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Interpretation of Gas Chromatographic Spectra in Routine Analysis of Exhaust Hydrocarbons

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Interpretation of Gas Chromatographic Spectra in Routine Analysis of Exhaust Hydrocarbons

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INTERPRETATION OF GAS CHROMATOGRAPHIC SPECTRA IN ROUTINE ANALYSIS OF EXHAUST HYDROCARBONS

by

B. Dimitriades,[1] C. J. Raible,[2] and C. A. Wilson[3]

ABSTRACT

Experimental work has been done to refine and to confirm an analytical procedure by which gas-liquid chromatographic (GLC) spectra are interpreted from retention time data alone. The rationale of this spectra interpretation technique involves whether or not a given peak invariably represents the same component or component mixture; if not, what factors influence changes in peak identifications. To answer these questions, peak-identification procedures, based mainly on the use of subtractive columns, were developed and applied to interpret GLC spectra of several exhaust (and fuel) samples.

INTRODUCTION

In studies of the atmospheric pollution from automobile emissions, a practical method is required for routinely analyzing the hydrocarbon component of the emission sample. That method must be sensitive and capable of discriminating hydrocarbons of different molecular size and different photochemical reactivity (1).[4] To meet this need, the Bureau has developed a GLC method as a part of its studies of environmental contamination from fuel combustion.

Development thus far has resulted in a chromatographic method with adequate simplicity, precision, and sensitivity, and acceptably short analysis time (2). Further, the resolving power of the system (fig. 1) has permitted adequate discrimination of exhaust hydrocarbons of different molecular size and class. However, interpretation of the chromatographic spectra has been of questionable accuracy because it has been based on the assumption that each chromatographic peak represents the same component or component mixture in differing exhaust samples. To what extent this assumption is valid has not been known with acceptable confidence, nor have guidelines been available for acceptable use of retention time/peak-identification correlation. With

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[2]Group leader.

[3]Research chemist.

[4]Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

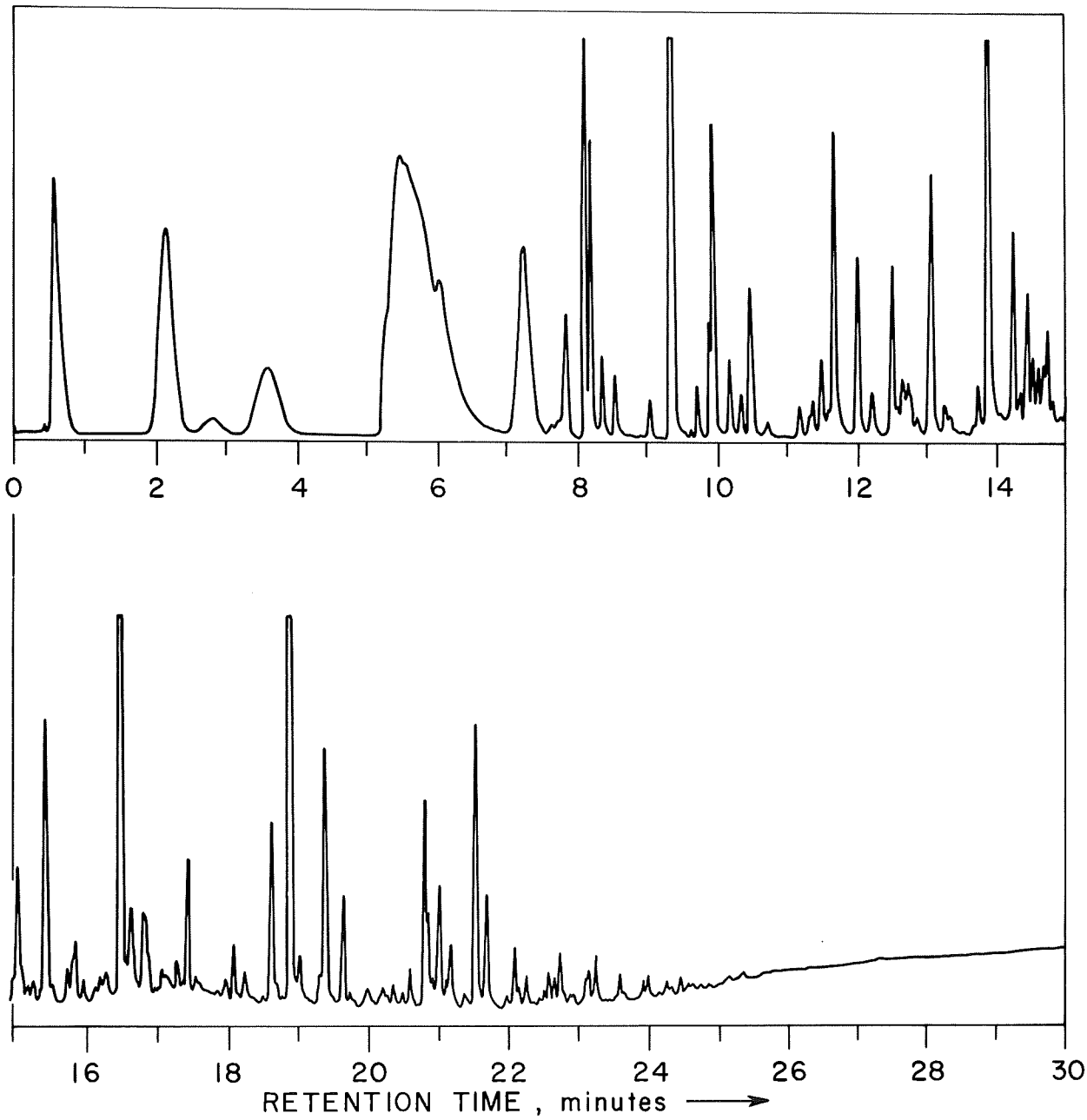

FIGURE 1. - Chromatogram of Hydrocarbons in Typical Exhaust.

respect to the questions raised, it is almost certain that in the light component part of the chromatographic spectrum (fig. 1), each peak does, in all analyses, represent one and the same component. In the heavier component part of the spectrum, however, such is not the case. Improved component resolution would eliminate some uncertainties in peak interpretation, but it would also entail unacceptable penalty in analysis time and introduce unwanted complexity. Thus, this work was performed to provide a better assessment of the GLC spectra interpretation technique presently in use in this laboratory; to determine inadequacies, as well as confirm validity of some practices; and, further, to provide direction for improvement.

EXPERIMENTAL PROCEDURES

Exhaust samples generated under varied engine conditions and fuels were analyzed chromatographically, and the resultant spectra were interpreted with peak-identification techniques that were designed to yield unambiguous determinations of the material associated with each peak.

Exhaust samples were obtained from a 1969 Valiant equipped with a 6-cylinder, 225-CID engine, and operated according to the 7-mode California cycle. The following combinations of engine adjustments were used: rich with vacuum spark advance (VSA); rich without VSA; lean with VSA; lean without VSA. Three fuels were used in tests with the Valiant; composition data are given in table 1 (fuels 1, 2, and 3). Additional data, similarly obtained, were used from another study in which four automobiles, a 1968 Delta 88 (455-CID), a 1968 Fury I (318-CID), a 1968 Impala (307-CID), and a 1968 Galaxie (302-CID), were operated at ambient temperatures of 70° and 95° F. One fuel (fuel 4, table 1) was used.

TABLE 1. - Hydrocarbon composition of test fuels by gas-liquid chromatography, mole pct

Fuel No.	Saturates	Olefins	Aromatics
1.....	66.0	15.1	18.9
2.....	60.7	10.2	29.1
3.....	53.1	1.9	45.0
4.....	41.8	12.4	45.8

Procedures for sampling exhaust and fuels have been described (2). Peak-identity data were obtained experimentally by the following three techniques.

1. Retention time. Retention-time data were used to establish identities of the light components and to provide suggestive evidence regarding the identity of others. Such data were obtained from chromatographic analyses of exhaust mixtures to which vapors of the test components had been added.

2. Subtractive column. Portions of each exhaust (or fuel vapor) sample were analyzed chromatographically both directly and after passing through two subtractive columns. These columns selectively subtracted (1) the aliphatic unsaturates and (2) the aliphatic unsaturated as well as the aromatic components. Thus, each peak in the chromatogram from the untreated exhaust was identified as a hydrocarbon type (paraffin, aliphatic unsaturate, or aromatic). If a mixture of hydrocarbons was found, the composition of that mixture was described. Subtractive columns were made of mercuric sulfate/sulfuric acid and of palladium sulfate/sulfuric acid (4). Columns were operated under conditions that were optimized for effective discrimination between saturates and unsaturates in the C_4 and heavier range--a molecule-weight range for which component resolution is relatively less complete. Thus for GLC analysis of gaseous mixtures using the subtraction technique, sample was drawn through the subtractive column and the sample loop of the injection system at 500 cm^3 min^{-1} for 1 minute, before injection. The column was maintained at room temperature; the sample loop, at 110° C. Column efficiencies were determined in tests using synthetic mixtures.

3. Component stability. Stability data on exhaust components in the dark and under solar irradiation were used primarily to identify unsaturates with conjugated double bonds, and secondarily to verify identities of olefins and reactive aromatics. In the absence of ultraviolet light, the aliphatic conjugated diolefins and aromatic olefins in exhaust react and disappear rapidly relative to other hydrocarbon components. Also, certain nonhydrocarbon components, such as acetone and benzaldehyde, were found to disappear rapidly. Sunlight irradiation of exhaust samples in Tedlar[5] bags for varying lengths of time revealed the GLC peaks which were due to reactive hydrocarbons, such as olefins and polyalkyl aromatics. However, the latter identification was often impossible because of the masking effect of reaction-product buildup.

DISCUSSION OF RESULTS

Results from measurements of efficiency of the subtractive columns and the related discussion are given in the appendix.

Results from the chromatographic analyses and peak-identification tests on fuel and exhaust samples from the one-car program are summarized in tables 2 to 4. Each table includes data taken for one fuel and for all exhaust samples obtained from that fuel. These data show the limits within which the composition of material represented by each peak varied from exhaust sample to exhaust sample, as well as the extent to which such variation in within-peak composition is caused by experimental error alone. Also, based on all peak-identification information, each peak was identified as a specific hydrocarbon or as a hydrocarbon mixture, and these specific peak identities are listed in each table under "assigned (peak) identification." Assigned peak identifications for the fuel and for the corresponding exhaust chromatograms are listed together in each table for comparison; such comparison would determine whether the fuel peak identifications would be used to interpret the corresponding exhaust chromatograms also.

Peak-identification data for the fuel and exhaust test samples from the four-car program are given in table 5.

For interpretation of these results, the experimental data were first examined for reliability.

Peak identification for the C_1 through C_3 components was based primarily on retention time, and secondarily on subtractive-column data. Considering the high resolving power of the chromatographic column and the relatively small number of isomers in this hydrocarbon-size range, such identification is believed to be unequivocal.

[5]Trade names are mentioned for identification only and do not imply endorsement by the Bureau of Mines.

TABLE 2. - Identification of chromatographic peaks in spectra of fuel 1 and of exhaust from fuel 1

Peak No.	Mole fraction in exhaust[1]	Exhaust peak identification[2] (average percent-composition and range): From subtractive columns	Variation owing to experimental error	Assigned identification	Fuel peak identification assigned
1	0.202	100 paraffin.....	0	100 methane.....	Not present.
2	.173	100 olefin.....	0	100 ethylene.....	Do.
3	.012	100 paraffin.....	0	100 ethane.....	Do.
4	.141	100 olefin.....	0	100 acetylene.....	Do.
5	.044	100 olefin.....	0	100 propylene.....	Do.
8	.003	100 olefin.....	0	100 propadiene.....	Do.
9	.005	100 olefin.....	0	100 methylacetylene.....	Do.
10	.002	100 paraffin.....	0	100 isobutane.....	100 isobutane.
11	.011	100 olefin.....	0	100 {isobutylene, 1-butene}.....	100 {isobutylene, 1-butene.
13	.028	{69.5±5.5 paraffin, 30.5±5.5 olefin}.	±1.0	{69.5 n-butane, 30.5 1,3-butadiene}.....	100 n-butane.
14	.002	100 olefin.....	0	100 trans-2-butene.....	100 trans-2-butene.
16	.003	100 olefin.....	0	100 cis-2-butene.....	100 cis-2-butene.
17	.001	100 olefin.....	0	100 1,2-butadiene.....	Not present.
18	.001	100 olefin.....	0	100 3-methyl-1-butene.....	100 3-methyl-1-butene.
19	.015	100 paraffin.....	0	100 isopentane.....	100 isopentane.
20	.002	100 olefin.....	0	100 1-pentene.....	100 1-pentene.
22	.023	{92.5±3.5 paraffin, 7.5±3.5 olefin}.	±2.5	{92.5 n-pentane, 7.5 2-methyl-1-butene}.....	{93 n-pentane, 7 2-methyl-1-butene.
23	.002	100 olefin.....	0	100 2-methyl-1,5-butadiene...	Not present.
24	.003	100 olefin.....	0	100 trans-2-pentene.....	100 trans-2-pentene.
25	.002	100 olefin.....	0	100 cis-2-pentene.....	100 cis-2-pentene.
26	.003	100 olefin.....	0	100 2-methyl-2-butene.....	100 2-methyl-2-butene.
27	.001	100 olefin.....	0	100 C_6 olefin.....	Not present.
28	.001	{19.0±6.0 paraffin, 81.0±6.0 olefin}.	±1.0	{19.0 2,2-dimethylbutane, 81.0 C_6 olefin}.....	100 2,2-dimethylbutane.
31	.001	100 olefin.....	0	100 cyclopentene.....	100 cyclopentene.
32	.003	{75.0±3.0 paraffin, 25.0±3.0 olefin}.	±2.0	{75.0 cyclopentane, 25.0 {3-methyl-1-pentene, 4-methyl-1-pentene}....	{77 cyclopentane, 23 {3-methyl-1-pentene, 4-methyl-1-pentene.
33	.002	100 paraffin.....	0	100 2,3-dimethylbutane.....	100 2,3-dimethylbutane.
35	.012	{94.0±1.0 paraffin, 6.0±1.0 olefin}.	±0.5	{94.0 2-methylpentane, 6.0 {2,3-dimethyl-1-butene, 4-methyl-cis-2-pentene}..	{96 2-methylpentane, 4 {2,3-dimethyl-1-butene, 4-methyl-cis-2-pentene.
37	.008	100 paraffin.....	0	100 3-methylpentane.....	100 3-methylpentane.
38	.003	100 olefin.....	0	100 {2-ethyl-1-butene, 2-methyl-1-pentene, 1-hexene}.....	100 {2-ethyl-1-butene, 2-methyl-1-pentene, 1-hexene.
40	.018	{98.5±1.5 paraffin, 1.5±1.5 olefin}.	±0.5	{98.5 n-hexane, 1.5 cis-3-hexene}.....	{95 n-hexane, 5 cis-3-hexene.
42	.002	100 olefin.....	0	100 {trans-2-hexene, 3-methylcyclopentene}...	100 {trans-2-hexene, 3-methylcyclopentene.
44	.002	100 olefin.....	0	100 {2-methyl-2-pentene, 3-methyl-cis-2-pentene}.	100 {2-methyl-2-pentene, 3-methyl-cis-2-pentene.
46	.001	100 olefin.....	0	100 cis-2-hexene.....	100 cis-2-hexene.
47	.012	{92.5±4.5 paraffin, 7.5±4.5 olefin}.	±1.0	{92.5 methylcyclopentane, 7.5 3-methyl-trans-2-pentene}	{88 methylcyclopentane, 12 3-methyl-trans-2-pentene.
48	.002	{70.0±3.0 paraffin, 30.0±3.0 olefin}.	±2.5	{70.0 2,4-dimethylpentane, 30.0 2,3-dimethyl-2-butene}..	100 2,4-dimethylpentane.
52	.002	100 olefin.....	0	100 methylcyclopentene.....	100 methylcyclopentene.
53[3]	.025	{53.0±17.0 paraffin, 47.0±17.0 aromatic}	±15.5	{53.0 cyclohexane, 47.0 benzene}.....	{56 cyclohexane, 44 benzene.
57	.009	{91.5±1.5 paraffin, 8.5±1.5 olefin}.	±0.5	{91.5 {2,3-dimethylpentane, 2-methylhexane}... 8.5 {cyclohexene, 4-methyl-1-hexene}	{88 {2,3-dimethylpentane, 2-methylhexane. {12 {cyclohexene, 4-methyl-1-hexene.
59	.006	100 paraffin.....	0	100 3-methylhexane.....	100 3-methylhexane.
61	.002	100 paraffin.....	0	100 dimethylcyclopentane.....	{88 dimethylcyclopentane, 12 3,4-dimethyl-trans-2-pentene.
64	.002	100 paraffin.....	0	100 dimethylcyclopentane.....	100 dimethylcyclopentane.
66	.004	{91.5±4.5 paraffin, 8.5±4.5 olefin}.	±2.0	{91.5 2,2,4-trimethylpentane, 8.5 C_7 olefin}.	{84 2,2,4-trimethylpentane, 16 C_7 olefin.
67	.001	100 olefin.....	0	100 C_7 olefin.....	100 C_7 olefin.
69	.010	{75.5±4.5 paraffin, 24.5±4.5 olefin}.	±1.0	{75.5 n-heptane, 24.5 C_7 olefin}.....	{71 n-heptane, 29 C_7 olefin.
70	.002	100 olefin.....	0	100 C_7 olefin.....	100 C_7 olefin.

See footnotes at end of table.

TABLE 2. - Identification of chromatographic peaks in spectra of fuel 1 and of exhaust from fuel 1--Continued

Peak No.	Mole fraction in exhaust[1]	Exhaust peak identification[3] (average percent-composition and range)			Fuel peak identification assigned
		From subtractive columns	Variation owing to experimental error	Assigned identification	
76	0.004	100 paraffin.....	0	100 methylcyclohexane.....	87 Methylcyclohexane. 13 C_7 olefin.
78	.001	100 paraffin.....	0	100 ethylcyclopentane.....	100 ethylcyclopentane.
79	.002	63.0±9.0 paraffin 37.0±9.0 olefin	±4.5	63.0 2,4-dimethylhexane, 2,5-dimethylhexane 37.0 C_7 olefin	100 2,4-dimethylhexane, 2,5-dimethylhexane.
80	.001	100 paraffin.....	0	100 2,2,3-trimethylpentane...	100 2,2,3-trimethylpentane.
89	.001	51.0±15.0 paraffin 49.0±15.0 olefin	±15.0	51.0 trimethylcyclopentane 49.0 C_7 olefin	45 trimethylcyclopentane. 55 C_7 olefin.
91	.002	13.5±5.5 paraffin 86.5±5.5 olefin	±3.5	13.5 2,3,3-trimethylpentane 86.5 C_7 olefin	5 2,3,3-trimethylpentane. 95 C_7 olefin.
92	.026	3.0±1.0 paraffin 97.0±1.0 aromatic	±0.5	3.0 2,3-dimethylhexane 97.0 toluene	100 toluene.
96	.005	100 paraffin.....	0	100 2-methylheptane.....	100 2-methylheptane.
97	.004	100 paraffin.....	0	100 3-methylheptane.....	100 3-methylheptane.
100	.002	57.5±8.5 paraffin 42.5±8.5 olefin	±8.5	57.5 2,2,5-trimethylhexane 42.5 C_8 olefin	78 2,2,5-trimethylhexane. 22 C_8 olefin.
104	.001	20.5±3.5 paraffin 79.5±3.5 olefin	±2.0	20.5 2,2,4-trimethylhexane 79.5 1-octene, trans-4-octene, 2,3-dimethyl-2-hexene	23 2,2,4-trimethylhexane. 77 1-octene, trans-4-octene, 2,3-dimethyl-2-hexene.
108	.005	80.5±9.5 paraffin 19.5±9.5 olefin	±8.5	80.5 n-octane 19.5 trans-2-octene	80 n-octane. 20 trans-2-octene.
110	.001	5.5±5.5 paraffin 94.5±5.5 olefin	±5.5	5.5 2,4,4-trimethylhexane 95.5 C_8 olefin	12 2,4,4-trimethylhexane. 88 C_8 olefin.
119	.001	100 paraffin.....	0	100 C_9 paraffin.....	100 C_9 paraffin.
123	.001	76.5±13.5 paraffin 23.5±13.5 olefin	±13.5	76.5 2,5-dimethylheptane, 3,5-dimethylheptane 23.5 C_8 olefin	75 2,5-dimethylheptane, 3,5-dimethylheptane.
126	.006	9.5±2.5 paraffin 90.5±2.5 aromatic	±1.5	9.5 2,3-dimethylheptane 90.5 ethylbenzene	20 2,3-dimethylheptane. 80 ethylbenzene.
129	.022	12.0±3.0 paraffin 88.0±3.0 aromatic	±1.5	12.0 4-methyloctane, 2-methyloctane 88.0 para-xylene, meta-xylene	13 4-methyloctane, 2-methyloctane. 87 para-xylene, meta-xylene.
131	.003	100 paraffin.....	0	100 3-methyloctane.....	100 3-methyloctane.
134	.002	100 olefin.....	0	100 styrene.....	100 styrene.
135	.009	5.5±2.5 paraffin 94.5±2.5 aromatic	±1.0	5.5 C_9 paraffin 94.5 ortho-xylene	100 ortho-xylene.
139	.002	100 paraffin.....	0	100 n-nonane.....	100 n-nonane.
142	.001	37.5±20.5 paraffin 62.5±20.5 aromatic	±20.5	37.5 2,4,5-trimethylheptane, 2,3,5-trimethylheptane 62.5 isopropylbenzene	57 2,4,5-trimethylheptane, 2,3,5-trimethylheptane. 43 isopropylbenzene.
152	.002	100 aromatic.....	0	100 n-propylbenzene.....	100 n-propylbenzene.
155	.007	7.0±2.0 paraffin 93.0±2.0 aromatic	±1.0	7.0 C_9 paraffin 93.0 1-methyl-3-ethylbenzene	4 C_9 paraffin. 96 1-methyl-3-ethylbenzene.
156	.003	100 aromatic.....	0	100 1-methyl-4-ethylbenzene..	100 1-methyl-4-ethylbenzene.
157	.001	100 paraffin.....	0	100 3,4,5-trimethylheptane, 3,4,4-trimethylheptane, 3,3,4-trimethylheptane	100 3,4,5-trimethylheptane, 3,4,4-trimethylheptane, 3,3,4-trimethylheptane.
158	.004	24.5±4.5 paraffin 75.5±4.5 aromatic	±3.5	24.5 C_9 paraffin 75.5 1-methyl-2-ethylbenzene	24 C_9 paraffin. 76 1-methyl-2-ethylbenzene.
160	.003	100 aromatic.....	0	100 1,3,5-trimethylbenzene...	100 1,3,5-trimethylbenzene.
163	.013	100 aromatic.....	0	100 1,2,4-trimethylbenzene...	100 1,2,4-trimethylbenzene.
164	.003	61.5±13.5 paraffin 38.5±13.5 aromatic	±9.5	61.5 n-decane 38.5 sec-butylbenzene, isobutylbenzene	100 n-decane.
165	.048	15.0±5.0 paraffin 10.0±1.0 olefin 79.5±10.5 aromatic	±4.5 0 ±4.5	15.0 C_{11} paraffin 10.0 C_{10} olefin 79.5 C_{10} aromatic	20 C_{11} paraffin. 80 C_{10} aromatic.

[1]Value represents average over all exhaust samples from fuel 1.

[2]The designation "olefin" is used to describe materials subtracted by the $HgSO_4$ column; therefore, it includes acetylenes and some oxygenates also. Likewise, materials designated as "aromatic" include some oxygenates also (see appendix).

[3]Large range in results reflects peculiar inadequacy of $HgSO_4 \cdot PdSO_4$ subtractive column in benzene scrubbing.

TABLE 3. - Identification of chromatographic peaks in spectra of fuel 2 and of exhaust from fuel 2

Peak No.	Mole fraction in exhaust[1]	Exhaust peak identification[2] (average percent-composition and range)			Fuel peak identification assigned
		From subtractive columns	Variation owing to experimental error	Assigned identification	
1	0.176	100 paraffin	0	100 methane	Not present.
2	.138	100 olefin	0	100 ethylene	Do.
3	.011	100 paraffin	0	100 ethane	Do.
4	.130	100 olefin	0	100 acetylene	Do.
5	.039	100 olefin	0	100 propylene	Do.
8	.002	100 olefin	0	100 propadiene	Do.
9	.005	100 olefin	0	100 methylacetylene	Do.
10	.008	100 paraffin	0	100 isobutane	100 isobutane.
11	.010	100 olefin	0	100 {isobutylene, 1-butene}	100 {isobutylene, 1-butene.}
13	.022	{66.5±4.5 paraffin, 33.5±4.5 olefin}	±3.5	{66.5 n-butane, 33.5 1,3-butadiene}	100 n-butane.
14	.002	100 olefin	0	100 trans-2-butene	100 trans-2-butene.
16	.005	100 olefin	0	100 cis-2-butene	100 cis-2-butene.
17	.001	100 olefin	0	100 1,2-butadiene	Not present.
18	.001	100 olefin	0	100 3-methyl-1-butene	100 3-methyl-1-butene.
19	.031	100 paraffin	0	100 isopentane	100 isopentane.
20	.002	100 olefin	0	100 1-pentene	100 1-pentene.
22	.022	{85.5±3.5 paraffin, 14.5±3.5 olefin}	±1.5	{85.5 n-pentane, 14.5 2-methyl-1-butene}	{88 n-pentane, 12 2-methyl-1-butene.
23	.001	100 olefin	0	100 2-methyl-1,3-butadiene	Not present.
24	.004	100 olefin	0	100 trans-2-pentene	100 trans-2-pentene.
25	.002	100 olefin	0	100 cis-2-pentene	100 cis-2-pentene.
26	.006	100 olefin	0	100 2-methyl-2-butene	100 2-methyl-2-butene.
27	.002	100 olefin	0	100 C_6 olefin	Not present.
28	.002	{65.0±23.0 paraffin, 35.0±23.0 olefin}	±9.0	{65.0 2,2-dimethylbutane, 35.0 C_6 olefin}	100 2,2-dimethylbutane.
31	.001	100 olefin	0	100 cyclopentene	100 cyclopentene.
32	.002	{71.0±5.0 paraffin, 29.0±5.0 olefin}	±5.0	{71.0 cyclopentane, 29.0 {3-methyl-1-pentene, 4-methyl-1-pentene}	{80 cyclopentane, 20 {3-methyl-1-pentene., 4-methyl-1-pentene.}
33	.003	100 paraffin	0	100 2,3-dimethylbutane	100 2,3-dimethylbutane.
35	.013	{92.0±2.0 paraffin, 8.0±2.0 olefin}	±2.0	{92.0 2-methylpentane, 8.0 {2,3-dimethyl-1-butene, 4-methyl-cis-2-pentene}	{94 2-methylpentane., 6 {2,3-dimethyl-1-butene., 4-methyl-cis-2-pentene.}
37	.008	100 paraffin	0	100 3-methylpentane	100 3-methylpentane.
38	.002	100 olefin	0	100 {2-ethyl-1-butene, 2-methyl-1-pentene, 1-hexene}	100 {2-ethyl-1-butene., 2-methyl-1-pentene., 1-hexene.}
40	.008	{90.5±2.5 paraffin, 9.5±2.5 olefin}	±1.5	{90.5 n-hexane, 9.5 cis-3-hexene}	{92 n-hexane., 8 cis-3-hexene.
42	.002	100 olefin	0	100 {trans-2-hexene, 3-methylcyclopentene}	100 {trans-2-hexene., 3-methylcyclopentene.
44	.003	100 olefin	0	100 {2-methyl-2-pentene, 3-methyl-cis-2-pentene}	100 {2-methyl-2-pentene., 3-methyl-cis-2-pentene.
46	.001	100 olefin	0	100 cis-2-hexene	100 cis-2-hexene.
47	.008	{81.5±3.5 paraffin, 18.5±3.5 olefin}	±1.5	{81.5 methylcyclopentane, 18.5 3-methyl-trans-2-pentene}	{80 methylcyclopentane., 20 3-methyl-trans-2-pentene.
48	.001	100 paraffin	0	100 2,4-dimethylpentane	100 2,4-dimethylpentane.
52	.002	100 olefin	0	100 1-methylcyclopentene	100 1-methylcyclopentene.
53[3]	.020	{58.5±21.5 paraffin, 41.5±21.5 aromatic}	±5.0	{58.5 cyclohexane, 41.5 benzene}	{34 cyclohexane., 66 benzene.
57	.007	{89.0±2.0 paraffin, 11.0±2.0 olefin}	±2.0	{89.0 {2,3-dimethylpentane, 2-methylhexane}, 11.0 {cyclohexene, 4-methyl-1-hexene}}	{87 {2,3-dimethylpentane., 2-methylhexane., 13 {cyclohexene., 4-methyl-1-hexene.}
59	.004	100 paraffin	0	100 3-methylhexane	100 3-methylhexane.
61	.002	100 paraffin	0	100 dimethylcyclopentane	100 dimethylcyclopentane.
64	.001	100 paraffin	0	100 dimethylcyclopentane	100 dimethylcyclopentane.
66	.002	{88.5±5.5 paraffin, 11.5±5.5 olefin}	±2.5	{88.5 2,2,4-trimethylpentane, 11.5 C_7 olefin}	100 2,2,4-trimethylpentane.
67	.001	100 olefin	0	100 C_7 olefin	100 C_7 olefin.
69	.005	{65.5±13.5 paraffin, 34.5±13.5 olefin}	±6.5	{65.5 n-heptane, 34.5 C_7 olefin}	{58 n-heptane., 42 C_7 olefin.
70	.001	100 olefin	0	100 C_7 olefin	100 C_7 olefin.
76	.004	100 paraffin	0	100 methylcyclohexane	{86 methylcyclohexane., 14 C_7 olefin.
78	.001	100 paraffin	0	100 ethylcyclopentane	100 ethylcyclopentane.
79	.002	{75.5±5.5 paraffin, 24.5±5.5 olefin}	±2.0	{75.5 {2,4-dimethylhexane, 2,5-dimethylhexane}, 24.5 C_7 olefin}	{100 {2,4-dimethylhexane., 2,5-dimethylhexane.}

See footnotes at end of table.

TABLE 3. - Identification of chromatographic peaks in spectra of fuel 2 and of exhaust from fuel 2--Continued

Peak No.	Mole fraction in exhaust[1]	Exhaust peak identification[2] (average percent-composition and range)			Fuel peak identification assigned
		From subtractive columns	Variation owing to experimental error	Assigned identification	
80	0.001	100 paraffin.....	0	100 2,2,3-trimethylpentane.....	100 2,2,3-trimethylpentane.
90	.001	100 paraffin.....	0	100 2,3,4-trimethylpentane.....	84 2,3,4-trimethylpentane. 16 C_7 olefin.
91	.002	40.5±19.5 paraffin 59.5±19.5 olefin	±8.0	40.5 2,3,3-trimethylpentane... 59.5 C_7 olefin	27 2,3,3-trimethylpentane. 73 C_7 olefin.
92	.028	4.0±2.0 paraffin 96.0±2.0 aromatic	±1.0	4.0 2,3-dimethylhexane..... 96.0 toluene	100 toluene.
96	.004	100 paraffin.....	0	100 2-methylheptane.....	100 2-methylheptane.
97	.004	100 paraffin.....	0	100 3-methylheptane.....	100 3-methylheptane.
100	.001	100 paraffin.....	0	100 2,2,5-trimethylhexane.....	100 2,2,5-trimethylhexane.
101	001	64.0±4.0 paraffin 36.0±4.0 olefin	±4.0	64.0 dimethylcyclohexane..... 36.0 C_8 olefin	100 dimethylcyclohexane.
104	.001	37.0±5.0 paraffin 63.0±5.0 olefin	±4.0	37.0 2,2,4-trimethylhexane 63.0 1-octene trans-4-octene 2,3-dimethyl-2-hexene	44 2,2,4-trimethylhexane. 56 1-octene. trans-4-octene. 2,3-dimethyl-2-hexene.
108	.003	68.0±3.0 paraffin 32.0±3.0 olefin	±2.0	68.0 n-octane..... 32.0 trans-2-octene	74 n-octane. 26 trans-2-octene.
110	.001	13.0±5.0 paraffin 87.0±5.0 olefin	±3.5	13.0 2,4,4-trimethylhexane.... 87.0 C_8 olefin	48 2,4,4-trimethylhexane. 52 C_8 olefin.
116	.001	100 paraffin.....	0	100 2,4-dimethylheptane.... 2,2,3-trimethylhexane	100 2,4-dimethylheptane. 2,2,3-trimethylhexane.
119	.001	100 paraffin.....	0	100 C_9 paraffin.....	100 C_9 paraffin.
123	.002	76.0±15.0 paraffin 24.0±15.0 olefin	±15.0	76.0 2,5-dimethylheptane 3,5-dimethylheptane..... 24.0 C_8 olefin	70 2,5-dimethylheptane. 3,5-dimethylheptane. 30 C_8 olefin.
125	.001	75.0±25.0 paraffin 25.0±25.0 olefin	±23.5	75.0 C_9 paraffin..... 25.0 C_8 olefin	75 C_9 paraffin. 25 C_8 olefin.
126	.009	8.0±2.0 paraffin 92.0±2.0 aromatic	±1.5	8.0 2,3-dimethylheptane..... 92.0 ethylbenzene	18 2,3-dimethylheptane. 82 ethylbenzene.
129	.036	6.5±0.5 paraffin 93.5±0.5 aromatic	±0.5	6.5 4-methyloctane 2-methyloctane..... 93.5 para-xylene meta-xylene	9 4-methyloctane. 2-methyloctane. 91 para-xylene. meta-xylene.
131	.004	100 paraffin.....	0	100 3-methyloctane.....	100 3-methyloctane.
134	.002	100 olefin.....	0	100 styrene.....	Not present.
135	.013	6.5±0.5 paraffin 93.5±0.5 aromatic	±0.5	6.5 C_9 paraffin..... 93.5 ortho-xylene	13 C_9 paraffin. 87 ortho-xylene.
139	.002	100 paraffin.....	0	100 n-nonane.....	100 n-nonane.
142	.001	52.0±18.0 paraffin 48.0±18.0 aromatic	±10.0	52.0 2,4,5-trimethylheptane 2,3,5-trimethylheptane.. 48.0 isopropylbenzene	61 2,4,5-trimethylheptane. 2,3,5-trimethylheptane. 39 isopropylbenzene.
144	.001	100 paraffin.....	0	100 2,2,3,3-tetramethylhexane 2,6-dimethyloctane	100 2,2,3,3-tetramethylhexane. 2,6-dimethyloctane.
148	.001	100 paraffin.....	0	100 C_{10} paraffin.....	100 C_{10} paraffin.
151	.001	100 paraffin.....	0	100 C_{10} paraffin.....	100 C_{10} paraffin.
152	.003	100 aromatic.....	0	100 n-propylbenzene.....	100 n-propylbenzene.
155	.011	4.0±4.0 paraffin 96.0±4.0 aromatic	±3.5	4.0 C_{10} paraffin.. 96.0 1-methyl-3-ethylbenzene	8 C_{10} paraffin. 92 1-methyl-3-ethylbenzene.
156	.005	100 aromatic.....	0	100 1-methyl-4-ethylbenzene....	100 1-methyl-4-ethylbenzene.
157	.001	100 paraffin.....	0	100 3,4,5-trimethylheptane 3,4,4-trimethylheptane.. 3,3,4-trimethylheptane	100 3,4,5-trimethylheptane. 3,4,4-trimethylheptane. 3,3,4-trimethylheptane.
158	.007	20.5±1.5 paraffin 79.5±1.5 aromatic	±0.5	20.5 C_{10} paraffin 79.5 1-methyl-2-ethylbenzene..	28 C_{10} paraffin. 72 1-methyl-2-ethylbenzene.
159	.001	100 paraffin.....	0	100 4-methylnonane..... 2-methylnonane	100 4-methylnonane. 2-methylnonane.
160	.004	100 aromatic.....	0	100 1,3,5-trimethylbenzene....	100 1,3,5-trimethylbenzene.
162	.001	43.5±4.5 paraffin 56.5±4.5 olefin	±2.0	43.5 C_{10} paraffin..... 56.5 C_9 olefin	100 C_{10} paraffin.
163	.020	0.5±0.5 paraffin 99.5±0.5 aromatic	±0.5	0.5 C_{10} paraffin... 99.5 1,2,4-trimethylbenzene	100 1,2,4-trimethylbenzene.
164	.004	58.0±7.0 paraffin 42.0±7.0 aromatic	±2.5	58.0 n-decane 42.0 sec-butylbenzene..... isobutylbenzene	100 n-decane.
165	.094	11.5±2.5 paraffin 10.5±2.5 olefin 77.0±4.0 aromatic	±1.5 ±2.5 ±2.5	11.5 C_{11} paraffin 10.5 C_{10} olefin..... 77.0 C_{10} aromatic	21 C_{11} paraffin. 79 C_{10} aromatic.

[1]Value represents average over all exhaust samples from fuel 2.

[2]The designation "olefin" is used to describe materials subtracted by the $HgSO_4$ column; therefore, it includes acetylenes and some oxygenates also. Likewise, materials designated as "aromatic" include some oxygenates also (see appendix).

[3]Large range in results reflects peculiar inadequacy of $HgSO_4 \cdot PdSO_4$ subtractive column in benzene scrubbing.

TABLE 4. - Identification of chromatographic peaks in spectra of fuel 3 and of exhaust from fuel 3

Peak No.	Mole fraction in exhaust[1]	Exhaust peak identification[2] (average percent-composition and range)			Fuel peak identification assigned
		From subtractive columns	Variation owing to experimental error	Assigned identification	
1	0.175	100 paraffin.....	0	100 methane.....	Not present.
2	.093	100 olefin.....	0	100 ethylene.....	Do.
3	.009	100 paraffin.....	0	100 ethane.....	Do.
4	.122	100 olefin.....	0	100 acetylene.....	Do.
5	.042	100 olefin.....	0	100 propylene.....	Do.
8	.003	100 olefin.....	0	100 propadiene.....	Do.
9	.006	100 olefin.....	0	100 methylacetylene.....	Do.
10	.006	100 paraffin.....	0	100 isobutane.....	100 isobutane.
11	.013	100 olefin.....	0	100 {isobutylene, 1-butene}.....	Not present.
13	.033	{89.5±4.5 paraffin, 10.5±4.5 olefin}.	±2.0	{89.5 n-butane, 10.5 1,3-butadiene}.....	100 n-butane.
14	.003	100 olefin.....	0	100 trans-2-butene.....	100 trans-2-butene.
16	.004	100 olefin.....	0	100 cis-2-butene.....	100 cis-2-butene.
18	.001	100 olefin.....	0	100 3-methyl-1-butene.....	100 3-methyl-1-butene.
19	.030	100 paraffin.....	0	100 isopentane.....	100 isopentane.
20	.001	100 olefin.....	0	100 1-pentene.....	100 1-pentene.
22	.005	{68.0±9.0 paraffin, 32.0±9.0 olefin}.	±3.5	{68.0 n-pentane, 32.0 2-methyl-1-butene}.....	{78 n-pentane., 22 2-methyl-1-butene.
23	.001	100 olefin.....	0	100 2-methyl-1,3-butadiene....	Not present.
24	.002	100 olefin.....	0	100 trans-2-pentene.....	100 trans-2-pentene.
25	.001	100 olefin.....	0	100 cis-2-pentene.....	100 cis-2-pentene.
26	.004	100 olefin.....	0	100 2-methyl-2-butene.....	100 2-methyl-2-butene.
27	.001	100 olefin.....	0	100 C_5 olefin.....	Not present.
32	.001	{52.0±13.0 paraffin, 48.0±13.0 olefin}	±6.0	{52.0 cyclopentane, 48.0 {3-methyl-1-pentene, 4-methyl-1-pentene}.....	{78 cyclopentane., 22 {3-methyl-1-pentene., 4-methyl-1-pentene.}
33	.004	100 paraffin.....	0	100 2,3-dimethylbutane.....	100 2,3-dimethylbutane.
35	.005	{86.0±8.0 paraffin, 14.0±8.0 olefin}.	±3.0	{86.0 2-methylpentane, 14.0 {2,3-dimethyl-1-butene, 4-methyl-cis-2-pentene}..	{96 2-methylpentane., 4 {2,3-dimethyl-1-butene., 4-methyl-cis-2-pentene.}
37	.002	100 paraffin.....	0	100 3-methylpentane.....	100 3-methylpentane.
38	.001	100 olefin.....	0	100 {2-ethyl-1-butene, 2-methyl-1-pentene, 1-hexene}.....	100 {2-ethyl-1-butene., 2-methyl-1-pentene., 1-hexene.}
40	.001	{67.5±21.5 paraffin, 32.5±21.5 olefin}	±6.0	{67.5 n-hexane, 32.5 cis-3-hexene}.....	{90 n-hexane., 10 cis-3-hexene.
44	.001	100 olefin.....	0	100 {2-methyl-2-pentene, 3-methyl-cis-2-pentene}..	100 {2-methyl-2-pentene., 3-methyl-cis-2-pentene.}
47	.001	{71.0±7.0 paraffin, 29.0±7.0 olefin}.	±4.5	{71.0 methylcyclopentane, 29.0 3-methyl-trans-2-pentene}	{79 methylcyclopentane., 21 3-methyl-trans-2-pentene.
48	.005	{97.5±2.5 paraffin, 2.5±2.5 olefin}.	±2.5	{97.5 2,4-dimethylpentane, 2.5 2,3-dimethyl-2-butene}....	100 2,4-dimethylpentane.
52	.004	100 olefin.....	0	100 methylcyclopentene.....	100 methylcyclopentene.
53[3]	.026	{51.0±43.0 paraffin, 49.0±43.0 aromatic}	±43.0	{51.0 cyclohexane, 49.0 benzene}.....	{4 cyclohexane., 96 benzene.
57	.015	100 paraffin.....	0	100 {2,3-dimethylpentane, 2-methylhexane}.....	99 {2,3-dimethylpentane., 2-methylhexane., 1 {cyclohexene., 4-methyl-1-hexene.}
59	.001	{70.0±9.0 paraffin, 30.0±9.0 olefin}.	±3.0	{70.0 3-methylhexane, 30.0 C_7 olefin}.....	100 3-methylhexane.
66	.014	{98.5±1.5 paraffin, 1.5±1.5 olefin}.	±1.5	{98.5 2,2,4-trimethylpentane, 1.5 C_7 olefin}..	100 2,2,4-trimethylpentane.
79	.005	100 paraffin.....	0	100 {2,4-dimethylhexane, 2,5-dimethylhexane}.....	100 {2,4-dimethylhexane., 2,5-dimethylhexane.}
90	.005	100 paraffin.....	0	100 2,3,4-trimethylpentane....	100 2,3,4-trimethylpentane.
91	.006	100 paraffin.....	0	100 2,3,3-trimethylpentane....	100 2,3,3-trimethylpentane.

See footnotes at end of table.

TABLE 4. - Identification of chromatographic peaks in spectra of fuel 3 and of exhaust from fuel 3--Continued

Peak No.	Mole fraction in exhaust[1]	Exhaust peak identification[2] (average percent-composition and range)			Fuel peak identification assigned
		From subtractive columns	Variation owing to experimental error	Assigned identification	
92	0.132	2 paraffin 98 aromatic	0	2 2,3-dimethylhexane 98 toluene	2 2,3-dimethylhexane. 98 toluene.
97	.001	100 paraffin	0	100 3-methylheptane	Not present.
100	.004	100 paraffin	0	100 2,2,5-trimethylhexane	100 2,2,5-trimethylhexane.
126	.019	1.5±0.5 paraffin 98.5±0.5 aromatic	±0.5	1.5 2,3-dimethylheptane 98.5 ethylbenzene	2 2,3-dimethylheptane. 98 ethylbenzene.
129	.067	1.0 paraffin 99.0 aromatic	0	1.0 4-methyloctane, 2-methyloctane 99.0 para-xylene, meta-xylene	100 para-xylene, meta-xylene.
133	.001	100 paraffin	0	100 C_9 paraffin	100 C_9 paraffin.
134	.003	100 olefin	0	100 styrene	100 C_9 paraffin.
135	.018	5.5±0.5 paraffin 94.5±0.5 aromatic	±0.5	5.5 C_9 paraffin 94.5 ortho-xylene	100 ortho-xylene.
139	.001	100 paraffin	0	100 n-nonane	100 n-nonane.
142	.001	50.5±6.5 paraffin 49.5±6.5 aromatic	±4.0	50.5 2,4,5-trimethylheptane, 2,3,5-trimethylheptane 49.5 isopropylbenzene	53 2,4,5-trimethylheptane, 2,3,5-trimethylheptane. 47 isopropylbenzene.
152	.003	100 aromatic	0	100 n-propylbenzene	100 n-propylbenzene.
155	.014	0.5±0.5 paraffin 99.5±0.5 aromatic	0	0.5 C_{10} paraffin 99.5 1-methyl-3-ethylbenzene	100 1-methyl-3-ethylbenzene.
156	.006	100 aromatic	0	100 1-methyl-4-ethylbenzene	100 1-methyl-4-ethylbenzene.
157	.002	100 paraffin	0	100 3,4,5-trimethylheptane, 3,4,4-trimethylheptane, 3,3,4-trimethylheptane	100 3,4,5-trimethylheptane, 3,4,4-trimethylheptane, 3,3,4-trimethylheptane.
158	.007	1.0±1.0 paraffin 99.0±1.0 aromatic	±1.0	1.0 C_{10} paraffin 99.0 1-methyl-2-ethylbenzene	100 1-methyl-2-ethylbenzene.
160	.005	11.5±2.5 paraffin 88.5±2.5 aromatic	±1.0	11.5 C_{10} paraffin 88.5 1,3,5-trimethylbenzene	13 C_{10} paraffin. 87 1,3,5-trimethylbenzene.
162	.001	100 paraffin	0	100 C_{10} paraffin	100 C_{10} paraffin.
163	.022	2.5±0.5 paraffin 97.5±0.5 aromatic	±0.5	2.5 C_{10} paraffin 97.5 1,2,4-trimethylbenzene	100 1,2,4-trimethylbenzene.
164	.001	37.0±22.0 paraffin 63.0±22.0 aromatic	±6.0	37.0 n-decane 63.0 sec-butylbenzene, isobutylbenzene	100 n-decane.
165	.033	9.5±2.5 paraffin 14.0±5.0 olefin 78.5±4.5 aromatic	±1.0 ±2.5 ±2.5	9.5 C_{11} paraffin 14.0 C_{10} olefin 78.5 C_{10} aromatic	11 C_{11} paraffin. 89 C_{10} aromatic.

[1]Value represents average over all exhaust samples from fuel 3.

[2]The designation "olefin" is used to describe materials subtracted by the $HgSO_4$ column; therefore, it includes acetylenes and some oxygenates also. Likewise, materials designated as "aromatic" include some oxygenates also (see appendix).

[3]Benzene not fully scrubbed.

TABLE 5. - Identification of chromatographic peaks in spectra of fuel 4 and of exhaust from fuel 4

Peak No.[1]	Exhaust peak identification[2] (within-peak composition or range)		Fuel peak identification assigned
	From subtractive column	Assigned identification	
1	Paraffin	Methane	Not present.
2	Olefin	Ethylene	Do.
3	Paraffin	Ethane	Do.
4	Olefin	Acetylene	Do.
5	...do...	Propylene	Propane.
8	...do...	Propadiene	Not present.
9	...do...	Methylacetylene	Do.
10	Paraffin	Isobutane	Isobutane.
11	Olefin	1-Butene and isobutylene	1-Butene and isobutylene.
13	5--18 percent paraffin Remainder olefin	10 percent n-butane 90 percent 1,3-butadiene	n-Butane.
14	Olefin	trans-2-Butene	trans-2-Butene.
16	...do...	cis-2-Butene	cis-2-Butene.
18	...do...	3-Methyl-1-butene	3-Methyl-1-butene.
19	Paraffin	Isopentane	Isopentane.
20	Olefin	1-Pentene	1-Pentene.
21	...do...	2-Methyl-1-butene	2-Methyl-1-butene.
22	Paraffin	n-Pentane	n-Pentane.
23	Olefin	2-Methyl-1,3-butadiene	Not present.
24	...do...	trans-2-Pentene	trans-2-Pentene.
25	...do...	cis-2-Pentene	cis-2-Pentene.
26	...do...	2-Methyl-2-pentene	2-Methyl-2-pentene.
27	...do...	C_5 Olefin	Not present.
28	Paraffin	2,2-Dimethylbutane	2,2-Dimethylbutane.
29	Olefin	C_5 Olefin	Not present.
30	...do...	C_6 Olefin	Do.
31	...do...	Cyclopentene	Cyclopentene.
32	50 percent paraffin 50 percent olefin	50 percent cyclopentane 50 percent 3- and 4-methyl-1-pentene	37 percent cyclopentane. 63 percent 3- and 4-methyl-1-pentene.
33	Paraffin	2,3-Dimethylbutane	2,3-Dimethylbutane.
34	Olefin	C_6 Olefin	Not present.
35	Paraffin	2-Methylpentane	2-Methylpentane.

See footnotes at end of table.

TABLE 5. - Identification of chromatographic peaks in spectra of fuel 4 and of exhaust from fuel 4--Continued

Peak No.[1]	Exhaust peak identification[2] (within-peak composition or range)		Fuel peak identification assigned
	From subtractive column	Assigned identification	
36	Olefin	C_6 Olefin	Not present.
37	Paraffin	3-Methylpentane	3-Methylpentane.
38	Olefin	2-Methyl-1-pentene 1-Hexene 2-Ethyl-1-butene	2-Methyl-1-pentene. 1-Hexene. 2-Ethyl-1-butene.
40	Paraffin	n-Hexane	n-Hexane.
41	Olefin	trans-3-Hexene	trans-3-Hexene.
42	ditto	trans-2-Hexene 3-Methylcyclopentene	trans-2-Hexene. 3-Methylcyclopentene.
44	ditto	2-Methyl-2-pentene 3-Methyl-cis-2-pentene	2-Methyl-2-pentene. 3-Methyl-cis-2-pentene.
46	ditto	cis-2-Hexene	cis-2-Hexene.
47	40--57 percent paraffin Remainder olefin	49 percent methylcyclopentane 51 percent olefin	45 percent methylcyclopentane. 55 percent 3-methyl-trans-2-pentene.
48	Paraffin	2,4-Dimethylpentane	2,4-Dimethylpentane.
49	Olefin	2,3-Dimethyl-2-butene	2,3-Dimethyl-2-butene.
51	ditto	C_6 Olefin	C_6 Olefin.
52	ditto	1-Methylcyclopentene	1-Methylcyclopentene.
53	ditto	Benzene[3]	Benzene.[3]
55	ditto	C_6 Olefin	C_6 Olefin.
57	Paraffin	2-Methylhexane 2,3-Dimethylpentane	2-Methylhexane. 2,3-Dimethylpentane.
59	ditto	3-Methylhexane	3-Methylhexane.
66	ditto	2,2,4-Trimethylpentane	2,2,4-Trimethylpentane.
69	75--81 percent paraffin Remainder olefin	78 percent n-heptane 22 percent C_7 olefin	60 percent n-heptane. 40 percent C_7 olefin.
70	Olefin	C_7 Olefin	C_7 Olefin.
76	78--88 percent paraffin Remainder olefin	83 percent methylcyclohexane 17 percent 2,3-dimethyl-2-pentene and cis-2-heptene	76 percent methylcyclohexane. 24 percent 2,3-dimethyl-2-pentene and cis-2-heptene.
79	Paraffin	2,4-Dimethylhexane 2,5-Dimethylhexane	2,4-Dimethylhexane. 2,5-Dimethylhexane.
90	ditto	2,3,4-Trimethylpentane	2,3,4-Trimethylpentane.

91	97--99 percent paraffin Remainder olefin	98 percent 2,3,3-trimethylpentane 2 percent C_7 olefin	94 percent 2,3,3-trimethylpentane. 6 percent C_7 olefin.
92	95 percent aromatic 5 percent paraffin	95 percent toluene 5 percent C_8 paraffin	97 percent toluene. 3 percent C_8 paraffin.
97	Paraffin	C_8 Paraffin	C_8 Paraffin.
100	do	2,2,5-Trimethylhexane	2,2,5-Trimethylhexane.
113	do	2,3,5-Trimethylhexane	2,3,5-Trimethylhexane.
126	Aromatic[4]	Ethylbenzene	98 percent ethylbenzene. 2 percent C_9 paraffin.
129	do.[4]	p- and m-Xylene	98 percent p- and m-xylene. 2 percent C_9 paraffin.
132	Paraffin	C_9 Paraffin	C_9 Paraffin.
135	Aromatic	o-Xylene	o-Xylene.
142	do	Isopropylbenzene	Isopropylbenzene.
152	do	n-Propylbenzene	n-Propylbenzene.
155	Aromatic[4]	1-Methyl-3-ethylbenzene 1-Methyl-4-ethylbenzene	98 percent 1-methyl-3-ethylbenzene. 1-methyl-4-ethylbenzene. 2 percent C_{10} paraffin.
158	Aromatic	1-Methyl-2-ethylbenzene	1-Methyl-2-ethylbenzene.
160	Aromatic[4]	1,3,5-Trimethylbenzene	94 percent 1,3,5-trimethylbenzene. 6 percent C_{10} paraffin.
163	do.[4]	1,2,4-Trimethylbenzene	98 percent 1,2,4-trimethylbenzene. 2 percent C_{10} paraffin.
165	do.[4]	C_9 and C_{10} Aromatic	99 percent C_9 and C_{10} aromatic. 1 percent C_{11} paraffin.

[1]Only fuel peaks greater than 0.1 mole pct are included.

[2]The designation "olefin" is used to describe materials subtracted by the $HgSO_4$ column; therefore, it includes acetylenes and some oxygenates also. Likewise, materials designated as "aromatic" include some oxygenates also (see appendix).

[3]Large range in results reflects peculiar inadequacy of $HgSO_4 \cdot PdSO_4$ subtractive column in benzene scrubbing.

[4]Contains trace of paraffin.

For the C_4 and heavier components, peak identifications were based primarily on subtractive-column data and were expressed in terms of hydrocarbon type (paraffin, aliphatic unsaturate, or aromatic) or in terms of a hydrocarbon mixture of known hydrocarbon type composition. Such identification data suffered from uncertainties (see the appendix). For example, initial tests with exhaust samples suggested the presence of "aromatic" component peaks in the light-component part of the chromatographic spectrum where aromatics cannot be present. Subsequent work with synthetic mixtures revealed that these suspect "aromatics" were in reality either oxygenates or olefins that were not removed quantitatively by the $HgSO_4$ column but were removed by the ($HgSO_4 \cdot PdSO_4$) column (table 2). This information and the fact that oxygenate peaks could be recognized easily from their characteristic peak tailing permitted correct identification of the suspect "aromatic" peaks in the C_1 through C_7 component range. In the heavier component part of the spectrum, where aromatics are abundantly present, uncertainty was unavoidable because the suspect "aromatics" could be either aromatics or olefins. Fortunately, this uncertainty was not critical because C_7 and heavier olefins do not seem to be present in fuels or exhaust at significant levels.

Comparison of the fuel-component hydrocarbon class identification established in this study showed excellent agreement with specific identification reported by others for the same fuels. Note that the reported evidence (5) is based on mass spectrometric and retention-time data that were obtained with an extremely high resolution chromatographic technique; such technique, albeit tedious, can provide unequivocal peak identification.

The reliability of the peak-identification data is further validated by the rational pattern that was observed in the relationship between the identities of fuel peaks and those of corresponding exhaust peaks. Thus, in the portion of the spectra that reflects C_7 and heavier components, exhaust and corresponding fuel peak identities are essentially the same except that in the exhaust chromatogram the nonaromatic portion of the fuel peaks appears to be suppressed and, on occasions, eliminated. Such a pattern is consistent with accepted suppositions that the heavier exhaust hydrocarbons are unburned fuel components and, that of these components, the aromatics are more combustion-resistant than the aliphatics.

Peak-identification errors of possible consequence include the misidentification of peaks involving oxygenated exhaust components. Recognizable exhaust oxygenate peaks, such as those for acetaldehyde and acetone, have a characteristic tail configuration that extends into several neighboring peaks. The oxygenate proportion of these neighboring composite peaks could not be determined because the subtractive columns do not clearly differentiate between oxygenates and paraffins, olefins, or aromatics (see the appendix). Therefore, oxygenates were unavoidably misidentified as paraffins, olefins, aromatics, or mixtures of these hydrocarbons. The magnitude of this misidentification could not be determined. It would depend on oxygenate level and on the hydrocarbon to which the oxygenate was attributed.

To summarize, the investigators feel that peak identification data were sufficiently specific and reliable to permit exploring the second and major

question posed in this study, "Does the composition of material represented by each peak vary among chromatograms of various fuels and among chromatograms of exhaust from various fuels and engines?"

The question of variation in within-peak composition among chromatograms of different fuels has practical significance only if the fuels in question are commercial blends. The fuels used in this and in previous studies at this laboratory are experimental fuels, but were prepared from commercially available blending stocks. Therefore, data obtained with these fuels are appropriate to the purpose of the study. In the course of this and previous studies, peak-identification data were obtained for chromatograms of 25 fuels. Examination of these data showed that of 165 measurable peaks (or groups of incompletely resolved peaks) in each chromatogram, as many as 35 peaks represented components or component mixtures that varied in within-peak composition from fuel to fuel. Therefore, the chromatographic method of this study requires that, in fuel analysis, chromatographic peaks be identified experimentally for each separate fuel.

Variation in the within-peak composition among exhaust chromatograms is shown by the data in tables 2 to 5. These data show that for several exhaust peaks, within-peak composition differs when the parent fuel differs. In contrast, for the same parent fuel but various automobile engines or engine conditions, the composition of material within each peak varies little among the respective exhaust chromatograms. To illustrate, peak 47 represents a paraffin/olefin mixture that is 92.5 percent paraffin for fuel 1 (table 2), 81.5 percent paraffin for fuel 2 (table 3), 71.0 percent for fuel 3 (table 4), and 49.0 percent for fuel 4 (table 5). Further, for the same fuel, variation in composition of material under peak 47 was only ±7 percent (table 4) at the most, and even this variation was for the greater part caused by experimental error (±4.5 percent, table 4). This variation in within-peak composition is best evaluated from its effect upon the exhaust-reactivity value that is computed from compositional data and specific reactivities. This computation is according to the equation, $R = \Sigma X_i r_i$, where R designates reactivity of the exhaust hydrocarbon mixture and X_i and r_i are mole fraction and specific reactivity, respectively, for the ith component. Using mole fraction values for a typical exhaust, and published values (3) for specific rate-of-NO_2-formation reactivities, the total variation in within-peak composition shown in tables 2 through 5 will cause variation in exhaust-reactivity value equivalent to ±2.3 percent, ±1.8 percent, ±1.7 percent, and ±2.0 percent, for fuels 1, 2, 3, and 4, respectively. Such a variation is considered unimportant.

These results suggest that for each parent fuel, exhaust peak identities must be established only once; these peak identities can then be used in interpreting chromatographic spectra of all exhaust samples obtained from different automobiles but from the same fuel. This method for interpreting chromatographic spectra is now in routine use in the Bartlesville laboratory (2).

The results and conclusions discussed in preceding paragraphs have been based on data obtained from automobiles either with emission control or not equipped with first-generation control. For automobiles with second-generation control devices (such as catalytic or thermal reactors), these

conclusions may not be valid. In fact, based on preliminary data, this limitation appears to be true, and if verified, it would suggest that it may be necessary to obtain separate sets of peak identities in order to interpret GLC spectra of exhaust from drastically different automotive combustion systems.

CONCLUSIONS

1. For pollution related emission studies, satisfactory interpretation of GLC spectra of exhaust and fuels can be accomplished through the use of subtractive-column techniques.

2. Of the subtractive materials used, the olefin-sensitive mercuric sulfate has the two following inadequacies: It does not subtract quantitatively certain olefins, and it causes formation of new products that may interfere with the subtractive column's function.

3. In GLC analysis of exhaust from different automobiles, it is not necessary to establish experimentally peak identities for each exhaust spectrum separately; the same set of peak-identity assignments can be used for spectra of all exhaust samples (different automobiles) obtained from one fuel.

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APPENDIX

Results from measurements of efficiency of the subtractive columns are given in table A-1. These data show two anomalies in the function of the $HgSO_4$ column. First, contrary to expectation, certain olefins were not removed quantitatively by the column. Second, new peaks appeared in the chromatograms of column-treated samples. These findings were verified by tests using a new column made of a regenerated packing mixture (4). Evidently, olefins of some undetermined type do not react quantitatively with $HgSO_4$ subtractive agent. Of the new peaks (table A-1), unknown 1 appeared in the spectrum where benzene (or cyclohexane) appears; unknown 2 was located just before toluene, where an unknown C_8 paraffin appears. Efforts to associate the appearance of these unknown peaks with the composition of the hydrocarbon mixture that entered the $HgSO_4$ column involved testing the following: Ethylene, propylene, trans-2-butene, 3-methyl-1-butene, 2-methyl-2-butene, 4-methyl-1-pentene, 3-methyl-trans-2-pentene, and trans-3-hexene. Of these hydrocarbons, 2-methyl-2-butene was found to cause the appearance of unknown 1 at a ppmC level ranging from 50 to 60 percent of that of 2-methyl-2-butene. The 3-methyl-trans-2-pentene was found to cause the appearance of unknown 2 at a ppmC level equal to about 25 percent of that of 3-methyl-trans-2-pentene. As expected, paraffins did not contribute to the buildup of the unknowns. Finally, from mass-spectrometry and GLC retention-time data, the unknowns 1 and 2 were identified as 3-methyl-2-butanone and 3-methyl-2-pentanone, respectively.

All oxygenates tested were subtracted quantitatively by the $HgSO_4 \cdot PdSO_4$ column, and some by the $HgSO_4$ column also. Therefore, on the basis of subtractive column data alone, the oxygenate peaks in the chromatographic spectra of exhaust are mistaken for aromatics or olefins. Such a mistake is not serious in the case of aldehydes because aldehydes have reactivity comparable to that of olefins and aromatics. For nonaldehyde oxygenates, however, this misidentification will cause error proportional to the relative levels of such oxygenates.

TABLE A-1. - Efficiencies of mercury ($HgSO_4$) and mercury-palladium ($HgSO_4 \cdot PdSO_4$) columns in removing hydrocarbons and oxygenates[1]

Compound	Column input concentration, ppm	Removal efficiency, pct	
		$HgSO_4$ column	$HgSO_4 \cdot PdSO_4$ column
Paraffins:			
Methane	195	0	-
Ethane	26	0	-
n-Butane	24	0	-
Isobutane	25	0	-
Isopentane	23	0	-
Cyclohexane	2- 25	5.4	3.9
Isooctane	2- 25	3.5	4.0
n-Undecane	2- 25	7.1	0

See footnotes at end of table.

TABLE A-1. - Efficiencies of mercury ($HgSO_4$) and mercury-palladium ($HgSO_4 \cdot PdSO_4$) columns in removing hydrocarbons and oxygenates[1]--Continued

Compound	Column input concentration, ppm	Removal efficiency, pct	
		$HgSO_4$ column	$HgSO_4 \cdot PdSO_4$ column
Olefins:			
Ethylene	101	100	-
Propylene	34	100	-
trans-2-Butene	23.5	84	-
trans-2-Pentene	4.4	72	100
3-Methyl-1-butene	15.4	99	-
2-Methyl-2-butene	15	100	100
1-Hexene	6.3	100	100
trans-2-Hexene	6.5	44	100
trans-3-Hexene	7.1	34- 68	100
4-Methyl-1-pentene	6.7	84-100	100
3-Methyl-trans-2-pentene	8.3	100	100
4-Methyl-trans-2-pentene	4.8	25	100
4-Methyl-cis-2-pentene	1.0	84	100
1-Octene	2- 25	100	100
1-Decene	2- 25	100	100
Aromatics:			
Benzene	2- 25	5.0	Varying
Toluene	2- 25	5.9	100
p-Xylene	2- 25	7.0	100
n-propyl-benzene	2- 25	0	100
1-Ethyl-2-isopropyl-benzene	2- 25	6.3	100
1,3,5-Trimethylbenzene	2- 25	9.0	100
Oxygenates:			
Acetaldehyde	30-100	58	100
Propionaldehyde	30-100	25	100
Methanol	30-100	100	100
Ethanol	30-100	100	100
Isopropanol	30-100	100	100
Acetone	30-100	98	100
Methyl-ethyl-ketone	30-100	85	100
Propylene oxide	30-100	96	100
Ethyl acetate	30-100	30	100
Unknowns:			
Unknown 1	0	([2])	-
Unknown 2	0	([2])	-

[1] Synthetic blends were prepared with each listed hydrocarbon and oxygenate at one or more concentration levels. When more than one concentration level was used, concentration ranges are shown. When efficiency was close to zero or 100, within experimental error, it was given a zero or 100 value.

[2] Peaks are of varying size and appear only in chromatograms of samples treated by this column. The unknown 1 peak is located at the point of the spectrum where the benzene peak appears. The unknown 2 peak is located at the point of the spectrum where a C_8 paraffin appears shortly before toluene.

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