS exhaust	10,320 EPA CVS exhaust with scrubber	11,725 EPA CVS exhaust	11,725 EPA CVS exhaust with scrubber	12,490 EPA CVS exhaust	12,490 EPA CVS exhaust with scrubber	12,840 EPA CVS exhaust	12,840 EPA CVS exhaust with scrubber
1	Methane.....	14.85	14.85	12.51	12.51	10.76	10.76	10.44	10.44
2	Ethylene.....	16.92	-	16.09	-	15.96	-	14.82	-
3	Ethane.....	1.35	1.35	1.37	1.37	1.40	1.40	1.25	1.25
4	Acetylene.....	21.98	-	17.75	-	15.60	-	16.21	-
5	Propylene, propane.....	7.90	.11	7.88	.19	7.26	.11	7.61	.12
6	Isobutane.....	.52	.08	.71	.11	-	.09	.80	.09
7	Butene-1, isobutylene.....	3.95	-	3.88	-	3.95	-	3.76	-
8	n-Butane, 1,3-butadiene.....	3.88	2.28	4.07	2.51	3.69	2.21	3.80	2.30
9	trans-2-Butene.....	.57	-	.64	-	.40	-	.65	-
10	cis-2-Butene.....	.71	-	.83	-	.54	-	.86	-
11	3-Methyl-1-butene.....	.19	-	.27	-	.06	-	.34	-
12	Isopentane.....	3.60	3.60	4.38	4.38	3.43	3.43	4.26	4.26
13	Pentene-1.....	.19	-	.23	-	.15	-	.30	-
14	n-Pentane, 2-methyl-1-butene.	2.90	2.76	3.18	2.14	2.93	2.63	3.52	3.43
15	trans-2-Pentene.....	.30	-	.13	-	.25	-	.41	-
16	cis-2-Pentene.....	.14	-	.04	-	.15	-	24	-
17	2-Methyl-2-butene.....	.39	-	.25	-	.40	-	.55	-
18	Cyclopentane, 3-methyl-1-pentene.....	5.30	5.12	6.31	4.04	5.27	5.02	6.77	6.39
19	2,3-Dimethylbutane.....	.38	.38	.32	.32	.35	.35	.63	.62
20	2-Methylpentane, 2,3-dimethyl-1-butene.....	.43	.37	.31	.32	.37	.35	.96	.63
21	3-Methylpentane.....	.19	.18	.11	.16	.23	.14	.52	.34
22	1-Hexene, 2-ethyl-1-butene...	.15	-	.07	-	.19	-	.55	-
23	n-Hexane, cis-3-hexene.....	.13	.21	.17	.10	.18	.14	.35	.26
24	Methylcyclopentane, 3-methyltrans-2-pentene....	.20	.16	.24	.17	.21	.15	.50	.21
25	2,4-Dimethylpentane.....	.12	.13	.15	.13	.12	.12	.47	.19
26	Benzene, cyclohexane.....	5.43	.14	5.03	.04	5.00	.05	4.95	.04
27	Cyclohexene, 2,3-dimethylpentane, 2-methylhexane.....	2.78	2.51	3.18	2.88	3.03	2.72	4.31	3.83
28	3-Methylhexane.....	.52	.47	.57	.52	.57	.50	.87	.70
29	Isooctane.....	5.17	5.17	5.85	5.85	5.71	5.71	8.12	8.12
30	n-Heptane.....	.74	.68	.79	.71	.84	.71	1.38	1.00
31	Methylcyclohexane.....	.39	.35	.41	.36	.44	.36	.77	.51
32	2,4-Dimethylhexane, 2,5-dimethylhexane.....	.89	.87	.93	.93	.96	.84	1.26	1.21
33	2,3,4-Trimethylpentane.....	.43	.43	.47	.48	.52	.51	.68	.69
34	2,3,3-Trimethylpentane.....	.19	.18	.19	.19	.23	.23	.31	.31
35	Toluene, 2,3-dimethylhexane..	17.38	.23	17.59	.25	18.45	.32	20.30	.34
36	2-Methylheptane.....	1.89	.79	1.96	.86	2.00	1.09	2.84	1.21
37	3-Methylheptane.....	1.25	.83	1.29	.89	1.36	1.14	1.87	1.29
38	2,2,5-Trimethylhexane.....	.11	.04	.12	.05	.12	.07	.18	.09
39	n-Octane.....	.72	.59	.75	.63	.85	.81	1.05	.86
40	2,3,5-Trimethylhexane.....	.03	.01	.03	.02	.04	.02	.03	.02
41	2,5-Dimethylheptane, 3,5-dimethylheptane.....	.14	.18	.15	.16	.19	.22	.22	.22
42	Ethylbenzene.....	1.29	.10	1.27	.08	1.41	.11	1.48	.15
43	p-Xylene, m-xylene.....	4.36	.36	4.28	.33	4.77	.44	5.32	.43
44	o-Xylene.....	2.08	.04	2.02	-	2.19	-	2.30	-
45	n-Propylbenzene.....	.11	-	.14	-	.17	-	.14	-
46	1-Methyl-3-ethylbenzene.....	1.03	.24	1.10	.14	1.15	.17	1.23	.14
47	1-Methyl-2-ethylbenzene.....	.41	.14	.42	.08	.45	.10	.47	.08
48	Mesitylene.....	.34	.14	.37	.09	.39	.11	.40	09
49	1,2,4-Trimethylbenzene.....	1.43	-	1.45	-	1.55	-	1.45	-
50	sec-Butylbenzene, n-decane...	.28	.16	.34	.10	.39	.09	.33	.08
	*Total hydrocarbons by GC.....	147.32		143.09		138.63		157.41	

* Includes exhaust hydrocarbons not reported in detailed analysis.

TABLE A-4. - Detailed Hydrocarbon Analysis
Stationary Engine A, ppmC

Peak No.	Compound	Accumulated mileage..	1,080		2,080		2,930		4,950		5,000	
		Fuel.....	Indolene		Indolene		Indolene		Indolene		Indolene + AF33X	
			CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber
1	Methane.....		9.28	9.28	7.68	7.68	6.83	6.83	7.53	7.53	6.58	6.58
2	Ethylene.....		10.56	-	11.07	-	10.20	-	11.07	-	10.44	-
3	Ethane.....		1.10	1.10	1.32	1.32	1.24	1.24	1.28	1.28	1.24	1.24
4	Acetylene.....		11.67	-	11.34	-	10.47	-	10.42	-	10.42	-
5	Propylene, propane.....		6.57	-	6.47	-	5.49	-	6.48	.07	6.97	.02
6	Isobutane.....		.93	.34	.43	.20	.31	.13	.76	.13	.33	.17
7	Butene-1, isobutylene.....		3.20	-	3.48	-	2.90	-	3.39	-	3.30	-
8	n-Butane, 1,3-butadiene.....		4.77	3.49	2.57	1.33	1.91	.92	2.43	1.18	3.21	1.99
9	trans-2-Butene.....		.71	-	.51	-	.40	-	.62	-	.47	-
10	cis-2-Butene.....		.72	-	1.01	-	.36	-	.68	-	.63	-
11	3-Methyl-1-butene.....		.18	-	.19	-	.10	-	.27	-	.14	-
12	Isopentane.....		4.15	4.24	1.63	1.63	1.10	1.10	1.53	1.53	2.45	2.45
13	Pentene-1.....		.17	-	.13	-	.06	-	.13	-	.12	-
14	n-Pentane, 2-methyl-1-butene		1.64	1.22	.85	.50	.56	.33	.74	.43	1.08	.67
15	trans-2-Pentene.....		.54	-	.48	-	.30	-	.32	-	.41	-
16	cis-2-Pentene.....		.24	-	.27	-	.09	-	.14	-	.20	-
17	2-Methyl-2-butene.....		.96	-	.69	-	.46	-	.64	-	.75	-
18	Cyclopentane, 3-methyl-1-pentene.....		.17	.08	.10	.05	.08	.02	.13	.03	.12	.05
19	2,3-Dimethylbutane.....		1.26	1.29	.51	.51	.39	.39	.53	.53	.77	.77
20	2-Methylpentane, 2,3-dimethyl-1-butene.....		1.35	1.26	.53	.53	.46	.40	.67	.53	.76	.75
21	3-Methylpentane.....		.75	.80	.37	.37	.25	.25	.40	.36	.49	.49
22	1-Hexene, 2-ethyl-1-butene..		.16	-	.16	-	.09	-	.23	-	.12	-
23	n-Hexane, cis-3-hexene.....		.65	.72	.30	.29	.21	.20	.31	.26	.40	.36
24	Methylcyclopentane, 3-methyltrans-2-pentene...		.62	.45	.26	.20	.23	.14	.34	.20	.43	.27
25	2,4-Dimethylpentane.....		1.21	1.14	.52	.53	.47	.38	.64	.51	.80	.69
26	Benzene, cyclohexane.....		4.70	.14	4.46	.09	3.97	.05	4.23	.06	4.32	.08
27	Cyclohexene, 2,3-dimethylpentane, 2-methylhexane.....		2.18	1.65	.87	.68	.83	.55	1.10	.76	1.28	1.06
28	3-Methylhexane.....		.82	.61	.29	.24	.27	.21	.36	.28	.45	.39
29	Isooctane.....		5.92	5.70	2.50	2.39	2.55	2.02	2.66	2.67	3.64	3.64
30	n-Heptane.....		.62	.47	.19	.16	.24	.16	.37	.21	.39	.34
31	Methylcyclohexane.....		.30	.23	.09	.08	.10	.07	.20	.11	.20	.17
32	2,4-Dimethylhexane, 2,5-dimethylhexane.....		1.67	1.67	.66	.67	.65	.64	.95	.95	1.03	1.01
33	2,3,4-Trimethylpentane.....		2.39	2.33	.95	.93	.76	.75	1.01	1.00	1.40	1.42
34	2,3,3-Trimethylpentane.....		2.70	2.68	1.07	1.05	.88	.88	1.21	1.21	1.61	1.61
35	Toluene, 2,3-dimethylhexane.		16.96	.74	11.47	.28	10.46	.26	12.05	.32	13.00	.46
36	2-Methylheptane.....		1.47	.41	.67	.15	-	.15	-	.18	.95	.25
37	3-Methylheptane.....		.75	.28	.31	.07	.42	.12	.57	.12	.51	.18
38	2,2,5-Trimethylhexane.....		1.05	.87	.42	.34	.58	.31	.65	.37	.68	.50
39	n-Octane.....		.19	.15	.05	.06	.07	.05	.14	.06	.14	.10
40	2,3,5-Trimethylhexane.....		.11	.08	.03	.04	.03	.03	.11	.04	.09	.06
41	2,5-Dimethylheptane, 3,5-dimethylheptane.....		.07	.05	.02	.02	.02	.02	.12	.03	.07	.04
42	Ethylbenzene.....		1.31	.02	.96	-	.86	.01	1.08	.01	1.08	.01
43	p-Xylene, m-xylene.....		2.97	.06	2.07	.04	1.79	.03	2.16	.03	2.26	.05
44	o-Xylene.....		1.75	.07	1.48	.09	1.33	.02	1.56	.03	1.53	.04
45	n-Propylbenzene.....		.18	-	.12	-	.09	-	.18	-	.14	-
46	1-Methyl-3-ethylbenzene.....		.98	-	.70	-	.57	-	1.00	.02	1.04	.01
47	1-Methyl-2-ethylbenzene.....		.39	-	.27	.02	.24	.02	.35	.05	.31	.04
48	Mesitylene.....		.39	.07	.30	-	.28	.01	.50	.02	.31	.02
49	1,2,4-Trimethylbenzene.....		2.19	.13	1.48	.02	1.80	.03	2.17	.01	1.70	.04
50	sec-Butylbenzene, n-decane..		-	-	.18	.03	-	.06	-	.02	.34	.03
	*Total hydrocarbons by GC....		131.75		92.13		89.77		95.01		98.78	

* Includes exhaust hydrocarbons not reported in detailed analysis.

TABLE A-4. - Detailed Hydrocarbon Analysis
Stationary Engine A, ppmC --
Continued

Peak No.	Compound	Accumulated mileage.. 963		5,000		6,400		8,250		[illegible]	
	Fuel..... EPA			FPA + F-310		FPA + F-310		FPA + F-310		FPA + F-1	
		CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	[illegible] with scrubber
1	Methane.....	7.23	7.23	7.85	7.85	7.49	7.49	7.77	7.77	7.09	7.09
2	Ethylene.....	11.46	-	14.57	-	10.99	-	11.47	-	11.84	-
3	Ethane.....	.87	.87	1.18	1.18	.87	.87	.92	.92	.90	.90
4	Acetylene.....	10.65	-	12.07	-	9.95	-	10.97	-	10.48	-
5	Propylene, propane.....	5.00	.06	5.77	.26	4.36	.18	3.84	.04	5.22	.06
6	Isobutane.....	.64	.11	.33	.16	.22	.06	-	.04	-	.05
7	Butene-1, isobutylene.....	2.29	-	3.15	-	2.49	-	2.46	-	2.64	-
8	n-Butane, 1,3-butadiene.....	2.95	1.96	3.64	2.26	2.51	1.49	2.18	1.21	2.54	1.42
9	trans-2-Butene.....	.48	-	.43	-	.31	-	.22	-	.33	-
10	cis-2-Butene.....	.57	-	.51	-	.39	-	.36	-	.46	-
11	3-Methyl-1-butene.....	.19	-	.09	-	.07	-	.03	-	.07	-
12	Isopentane.....	3.02	3.02	3.43	3.43	2.44	2.44	1.99	1.99	2.29	2.29
13	Pentene-1.....	.14	-	.11	-	.08	-	.07	-	.08	-
14	n-Pentane, 2-methyl-1-butene	2.32	2.35	2.74	2.62	2.00	1.86	1.70	1.51	1.88	1.72
15	trans-2-Pentene.....	.25	-	.24	-	.16	-	.14	-	.16	-
16	cis-2-Pentene.....	.11	-	.11	-	.07	-	.08	-	.07	-
17	2-Methyl-2-butene.....	.31	-	.34	-	.25	-	.23	-	.26	-
18	Cyclopentane, 3-methyl-1-pentene.....	4.14	4.16	5.10	4.30	3.63	3.36	3.08	2.70	3.35	2.95
19	2,3-Dimethylbutane.....	.34	.34	.35	.35	.25	.25	.20	.20	.24	.24
20	2-Methylpentane, 2,3-dimethyl-1-butene.....	.47	.33	.44	.37	.24	.24	.20	.19	.23	.23
21	3-Methylpentane.....	.25	.17	.20	.24	.14	.09	.11	.08	.15	.10
22	1-Hexene, 2-ethyl-1-butene..	.25	-	.17	-	.12	-	.08	-	.12	-
23	n-Hexane, cis-3-hexene.....	.16	.11	.15	.19	.09	.08	.10	.07	.10	.07
24	Methylcyclopentane, 3-methyltrans-2-pentene...	.23	.10	.24	.14	.15	.08	.11	.07	.12	.07
25	2,4-Dimethylpentane.....	.17	.08	.12	.11	.07	.07	.05	.05	.05	.06
26	Benzene, cyclohexane.....	3.05	.01	4.29	.02	3.31	.04	3.31	.02	3.29	.02
27	Cyclohexene, 2,3-dimethylpentane, 2-methylhexane.....	2.01	1.89	2.55	2.23	1.87	1.80	1.53	1.33	1.71	1.48
28	3-Methylhexane.....	.36	.33	.47	.40	.39	.29	.28	.24	.34	.26
29	Isooctane.....	3.89	3.89	4.61	4.61	3.42	3.42	2.68	2.68	3.01	3.01
30	n-Heptane.....	.55	.49	.66	.59	.47	.39	.40	.34	.44	.38
31	Methylcyclohexane.....	.28	.22	.36	.29	.24	.20	.20	.17	.22	.19
32	2,4-Dimethylhexane, 2,5-dimethylhexane.....	.59	.56	.79	.77	.53	.49	.39	.33	.45	.46
33	2,3,4-Trimethylpentane.....	.29	.29	.40	.39	.26	.26	.21	.18	.22	.23
34	2,3,3-Trimethylpentane.....	.15	.15	.22	.22	.11	.11	.08	.08	.09	.09
35	Toluene, 2,3-dimethylhexane.	10.11	.19	14.82	.26	11.11	.15	10.02	.11	10.61	.15
36	2-Methylheptane.....	1.29	.51	1.70	.76	1.21	.45	1.00	.32	1.09	.41
37	3-Methylheptane.....	.83	.54	1.14	.81	.76	.46	.62	.33	.68	.41
38	2,2,5-Trimethylhexane.....	.08	.04	.13	.07	.07	.03	.06	.02	.06	.04
39	n-Octane.....	.43	.45	.70	.67	.40	.31	.30	.25	.35	.29
40	2,3 5-Trimethylhexane.....	.04	.02	.05	.07	-	-	.01	.01	.01	.01
41	2,5-Dimethylheptane, 3,5-dimethylheptane.....	.12	.07	.21	.26	.08	.09	.06	.09	.06	.09
42	Ethylbenzene.....	.74	.04	1.20	.40	.82	.03	.72	.03	.78	.07
43	p-Xylene, m-xylene.....	2.27	.16	3.65	.32	2.67	.17	2.26	.11	2.39	.17
44	o-Xylene.....	1.24	-	2.00	-	1.34	-	1.20	-	1.33	-
45	n-Propylbenzene.....	.10	-	.18	-	.07	-	.12	-	.17	-
46	1-Methyl-3-ethylbenzene.....	.56	.02	.95	.05	.67	.07	.57	.04	.67	.06
47	1-Methyl-2-ethylbenzene.....	.22	.03	.41	.07	.26	.04	.25	.02	.30	.03
48	Mesitylene.....	.19	-	.39	-	.22	.04	.21	.02	.26	.03
49	1,2,4-Trimethylbenzene.....	1.12	-	1.77	-	1.03	.01	.96	-	1.09	-
50	sec-Butylbenzene, n-decane..	.32	.06	.51	.09	.32	.06	.39	.03	.42	.04
	*Total hydrocarbons by GC....	92.51		126.82		89.54		82.53		89.43	

* Includes exhaust hydrocarbons not reported in detailed analysis.

TABLE A-4. - Detailed Hydrocarbon Analysis
Stationary Engine A, ppmC--
Continued

Peak No.	Compound	Accumulated mileage...	6,090		8,180		9,140		10,040		10,060	
		Fuel.....	Indolene + AK33X		Indolene + AK33X		Indolene + AK33X		Indolene + AK33X		Indolene + AK33X	
			CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber
1	Methane.....		9.50	9.50	9.00	9.00	8.61	8.61	8.66	8.66	7.37	7.37
2	Ethylene.....		14.82	-	13.85	-	12.25	-	12.88	-	14.44	-
3	Ethane.....		1.85	1.85	1.87	1.87	1.46	1.38	1.43	1.43	1.76	1.76
4	Acetylene.....		15.70	-	14.24	-	13.04	-	13.85	-	12.73	-
5	Propylene, propane.....		8.67	.05	8.18	.05	7.45	.19	6.72	.22	8.00	.18
6	Isobutane.....		1.10	.17	1.01	.18	1.14	.40	.63	.48	.80	.19
7	Butene-1, isobutylene.....		4.09	-	3.80	-	3.68	-	3.74	-	4.25	-
8	n-Butane, 1,3-butadiene.....		3.34	1.79	3.48	1.58	5.63	4.06	5.12	3.47	3.58	1.86
9	trans-2-Butene.....		.78	-	.79	-	.85	-	.70	-	.74	-
10	cis-2-Butene.....		1.04	-	1.00	-	.99	-	.94	-	.90	-
11	3-Methyl-1-butene.....		.30	-	.30	-	.37	-	.29	-	.34	-
12	Isopentane.....		2.18	2.18	2.06	2.06	5.36	5.36	4.75	4.75	2.50	2.50
13	Pentene-1.....		.19	-	.08	-	.29	-	.22	-	.15	-
14	n-Pentane, 2-methyl-1-butene		1.02	.59	.93	.61	2.20	1.67	1.98	1.56	1.15	.68
15	trans-2-Pentene.....		.42	-	.36	-	.76	-	.74	-	.47	-
16	cis-2-Pentene.....		.21	-	.14	-	.35	-	.39	-	.20	-
17	2-Methyl-2-butene.....		.75	-	.68	-	1.27	-	1.26	-	.83	-
18	Cyclopentane, 3-methyl-1-pentene.....		.18	.05	.08	.05	.22	.14	.22	.16	.17	.05
19	2,3-Dimethylbutane.....		.69	.69	.66	.66	1.71	1.71	1.53	1.53	.85	.85
20	2-Methylpentane, 2,3-dimethyl-1-butene.....		.82	.70	.68	.65	1.83	1.69	1.66	1.55	.81	.82
21	3-Methylpentane.....		.46	.45	.39	.40	1.03	1.15	.92	1.09	.56	.53
22	1-Hexene, 2-ethyl-1-butene..		.15	-	.08	-	.27	-	.22	-	.23	-
23	n-Hexane, cis-3-hexene.....		.35	.34	.34	.32	.88	1.04	.75	.92	.44	.41
24	Methylcyclopentane, 3-methyltrans-2-pentene...		.35	.24	.34	.23	.86	.72	.74	.60	.34	.29
25	2,4-Dimethylpentane.....		.68	.63	.71	.62	1.71	1.79	1.50	1.46	.91	.78
26	Benzene, cyclohexane.....		5.49	.08	5.38	.09	5.07	.29	5.30	.22	5.01	.10
27	Cyclohexene, 2,3-dimethylpentane, 2-methylhexane.....		1.28	.98	1.22	1.00	2.79	2.48	2.48	2.10	1.54	1.17
28	3-Methylhexane.....		.44	.37	.51	.37	.95	.94	.83	.77	.50	.43
29	Isooctane.....		3.53	3.53	3.56	3.44	8.09	8.09	7.09	7.09	4.20	4.20
30	n-Heptane.....		.40	.31	.34	.30	.97	.82	.71	.57	.58	.35
31	Methylcyclohexane.....		.20	.15	.19	.15	.50	.43	.35	.29	.28	.18
32	2,4-Dimethylhexane, 2,5-dimethylhexane.....		.95	.91	.93	.99	2.42	2.53	2.07	2.14	1.25	1.22
33	2,3,4-Trimethylpentane.....		1.20	1.28	1.28	1.27	3.39	3.31	2.96	2.94	1.62	1.64
34	2,3,3-Trimethylpentane.....		1.37	1.37	1.49	1.49	3.92	3.92	3.37	3.37	1.91	1.91
35	Toluene, 2,3-dimethylhexane.		15.22	.44	14.78	.45	21.44	1.15	20.57	.95	16.67	.56
36	2-Methylheptane.....		-	.23	.92	.25	2.09	.67	1.56	.52	-	.30
37	3-Methylheptane.....		.60	.18	.41	.21	1.09	.64	.74	.40	.64	.24
38	2,2,5-Trimethylhexane.....		.86	.48	.69	.52	1.56	1.30	1.21	1.04	.97	.63
39	n-Octane.....		.14	.11	.10	.11	.32	.32	.23	.21	.17	.10
40	2,3,5-Trimethylhexane.....		.09	.05	.04	.06	.20	.18	.12	.12	.12	.07
41	2,5-Dimethylheptane, 3,5-dimethylheptane.....		.07	.04	.04	.05	.11	.19	.08	.08	.10	.05
42	Ethylbenzene.....		1.24	.01	1.31	.03	1.65	.11	1.60	.04	1.46	.02
43	p-Xylene, m-xylene.....		2.59	.05	2.69	.07	3.80	.17	3.58	.09	2.78	.06
44	o-Xylene.....		1.84	.06	1.95	.12	2.28	.26	2.23	.10	2.05	.06
45	n-Propylbenzene.....		.14	-	.17	-	.31	-	.28	-	.28	-
46	1-Methyl-3-ethylbenzene.....		1.09	.01	.89	.01	1.35	.03	1.91	.02	1.47	.01
47	1-Methyl-2-ethylbenzene.....		.36	.04	.34	.05	.59	.18	.55	.13	.48	.06
48	Mesitylene.....		.36	.01	.36	.02	.61	.09	.58	.05	.49	.01
49	1,2,4-Trimethylbenzene.....		2.18	.03	2.00	.08	2.92	.21	2.67	.10	3.31	.05
50	sec-Butylbenzene, n-decane..		-	.03	-	.04	.61	.15	.49	.06	-	.03
	Total hydrocarbons by GC....		120.24		115.23		158.19		147.40		125.67	

* Includes exhaust hydrocarbons not reported in detailed analysis.

TABLE A-5. - Detailed Hydrocarbon Analysis
Stationary Engine B, ppmC

Peak No.	Compound	Accumulated mileage.. Fuel.....	4,000 Indolene + AK33X		4,930 Indolene + AK33X		6,164 Indolene + AK33X		8,515 EPA + AK33X		4,350 EPA + F-310	
			CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber
1	Methane		7.11	7.11	9.70	9.70	11.24	-	8.03	8.03	10.36	10.36
2	Ethylene		11.28	-	13.03	-	15.47	-	20.34	-	15.08	-
3	Ethane		1.18	1.18	1.46	1.46	1.81	-	1.60	1.60	1.05	1.05
4	Acetylene		10.39	-	12.28	-	15.42	-	11.97	-	15.14	-
5	Propylene, propane		6.70	.07	9.06	.10	10.38	-	9.03	.71	7.18	.07
6	Isobutane		.40	.18	.92	.17	1.03	-	.66	.45	.65	.10
7	Butene-1, isobutylene		3.76	-	4.71	-	4.97	-	5.32	-	3.86	-
8	n-Butane, 1,3-butadiene		3.26	1.85	3.54	1.80	3.46	-	5.59	3.43	4.05	2.52
9	trans-2-Butene		.59	-	.89	-	.74	-	.75	-	.56	-
10	cis-2-Butene		.72	-	1.23	-	-	-	.97	-	.67	-
11	3-Methyl-1-butene		.22	-	.37	-	.23	-	.26	-	.19	-
12	Isopentane		2.52	2.52	2.71	2.71	2.43	-	5.23	5.27	3.90	3.90
13	Pentene-1		.13	-	.25	-	.09	-	20	-	.18	-
14	n-Pentane, 2-methyl-1-butene		1.17	.73	1.33	.88	1.15	-	4.24	4.08	3.14	2.92
15	trans-2-Pentene		.46	-	.57	-	.44	-	.42	-	.29	-
16	cis-2-Pentene		.20	-	.28	-	.16	-	.22	-	.15	-
17	2-Methyl-2-butene		.86	-	1.02	-	.89	-	.65	-	.47	-
18	Cyclopentane, 3-methyl-1-pentene		.15	.06	.22	.10	.12	-	7.50	6.06	5.63	5.45
19	2,3-Dimethylbutane		.83	.83	.94	.94	.86	-	.57	.57	.45	.45
20	2-Methylpentane, 2,3-dimethyl-1-butene		.82	.81	1.17	.97	.91	-	.56	.65	.43	.42
21	3-Methylpentane		.53	.47	.66	.68	.51	-	.43	.49	.31	.20
22	1-Hexene, 2-ethyl-1-butene		.15	-	.25	-	.09	-	.39	-	.29	-
23	n-Hexane, cis-3-hexene		.43	.42	.51	.61	.45	-	.29	.43	.20	.14
24	Methylcyclopentane, 3-methyltrans-2-pentene		.44	.30	.54	.40	.46	-	.38	.18	.27	.16
25	2,4-Dimethylpentane		.88	.79	1.06	1.04	.91	-	.27	.15	.17	.12
26	Benzene, cyclohexane		4.89	.10	5.80	.24	6.41	-	4.96	.05	4.49	.03
27	Cyclohexene, 2,3-dimethylpentane, 2-methylhexane		1.39	1.21	1.68	1.40	1.70	-	3.88	3.31	2.87	2.40
28	3-Methylhexane		.54	.45	.58	.53	.66	-	.73	.63	.54	.44
29	Isooctane		4.34	4.34	4.86	4.86	5.09	-	7.26	7.26	4.90	4.90
30	n-Heptane		.46	.37	.45	.50	.47	-	1.03	.89	.89	.63
31	Methylcyclohexane		.24	.17	.21	.25	.22	-	.53	.44	.46	.32
32	2,4-Dimethylhexane, 2,5-dimethylhexane		1.40	1.44	1.62	1.65	1.57	-	1.22	1.16	.89	.75
33	2,3,4-Trimethylpentane		1.70	1.67	1.98	1.95	2.01	-	.62	.60	.43	.41
34	2,3,3-Trimethylpentane		1.96	1.96	2.23	2.23	2.24	-	.31	.31	.23	.23
35	Toluene, 2,3-dimethylhexane		19.70	.56	19.16	.65	22.42	-	22.29	.36	16.30	.31
36	2-Methylheptane		1.11	.32	1.32	.37	-	-	2.46	1.20	2.06	.94
37	3-Methylheptane		.35	.26	.64	.30	.78	-	1.65	1.24	1.34	.92
38	2,2,5-Trimethylhexane		.78	.65	.93	.76	1.06	-	.16	.08	.16	.07
39	n-Octane		.16	.14	.16	.21	.17	-	.93	.81	.75	.69
40	2,3,5-Trimethylhexane		.09	.11	.08	.10	.08	-	.05	.02	.06	.03
41	2,5-Dimethylheptane, 3,5-dimethylheptane		.03	.11	.06	.07	.05	-	.23	.23	.19	.19
42	Ethylbenzene		1.23	.02	1.59	.03	1.75	-	1.72	.11	1.32	.18
43	p-Xylene, m-xylene		2.83	.06	3.75	.08	4.08	-	5.28	.44	4.24	.40
44	o-Xylene		1.85	.05	2.30	.07	2.64	-	2.68	-	2.18	-
45	n-Propylbenzene		1.18	-	.29	-	.24	-	.16	-	.22	-
46	1-Methyl-3-ethylbenzene		1.31	.01	1.87	.02	1.47	-	1.36	.17	1.23	.26
47	1-Methyl-2-ethylbenzene		.40	.05	.60	.12	.59	-	.49	.10	.48	.15
48	Mesitylene		.40	.01	.57	.05	.56	-	.41	.11	.42	.11
49	1,2,4-Trimethylbenzene		2.21	.04	2.85	.13	3.26	-	1.93	-	1.75	-
50	sec-Butylbenzene, n-decane		.10	.03	.50	.10	.48	-	.42	.11	.56	.18
	*Total hydrocarbons by GC ...		114.98		137.23		144.58		163.93		138.36	

* Includes exhaust hydrocarbons not reported in detailed analysis.

TABLE A-5. - Detailed Hydrocarbon Analysis
Stationary Engine B, ppmC--
Continued

Peak No.	Compound	Accumulated mileage..	5,540		6,125		7,070		7,930	
		Fuel.....	EPA + F-310		EPA + F-310		EPA + F-310		EPA + F-310	
			CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber	CVS exhaust	CVS exhaust with scrubber
1	Methane.....		11.36	11.36	8.31	8.31	7.25	7.25	7.39	7.39
2	Ethylene.....		14.14	-	11.85	-	11.87	-	11.75	-
3	Ethane.....		.99	.99	.77	.77	.75	.75	.64	.64
4	Acetylene.....		15.77	-	11.41	-	9.94	-	9.89	-
5	Propylene, propane.....		6.91	.07	5.68	.06	4.39	.06	5.85	.07
6	Isobutane.....		.78	.09	.89	.21	.16	.06	.66	.07
7	Butene-1, isobutylene.....		3.63	-	3.00	-	2.80	-	3.15	-
8	n-Butane, 1,3-butadiene.....		3.47	1.92	5.67	4.37	2.12	1.13	2.65	1.38
9	trans-2-Butene.....		.63	-	.56	-	.33	-	.52	-
10	cis-2-Butene.....		.81	-	.69	-	.21	-	.68	-
11	3-Methyl-1-butene.....		.33	-	.22	-	.04	-	.21	-
12	Isopentane.....		3.27	3.27	4.31	4.31	1.95	1.95	2.48	2.48
13	Pentene-1.....		.12	-	.11	-	.10	-	.11	-
14	n-Pentane, 2-methyl-1-butene..		2.67	2.53	3.14	3.00	1.62	1.52	2.08	1.92
15	trans-2-Pentene.....		.25	-	.25	-	.18	-	.19	-
16	cis-2-Pentene.....		.12	-	.12	-	.08	-	.09	-
17	2-Methyl-2-butene.....		.36	-	.36	-	.25	-	.32	-
18	Cyclopentane, 3-methyl-1-pentene.....		5.01	4.61	5.22	4.41	3.16	3.10	3.81	3.38
19	2,3-Dimethylbutane.....		.38	.38	.37	.37	.26	.26	.31	.31
20	2-Methylpentane, 2,3-dimethyl-1-butene.....		.49	.39	.45	.37	.37	.25	.31	.32
21	3-Methylpentane.....		.22	.18	.21	.18	.18	.10	.25	.18
22	1-Hexene, 2-ethyl-1-butene....		.19	-	.15	-	.17	-	.23	-
23	n-Hexane, cis-3-hexene.....		.16	.12	.14	.12	.12	.08	.17	.17
24	Methylcyclopentane, 3-methyltrans-2-pentene.....		.23	.12	.20	.10	.16	.09	.21	.14
25	2,4-Dimethylpentane.....		.14	.10	.11	.09	.09	.07	.13	.15
26	Benzene, cyclohexane.....		4.25	.04	3.43	.02	2.87	.02	3.10	.05
27	Cyclohexene, 2-3-dimethylpentane, 2-methylhexane.....		2.59	2.39	2.37	2.20	1.84	1.59	2.06	1.88
28	3-Methylhexane.....		.47	.43	.43	.39	.33	.28	.37	.35
29	Isooctane.....		4.82	4.82	4.43	4.43	3.25	3.25	3.82	3.82
30	n-Heptane.....		.74	.59	.65	.54	.57	.39	.58	.45
31	Methylcyclohexane.....		.39	.30	.35	.30	.32	.21	.29	.23
32	2,4-Dimethylhexane, 2,5-dimethylhexane.....		.76	.76	.71	.68	.53	.49	.61	.56
33	2,3,4-Trimethylpentane.....		.38	.38	.36	.35	.26	.26	.31	.31
34	2,3,3-Trimethylpentane.....		.19	.19	.18	.18	.12	.12	.15	.15
35	Toluene, 2,3-dimethylhexane...		15.00	.22	13.36	.20	10.74	.14	11.68	.18
36	2-Methylheptane.....		1.88	.77	1.64	.69	1.49	.54	1.51	.65
37	3-Methylheptane.....		1.19	.81	1.06	.69	.89	.53	.95	.63
38	2,2,5-Trimethylhexane.....		.13	.05	.12	.03	.10	.03	.11	.05
39	n-Octane.....		.64	.57	.53	.48	.35	.32	.49	.43
40	2,3,5-Trimethylhexane.....		.03	.02	-	-	-	-	.02	-
41	2,5-Dimethylheptane, 3,5-dimethylheptane.....		.13	.17	.10	.10	.07	.07	.10	.10
42	Ethylbenzene.....		1.14	.10	1.00	.06	.80	.03	.85	.05
43	p-Xylene, m-xylene.....		3.86	.34	3.45	.23	2.65	.15	2.85	.21
44	o-Xylene.....		1.92	-	1.67	-	1.40	-	1.43	-
45	n-Propylbenzene.....		.14	-	.10	-	.07	-	.12	-
46	1-Methyl-3-ethylbenzene.....		1.04	.27	.93	.09	.67	.06	.77	.12
47	1-Methyl-2-ethylbenzene.....		.40	.08	.35	.05	.26	.03	.30	.07
48	Mesitylene.....		.35	.12	.32	.06	.23	.03	.29	.09
49	1,2,4-Trimethylbenzene.....		1.42	.06	1.34	-	1.15	-	1.64	-
50	sec-Butylbenzene, n-decane....		.39	.13	.36	.05	.18	.05	.52	.10
	*Total hydrocarbons by GC.....		126.48		112.15		88.10		97.76	

* Includes exhaust hydrocarbons not reported in detailed analysis.

TABLE A-6. - Effect of mileage accumulation on exhaust emissions
Stationary Engine A

Miles	Test temp., °F	Barometric pressure, mmHg	Fuel consumed, lbs/test	Emissions, grams/mile							
				CO	HC	NO_x, uncorrected	NO_x, FTP corrected	Total aldehydes	MCMT x 10^6	Inorganic Mn x 10^6	MCMT percent emitted
CLEAR FUEL											
0	100	750.5	4.30	22.0	2.18	2.34	3.42	-	-	-	-
1,080	76	755.6	4.23	23.5	1.97	2.53	2.83	-	-	-	-
1,400	85	741.5	4.05	23.4	1.39	2.47	3.12	-	-	-	-
2,080	91	749.7	4.17	22.5	1.51	2.35	3.18	-	-	-	-
2,930	83	745.5	4.21	18.6	1.24	2.53	3.38	-	-	-	-
3,900	90	742.5	4.29	17.9	-	2.59	3.66	-	-	-	-
4,950	86	743.3	4.11	17.5	1.29	2.45	2.86	-	0.00	-	0.000
CHANGE TO FUEL CONTAINING AK33X ADDITIVE - 0.125 gMn/GAL											
5,000	85	744.3	4.23	21.6	1.62	2.51	2.73	0.074	0.00	992	0.000
6,090	95	740.0	4.34	22.6	1.85	2.72	4.02	.074	.00	1,747	.000
8,180	83	745.0	4.80	18.9	1.80	2.70	3.14	.103	.37	2,127	.003
9,140	77	747.8	4.30	16.1	2.50	2.93	3.07	.125	2.46	2,527	.021
10,040	84	742.7	4.14	15.9	2.72	2.78	3.79	.148	2.99	1,691	.027
NEW SPARK PLUGS INSTALLED											
1,006	84	747.6	4.16	15.0	2.11	3.00	3.74	0.146	1.02	1,111	0.009
NEW TEST CYCLE											
0	88	741.1	4.61	26.3	1.64	2.05	2.48	-	-	-	-
963	84	744.0	4.25	19.8	1.39	2.01	2.79	-	-	-	-
1,120	85	743.1	4.47	17.7	1.41	2.28	2.32	-	-	-	-
2,930	80	743.2	3.85	27.2	1.86	2.09	2.76	-	-	-	-
4,012	76	751.9	4.07	27.6	1.84	2.66	2.65	-	-	-	-
4,940	94	746.4	3.73	23.6	1.86	2.27	2.97	-	-	-	-
CHANGE TO FUEL CONTAINING F-310 ADDITIVE - 14.2 ML/GAL											
5,000	82	748.2	4.02	21.0	1.79	2.52	3.12	0.108	-	-	-
6,400	60	740.0	4.23	29.3	1.50	2.56	2.18	.052	-	-	-
8,250	68	744.2	4.20	27.4	1.50	3.00	2.61	.071	-	-	-
9,130	75	757.0	4.07	24.9	1.44	2.76	2.56	.101	-	-	-

TABLE A-7. - Effect of mileage accumulation on exhaust emissions
Stationary Engine B

Miles	Test temp., °F	Barometric pressure mmHg	Fuel consumed, lbs/test	Emissions, grams/mile							
				CO	HC	NO_x, uncorrected	NO_x, FTP corrected	Total aldehydes	MCMT x 10^6	Inorganic Mn x 10^6	MCMT percent emitted
CLEAR FUEL											
0	80	747.1	2.96	18.2	1.37	1.56	1.79	-	-	-	-
1,240	90	749.6	4.65	16.1	1.59	2.42	2.75	-	-	-	-
2,030	93	749.9	4.04	16.5	1.62	1.97	2.45	-	-	-	-
3,990	78	746.4	4.44	20.5	1.79	2.33	2.86	-	-	-	-
CHANGE TO FUEL CONTAINING AK33X ADDITIVE - 0.125 gMn/GAL											
4,000	85	755.0	4.56	23.0	1.82	2.67	3.57	0.109	Trace	1,031	Trace
4,930	75	754.0	4.07	35.0	2.17	2.50	2.59	.164	<0.50	1,267	<0.005
5,870	74	747.8	4.29	25.5	1.85	2.79	2.77	.130	.35	1,746	.003
8,515	80	746.0	4.96	24.9	2.52	2.80	2.89	.130	.58	608	.004
9,085	71	745.3	4.79	36.7	2.98	3.29	3.09	-	.87	2,266	.008
NEW TEST CYCLE											
0	76	740.0	4.89	25.1	1.68	2.64	2.61	-	-	-	-
1,420	66	744.2	4.88	38.4	1.98	3.72	3.27	-	-	-	-
2,840	71	740.5	4.92	33.8	2.15	3.49	3.59	-	-	-	-
3,650	74	748.7	5.08	38.9	2.09	4.15	3.84	-	-	-	-
4,050	78	739.0	5.04	34.8	1.73	3.64	4.27	-	-	-	-
CHANGE TO FUEL CONTAINING F-310 ADDITIVE - 14.2 ML/GAL											
4,350	78	739.1	4.89	32.8	1.81	3.82	4.36	0.091	-	-	-
5,540	70	743.3	4.91	45.3	1.77	3.96	3.87	.089	-	-	-
6,125	76	749.3	4.98	38.6	1.66	4.45	4.08	.094	-	-	-
7,070	71	741.4	5.24	34.1	1.55	3.99	4.00	.103	-	-	-
7,930	80	755.7	5.39	43.0	1.66	4.82	4.10	.092	-	-	-

TABLE A-8. - Effect of mileage accumulation on exhaust emissions
F-310 Vehicle

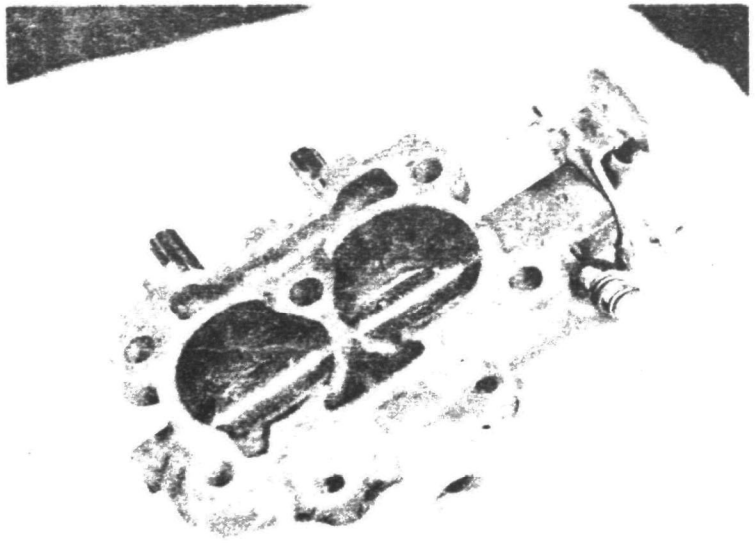
Miles	Test temp., °F	Barometric pressure mmHg	Fuel consumed, lbs/test	Emissions, grams/mile							
				CO	HC	NO_x, uncorrected	NO_x, FTP corrected	Total aldehydes	MCMT x 10^6	Inorganic Mn x 10^6	MCMT percent emitted
CLEAR FUEL											
0	72	748.2	4.60	59.5	2.76	4.78	4.55	-	-	-	-
1,710	67	745.0	3.46	69.6	2.96	5.46	5.08	-	-	-	-
2,743	83	745.9	4.61	65.5	2.62	4.40	5.33	-	-	-	-
4,030	82	748.8	4.92	65.6	2.51	3.86	5.06	-	-	-	-
4,700	93	741.6	4.62	62.1	2.77	4.44	5.81	-	-	-	-
CHANGE TO FUEL CONTAINING F-310 ADDITIVE - 14.2 ML/GAL											
4,750	81	745.9	4.77	64.7	3.11	4.00	4.91	0.086	-	-	-
6,070	86	742.5	4.92	75.8	2.85	4.02	6.51	.093	-	-	-
7,420	94	749.6	4.98	62.2	2.41	4.40	6.45	.065	-	-	-
8,550	79	743.2	4.77	58.0	2.39	4.43	5.58	.089	-	-	-
9,150	80	742.2	4.43	63.4	2.73	3.60	4.57	.072	-	-	-
9,550	84	740.0	4.62	63.2	2.66	3.59	4.99	.077	-	-	-
10,550	76	744.0	4.66	66.5	2.66	3.81	4.60	.090	-	-	-
11,880	66	751.1	4.70	52.7	2.58	5.03	5.63	.105	-	-	-
12,840	66	737.9	4.70	45.7	2.53	5.63	5.25	.054	-	-	-
13,940	66	744.0	4.67	49.7	2.53	5.48	5.00	.086	-	-	-

TABLE A-9. - Effect of mileage accumulation on exhaust emissions
AK33X Vehicle

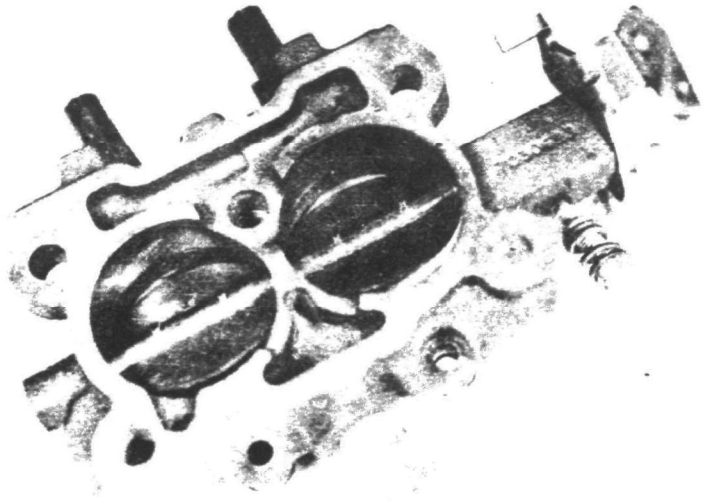
Miles	Test temp., °F	Barometric pressure mmHg	Fuel consumed, lbs/test	Emissions, grams/mile							
				CO	HC	NO_x, uncorrected	NO_x, FTP corrected	Total aldehydes	MCMT x 10^6	Inorganic Mn x 10^6	MCMT percent emitted
CLEAR FUEL											
0	86	741.1	5.07	74.4	3.09	4.34	4.85	-	-	-	-
1,600	80	744.5	4.94	74.4	3.43	5.65	5.96	-	-	-	-
1,910	77	739.0	4.74	79.5	3.72	4.68	4.93	-	-	-	-
3,190	83	745.9	4.58	59.3	2.89	4.89	5.93	-	-	-	-
4,010	80	747.7	5.24	78.3	2.80	4.51	6.09	-	-	-	-
4,700	90	748.0	4.16	63.5	2.92	3.97	5.16	-	-	-	-
CHANGE TO FUEL CONTAINING AK33X ADDITIVE - 0.125 gMn/GAL											
4,740	90	750.0	4.86	61.9	3.02	4.03	5.88	0.088	-	915	-
5,305	80	746.6	4.35	57.4	2.98	4.57	5.48	-	1.86	1,857	0.016
7,170	87	744.4	4.89	79.2	2.87	4.54	5.77	.089	0.80	905	.006
8,030	81	744.1	4.89	57.8	3.69	4.43	5.68	.109	4.97	1,440	.037
9,434	60	752.0	5.02	69.7	4.29	5.53	5.04	.105	4.63	846	.042
10,353	70	744.0	4.96	70.3	3.97	4.70	5.00	.126	1.29	800	.010
11,390	62	750.4	4.66	56.3	3.52	5.45	5.45	.096	.82	1,452	.007
12,140	55	740.3	4.72	58.8	3.47	5.59	5.59	.096	1.70	500	.013
12,740	76	742.5	4.56	51.8	3.63	4.84	5.31	.085	2.98	1,471	.024
14,050	63	755.5	5.00	56.4	3.52	6.22	5.53	.093	1.44	1,095	.011

TABLE A-10.- Effect of mileage accumulation on exhaust emissions
Control Vehicle

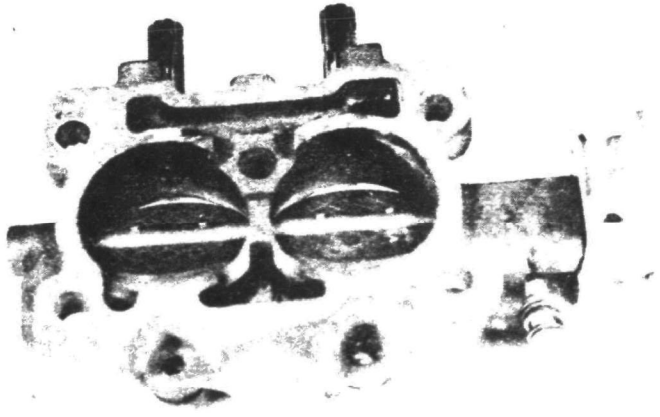
Miles	Test temp., °F	Barometric pressure mmHg	Fuel consumed, lbs/test	Emissions, grams/mile							MCMT percent emitted
				CO	HC	NO_x, uncorrected	NO_x, FTP corrected	Total aldehydes	MCMT x 10^6	Inorganic Mn x 10^6	
CLEAR FUEL											
0	65	748.6	4.76	46.7	2.92	5.18	4.62	-	-	-	-
1,400	67	745.0	4.59	48.3	2.65	5.28	4.78	-	-	-	-
2,250	83	745.9	4.68	59.2	2.81	4.27	5.18	-	-	-	-
3,200	85	748.8	5.03	66.6	2.69	4.51	5.97	-	-	-	-
4,550	95	748.4	4.89	63.6	2.78	3.70	5.60	-	-	-	-
5,950	85	747.8	4.73	65.7	2.99	4.52	6.80	0.103	-	-	-
7,700	92	746.0	5.00	82.7	2.07	4.28	5.97	.093	-	-	-
8,725	84	744.1	4.77	67.3	2.64	3.91	5.65	.083	-	-	-
9,865	80	742.5	4.34	70.2	2.65	4.23	5.01	.069	-	-	-
10,320	70	744.6	4.27	63.3	2.43	4.08	4.39	.086	-	-	-
11,200	89	740.2	5.03	80.2	2.96	4.17	6.47	.092	-	-	-
11,725	74	748.0	4.41	57.8	2.30	4.78	4.86	.096	-	-	-
12,490	60	740.3	4.63	52.9	2.00	5.12	5.29	-	-	-	-
13,490	82	737.5	4.57	59.8	2.28	4.28	5.03	-	-	-	-
13,840	65	740.0	4.50	53.0	2.47	5.32	4.85	.066	-	-	-



AK33X vehicle

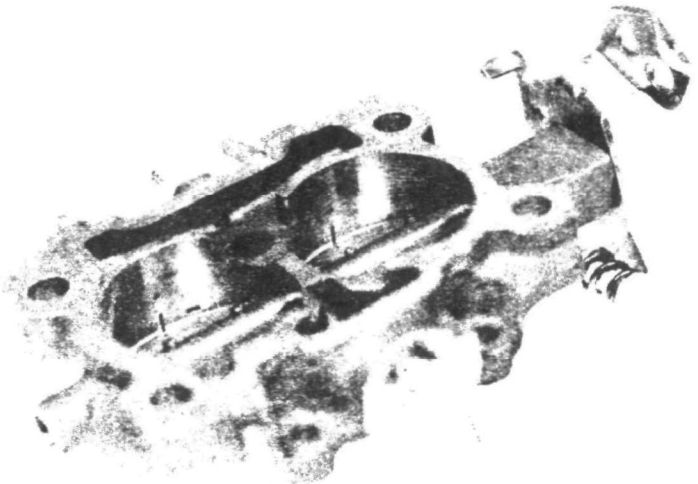


F310 vehicle



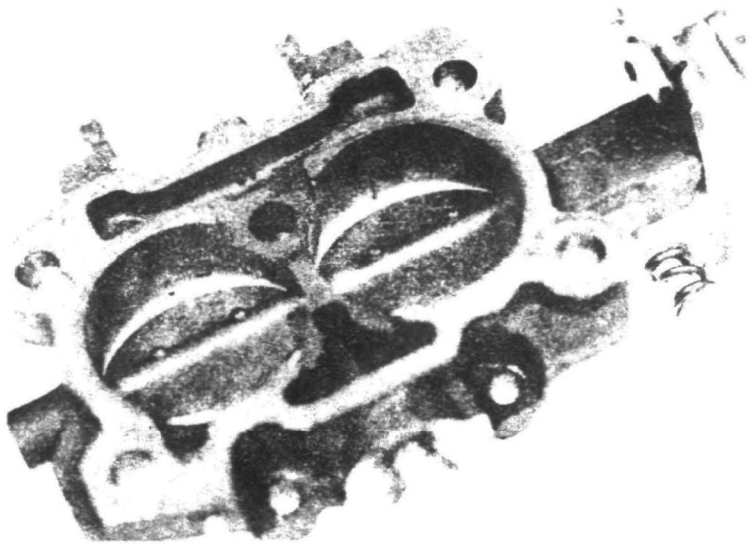
Control vehicle

FIGURE B-1.-Carburetor bases for the AK33X, F310, and control vehicles.



AK33X engine A

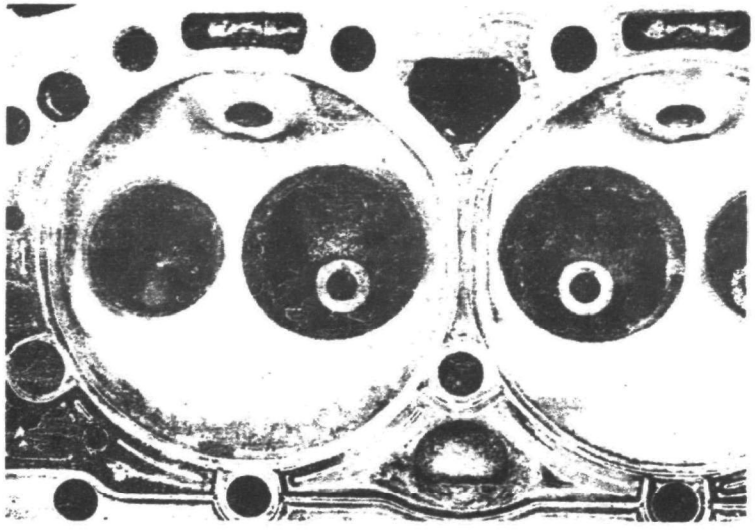
AK33X engine B



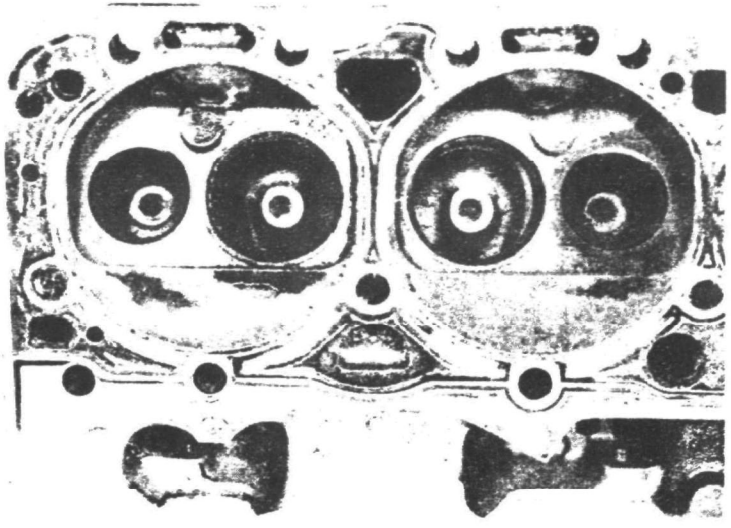
F310 engine A

F310 engine B

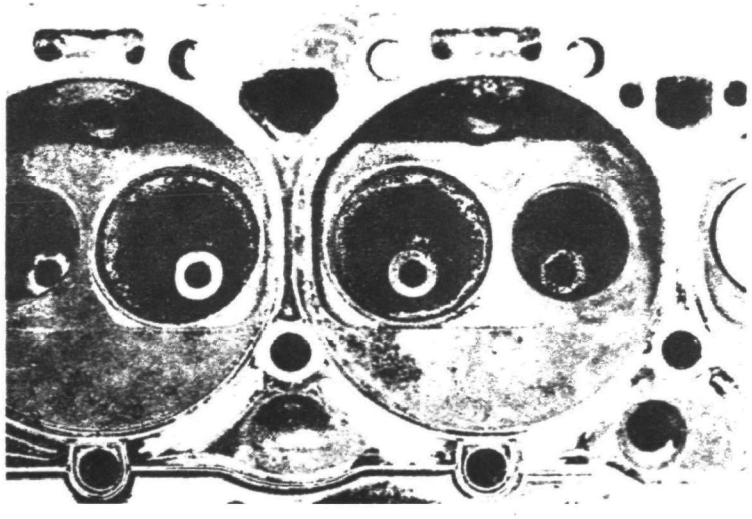
FIGURE B-2.- Carburetor bases for the stationary engines.



AK33X vehicle

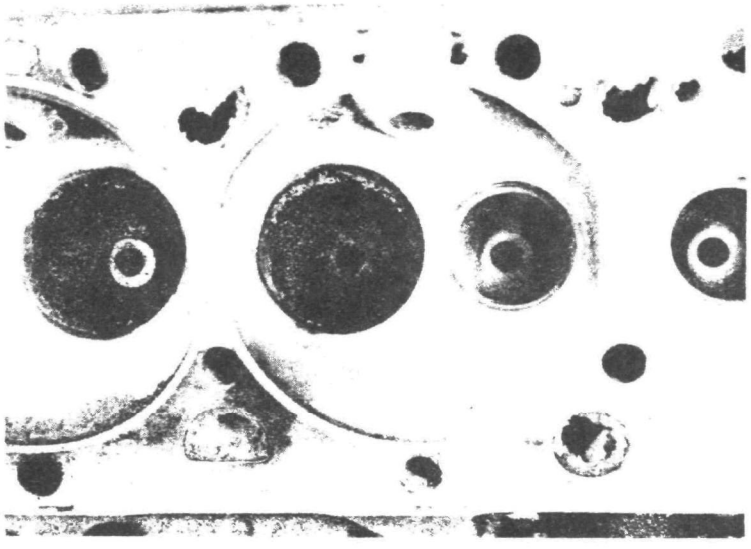


F310 vehicle

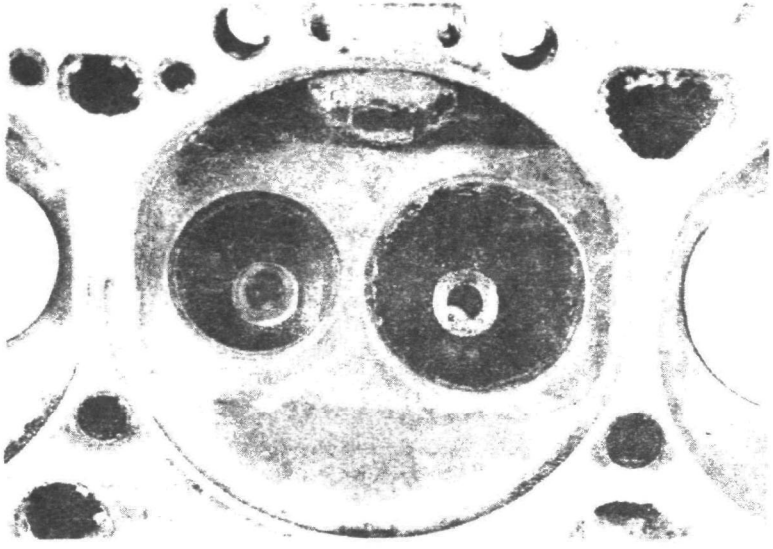


Control vehicle

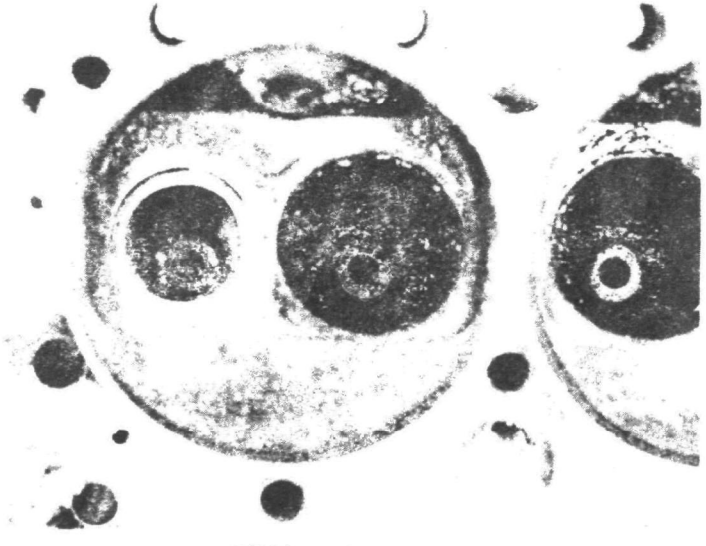
FIGURE B-3.- Intake and exhaust ports for the AK33X, F310, and control vehicles.



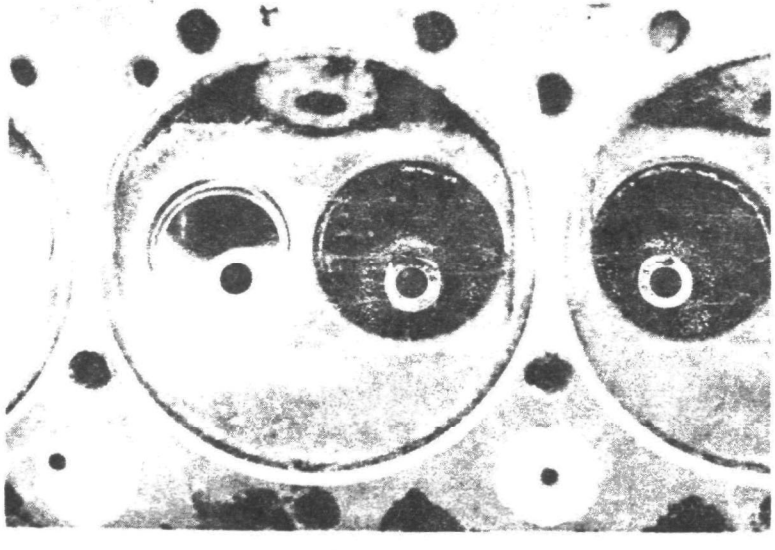
AK33X engine A



AK33X engine B

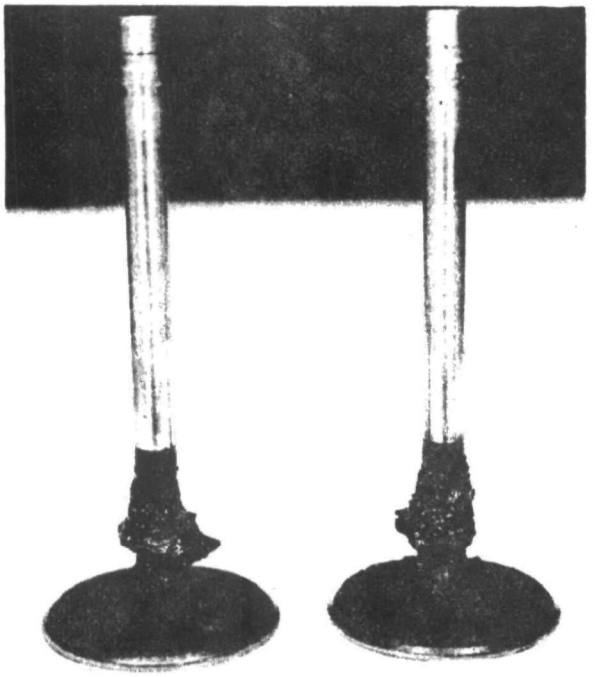


F310 engine A

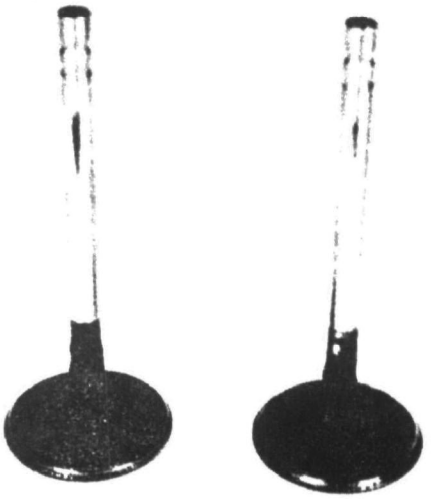


F310 engine B

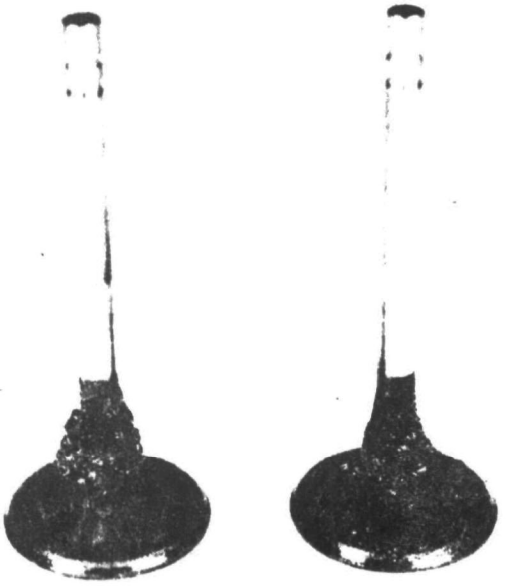
FIGURE B-4. – Intake and exhaust ports for the stationary engines.



AK33X vehicle



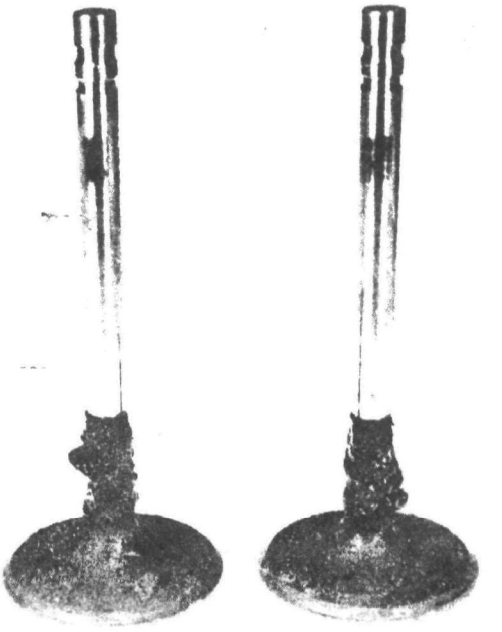
F310 vehicle



Control vehicle

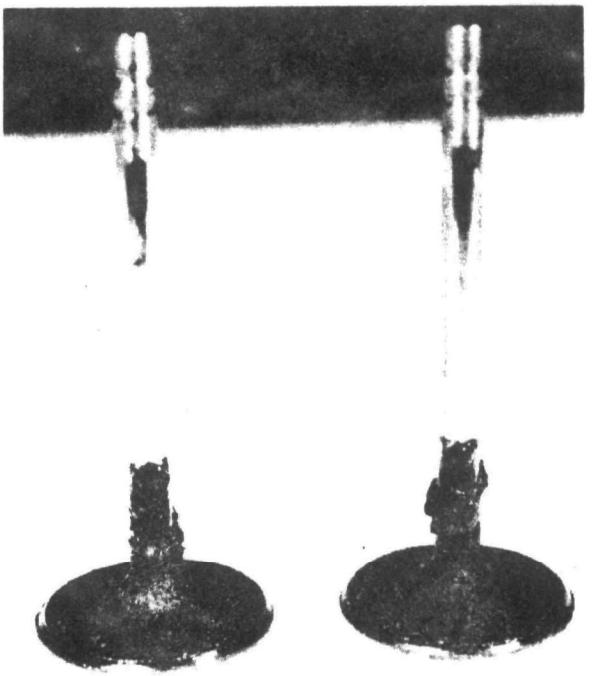
FIGURE B-5.-Intake valve stems for the AK33X, F310, and control vehicles.

AK33X engine A



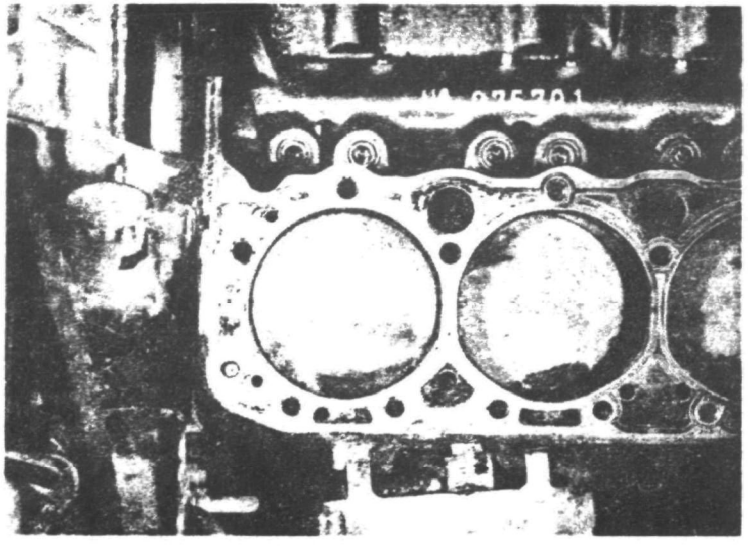
AK33X engine B

F310 engine A

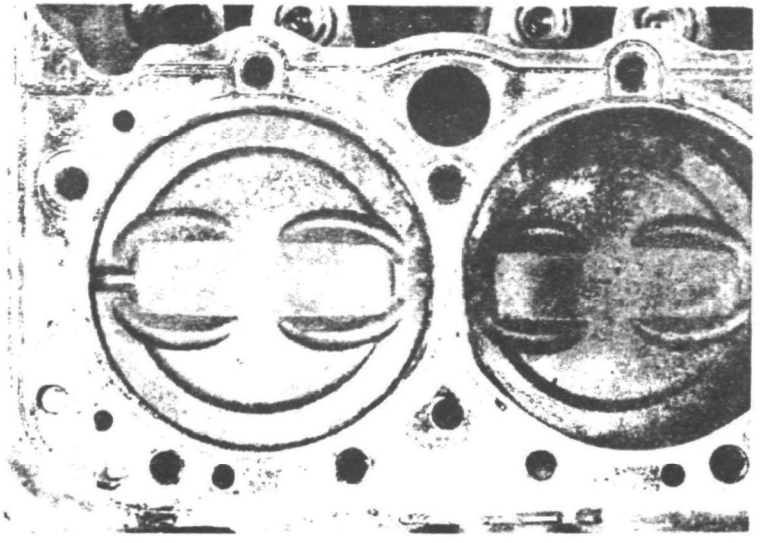


F310 engine B

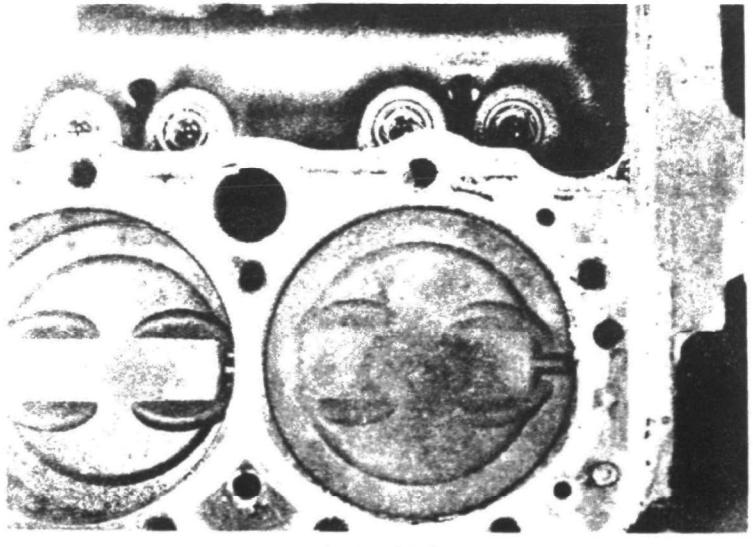
FIGURE B-6.-Intake valve stems for the stationary engines.



AK33X vehicle

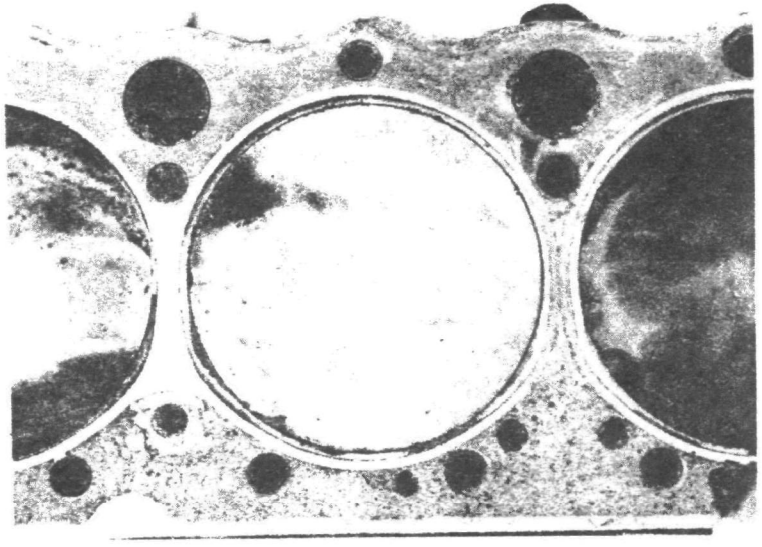


F310 vehicle

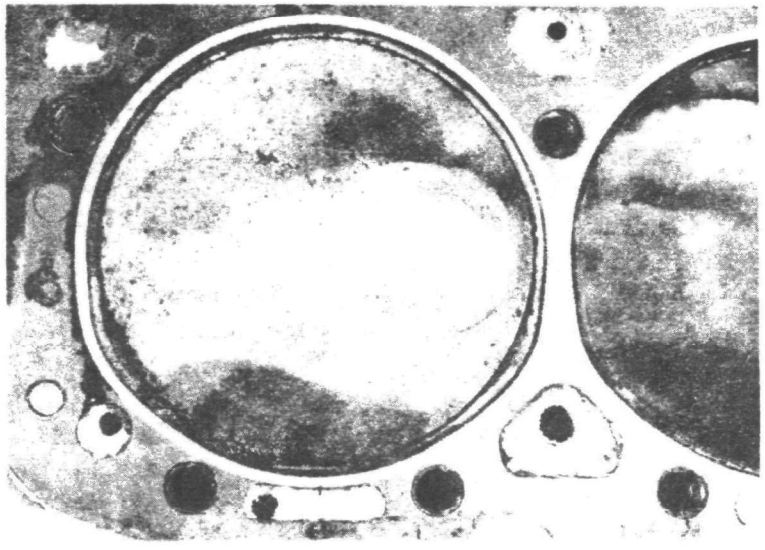


Control vehicle

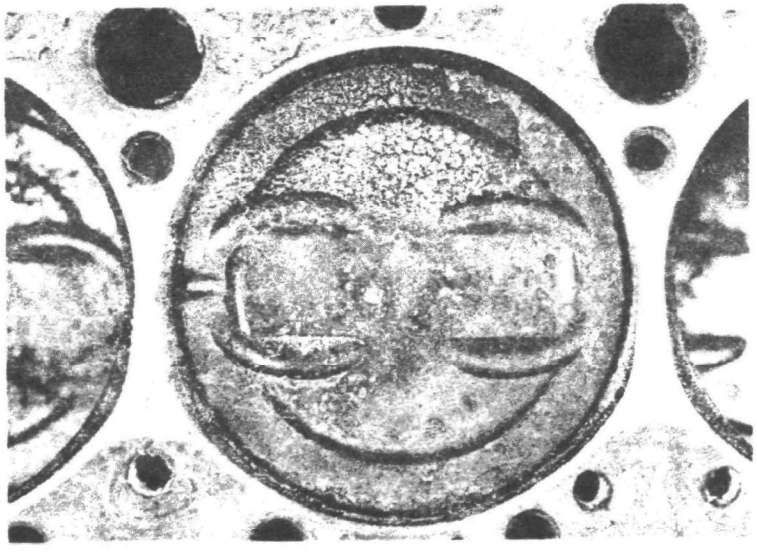
FIGURE B-7.-Piston head for the AK33X, F310, and control vehicles.



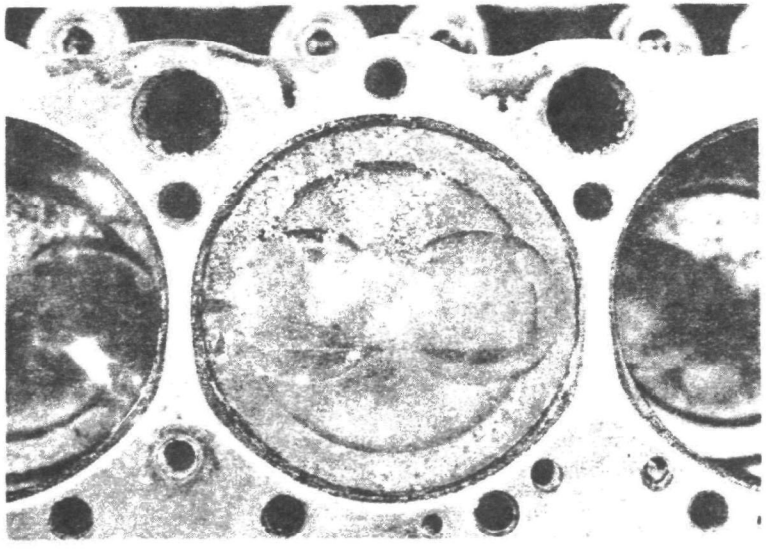
AK33X engine A



AK33X engine B

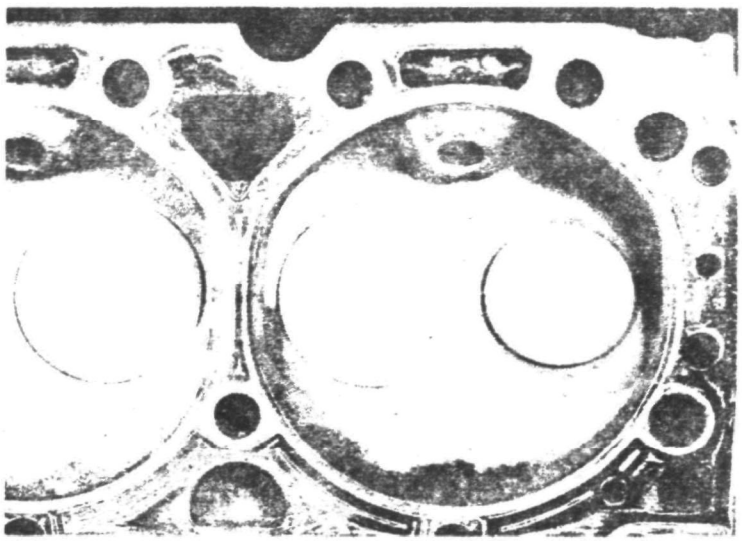


F310 engine A

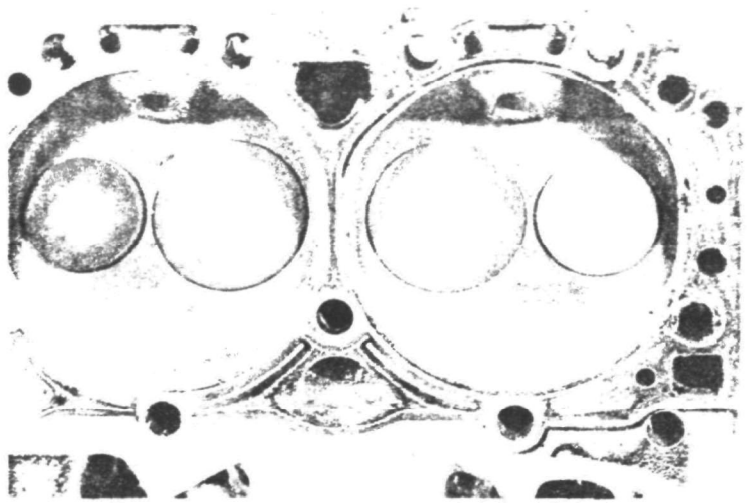


F310 engine B

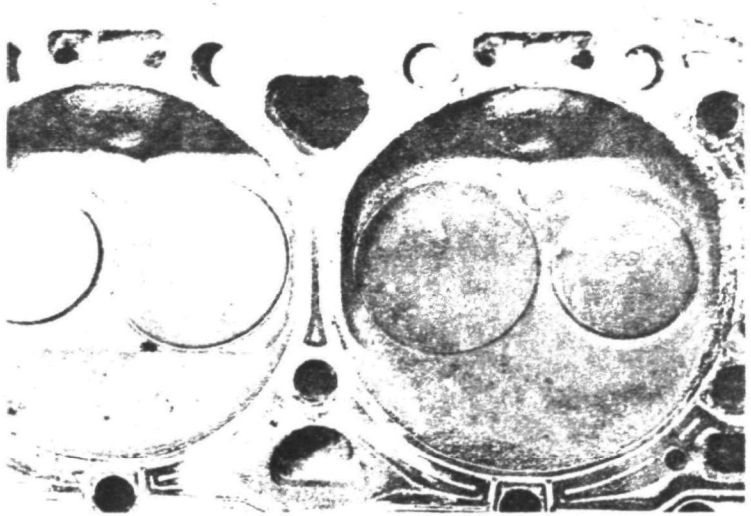
FIGURE B-8.-Piston head for the stationary engines.



AK33X vehicle

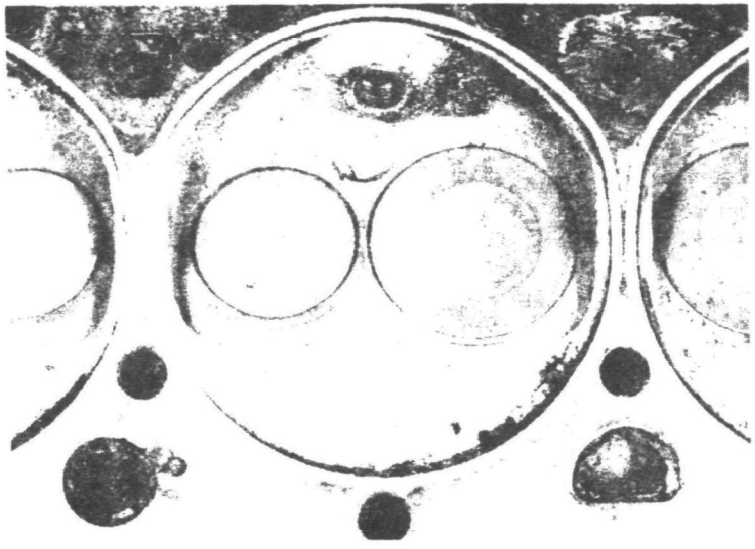


F310 vehicle

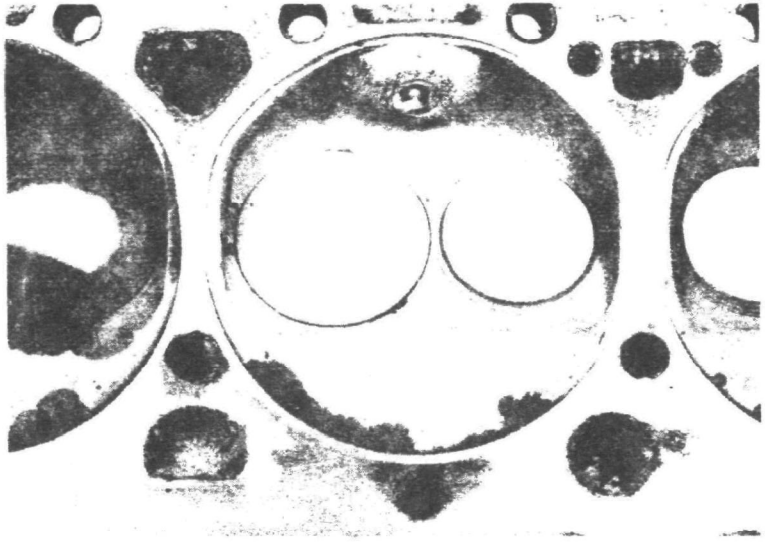


Control vehicle

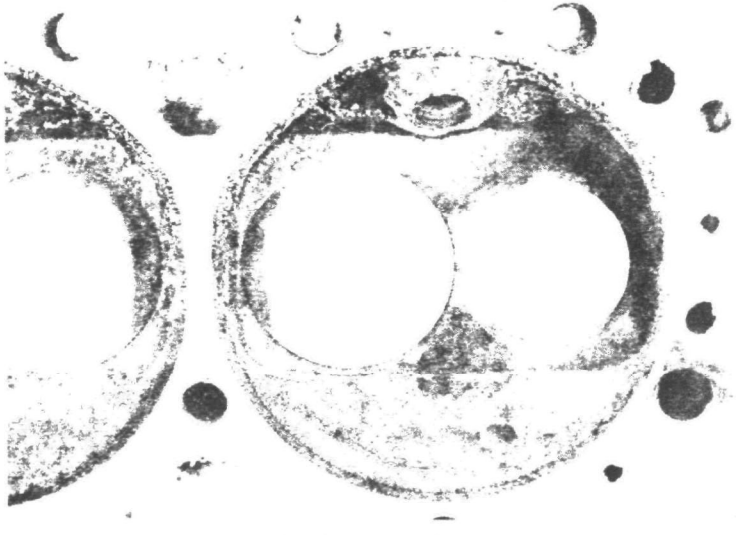
FIGURE B-9.-Cylinder heads for the AK33X, F310, and control vehicles.



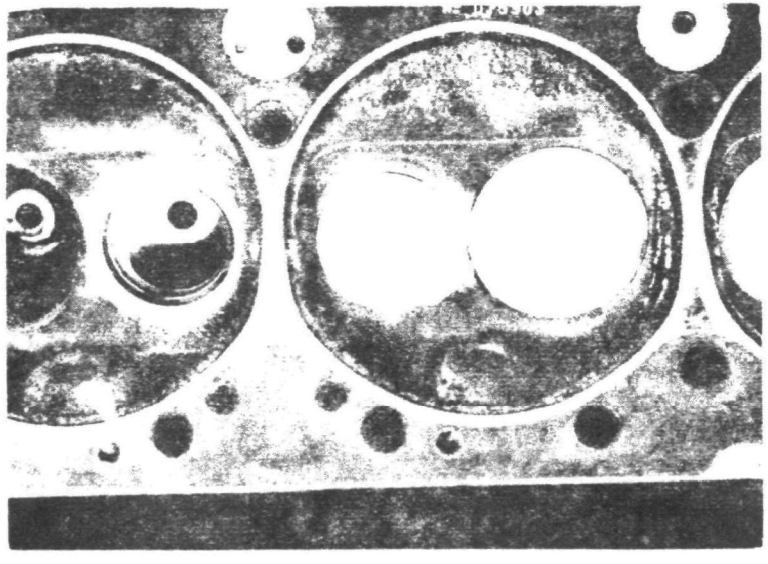
AK33X engine A



AK33X engine B

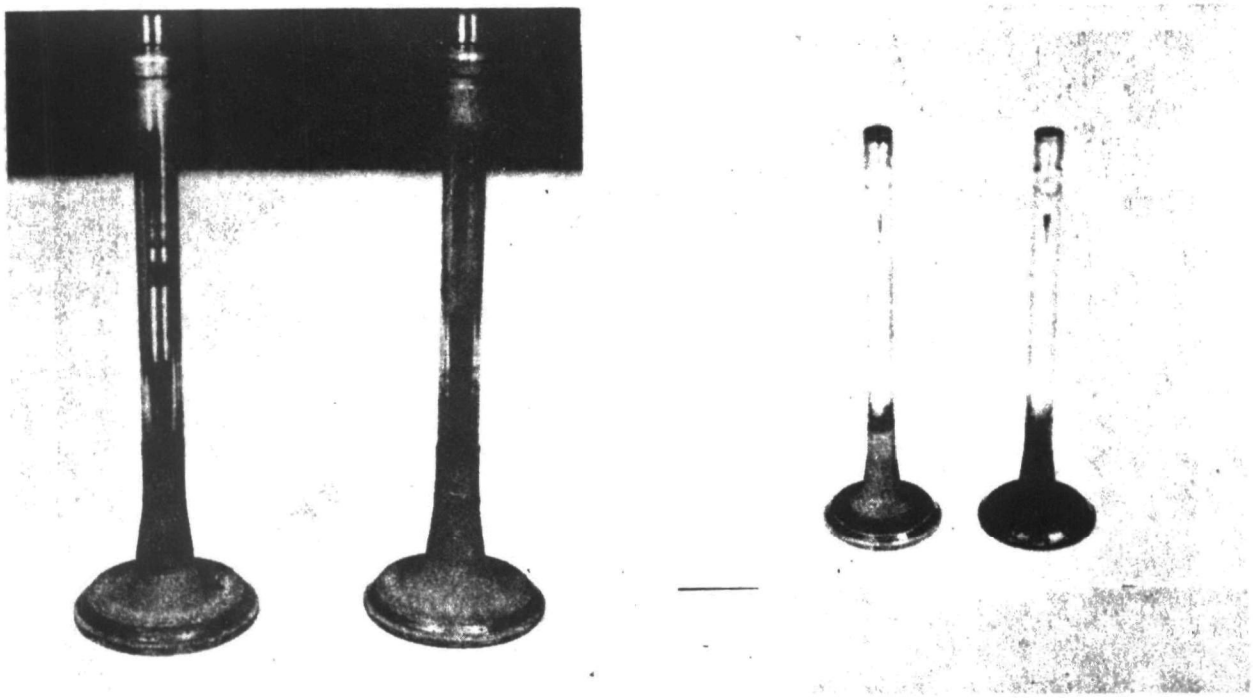


F310 engine A



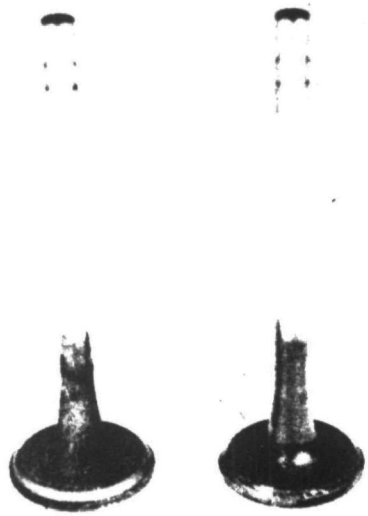
F310 engine B

FIGURE B-10.-Cylinder heads for the stationary engines.



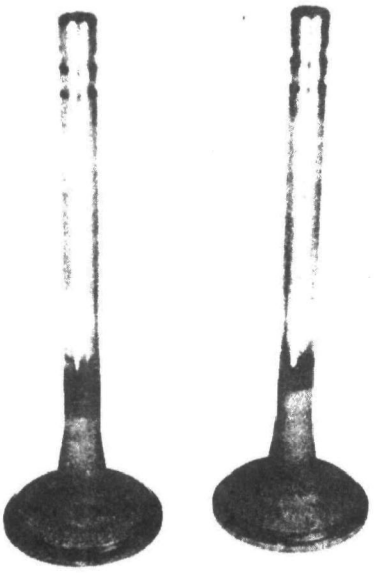
AK33X vehicle

F310 vehicle

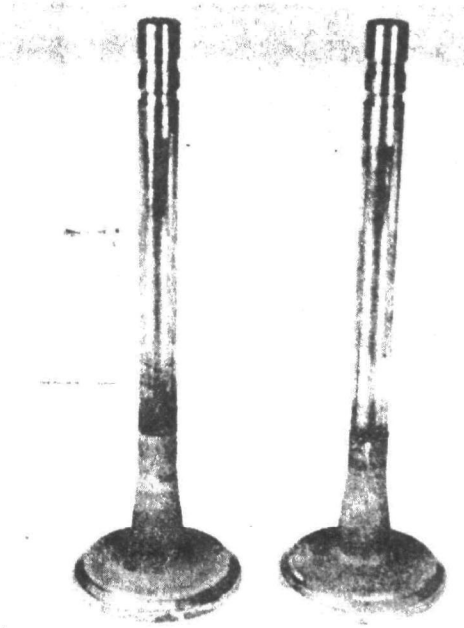


Control vehicle

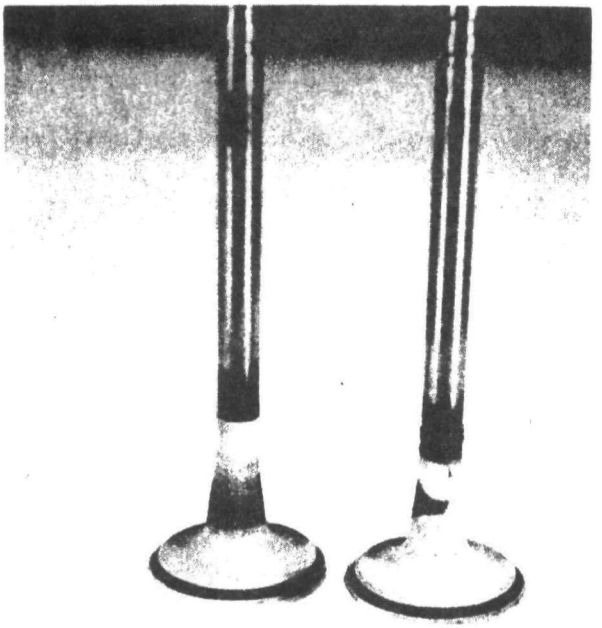
FIGURE B-11.- Exhaust valve stems for the AK33X, F310, and control vehicles.



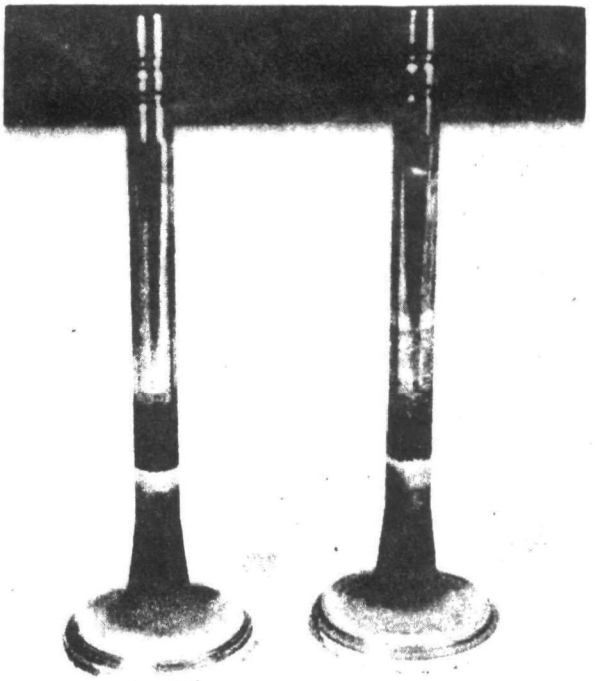
AK33X engine A



AK33X engine B



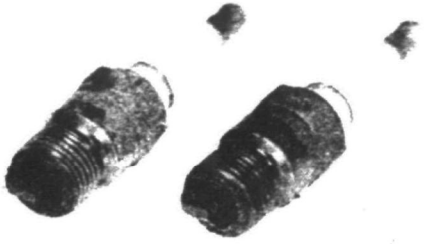
F310 engine A



F310 engine B

FIGURE B-12.-Exhaust valve stems for the stationary engines.

AK33X vehicle



F310 vehicle

Control vehicle

FIGURE B-13.–Spark plugs for the AK33X, F310, and control vehicles.

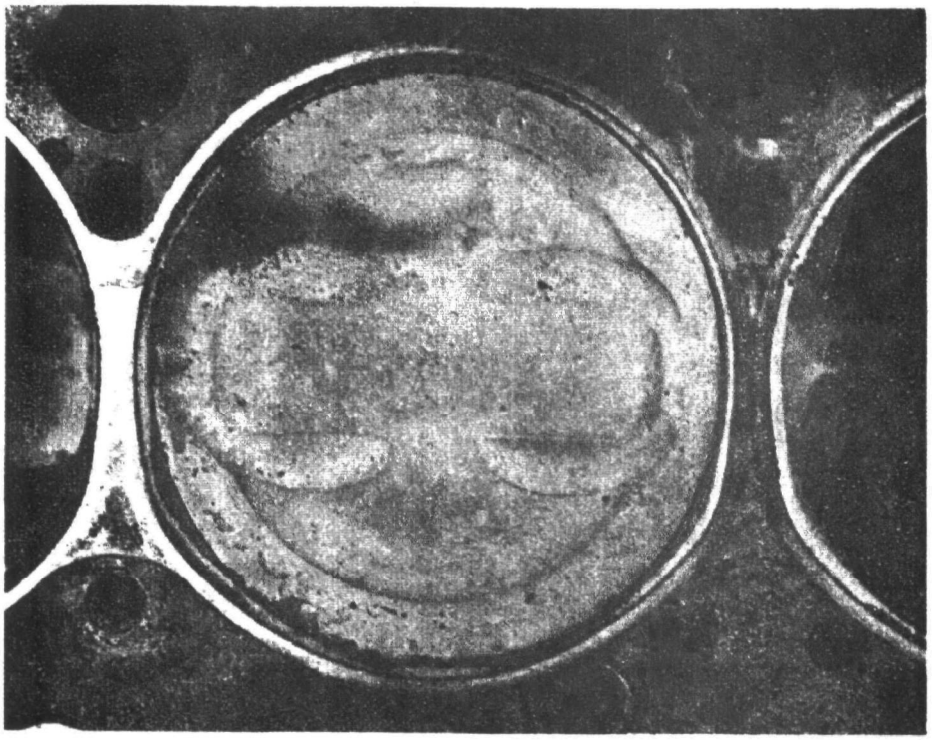
AK33X engine A

AK33X engine B

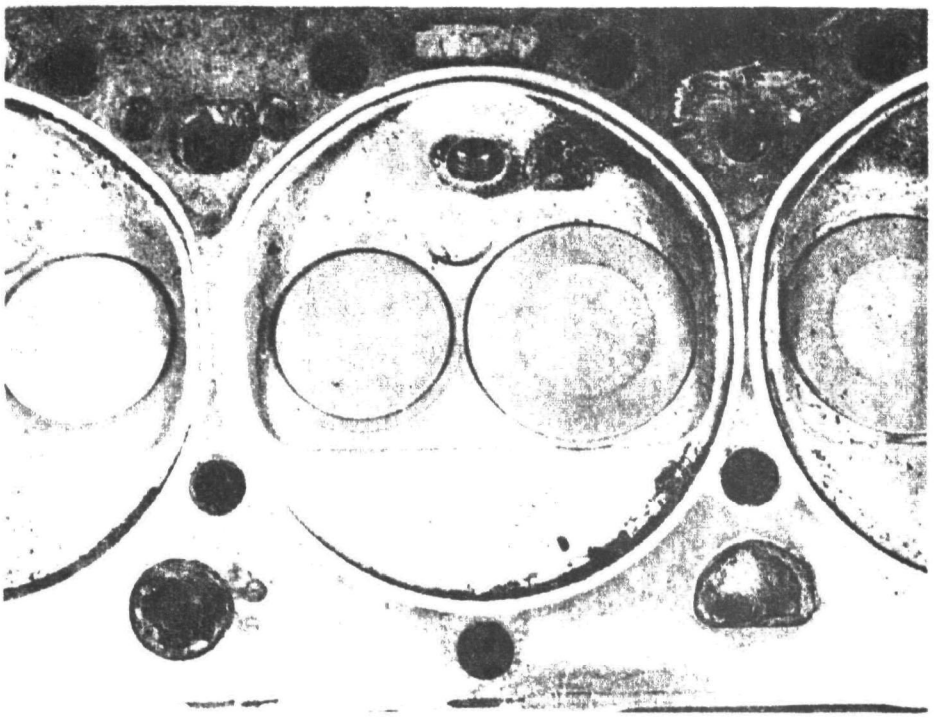
F310 engine A

F310 engine B

FIGURE B-14.-Spark plugs for the stationary engines.



Piston head -- AK33X engine A



Cylinder head -- AK33X engine A

FIGURE B-15.- Piston and engine head for AK33X engine A.

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BARTLESVILLE ENERGY RESEARCH CENTER

P. O. BOX 1398

BARTLESVILLE, OKLAHOMA 74003

AIRMAIL

October 9, 1974

Memorandum

To: John E. Sigsby, Jr., Environmental Protection Agency, Research Triangle Park, NC

From: R. W. Hurn, Research Supervisor, BERC

Subject: Monthly progress reports

Accompanying as attachment A and B is a copy of the monthly progress reports covering work accomplished through September 1974, on the projects "Gaseous Emissions Associated with Gasoline Additives--Reciprocating Engines" and "Characterization of Gaseous Emissions from Rotary Engines Using Additive Fuel."

R. W. Hurn
dw

Attachment A & B

cc w/attach:
Sigsby (4)
Gooding
Cox
Allsup
Seizinger
Fleming
Williams
General files

United States Department of the Interior

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BARTLESVILLE ENERGY RESEARCH CENTER

P. O. BOX 1398

BARTLESVILLE, OKLAHOMA 74003

October 9, 1974 Attachment A to memo dated October 9, 1974

Monthly Progress Report
Work accomplished through
September 1974
Project No. 4844

Gaseous Emissions Associated with
Gasoline Additives--Reciprocating Engines

Experimental work has been completed on all cars and additives for this study. The final report is in progress and will combine the results of both the reciprocating and rotary engines work. This report completes monthly reporting procedures for this project.

United States Department of the Interior

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BARTLESVILLE ENERGY RESEARCH CENTER

P. O. BOX 1398

BARTLESVILLE, OKLAHOMA 74003

October 9, 1974 Attachment B to memo dated October 9, 1974

Monthly Progress Report
Work accomplished through
September 1974
Project No. 4851

Characterization of Gaseous Emissions from Rotary Engines Using Additive Fuel

Experimental work has been completed on all cars and additives for this study. The final report is in progress and will combine the results of both the reciprocating and rotary engines work. This report completes monthly reporting procedures for this project.

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BARTLESVILLE ENERGY RESEARCH CENTER

P. O. BOX 1398

BARTLESVILLE, OKLAHOMA 74003

September 12, 1974 Attachment B to memo dated Sept. 12, 1974

Monthly Progress Report
Work Accomplished Through
August 1974
Project No. 4851

Characterization of Gaseous Emissions from Rotary Engines Using Additive Fuel

Tests were completed on the Mazda stationary engine using Lubrizol 8101 fuel additive for 15,000 miles. The Lubrizol 8101, a succamid, is a multifunctional dispersant-type additive for gasoline and was used at a dosage of 140 lbs per 1,000 barrels gasoline. No statistical trend was apparent in the routine emissions during the 5,000 mile period. Exhaust emission data is presented in table 5.

Tests were completed on the Mazda vehicle using both the Texaco TFA 318 polyisopropylene fuel additive and the combination of Texaco TFA 318 and Lubrizol 8101 fuel additives. Additive dosage was the same as used in the reciprocating engine tests. Exhaust emission data for the vehicle is presented in table 6 and 7.

This series of tests completes the experimental work outlined in the program. Compilation of all experimental data and drafting of the final report is now in progress.

TABLE 5. - Exhaust emissions from 1973 Mazda engine using Lubrizol 8101 fuel additive

Fuel	Elapsed miles	1975 FTP g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	21.8	2.60	0.59	0.201
Clear + 8101.....	0	25.8	2.90	.60	-
Clear + 8101.....	800	27.1	4.13	.58	.334
Clear.....	810	21.6	2.14	.63	.234
Clear + 8101.....	2,900	26.5	3.17	.65	.260
Clear.....	2,910	24.1	3.05	.77	.362
Clear + 8101.....	5,900	28.4	2.68	1.01	.292
Clear + 8101.....	8,900	22.9	2.77	.73	.164
Clear.....	8,910	24.1	2.70	.82	.187
Clear + 8101.....	11,700	22.7	2.19	.80	.122
Clear + 8101.....	14,800	19.3	2.10	.70	.133
Clear.....	14,810	20.4	2.25	.54	.133

TABLE 6. - Exhaust emissions from 1974 Mazda vehicle using Texaco TFA 318 fuel additive

Fuel	Elapsed miles	1975 FTP g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	23.4	2.05	1.17	0.166
Clear + TFA 318..	10	24.1	2.19	1.20	.170
Clear + TFA 318..	30	24.0	2.05	1.21	.203
Clear + TFA 318..	1,000	20.9	1.72	1.25	.148
Clear + TFA 318..	1,860	22.5	2.34	1.23	.292
Clear + TFA 318..	2,870	20.2	2.08	1.18	.143
Clear.....	2,900	18.0	1.95	1.14	.135

TABLE 7. - Exhaust emissions from 1974 Mazda vehicle using Lubrizol 8101 and Texaco TFA 318 fuel additives

Fuel	Elapsed miles	1975 FTP g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	20.8	1.77	1.21	0.130
Clear + 318 + 8101	20	26.7	1.75	1.28	.137
Clear + 318 + 8101	30	23.7	2.12	1.33	.146
Clear + 318 + 8101	1,050	22.2	2.37	1.23	.154
Clear + 318 + 8101	2,050	19.8	1.89	1.22	.125
Clear + 318 + 8101	3,050	19.6	1.72	1.32	.151
High Aromatic + 318 + 8101....	3,070	17.9	1.61	1.25	.124

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P. O. BOX 1398

BARTLESVILLE, OKLAHOMA 74003

August 19, 1974 Attachment B to memo dated August 19, 1974

Monthly Progress Report
Work Accomplished Through
July 1974
Project No. 4851

Characterization of Gaseous Emissions from Rotary Engines Using Additive Fuel

Tests have been completed on the Mazda stationary engine using Du Pont DMA-4 fuel additive. The DMA-4, an amine neutralized alkyl phosphate, is a multifunctional cleaning additive and was used at the recommended dosage of 15 lbs per 1,000 barrels. No significant trends of CO, HC, or NO_x were apparent during the 15,000 mile use with the DMA-4 (table 6). Tests are now underway using Lubrizol 8101 (a succinamid) at a dosage of 140 lbs per 1,000 barrels.

Tests with the Mazda vehicle using DMA-51 (described in reciprocating engine report) were completed and the emission data is presented in table 7. Presently Texaco TFA 318 fuel additive is being used in the Mazda vehicle.

TABLE 6. - Exhaust emissions from 1973 Mazda engine using DMA-4 fuel additive

Fuel	Elapsed miles	1975 FTP g/mile			
		CO	HC	NO_x	Aldehydes
Clear.	0	18.4	2.54	0.76	0.164
Clear + DMA-4. . .	10	19.2	2.80	.80	.163
Clear + DMA-4. . .	1020	16.4	2.58	.71	.142
Clear.	1030	15.3	2.17	.70	.133
Clear + DMA-4. . .	3030	13.7	2.03	.74	.122
Clear.	3040	14.1	1.89	.71	-
Clear + DMA-4. . .	5500	18.4	2.15	.79	.143
Clear + DMA-4. . .	8580	17.6	1.78	.66	.107
Clear.	8590	20.8	2.46	.60	.233
Clear + DMA-4. . .	11500	21.2	2.64	.69	.210
Clear + DMA-4. . .	14800	26.2	2.92	.64	-
Clear.	14840	26.0	2.55	.68	.120

TABLE 7. - Exhaust emissions from 1974 Mazda vehicle using DMA-51 fuel additive

Fuel	Elapsed miles	1975 FTP g/mile			
		CO	HC	NO_x	Aldehydes
Clear.	0	37.2	2.51	1.23	0.238
Clear + DMA-51 . .	20	31.3	1.72	1.24	.122
Clear + DMA-51 . .	40	20.0	1.63	1.15	.115
Clear + DMA-51 . .	1050	22.0	1.92	1.25	.165
Clear + DMA-51 . .	1850	15.6	1.25	1.07	.090
Clear + DMA-51 . .	2840	17.7	1.42	1.17	.118
Clear.	2860	20.5	1.69	1.13	.099

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P. O. BOX 1398

BARTLESVILLE, OKLAHOMA 74003

July 22, 1974 Attachment B to memo dated July 22, 1974

Monthly Progress Report
Work Accomplished Through
June 1974
Project No. 4851

Characterization of Gaseous Emissions from Rotary Engines Using Additive Fuel

Tests with the rotary engine vehicle were completed with the amine neutralized alkyl phosphate fuel additive (Du Pont DMA-4) and the succinamide fuel additive (Lubrizol 8101). Emission data are presented in tables 6-7.

Stationary rotary engine tests were completed with the F-310 fuel additive and are in progress with the DMA-4 with about 6,000 miles of the planned 15,000 miles accumulated to date. Emission data for the stationary engine data are presented in tables 8-9.

TABLE 6. - Exhaust emissions from 1974 Mazda vehicle using DMA4 fuel additive

Fuel	Elapsed miles	1975 FTP, g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	18.1	1.64	1.30	0.091
Clear + DMA4..	20	16.9	1.71	1.40	.116
Clear + DMA4..	40	17.0	1.69	1.34	.108
Clear + DMA4..	990	15.7	1.48	1.30	.104
Clear + DMA4..	2,000	23.7	2.45	1.24	.164
Clear + DMA4..	3,000	18.3	1.73	1.22	.110
Clear.....	2,010	18.3	1.87	1.24	.109

TABLE 7. - Exhaust emissions from 1974 Mazda vehicle using Lubrizol 8101 fuel additive

Fuel	Elapsed miles	1975 FTP, g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	20.0	1.89	1.27	0.129
Clear + 8101..	10	20.5	1.90	1.22	.132
Clear + 8101..	20	19.1	1.74	1.18	.131
Clear + 8101..	1,010	17.7	1.63	1.33	.123
Clear + 8101..	1,980	22.1	1.81	1.30	.164
Clear + 8101..	2,990	20.7	1.80	1.49	.157
Clear.....	3,010	34.7	1.59	1.35	.110

TABLE 8. - Exhaust emissions from 1973 Mazda stationary engine using F-310 fuel additive

Fuel	Elapsed miles	1975 FTP, g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	25.9	3.64	1.24	0.195
Clear + F-310..	10	30.4	3.47	1.15	-
Clear + F-310..	20	28.3	3.18	1.14	.208
Clear + F-310..	1,000	21.3	2.70	.94	.177
Clear.....	1,100	18.3	2.44	.96	.131
Clear + F-310..	3,000	23.5	2.98	1.27	.216
Clear.....	3,020	18.8	2.47	1.30	.185
Clear + F-310..	6,000	19.9	2.71	.71	.148
Clear.....	9,000	19.5	2.63	.86	.159
Clear + F-310..	9,010	16.5	2.51	.70	.123
Clear + F-310..	12,000	28.7	3.55	1.10	.253
Clear.....	12,010	25.7	3.35	.87	.190
Clear + F-310..	15,000	22.3	2.76	.74	.253
Clear.....	15,010	24.7	3.15	.76	.179

TABLE 9. - Exhaust emissions from 1973 Mazda stationary engine using DMA4 fuel additive

Fuel	Elapsed miles	1975 FTP, g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	18.4	2.54	0.76	0.164
Clear + DMA4...	10	19.2	2.80	.80	.163
Clear + DMA4...	1,020	16.4	2.58	.71	.142
Clear	1,030	15.3	2.17	.70	.133
Clear + DMA4...	3,030	13.7	2.03	.74	.122
Clear ...	3,040	14.1	1.89	.71	-
Clear + DMA4...	5,500	18.4	2.15	.79	.143

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BARTLESVILLE ENERGY RESEARCH CENTER

P. O. BOX 1398

BARTLESVILLE, OKLAHOMA 74003

June 18, 1974 Attachment B to memo dated June 18, 1974

Monthly Progress Report
Work Accomplished Through
May 1974
Project No. 4851

Characterization of Gaseous Emissions from Rotary Engines Using Additive Fuel

Vehicle

Tests with the rotary engine vehicle were completed using the F-310 fuel additive for a 3,000 mile period. No trend in vehicle emissions occurred during the use of F-310. After the test period with F-310 the vehicle was driven at highway speeds for 1,000 miles using additive-free fuel. Apparently the severe driving resulted in a CO and HC reduction of about 25 pct which has been observed until the present time at 1,000 miles during the test sequence using DMA4 fuel additive.

Stationary Engine

The stationary rotary engine presently has 9,000 miles accumulated of the planned 15,000 miles using the F-310 fuel additive. The stationary engine emission data show a slight decrease in HC emissions during the 0 to 1,000 mile point after which HC emissions have apparently stabilized. The emissions data for both the vehicle and stationary engine are presented in tables 4-6.

Analytical Procedures

Analytical procedures that serve this project are identical to those that serve the project "Gaseous Emissions Associated with Gasoline Additives--Reciprocating Engines." For general discussion of the status of analytical procedures development see the report covering that project for the current month.

TABLE 4. - Exhaust emissions from 1974 Mazda using F-310 fuel additive

Fuel	Elapsed miles	1975 FTP, g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	22.2	2.04	1.12	0.129
Clear + F-310..	10	20.8	2.22	1.34	.148
Clear + F-310..	20	21.2	2.20	1.26	.149
Clear + F-310..	1,000	22.9	2.59	1.26	.168
Clear + F-310..	2,000	22.4	2.37	1.19	.157
Clear + F-310..	3,000	25.3	2.63	1.59	.187
Clear.....	3,010	26.9	2.75	1.77	.133

TABLE 5. - Exhaust emissions from 1973 Mazda stationary engine using DMA4 fuel additive

Fuel	Elapsed miles	1975 FTP, g/mile			
		CO	HC	NO_x	Aldehydes
Clear	0	18.1	1.64	1.30	0.091
Clear + DMA4...	20	16.9	1.71	1.40	.116
Clear + DMA4...	40	17.0	1.69	1.34	.108
Clear + DMA4...	990	15.7	1.48	1.30	.104

TABLE 6. - Exhaust emissions from 1973 Mazda stationary engine using F-310 fuel additive

Fuel	Elapsed miles	1975 FTP, g/mile			
		CO	HC	NO_x	Aldehydes
Clear.....	0	25.9	3.64	1.24	0.195
Clear + F-310..	10	30.4	3.47	1.15	-
Clear + F-310..	20	28.3	3.18	1.14	.208
Clear + F-310..	1,000	21.3	2.70	.94	.177
Clear.....	1,100	18.3	2.44	.96	.131
Clear + F-310..	3,000	23.5	2.98	1.27	.216
Clear.....	3,020	18.8	2.47	1.30	.185
Clear + F-310..	6,000	19.9	2.71	.71	.148
Clear.....	9,000	19.5	2.63	.86	.159
Clear + F-310..	9,010	16.5	2.51	.70	.123

Appendix B2.9

Status Report

ROAP 26AAE

Task 023

Exploratory Investigation of the Toxic and Carcinogenic Partial Combustion Products from Oxygen- and Sulfur-Containing Fuel Components

Concept:

A specific chemiluminescence detector with sensitivity below 10ppb has been developed by the University of Michigan and applied to the search for new combustion products from gasoline additives. Two commonly-used additives different from those used in other aspects of the fuel additive program were studied in simplified combustors. No new products were found.

Current work in this project involved construction of a new even more sensitive detector for use in the in-house program and search of engine exhaust for carcinogens.

Appendix B2.10

Status Report
ROAP 26AAE
Task 023

Exploratory Investigation of the Toxic and Carcinogenic Partial Combustion Products from Various Nitrogen-Containing Additives

Concept:

Gas chromatography - mas spectroscopy is being used as the principal analytical tool in a program which reaches for new products from fuel additives. A constant volume bomb is used to combustion isooctane - additive mixtures in a way that potential product yeilds can be maximized. Thus far, no new products have been found in tests of two commonly used nitrogenous additives.

Appendix B2.11

Status Report
ROAP 26AAE
Task 019

Characterize Diesel Gaseous and Particulate Emissions

Concept:

Fuel economy considerations strongly suggest the desirability of significant numbers of vehicles fuels with middle distillates in the U.S. car population. The introduction of diesel or stratified charge cars is likely to significantly change light-duty vehicle emissions patterns and an integrated research program to assess these hanges is necessary.

The attack on this problem will be two-pronged. First, it is suggested that the complex problem of heavy molecule identification by guided by health effects studies. This approach has been discussed in detail and a copy of the proposed research program is attached Secondly, a general characterization program in cooperation with OAWM is proposed to survey the gross emissions potentials of light-duty engines. Cooperative studies are currently underway and preliminary test data from that study are attached.

It appears that diesel and stratified charge cars can appreciably limit urban hydrocarbon and CO vehicular emissions. Particulate carbon may be a problem, however, For NO_x it appears that present humidity corrections designed for gasoline-powered vehicles and presently applied to light-duty diesel and stratified charge engines, probably unfairly increase reported NO_x values. Better humidity corrections for light duty engines are necessary and it is proposed that these emission factors be determined in the current program.

LIGHT DUTY DIESEL EXHAUST EMISSIONS

by

Ronald L. Bradow
Chief, ETCS

INTRODUCTION:

A light-duty diesel characterization program has been in progress for some time at Southwest Research Institute under the auspices of OAWM. In a cooperative effort with OAWM a series of particulate samples have been obtained and analyzed in our laboratory in order to assess the impact of such vehicles on localized emissions problems. Since diesel and stratified charge cars appear to be the most reasonable alternatives to current year catalyst technology, it is important to assess their relative impact on atmospheric aerosol problems.

EXPERIMENTAL:

Samples of particulate matter were obtained on fluoropore and glass-fiber filters, using a Nissan and an Opel diesel powered automobile on the 1975 FTP. An air dilution aerosol handling system-CVS identical in design to the EPA system previously described was used to obtain the samples. Conditions for the tests, fuel properties and analytical methods for gaseous emissions are given in an SWRI interim report to OAWM on contract PH-22-68-23, dated June, 1974.

Filter samples were mailed to RTP, humidity conditioned, and reweighed prior to analysis. Filter analysis procedures on glass fiber samples included automated carbon, hydrogen, and nitrogen analysis and extraction with methylene chloride, followed by evaporation and weighing the extract. Fluoropore filter samples were analyzed by X-ray fluoresence spectroscopy and by an automated barium chloranilate procedure.

RESULTS AND DISCUSSION:

Table 1 presents mass emissions and fuel economy data from SWRI for 3 diesel cars, compared with similar data from Exxon on a GM "75 prototype using high sulfur fuel. Hydrocarbons, CO and NOx from the diesels compare favorably with the catalyst cars and particulates are only slightly higher for high sulfur fuels. For lower fuel sulfur content, the catalyst car is considerably better with respect to particulate emission rate. Catalyst car particulate matter is composed of sulfuric acid-water droplets, while diesel particles are mainly elemental carbon. Consequently, the trade-off between these two control options is not all that clear cut.

Fuel economy considerations are really one-sided as Table 1 shows. These diesel cars in the 3500 lb. class had exceptional fuel economy, far exceeding any recently reported for gasoline powered passenger cars in this weight. It should also be remembered that diesel engines burn middle distillate fuel oil fractions rather than energy-expensive high octane gasoline.

Analysis of filter samples is shown in Table 2. Carbon clearly makes up the bulk of the material, together with lesser amounts of organic material, possibly adsorbed on carbon particles. Only small amounts of metallic components (iron, copper, and zinc), probably from wear of engine and exhaust components, were found. In a few cases phosporous, possibly derived from the lubricant, was detected. Lead was also found in traces in the Opel samples.

Sulfur compound emissions were relatively low and did not appear to be sulfate.

Consequently the form of this sulfur emission is of considerable interest. It is possible that sulfur-bearing fuel components are emitted with the heavy organics. Therefore, sulfur analysis of the heavy organics is planned. It is also possible that some of the SO_2 in the exhaust is adsorbed on carbon particles and is consequently retained in the particulate matter. Sulfite determinations are also planned to settle this point.

Nitrogen values are especially high. This may be an artifact from interaction of NO_2 with the glass-fiber to produce nitrate. It is not as yet known whether there are significant amounts of organic nitrogen compounds in the exhaust.

Only two extractions have been made to date. One with a 7.5 hot start run on the Opel gave 10.5% extractable. With the Nissan only 2.0% was extractable. This difference can be confirmed by comparing the filter weight gain with the sum of carbon, nitrogen and water, assuming all the hydrogen is present as water. In the case of the Nissan samples, the C, N, H_2O sum was 95-98% of the filter weight gain. In the case of the Opel samples this sum is 115-135% of the filter gain. Clearly the hydrogen can not be mainly in the form of water with the Opel samples, and the organic content is relatively higher.

It is clear that the main hazard from diesel exhaust would be from toxic organics in the exhaust. Consequently, the main thrust of the current year's contract program should be towards characterization of this material.

CONCLUSION:

The current year's OAWM program at Southwest relies

heavily on analytical technology developed by previous ORD efforts in the heavy duty diesel field. We plan to coordinate ORD and OAWM efforts in cooperative experiments, such as this one, to get maximum benefit for the Government's contract dollar. Thus, ORD is supplying methodology for improved gas analysis for SO_2 and SO_3, detailed hydrocarbons, odor components, and aldehydes. Analysis for particulate sampling, PNA, metals, and organics in filterable particulate also result from ORD programs. OAWM supplies engineering guidance for vehicle and engine choice, noise, fuel economy, and regulated emissions testing, as well as a wealth of background information on diesel technology. Current year plans include integration of bioassay techniques by ORD-EBL to help guide the characterization program. The efforts in this field are mutually supportive and represent a high degree of cooperative by all concerned.

TABLE 1

1975 FTP - Light Duty Diesel Test Results

A. Emissions Data - gms/mile
Average of 4 tests

CAR	NISSAN	OPEL	PEUGEOT	GM PROTOTYPE*	
HC $\bar{x}$	0.354	0.386	1.96	0.32	
(Hot FID) σ	0 019	0.019	0.075		
CO $\bar{x}$	1.35	0.982	2.37	3 01	
σ	0.22	0.123	0.201		
NO_x $\bar{x}$	1.53	1.32	1.00	2.75	
σ	0 058	0.050	0.029		
Formaldehyde	0 034	0.038	0.074	0.009	
Acrolein	0.038	0.032	0.076	Not detectable	
Particulate $\bar{x}$	0.399	0.251	———	0.118[a]	0.244[b]
σ	0.001	0.062		0.037	0.072

B Fuel Economy - miles/gallon

28.8	28.8	28.2	10.1

* Exxon Data
[a] 0.065 % Fuel
[b] 0.14% Fuel

TABLE 2

Particle Emissions

A. Nissan Diesel

Run Mode	Filter No.	Part. g/mile	Filter Wt.	Wt. % C	H	N	Fe	Cu	Zn	P	S	SO_4
FTP 7.5 mile Hot Start	30	0.348	2.03	70.65	2.23	6.23	0.15	—	0.16	—	0.51	
	32	0.348	1.56	72.84	1.70	8.81	0.15	—	0.14	—	0.70	
	34	0.349	1.85	70.42	1.11	6.54	—	0.03	0.10	—	0.88	
	36	0.349	1.65	—	—	—	—	—	0.07	—	0.75	
FTP 11.09 mile Cold Start	38	0.300	2.53	65.75[a]	1.27	5.51	0.16	0.03	0.13	—	1.12	
	40	0.300	2.31	78.8[a]	0.43	8.04	0.13	0.02	0.09	—	1.04	

B. Opel Emissions

FTP 11.09 mile Cold Start	54	0.325	2.62	72.38	4.73	0.94	1.01	—	0.22	0.03	0.83	
	56	0.325	2.63									
FTP 7.5 mile Hot Start	58	0.313	1.24	77.90	4.83	1.07	0.19	—	0.16	—	0.49	
	60	0.331	1.29				Filter Destroyed In Handling					
FTP 11.09 mile Cold Start	74	0.339	2.75	72.43	6.13	3.51	0.74	0.01	0.25	0.07	1.05	
	76	0.335	2.72				1.08	0.01	0.29	0.09	1.06	
FTP 7.5 mile Hot Start	78	0.296	1.73				0.13	—	0.19	—	0.73	
	80	0.281	1.64				0.14	—	0.22	—	0.70	

a. 1st 1373 sec. b: 2nd 505 sec.

Appendix B2.12

Status Report

Characterize Rotary Emissions as a Function of Lubricant Composition and Fuel/Lubricant Interaction

Report:

Attempts to arrange this work as a grant program in 1974 were unsuccessful. No reasonable acceptable grant proposals were received. It is planned to reprogram this project to a contract status and issue a new RFP. Since rotary engines are not likely to represent a substantial number of cars, only the potential increased PNA, and metals emissions are worthy of significant additional study. This will not be funded in FY75.

Appendix B2.13

Status Report
ROAP 26AAE
Task 017

Characterize Particulate Emissions -- Alternate Power Systems (Rotary)

Report:

This task will be adequately covered under Task 13. It is planned to reprogram the funds to diesel and stratified charge engine exhaust characterization studies.

This reprogramming is based upon our current view that rotary power plants will not constitute an increasing alternate automotive power source in the U.S. in this decade while diesel and stratified charge engine likely will become more prevelant.

1 REPORT NO	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/3-75-010 c		

4 TITLE AND SUBTITLE	5. REPORT DATE
ANNUAL CATALYST RESEARCH PROGRAM REPORT Appendices, Volume II	September 1975 6. PERFORMING ORGANIZATION CODE

7 AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Criteria and Special Studies Office	

9 PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Health Effects Research Laboratory Office of Research & Development U.S. Environmental Protection Agency Research Triangle Park, N.C. 27711	1AA002 11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS	13 TYPE OF REPORT AND PERIOD COVERED
Same as above	Annual Program Status 1/74-9/7 14 SPONSORING AGENCY CODE EPA-ORD

15 SUPPLEMENTARY NOTES

This is the Summary Report of a set (9 volumes plus Summary).
See EPA-600/3-75-010a,010b, & 010d thru 010j. Report to Congress.

16. ABSTRACT

This report constitutes the first Annual Report of the ORD Catalyst Research Program required by the Administrator as noted in his testimony before the Senate PUblic Works Committee on November 6, 1973. It includes all research aspects of this broad multi-disciplinary program including: emissions characterization, measurement method development, monitoring, fuels analysis, toxicology, biology, epidemiology, human studies, and unregulated emissions control options. Principal focus is upon catalyst-generated sulfuric acid and noble metal particulate emissions.

17 KEY WORDS AND DOCUMENT ANALYSIS

a DESCRIPTORS	b IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Catalytic converters Sulfuric acid Desulfurization Catalysts Sulfates Sulfur Health	Automotive emissions Unregulated automotive emissions Health effects (public)	

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