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STABILITY CHARACTERISTICS OF HYDROCARBON FUELS FROM ALTERNATIVE SOURCES

DEPARTMENT OF ENERGY, BARTLESVILLE, OK.
BARTLESVILLE ENERGY TECHNOLOGY CENTER

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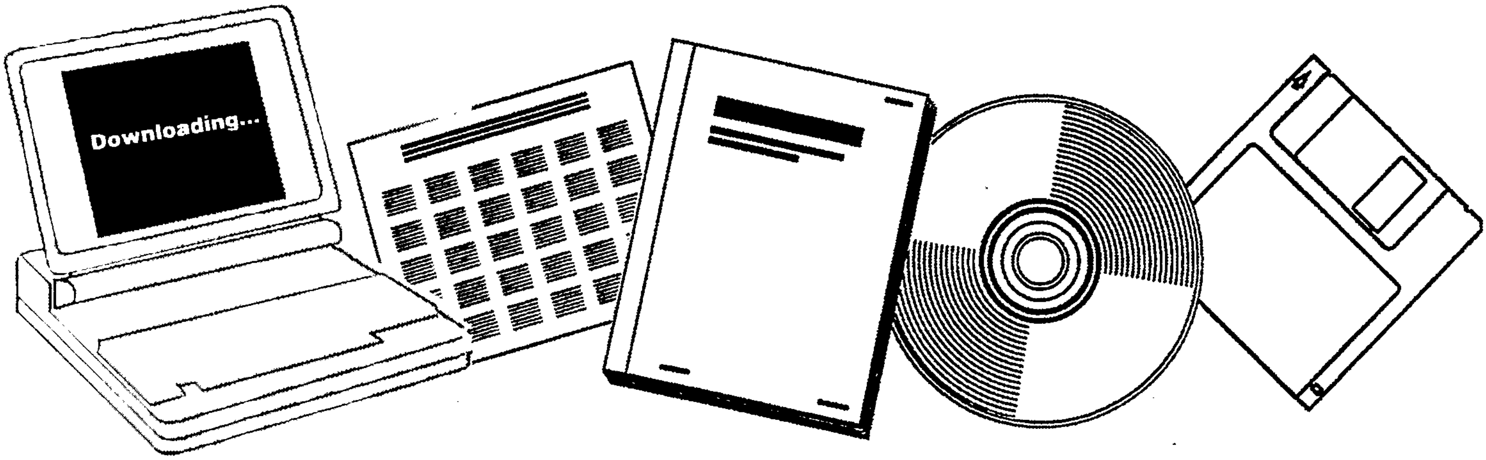

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BETCRI7823

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Date Published—March 1979

UNITED STATES DEPARTMENT OF ENERGY
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CONTENTS

CONTENTS—Continued

ILLUSTRATIONS

TABLES

STABILITY CHARACTERISTICS OF HYDROCARBON FUELS FROM ALTERNATIVE SOURCES

by

Dennis W. Brinkman,[1] Marvin L. Whisman,[2]
and John N. Bowden[3]

ABSTRACT

Two samples of gasoline and six samples of jet fuel derived from coal, tar sands or oil shale were subjected to accelerated storage stability tests at 43.3° C (110° F) and 93.3° C (200° F). Two samples of commercial, petroleum-based gasoline and one sample of a petroleum based jet fuel also were evaluated in this program for comparative purposes. One gasoline, which was derived from coal via the Fischer-Tropsch process, exhibited a high initial gum content which did not vary over a period of 16 weeks at 43.3° C (110° F), but increased significantly from 16 to 32 weeks. A sample of naphtha from tar sands showed moderately high gum level after 32 weeks. Petroleum-based gasolines had moderate gum levels at the end of the storage period. Most of the jet fuels appeared to be relatively stable after 16 weeks of storage; however, after 32 weeks, three of the fuels developed a large amount of gum. After 16 hours at 93.3° C (200° F), the coal-derived gasoline had the highest gum content. Correlation of the gum concentration after 32 weeks storage with predicted gum levels based on 16 hours test results was reasonably good for the gasoline samples, but very poor for the jet fuel samples. High-temperature thermal stability test results showed considerable scatter. Considering the primitive nature of some of the synfuels, relative stabilities seem reasonable as initial attempts, but much improvement will be required for commercial acceptance.

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INTRODUCTION

The United States is now importing nearly 50 percent of its crude petroleum requirements and this number could increase as domestic production decreases and reserves are depleted. Alternative domestic energy sources are needed. Among the possible choices, synthetic fuels derived from coal, oil shale, and tar sands can be generally compatible with today's automobile, diesel and aircraft engines and with the existing system for refining and distributing petroleum products. Technology exists for manufacture of synthetic fuels, but little information is available on their characteristics (3,8).[4] Preliminary characterization of a synthetic crude oil from coal shows relatively high percentages of sulfur, nitrogen, oxygen, trace metals, unsaturated hydrocarbons, and polar materials (9). Earlier studies on petroleum fuels have shown all these types of compounds contribute to fuel instability during storage (4,7). Therefore it is essential that information be developed on the storage and thermal characteristics of fuels derived from nonpetroleum sources.

The objectives of the current work are to determine the storage characteristics of representative liquid fuels derived from coal, oil shale, and tar sands, to analyze representative gasolines, diesel fuels and jet fuels for hydrocarbons and nonhydrocarbons that are known precursors of deterioration products, and to provide information that will guide refiners in selecting processes to minimize fuel deterioration through removal or inhibition of reactive components.

In the interest of disseminating research results on synfuel stability as rapidly as possible, this report summarizes the status of the project to date, with a more in-depth, detailed discussion to follow at a later date.

EXPERIMENTAL

Description of Test Fuels

A number of samples of hydrocarbon fuels derived from coal, shale, and tar sands were obtained for this investigation and are identified and described as follows:

G-C1 - SASOL Gasoline

This material was produced in South Africa by conversion of coal to liquid hydrocarbon fuels in two major steps. The first was gasification of coal by the Lurgi process where the coal was reacted with steam and oxygen to yield primarily a mixture of hydrogen and carbon monoxide which is known as synthesis gas. This gas was subjected to the Fischer-Tropsch synthesis reaction to produce hydrocarbons for blending into gasoline. The material

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[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

used here is a finished gasoline containing lead antiknock additives and was obtained through the Lawrence Livermore Laboratory in California. The sample was received on February 22, 1977 and was kept in cold storage prior to evaluation.

G-T1 - Tar Sands Naphtha

The Athabasca oil sands (sometimes called tar sands) yield a heavy oil or bitumen after strip mining and an elaborate hot water process for separating the bitumen from the sand, shale and clay mixture. The bitumen is processed through a refinery where a coker produces naphtha, kerosene and gasoline fractions in addition to gas which is recovered. The three liquid fractions are hydrotreated. Sample G-T1 is representative of the naphtha fraction derived from tar sands bitumen as described above. This material was received from Suntech, Inc. on December 2, 1976 and maintained in cold storage.

G-P1 - Commercial Leaded, Regular Grade Gasoline

This material was obtained from a local service station on June 6, 1977, just prior to initiation of the storage program.

G-P2 - Commercial Unleaded Gasoline

This sample also was obtained from a local service station on June 16, 1977 prior to the investigation and, as in the case of G-P1, was included in the program to establish a base line with petroleum-derived products.

J5-P1 - Petroleum JP-5

This fuel meets the requirements of Military Specification, MIL-T-5624-J, Turbine Fuel, Aviation, Grade JP-5, and was obtained from a San Antonio, TX refinery on May 20, 1976. J5-P1 was included in this investigation as a representative of a petroleum-derived fuel.

J5-S1 - JP-5 Produced from Shale Oil

This fuel resulted from a program conducted by Applied Systems Corporation under an Office of Naval Research Contract in which 9,956 barrels of crude shale oil produced by the Paraho process plant located at the Naval Oil Shale Reserve, Anvil Points, CO, were refined into a number of military fuels, including 650 barrels of JP-5. The material as received at the Naval Air Propulsion Test Center did not meet some of the JP-5 requirements such as particulate contaminant, gum content, thermal stability and freezing point. The samples received for this study from the Naval Air Propulsion Test Center had considerably improved gum content and particulate contaminant; however the other properties were virtually equivalent to those reported by the NAPTC. Some improvement is occasionally observed when initial reactive impurities combine and settle out, and this is probably what happened with this fuel.

J5-T1 - JP-5 Derived from Athabasca Tar Sands

A hydrotreated kerosene is one of three fractions derived from the processing of bitumen extracted from oil sands as described in the production of sample G-T1, Tar Sands Naphtha. This kerosene as it leaves the hydrotreater has properties that meet most of the requirements of JP-5. This was received from NAPTC on December 2, 1976.

J5-C1 - JP-5 Refined from Coal Syncrude Produced by the COED Process

A synthetic crude oil derived from Western Kentucky coal was processed further by Sun Oil Co. using severe hydrogenation to obtain a fuel that met most of the requirements of JP-5. This COED product was received from NAPTC on March 15, 1977.

JA-S1 - Jet A Fuel Produced from Paraho Shale Oil

The Air Force Wright Aeronautical Laboratories at Wright-Patterson AFB obtained 22 samples of Jet A derived from Paraho shale oil which had been refined by Exxon to varying levels of sulfur and nitrogen content. Three of these samples containing low sulfur and a wide range of nitrogen were received on July 9, 1977 and included in this program. The first one, JA-S1, had the highest nitrogen level.

JA-S2 - Jet A Fuel Produced from Paraho Shale Oil

This sample had the lowest level of nitrogen of the three shale oil Jet A samples.

JA-S3 - Jet A Fuel Produced from Paraho Shale Oil

This fuel contained an intermediate level of nitrogen.

Fuel Properties

Physical and chemical properties of the gasolines in this program are shown in table 1. These characteristics as well as those for the synthetic jet fuels investigated were measured by the procedures listed in table A-1 of Appendix A. Most test methods are identified by ASTM numbers or are described elsewhere in the appendix.

The properties of the SASOL gasoline, G-C1, appear to be typical of a petroleum base gasoline with the exception of a high unwashed existent gum value. As would be expected from a straight run product, the naphtha from tar sands has very low octane ratings compared to commercial gasolines. Simulated distillations and aromatic distribution by gas chromatography were performed on the gasoline samples and the data appear in table 2. The simulated distillation data for the SASOL gasoline imply a typical hydrocarbon composition, while the aromatic distribution shows a relatively high benzene content. The naphtha from tar sands has less-low-boiling components, and most of the aromatic

TABLE 1. - Properties of gasolines

Properties	SASOL gasoline	Tar Sands naphtha	Regular leaded gasoline	ASTM D439 limits for "regular" gasoline[1]	Unleaded gasoline	ASTM D439 limits for unleaded gasoline[2]
Code Number	G-C1	G-T1	G-P1		G-P2	
Specific gravity 15.6/15.6° C	0.7385	0.7424	0.7320	NR[3]	0.7459	NR
Gravity, °API	60.1	59.1	61.8	NR	58.2	NR
RVP, kPa (lbs)	57.8(8.4)	32.4(4.7)	66.2(9.6)	79(11.5) max	63.4(9.2)	79(11.5) max
Distillation, °C(°F)						
IBP	37(98)	39(103)	31(87)	NR	31(87)	NR
10 percent evaporated	54(130)	63(146)	51(123)	60(140) max	53(128)	60(140) max
20 percent evaporated	67(152)	82(180)	61(141)	NR	69(156)	NR
30 percent evaporated	78(173)	101(213)	72(161)	NR	83(182)	NR
40 percent evaporated	89(193)	116(241)	84(183)	NR	95(203)	NR
50 percent evaporated	101(213)	131(267)	98(209)	77-116(170-240)	107(225)	77-116(170-240)
60 percent evaporated	112(234)	144(292)	116(240)	NR	121(250)	NR
70 percent evaporated	124(256)	158(317)	133(272)	NR	138(280)	NR
80 percent evaporated	141(286)	170(338)	151(304)	NR	153(308)	NR
90 percent evaporated	163(326)	183(362)	172(342)	185(365) max	172(342)	185(365) max
EP	192(378)	211(412)	212(414)	225(437) max	199(390)	225(437) max
percent recovered	97.0	98.0	98	NR	97.0	NR
percent residue	1.8	1.7	1	2 max	1.8	2 max
percent loss	1.2	0.3	1	NR	1.2	NR
Existent gum, unwashed, mg/100 ml	19.6	2.8	2.9	NR	1.1	NR
washed, mg/100 ml	3.4	1.0	2.5	5 max	1.1	5 max
Oxidation stability, minutes	952	>1440	>1440	NR	>1440	NR
Copper corrosion, ASTM rating	1A	1A	1A	1 max	1A	1 max
Research octane number	94.6	48.5	93.4	[4]	91.0	[5]
Motor octane number	83.8	41.4	88.7	[4]	83.6	[5]
Water and sediment	Trace	0	Trace	NR	0	NR
Lead, g/1 (g/gal)	0.29(1.1)	<0.001(<0.001)	0.86(3.25)	1.1(4.2) max	0.001(0.006)	0.013(0.05) max
Phosphorus, mg/1 (mg/gal)	1.84(7.0)	0.32(0.001)	0.15(0.58)	NR	0.03(0.11)	1.3(5.0) max
Sulfur, wt-pct	0.004	0.05	0.01	0.10 max	0.003	0.10 max
Carbon, wt-pct	85.96	84.80	85.83	NR	85.81	NR
Hydrogen, wt-pct	13.42	14.73	13.50	NR	13.83	NR
Oxygen, wt-pct	0.45	0.54	0.22	NR	0.18	NR
Nitrogen, wt-pct	0.015	0.015	0.49	NR	0.05	NR
Aromatics, vol-pct (FIA)	23	8	23	NR	29	NR
Olefins, vol-pct (FIA)	0	0	4	NR	4	NR

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[1] Medium volatility (Class C), leaded.

[2] Medium volatility (Class C), unleaded.

[3] NR - No requirement.

[4] (R + M)/2 = 89 min.

[5] (R + M)/2 = 87 min.

TABLE 2. - Gas chromatography analyses of gasolines

Properties Code Number	SASOL gasoline G-C1	Tar Sands naphtha, G-T1	Regular leaded gasoline, G-P1	Unleaded gasoline, G-P2
Simulated distillation, GC, °C				
IBP	-5	-4	-10	-8
10 percent over	37	39	31	32
20 percent over	63	72	50	63
30 percent over	85	98	68	89
40 percent over	92	117	90	98
50 percent over	101	133	105	114
60 percent over	114	147	122	137
70 percent over	137	166	140	148
80 percent over	147	181	164	167
90 percent over	176	200	185	182
95 percent over	196	212	204	194
98 percent over	217	226	228	212
FBP	237	250	251	242
Propane, wt-pct	0.01	0	0.08	0.04
Isobutane, wt-pct	0.3	0.1	0.6	1.0
n-Butane, wt-pct	1.6	2.5	2.9	4.3
Isopentane, wt-pct	5.1	3.5	8.3	5.8
n-Pentane, wt-pct	5.5	5.7	7.2	3.9
Others boiling below 38° C	1.7	0	0.04	0.04
Total below 38° C	14.1	11.8	19.2	15.1
Aromatic distribution, GC				
Benzene, vol-pct	3.8	0.1	1.3	1.1
Toluene, vol-pct	4.7	0.5	4.6	4.7
Ethylbenzene, vol-pct	1.1	0.2	1.0	1.5
m- & p-Xylene, vol-pct	3.5	0.7	4.3	5.5
o-Xylene, vol-pct	1.3	0.3	1.6	2.4
C9+ Aromatics, vol-pct	7.0	6.0	12.0	20.6
Total, vol-pct	21.4	7.8	24.8	35.8

compounds present have nine or more carbon atoms. The aromatic distribution for the two commercial gasolines appear to be typical. The unleaded fuel has higher aromatic content than the leaded fuel as would be expected.

Characteristics for the aviation turbine engine fuels, JP-5, are shown in table 3. The physical and chemical properties of jet fuels compare favorably with those properties of petroleum-derived jet fuels with a few exceptions. Although the aromatic content of the shale oil jet fuel is high, it is still below the limit for JP-5. The freezing point for this fuel is above the specification limit for this property, so that the viscosity at -34.4° C (-30° F) could not be measured. The net heating value of the coal-derived JP-5 is below the limit of 42.6 MJ/kg (18,300 BTU/lb), and the aniline-gravity product for the same sample is below the specification minimum.

The physical and chemical properties for three samples of Jet A fuels processed by Exxon to different levels of nitrogen contents are shown in table 4. These properties are compared to those for ASTM D1655, Specification for Aviation Turbine Fuels, Jet A. The Jet A No. 4 sample from Paraho shale oil, JA-S1, fails to meet the limits for freezing point, net heat of combustion, and copper corrosion. This same sample contains considerably more nitrogen compounds than JA-S2and JA-S3.

43.3° C Storage Stability Tests

The 11 fuels described previously were submitted to 32-week storage tests at 43.3° C (110° F). The procedure for the test was originally described in Bulletin 660 of the Bureau of Mines (5) (now Department of Energy - Bartlesville Energy Technology Center). Some minor changes were necessary because the recommended 40 oz. amber glass bottles were not available. Therefore, 32 oz. amber glass bottles were used and 280 ml of fuel in each instead of 350 ml to maintain the same relative air/fuel ratio as in the original procedure. The procedure utilized in this program is described in Appendix A, Section II.

Results from these storage tests are shown in table 5. The petroleum-based fuels show good storage stability while most of the synthetic fuels developed high levels of deposits after 32 weeks. There appeared to be an induction period in excess of 16 weeks because the deposits were for the most part at low levels at 16 weeks. The SASOL gasoline, G-C1 had the highest gum level among these lighter fuels after 32 weeks; however, this fuel had a relatively high level originally. Of the Jet A samples, JA-S1 had the highest nitrogen content and failed to meet the copper strip corrosion requirement for Jet A fuels.

Acid Numbers and Viscosities

Acid numbers of all test fuels and viscosities at 37.8° C (100° F) of jet fuels were determined after 4, 8, 16, and 32 weeks at 43.3° C (110° F). The results of these measurements are shown in table 6 and indicate that these properties were not significantly affected by the storage period. Slight increases in acid numbers were observed after 32 weeks for the tar sands naphtha (G-T1), the tar sands JP-5 (J5-T1) and the COED coal JP-5 (J5-C1),

TABLE 3. - Physical and chemical properties of JP-5 fuels

Properties	Petroleum based JP-5	Paraho shale oil JP-5	Tar Sands JP-5	COED Coal JP-5	Requirements of MIL-T-5624K for JP-5
Code Number	J5-P1	J5-S1	J5-T1	J5-C1	
Total acid number, mg KOH/g	0.01	0.02	0.04	0.08	0.015 max
Aromatics, vol-pct	12.9	23.2	20.1	15.6	25.0 max
Olefins, vol-pct	0.8	1.0	0.5	0.4	5.0 max
Sulfur, mercaptan, ppm	1.3	<1	<1	<1	10 max
Sulfur, total wt-pct	0.027	0.015	<0.001	<0.001	0.40 max
Distillation temp., °C (°F)					
Initial boiling point	188(370)	173(344)	188(370)	181(358)	Report
10 percent recovered	195(383)	192(378)	202(396)	189(372)	205(401) max
20 percent recovered	196(385)	199(390)	207(404)	192(378)	Report
50 percent recovered	202(395)	217(422)	221(429)	202(396)	Report
90 percent recovered	227(440)	250(482)	250(482)	234(454)	Report
End point	263(505)	268(515)	278(532)	270(518)	290(554) max
Distillation residue, pct	1.3	1.3	1.6	1.0	1.5 max
Distillation loss, pct	0.7	0.2	0.4	0.5	1.5 max
Flash point, °C(°F)	61(141)	55(131)	59(138)	65(149)	60(140) min
Specific gravity 15.6/15.6° C	0.8109	0.8054	0.8289	0.8488	0.788-0.845
Gravity, °API	43.0	44.2	39.2	35.2	36-48
Freezing point, °C(°F)	-57(-71)	-33(-27)	-57(-71)	-68(-90)	-46(-51) max
Viscosity at -34.4° C(-30°F), cSt	8.25	-	12.77	8.90	NR[1]
Net heat of combustion, MJ/kg	42.994	42.810	43.131	42.480	42.6 min
BTU/lb	18,484	18,405	18,543	18,263	18,300 min
Aniline point, °C(°F)	61.0(141.8)	64.8(148.6)	59.7(139.5)	41.0(105.8)	NR
Aniline gravity product	6097	6568	5468	3724	4500 min
Corrosion, copper strip, rating	1A	1A	1A	1A	1B max
Existent gum, mg/100 ml	0.8	1.7	2.7	1.1	7 max
Hydrogen, wt-pct	13.68	13.32	13.32	13.24	NR
Carbon, wt-pct	85.94	86.20	86.61	86.69	NR
Oxygen, wt-pct	0.42	0.28	None	None	NR
Nitrogen, wt-pct	0.006	0.15	0.004	0.004	NR

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[1] No requirement. (Viscosity requirement at -20° C is 8.5 cSt max.)

TABLE 4. - Physical and chemical properties of Jet A fuels[1]

Properties	Paraho shale oil Jet A #4	Paraho shale oil Jet A #23	Paraho shale oil Jet A #10	Requirements ASTM D 1655 for Jet A
Code Number	JA-S1	JA-S2	JA-S3	
Total acid number, mg KOH/g	0.05	0.03	0.06	0.1 max
Aromatics, vol-pct	17.9	7.6	17.2	20 max
Olefins, vol-pct	0.8	1.2	0.7	NR[2]
Sulfur, mercaptan, ppm	--	--	--	0.003 max
Sulfur, total wt-pct	0.007	0.005	0.006	0.3 max
Distillation temp., °C(°F)				
Initial boiling point	172(342)	167(333)	167(332)	NR
10 percent recovered	194(382)	187(386)	192(378)	204.4(400) max
20 percent recovered	201(394)	192(378)	196(385)	NR
50 percent recovered	215(419)	208(407)	213(415)	Report
90 percent recovered	239(462)	231(447)	235(455)	Report
End point	262(504)	268(515)	264(507)	300(572) max
Distillation residue, percent	1.5	1.0	1.0	1.5 max
Distillation loss, percent	0	0	0.5	1.5 max
Flash point, °C(°F)	57(134)	52(126)	59(138)	37.8(100) min
Specific gravity 15.6/15.6° C	0.8054	0.7927	0.8026	0.7753-0.8398
Gravity, °API	44.2	47.0	44.8	37-51
Freezing point, °C(°F)	-37(-35)	-41(-42)	-40(-40)	-40(-40) max
Viscosity @ -34.4° C(-30° F), cSt	10.38	9.39	10.09	NR[3]
Net heat of combustion, MJ/kg	42.503	42.617	43.031	42.6 min
BTU/lb	18,273	18,322	18,500	18,400 min
Aniline point, °C(°F)	66.1(151.0)	71.9(161.4)	65.8(150.4)	NR
Aniline gravity product	6674	7586	6738	NR
Corrosion, copper strip, rating	2	1A	1A	1 max
Existent gum, mg/100 ml	5.8	2.7	3.1	7 max
Hydrogen, wt-pct	13.87	14.42	13.93	NR
Carbon, wt-pct	85.81	85.43	85.72	NR
Oxygen, wt-pct	0.05	0.05	0.05	NR
Nitrogen, wppm	347	3.2	146	NR

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[1] Some data supplied by Air Force Wright Aeronautiaal Laboratories.

[2] NR - No requirement

[3] Viscosity requirement at -20° C is 8 cSt max.

TABLE 5. - Storage stability test results at 43.3° C (110° F)[1]

			4 Weeks				8 Weeks			
Sample No.	Description	Initial total gum	Inorg. residue	Fuel insol. gum	Soluble gum	Total gum	Inorg. residue	Fuel insol. gum	Soluble gum	Total gum
G-C1	SASOL gasoline	19.6	0.1	0.3	19.0	19.3	0.1	0.5	19.2	19.7
G-T1	Tar Sands naphtha	2.3	0.1	0.5	0.8	1.3	0.1	1.2	2.9	4.1
G-P1	Commercial regular Gasoline - leaded	2.3	0	0.5	1.5	2.0	0	0.7	3.9	4.6
G-P2	Commercial unleaded Gasoline	4.0	0	0.6	2.3	2.9	0.1	0.4	4.2	4.6
J5-P1	Petroleum based JP-5	0.3	0.1	1.4	0.6	2.0	0	0.5	1.7	2.2
J5-S1	Paraho Shale Oil JP-5	4.1	0	0.7	2.9	3.6	0	0.8	2.7	3.5
J5-T1	Tar Sands JP-5	1.6	0.1	0.1	0.9	1.0	0.2	0.3	1.9	2.2
J5-C1	COED coal liquid JP-5	2.0	0	0.4	2.4	2.8	0.1	0.4	1.6	2.0
JA-S1	Paraho Shale Oil Jet A #4	2.5	0.1	0.1	1.9	2.0	0.1	0.4	3.4	3.9
JA-S2	Paraho Shale Oil Jet A #23	2.7	0	0.6	3.3	3.9	0.04	0.2	4.4	4.6
JA-S3	Paraho Shale Oil Jet A #10	3.1	0.04	0.1	1.5	1.6	0.1	0.4	2.0	2.4
			16 Weeks				32 Weeks			
G-C1	SASOL gasoline		0	0.2	21.2	21.4	2.5	2.2	33.6	35.8
G-T1	Tar Sands naphtha		0.3	0.5	5.8	6.3	0.3	1.2	19.5	20.7
G-P1	Commercial regular Gasoline - leaded		0.2	0.3	4.2	4.5	0.2	1.0	5.4	6.4
G-P2	Commercial unleaded Gasoline		0.1	0.4	4.0	4.4	0	1.4	9.5	10.9
J5-P1	Petroleum based JP-5		0.02	0.7	0.5	1.2	0	0.9	1.7	2.6
J5-S1	Paraho Shale Oil JP-5		0.2	1.7	3.4	5.1	0	1.7	4.7	6.4
J5-T1	Tar Sands JP-5		0.1	1.0	7.3	8.3	0	1.0	25.0	26.0
J5-C1	COED coal liquid JP-5		0.2	0.9	2.6	3.5	0.3	2.9	25.0	27.9
JA-S1	Paraho Shale Oil Jet A #4		0.04	0.4	4.4	4.8	0	0.1	116.4	116.5
JA-S2	Paraho Shale Oil Jet A #23		0.04	0.4	1.8	2.2	0	0.2	1.6	1.8
JA-S3	Paraho Shale Oil Jet A #10		0.04	0.2	1.6	1.8	0	0.3	1.8	2.1

---

[1] Data presented as mg gum/100 ml fuel.

TABLE 6. - Effect of 43.3° C (110° F) storage on acid numbers and viscosities

		Initial		4 Weeks		8 Weeks		16 Weeks		32 Weeks	
Sample No.	Description	TAN[1]	Viscosity at 37.8° C	TAN	Viscosity at 37.8° C	TAN	Viscosity at 37.8° C	TAN	Viscosity at 37.8° C	TAN	Viscosity at 37.8° C
G-C1	SASOL gasoline	0.04	NA[a]	0.04	NA	0.05	NA	0.01	NA	0.03	NA
G-T1	Tar Sands naphtha	0.03	NA	0.05	NA	0.05	NA	0.01	NA	0.16	NA
G-P1	Commercial regular Gasoline - leaded	0.05	NA	0.04	NA	0.06	NA	0	NA	0.01	NA
G-P2	Commercial unleaded Gasoline	0.02	NA	0.03	NA	0.05	NA	0.02	NA	0.03	NA
J5-P1	Petroleum based JP-5	0.01	1.45	0.06	1.45	0.05	1.45	0.01	1.45	0.04	1.46
J5-S1	Paraho Shale Oil JP-5	0.02	1.46	0.03	1.48	0.06	1.48	0.04	1.43	0.04	1.46
J5-T1	Tar Sands JP-5	0.04	1.72	0.04	1.76	0.04	1.77	0.05	1.72	0.10	1.79
J5-C1	COED coal liquid JP-5	0.08	1.49	0.03	1.54	0.02	1.53	0.03	1.50	0.11	1.60
JA-S1	Paraho Shale Oil Jet-A #4	0.05	1.60	0.03	1.60	0.02	1.61	0.04	1.62	0.04	1.61
JA-S2	Paraho Shale Oil Jet-A #23	0.03	1.47	0.04	1.50	0.03	1.48	0.01	1.48	0.02	1.47
JA-S3	Paraho Shale Oil Jet-A #10	0.06	1.53	0.04	1.53	0.03	1.54	0.03	1.53	0.02	1.53

[1] TAN - total acid number.

[a] NA - not analyzed.

while the viscosities of the jet fuels throughout the storage period showed no significant changes. The differences observed were within the experimental error of the test.

Accelerated Storage Test. 16 Hours at 93.3° C (200° F)

The fuel samples under study were submitted to a 16 hour stability test at 93.3° C (200° F), also described in Bulletin 660 (5) as a "16 Hour Oven Test for Predicting Storage Stability." The materials used in the current study were modified as follows: an oil bath, at 93.3° C was used rather than an oven, and 28 oz. beverage bottles were used in place of 16 oz. bottles, thus 228 ml of sample were used rather than 130 ml to maintain the same relative air-fuel ratio. The procedure used is described in more detail in appendix A, section III. The results of this test appear in table 7 and show that, in general, the gasolines gave considerable increase in gum content while the jet fuels had very little gum increase. The predicted gum contents for 32 weeks at 43.3° C (100° F), calculated by the procedure described in appendix A section V from the 16 hours 93.3° C test data, are also shown in table 7. As expected, reasonable correlations exist between the predicted and measured gum values for the gasoline and naphtha samples, but very poor correlation is found for the jet fuel samples. This test was developed for gasolines and separate correlations would seem to be required for other fuels.

Thermal Oxidation Stability Evaluation

The Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure ASTM D3241) was conducted on all fuels in this investigation. Although the test is primarily designed for aviation turbine fuels, the gasolines were evaluated also, and the results are shown in table 8. The tests were conducted for 2.5 hours at 260° C (500° F) control temperature. The requirements for aviation turbine fuels are a visual rating of less than three for preheater deposits and a maximum filter pressure drop of 25 mm of Hg during the test period. The data indicate that the petroleum-derived fuels, gasoline and JP-5, meet the visual rating requirements, while the synthetic fuels do not. On the other hand, the leaded commercial regular gasoline and the COED JP-5 failed the filter pressure drop limit.

The suppliers of the JP-5 type fuels J5-S1, J5-T1, and J5-C1 have indicated that these met the MIL-T-5624K requirements for the JFTOT test; however, the tests reported herein do not agree with those reports. It is known that considerable time elapsed between the tests conducted by the suppliers and those conducted at this laboratory; therefore, some deterioration of these fuels could have occurred.

Analyses of Fuels Following Storage Tests

Samples of each fuel were analyzed by high performance liquid chromatography (HPLC) and gas chromatography (GC) (gasolines only) before and after the 32-week (43.3° C) storage test in an effort to detect changes in composition during the test. Both techniques indicated that the gasoline samples lost some of the lighter components during the storage test. These lighter components are mostly paraffins, thus the net effect was an increase in percent

TABLE 7. - Accelerated storage test: 16 hours at 93.3° C (200° F)[1]

	SASOL gasoline	Tar Sands naphtha	Regular leaded gasoline	Unleaded gasoline	Petroleum JP-5	Shale JP-5
Code Number	G-C1	G-T1	G-P1	G-P2	J5-P1	J5-S1
Soluble gum	37.6	13.6	9.8	10.0	0.6	3.6
Insoluble gum	0.4	0.4	0.6	0.6	0.4	1.3
Total gum	38.0	14.0	10.4	10.6	1.0	4.9
Inorganic residue	0.1	0.1	1.3	0.1	0.1	0
Oxygen, percent (in ullage)	20.9	21.0	18.7	18.3	20.2	19.9
Predicted gum after 32 weeks storage at 110° F[2]	21.6	3.6	11.6	13.0	1.8	5.7
Measured gum after 32 weeks storage at 110° F	35.8	20.7	6.4	10.9	2.6	6.4

	Tar Sands JP-5	COED JP-5	Shale Jet A #4	Shale Jet A #23	Shale Jet A #10
Code Number	J5-T1	J5-C1	JA-S1	JA-S2	JA-S3
Soluble gum	2.0	1.8	1.8	0.6	1.2
Insoluble gum	0.7	0.4	0.2	0.9	1.4
Total gum	2.7	2.2	2.0	1.5	2.6
Inorganic residue	0.1	0.1	0.2	0.1	0.1
Oxygen, percent (in ullage)	20.2	13.7	20.6	20.8	20.2
Predicted gum after 32 weeks storage at 110° F[2]	3.2	3.9	3.2	2.5	3.8
Measured gum after 32 weeks storage, at 110° F	26.0	27.9	116.5	1.8	2.1

[1] Gum data presented as mg gum/100 ml fuel.

[2] Calculated by method shown in Appendix A, Section V.

TABLE 8. - JFTOT evaluations by ASTM test method D 3241 conducted for 2.5 hours at 260° C control temperature

Sample No.	Description	JFTOT Ratings							
		Visual	Spun Tube	Spot Deposit	ΔP, mm Hg/time, minutes				
G-C1	SASOL gasoline	4	19	22	0/30	0/60	0/90	0/120	0/150
G-T1	Tar sands naphtha	1	2.5	2.5	0/30	0/60	0/90	2/120	5/150
G-P1	Commercial regular gasoline-leaded	1	1.5	6.0	145/30	145/60	148/90	148/120	148/150
G-P2	Commercial unleaded	3	27	31	0/30	0/60	0/90	0/120	0/150
J5-P1	Petroleum based JP-5	1	4	6	1/30	1/60	1/90	2/120	2/150
J5-S1	Paraho shale oil JP-5	4	24.5	34.5	1/30	1/60	1/90	1/120	1.5/150
J5-T1	Tar sands JP-5	4	15	17	0/30	0/60	0.5/90	0.5/120	0.5/150
J5-C1	COED coal liquid JP-5	4	12	24	2/30	15/60	76/90	150/120	197/150
JA-S1	Paraho shale oil, Jet A (#4)	3	15	18	1/30	1/60	1/90	1/120	1/150
JA-S2	Paraho shale oil, Jet A (#23)	4	17	19	0.5/30	0.5/60	0.5/90	0.5/120	0.5/150
JA-S3	Paraho shale oil, Jet A (#10)	4	30	35	1/30	1/60	1/90	1/120	1/150

aromatics in the fuels after 32 weeks. The volumes of fuel remaining in the bottles containing gasoline and naphtha samples indicated that in some cases up to 25 percent of the fuels were lost through evaporation of lighter components, probably during the aeration procedure every four weeks. This loss of fuel did not occur with the jet fuels, presumably due to their lower volatility.

The HPLC analyses of the jet fuels before and after 32 weeks storage show slight compositional changes in a few of the fuels and none in others. Those with no changes were J5-P1, the petroleum base JP-5; J5-T1, the tar sands JP-5; JA-S1, and the high nitrogen level Jet A; and JA-S3, the medium nitrogen level Jet A. The others showed slight compositional changes and were: J5-S1, Paraho shale oil JP-5; J5-C1 COED coal JP-5; and J5-S2, the low nitrogen level Jet A. Identification of compounds undergoing change during storage was not possible; however, indications are that mostly aromatic compounds may be involved.

Analyses of Gum Residues Developed During 43.3° C (110° F) 32-Week Storage Tests

The soluble gums recovered from the test samples after 32 weeks of storage at 43.3° C were retained for analyses. In a few instances the amount of gum developed was so small that the analyses were necessarily somewhat limited. Table 9 shows the data obtained on these gums. The sulfur measurements were made quantitatively, and the other elements shown were detected as being present.

Infrared spectroscopy measurements were made on the gum residues from nine of the samples after 32 week storage. Two Jet A fuels JA-S2 and JA-S3 had such low gum levels that IR measurements could not be made. Infrared spectra for those that were measured are shown as figures 1 through 9. In all but one case, the spectra were obtained on KBr pellets containing the gum residues. Jet A fuel JA-S1, yielded a large quantity of gum which was in fact a viscous liquid. This residue was placed in a 0.025 mm thickness cell for the IR measurement. The very strong absorption at 1720 cm^{-1} frequency is indicative of a ketone. Since the sample was dissolved in toluene-acetone-methanol solvent prior to the infrared measurement, it was suspected that the acetone was not completely removed during the evaporation step. However, further investigation showed that this absorption was due to a material in the gum residue and not to acetone.

The spectra from the other gum residues indicate the presence of amides in some cases (G-C1, G-T1), aldehydes and amides in others (G-P1, G-P2, J5-T1) and aldehydes or ketones in others (J5-C1, J5-P1 and J5-S1).

The gum residues from 32 week storage of fuels G-C1 and G-T1 were submitted to nuclear magnetic resonance analyses (NMR) for determination of hydrogen/carbon ratio, volume percent aromatics, olefins and paraffins. The results obtained were as follows:

TABLE 9. - X-Ray analysis of gum deposits after 32 weeks storage at 110° F

Code	Description	S, wt-pct	Pb	Cl	P
G-C1	SASOL gasoline	1.5	present	present	---
G-T1	Tar sands naphtha	0.15	---	---	---
G-P1	Leaded gasoline	0.30	present	present	---
G-P2	Unleaded gasoline	0.08	---	present	---
J5-P1	Petroleum JP-5	0.13	---	---	---
J5-S1	Shale oil JP-5	0.09	present	---	---
J5-T1	Tar sands JP-5	0.03	---	---	---
J5-C1	Coal (COED) JP-5	0.09	---	---	---
JA-S1	Shale Jet A (high N)	0.04	---	---	present
JA-S2	Shale Jet A (low N)	0.16	---	---	---
JA-S3	Shale Jet A (medium N)	0.15	---	present	---

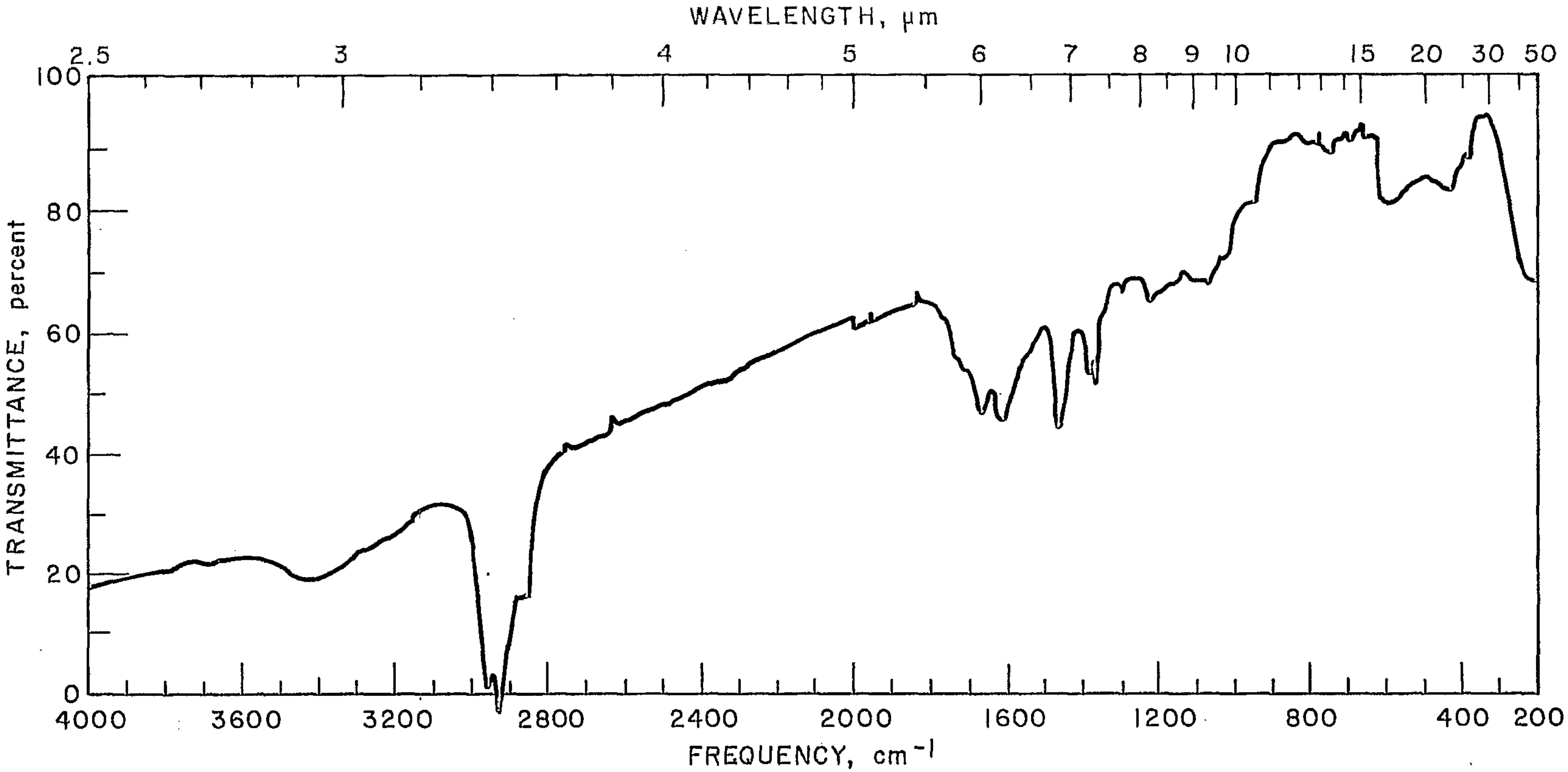

FIGURE 1. - Infrared spectra of gum residue from SASOL gasoline.

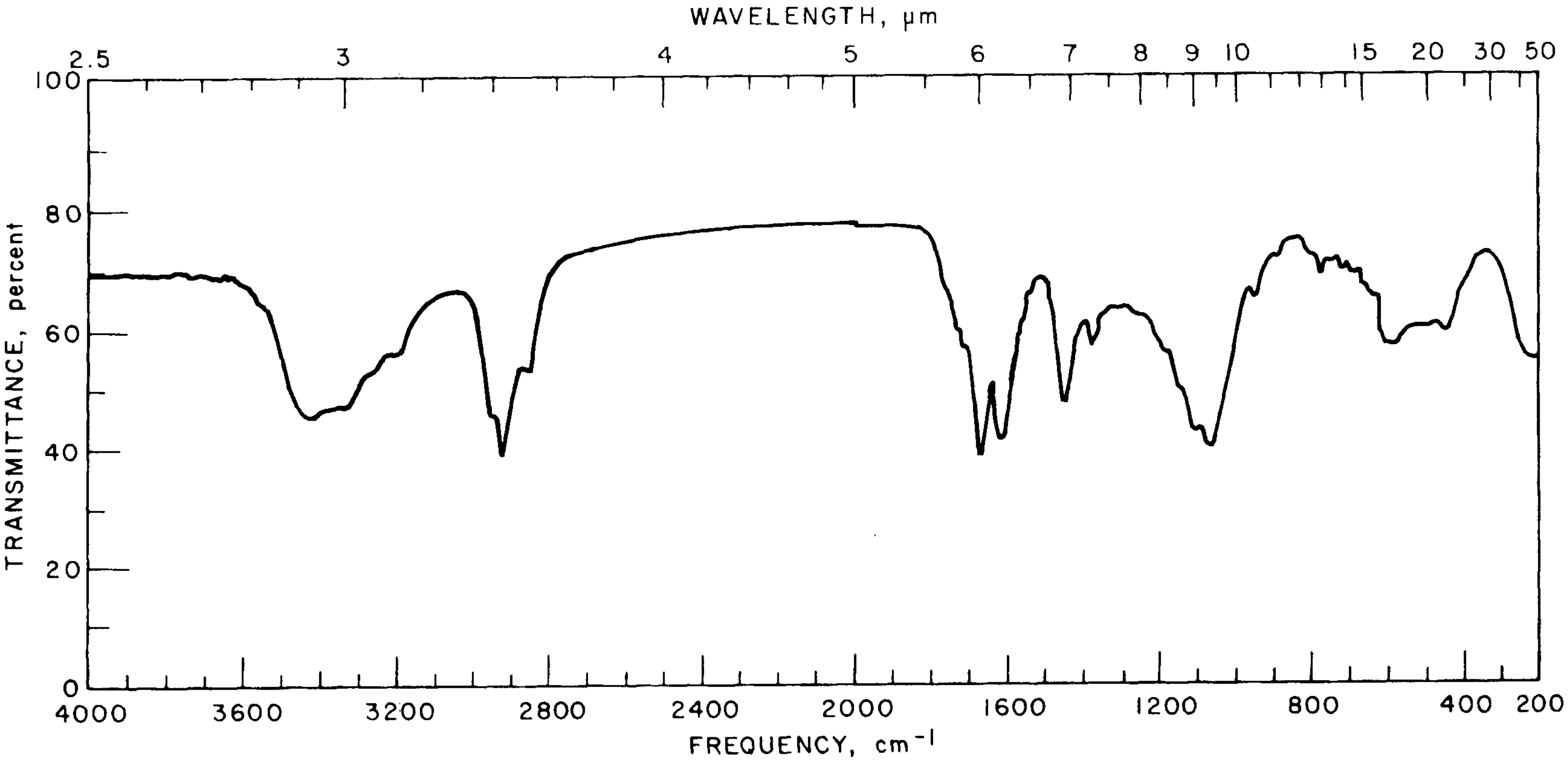

FIGURE 2. - Infrared spectra of gum residue from tar sands naphtha.

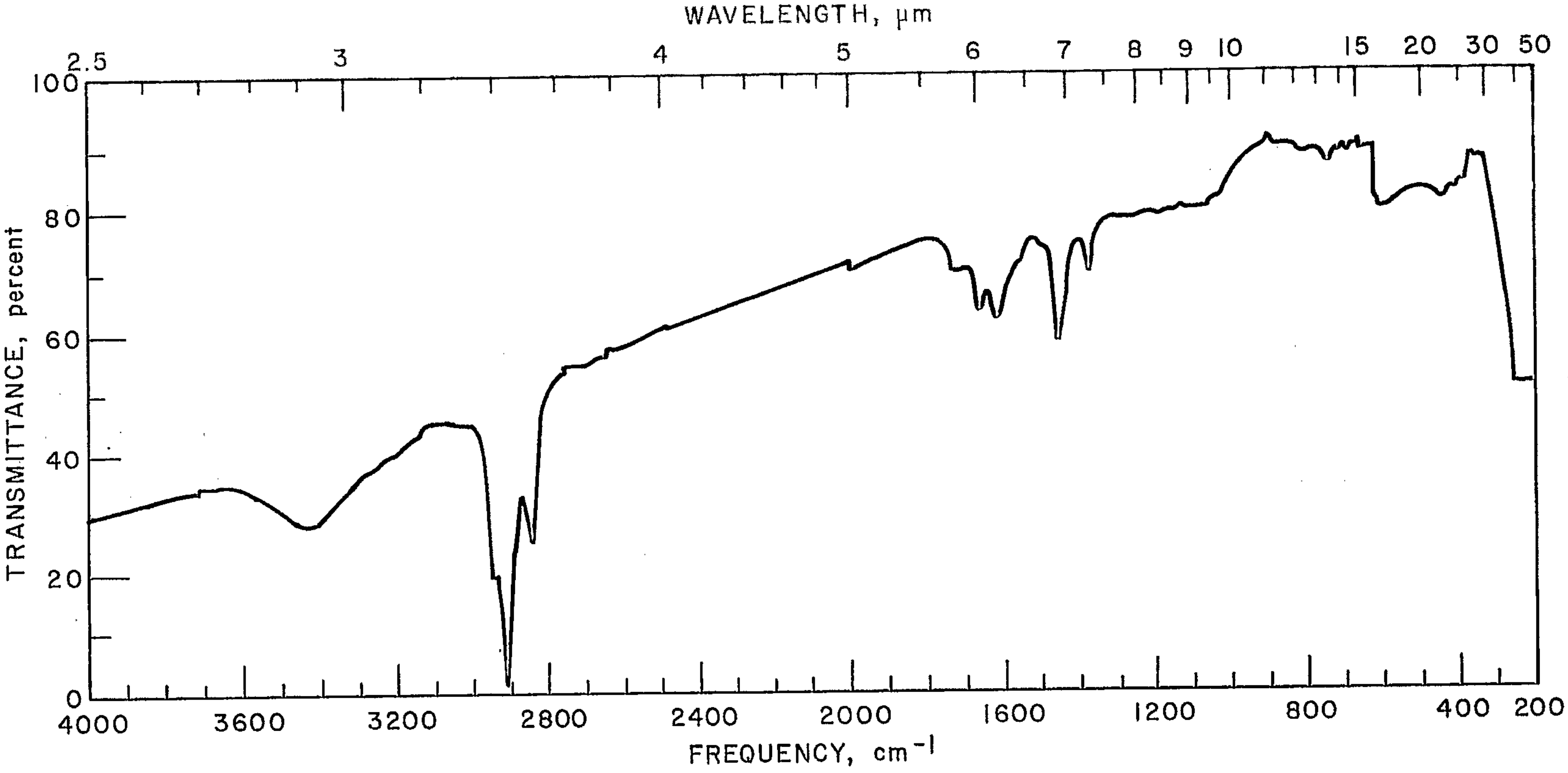

FIGURE 3. - Infrared spectra of gum residue from petroleum-based gasoline, leaded.

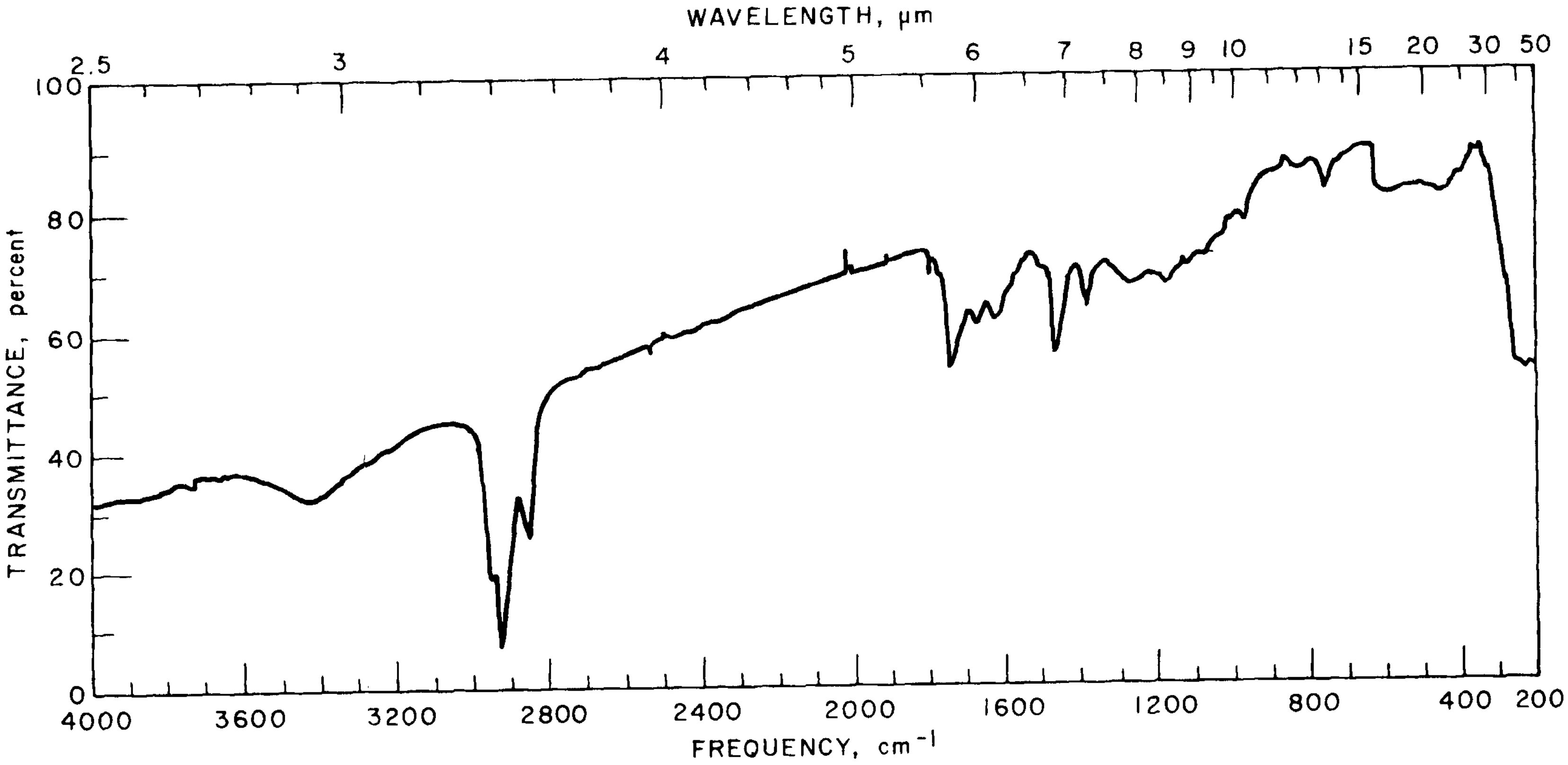

FIGURE 4. - Infrared spectra of gum residue from petroleum-based gasoline, unleaded.

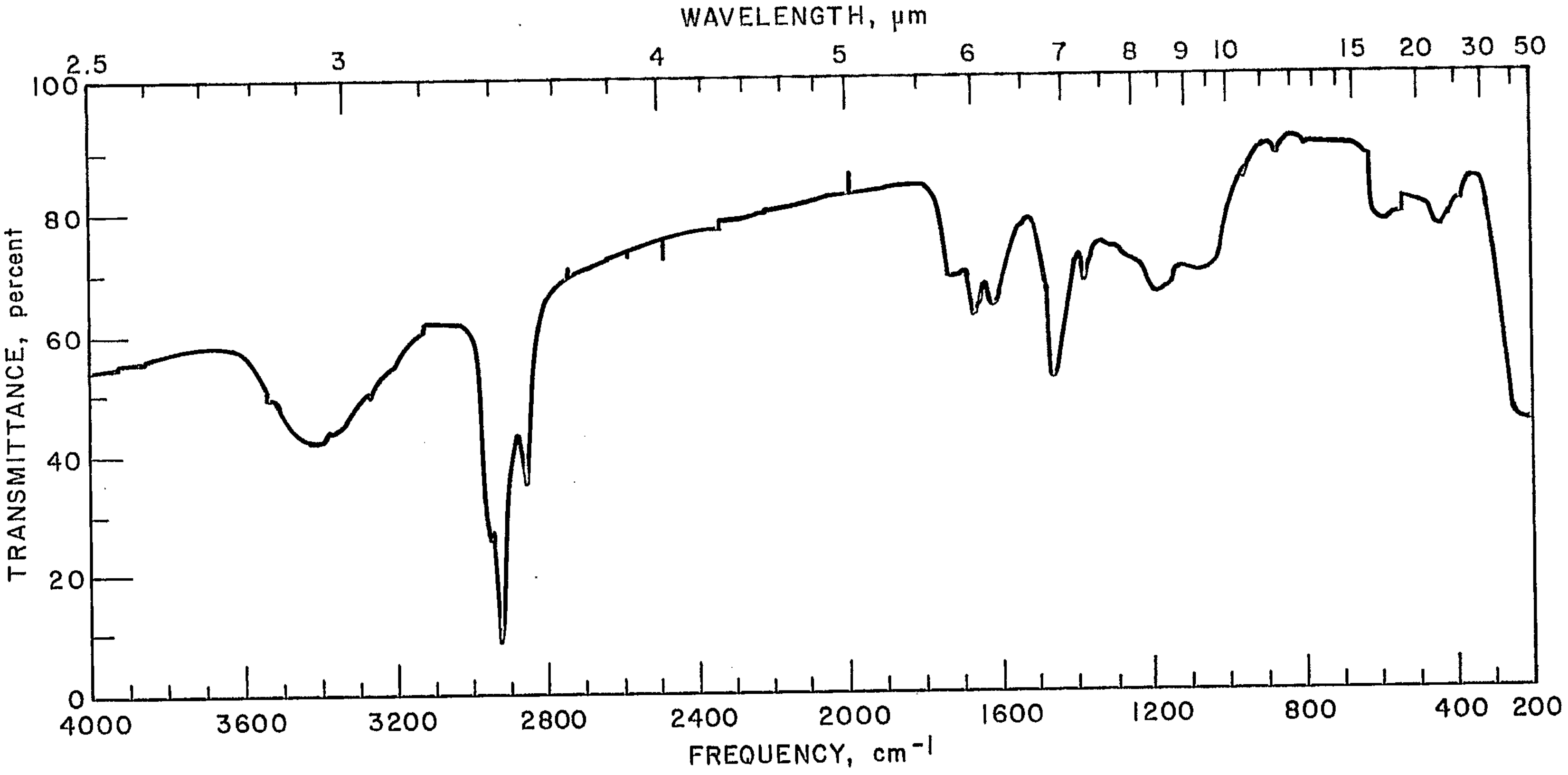

FIGURE 5. - Infrared spectra of gum residue from petroleum-based gasoline, JP-5.

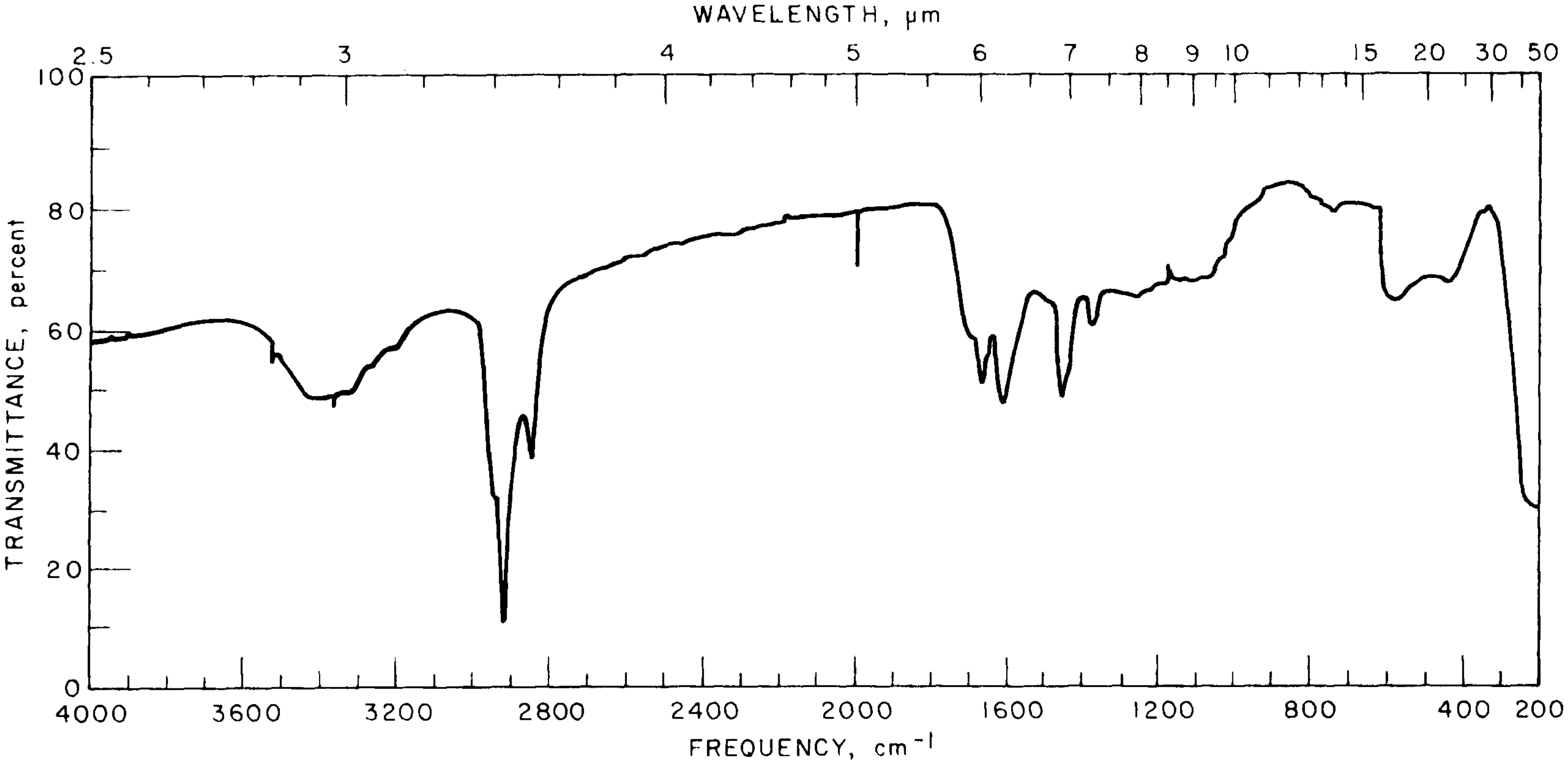

FIGURE 6. - Infrared spectra of gum residue from shale oil JP-5.

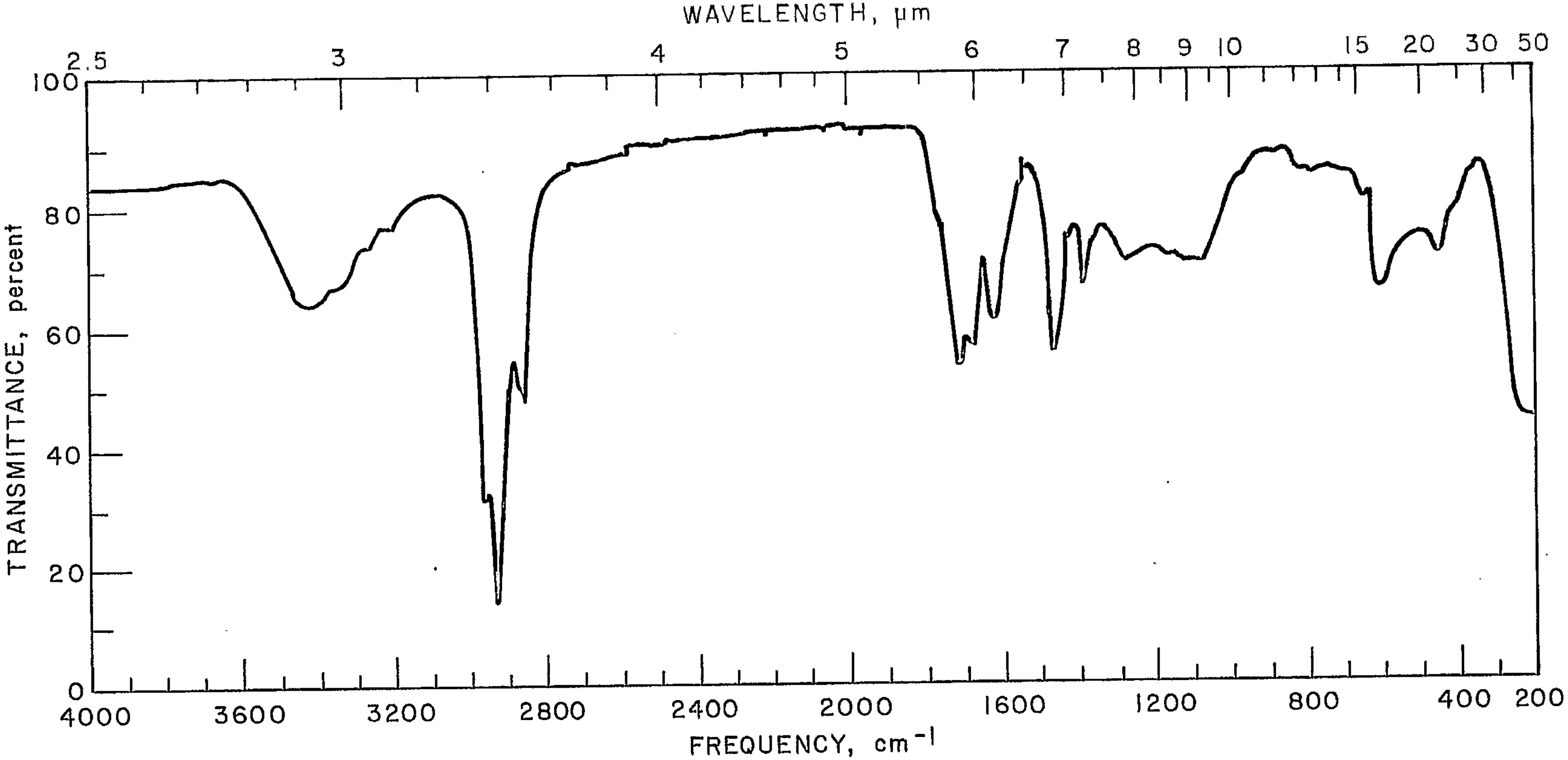

FIGURE 7. - Infrared spectra of gum residue from tar sands-based kerosene fraction.

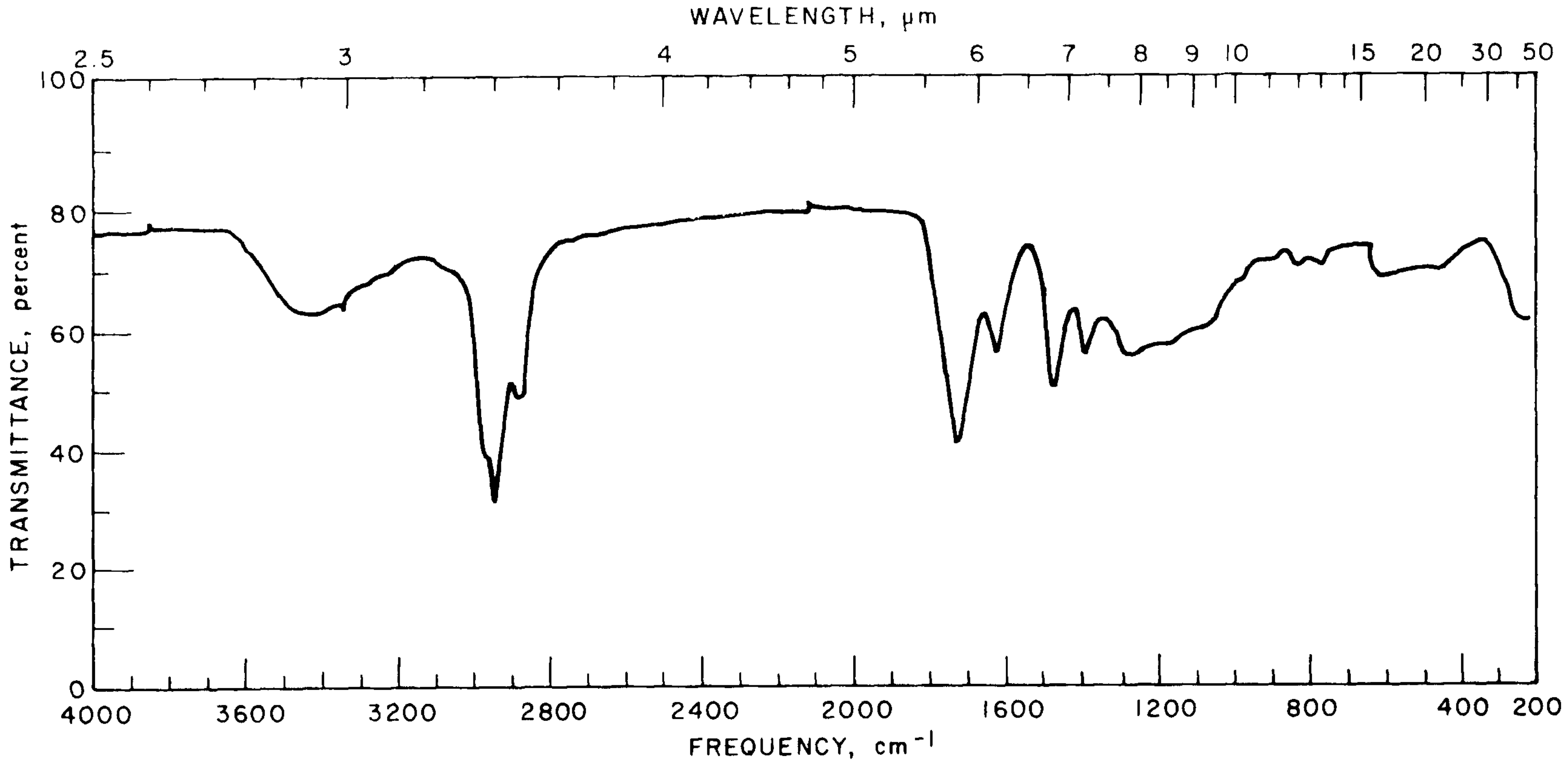

FIGURE 8. - Infrared spectra of gum residue from coal-derived JP-5.

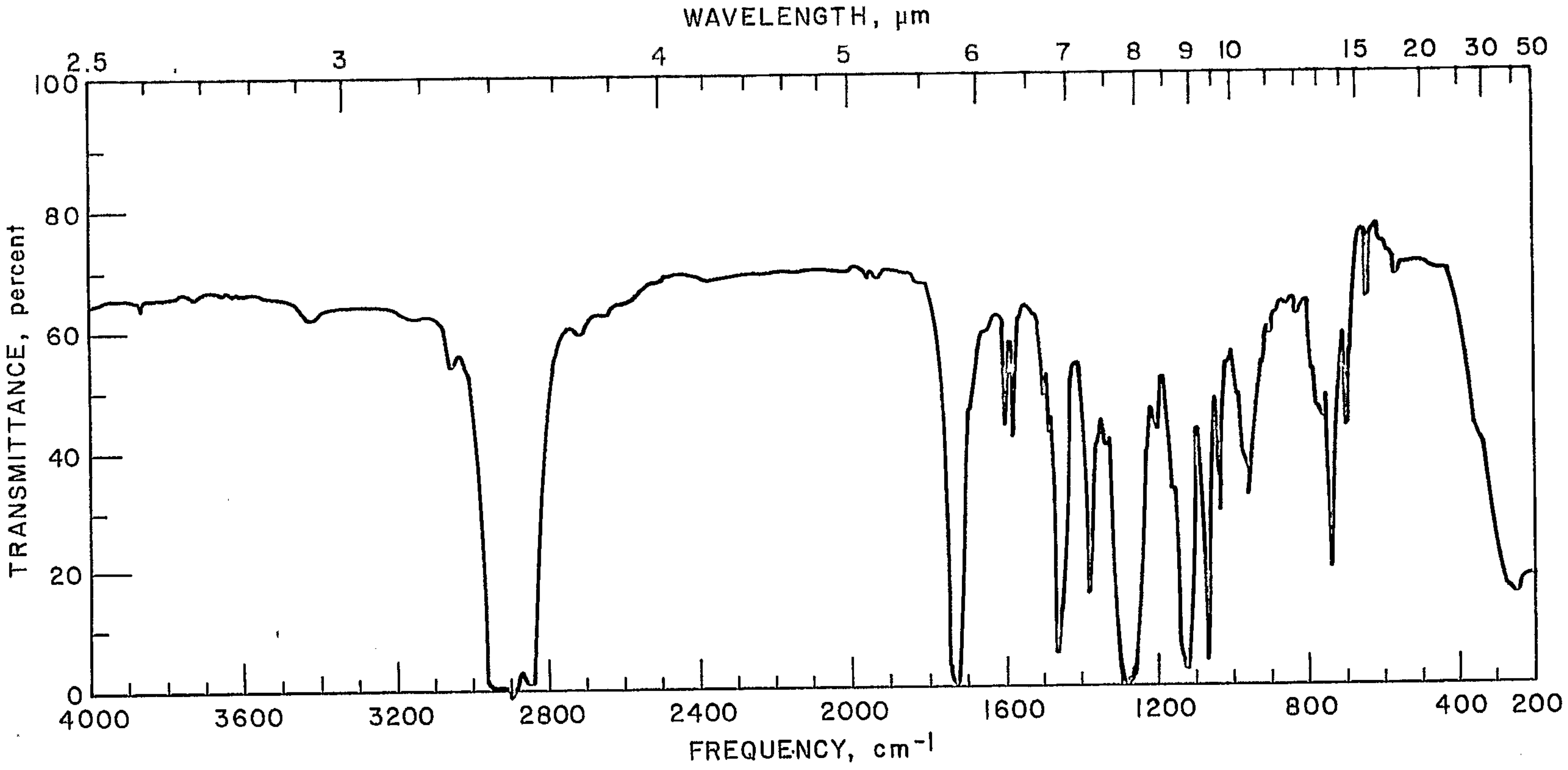

FIGURE 9. - Infrared spectra of gum residue from high nitrogen, shale oil Jet A.

	H/C	Aromatics, Vol.-pct.	Olefins, Vol.-pct.	Paraffins, Vol.-pct.
G-C1	1.82	8.94	0	91.06
G-T1	1.48	35.5	39.8	24.7

These measurements and calculations were made by techniques developed for gasolines as described by Myers, and others (2), and the applicability of the method to residues is not known. It is known that compounds other than hydrocarbons, such as nitrogen, oxygen and sulfur containing compounds are present in the gum, which are not accounted for in this NMR technique.

Molecular weight and other elemental analyses will be performed on gum residues where sample size is sufficient.

Analysis of Gum From SASOL Gasoline Before Storage

The pentane-insoluble gum from sample G-C1, SASOL gasoline, was high compared to other samples in this program. Therefore, the residue was analyzed by x-ray and by infrared. The x-ray fluorescence indicated the presence of S (0.026 percent), P, Cl, Mn, Fe, Zn. The infrared shows amides and aldehydes may be present in the gum.

CONCLUSIONS

The storage stability of the synthetic fuels evaluated to date in this program varied considerably. Based on the 43.3° C 32-week storage test, some samples exhibited good storage stability while others were poor. The Jet A sample from Paraho shale oil had the highest gum content after 32 weeks and also had the highest nitrogen content. Another sample with high nitrogen content, JA-S3, developed a low level of gum, which suggests that the type of nitrogen compounds present in the fuel may have a significant effect on the level of gum developed, as has been suggested by Frankenfeld and Taylor (1).

The evaluated fuels had very low concentrations of olefins; therefore, the presence of olefinic gum precursors, such as conjugated diolefins, is considered unlikely. Nonetheless, the thermal stability of all the synthetic fuels was considered poor based on failure to meet the requirements of the JFTOT test.

Future plans call for continued detailed analyses of the gum residues from the storage tests. Storage tests for SRC II coal liquid samples are in progress, and samples of kerosene and gas oil from tar sands also have been placed in storage. The thermal stability of jet fuels before and after the storage tests are being compared and will be discussed along with the other investigations in a future publication.

ACKNOWLEDGMENTS

The authors would like to thank those who supplied fuel samples and information -- both of which were invaluable during this study. Specifically, we appreciate the help of Fred Eison and Fred Camp, Suntech, Inc.; Herb Lander and Chuck Delaney, Wright-Patterson AFB; Ed White, Navy Ship Research and Development; Buck Norwack, Naval Air Propulsion Test Center; and Lt. Larry Lukens, U.S. Navy; in sample procurement. The support of Dr. M. Kolobielski of the U.S. Army Mobility Equipment Research and Development Command, Ft. Belvoir, VA, in the performance of this work is also acknowledged.

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APPENDIX A. – ANALYTICAL METHODS

The methods employed for analysis and evaluations of the fuels investigated are listed in table A-1 with identifying ASTM method numbers or other descriptions.

I. Storage Stability Test at 43.3° C (110° F)

This procedure was originally described in Bureau of Mines Bulletin 660 and was modified slightly in this program

Cleaning the Storage Bottles

1. Scrub with a detergent solution and rinse with water.
2. Fill the bottle about half full with chromic acid cleaning solution, roll the bottle for complete contact of acid with the inner surface, pour out the acid, and allow the bottle to stand for at least 1 hour.
3. Rinse with tapwater, then invert and flush with a stream of distilled water.
4. Allow the bottle to drain. Dry overnight in a 150° C (300° F) oven.

Aging at 43.3° C (110° F)

Filter the fuel through a membrane filter having 0.45-micron pore size to remove particles. Place 280 ml of fuel in each of ten 32 oz (946 ml), screw cap, amber bottles. Seal with screw caps lined with Teflon. Store in the dark at a constant temperature of 43.3° C. After each storage interval--4, 8, 16, and 32 weeks from the beginning of storage--remove two samples and analyze for gum. Use two samples as "floaters" for additional analysis at unscheduled times. Every four weeks during the storage, replenish the oxygen in the vapor space. To do this, remove all bottles, cool, aerate, and return to storage.

Aerating Storage Samples

1. Remove the sample from 43.3° C storage and cool to 0-4.5° C.
2. Sweep the interior of the cooled bottle above the surface of the gasoline with a gentle stream of dried, compressed air for two minutes to insure that an adequate supply of air is in contact with the gasoline.
   NOTE 1: Use of this aerating procedure resulted in excessive evaporation of the gasoline and naphtha samples, therefore, step 2 was replaced with the following: 2. After overnight cooling at 0-4.5° C, remove bottle caps for five minutes.
3. Recap the sample; when the sample has warmed to room temperature, return it to 43.3° C storage.

TABLE A-1. - Analytical Methods Used In This Program

Method	ASTM No. or other Description
Specific gravity, 15.6°/15.6° C	D 1298
Gravity, API°	D 1298
Reid vapor pressure, kPa(lbs)	D 323
Distillation, percent evaporated at various temperatures, °C (°F)	D 86
Existent gum, g/100 ml	D 381
Oxidation stability, minutes	D 525
Copper corrosion, ASTM rating	D 130
Research octane number	D 2699
Motor octane number	D 2700
Water and sediment, volume-percent	D 1796
Lead content, g/l (g/gal)	D 3237
Phosphorus content, weight-percent	D 3231
Sulfur content, weight-percent	D 1266
Carbon content, weight-percent	1/
Hydrogen content, weight-percent	1/
Oxygen content, weight-percent	2/
Nitrogen content, weight-percent	3/
Aromatics, volume-percent	D 1319
Olefins, volume-percent	D 1319
Gas chromatography simulated distillation	D 2887
Aromatic distribution, weight-percent	AFLRL Procedure (6)
Total acidity, mg KOH/g	D 3242
Mercaptan sulfur, weight-percent	D 1323
Flash point, °C (°F)	D 93
Freezing point, °C (°F)	D 2386
Kinematic viscosity at -34.4° C (-30° F)	D 445
Kinematic viscosity at 32.8° C (100° F)	D 445
Net heat of combustion, MJ/kg	D 240
Aniline point, °C (°F)	D 611
Aniline gravity product	D 1405
Storage stability test at 43.3° C (110° F)	See appendix A-I
Accelerated storage test at 93.3° C (200° F)	See appendix A-II
Thermal stability (JFTOT)	D 3241

1/ Carbon and hydrogen were determined with an Elemental Analyzer. Combustion of the sample occurs in pure oxygen under static conditions. The combustion products, CO_2 & H_2O are analyzed automatically in a thermal conductivity analyzer.

2/ The "Elemental Analyzer" with an oxygen analysis kit was utilized to determine oxygen content. The sample is pyrolysized in helium at 975° C, over platinized carbon, and the oxygen is converted to carbon monoxide.

3/ Nitrogen was determined by the Kjeldahl procedure and in some instances, when the values were extremely low, a Nessler titration was employed.

Analyzing Storage Samples

The fuel-insoluble gum and the precipitate are separated from the fuel by filtration. Soluble gum is determined on the filtered fuel as is "unwashed" gum by ASTM Method D 381. Insoluble gum is dissolved in organic solvents and weighed after evaporation of solvent. Precipitate is determined by weighing the filter.

Materials and Apparatus

Glass reservoir, with air-pressure connection and an approximately 9-mm-OD delivery tube.

Size 9 neoprene stopper, bored to accept delivery tube.

Gooch low-form filtering crucible: Pyrex, fritted disk, 30 ml, fine porosity.

Crucible holder.

Eight ASTM D 381 air-jet gum beakers.

Two graduated bottles, at least 12 oz (355 ml).

Stirring rod with policeman.

Gum solvent (1:1:1 acetone-toluene-methanol).

n-Heptane.

D 381 gum bath; analytical balance; 93.3° C oven; covered container for beakers and filter.

Determining Soluble Gum

Weigh a filtering crucible (hereafter called "filter") and eight gum beakers. Assemble the reservoir-stopper-filter-holder arrangement for filtration, as shown in figure A-1. With gentle air pressure, pass the aged fuel from bottle A through the filter and collect the filtrate in a graduated bottle. Set aside. Pass the fuel from bottle B through the same filter, collecting in a separate bottle. Measure two 50 ml portions of the filtrate from bottle A, and from bottle B into gum beakers. Determine air-jet gum on each by ASTM Method D 381. Average the results and report as soluble gum, in mg/100 ml.

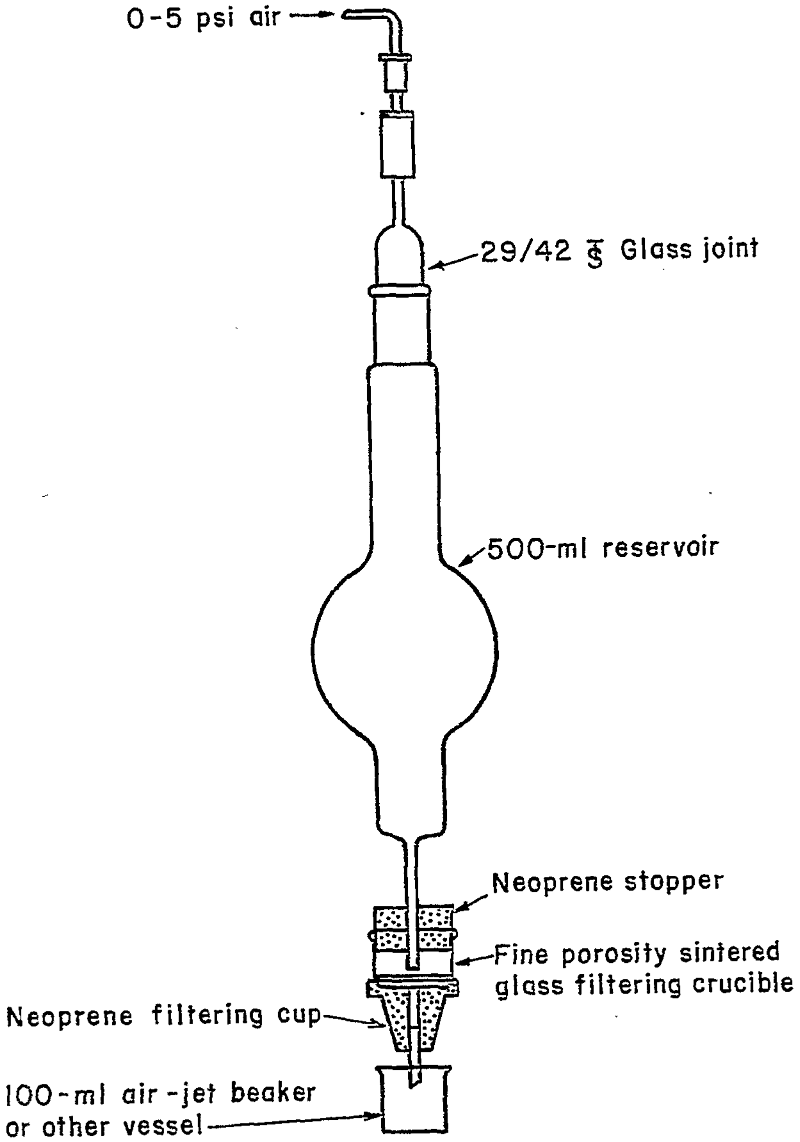

FIGURE A-1. - Filtering assembly.

Determining Insoluble Gum

Place a container beneath the filter. Rinse each bottle and the filter free of fuel by adding three successive 50-ml portions of heptane into each bottle by gently swirling, and pass rinsings through filter. Discard rinsings.

Place a weighed gum beaker beneath the filter. Rinse and police bottle A with 15 ml of gum solvent, then pass the solution through filter into beaker. Repeat twice with 15- to 20-ml portions of solvent for a total of not more than 50 ml of solution in gum beaker.

Place another gum beaker beneath filter and carry out the gum solvent steps on bottle B.

Evaporate solvent from the two solutions by the air-jet method described in ASTM D381 and weigh the residues.

$$\text{Insoluble gum, mg/100 ml} = \frac{\text{residue A, mg} + \text{residue B, mg}}{5.6^{1}}$$

To obtain total gum, add the insoluble gum and soluble gum values.

Determining Precipitate

To determine the precipitate collected on the filter, dry the filter in a 93.3° C oven for 1 hour, cool at least 2 hours, and weigh.

$$\text{Precipitate, mg/100 ml} = \frac{\text{precipitate, mg}}{5.6}$$

II. Accelerated Storage Test at 93.3° C (200° F)

Method of Cleaning Beverage Bottles

1. Scrub with a detergent solution, and rinse with water.
2. Add chromic acid cleaning solution to the bottle, swirl, and roll the bottle to insure complete contact of acid with entire inner surface.
3. Rinse with tap water, then invert the bottle and flush with a stream of distilled water.
4. Allow the bottle to drain. Dry overnight in a 150° C oven.

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[1] This number represents the combined filtered volume of fuel from bottles A and B divided by 100. If the total volume differs from 560 ml this denominator should be changed accordingly.

Aging at 93.3° C

Filter the fuel through a 0.45-micron pore-size membrane filter to remove particles. Place 228 ml of fuel in each of two 28 oz (828 ml) beverage bottles at room temperature. Seal the bottles with special crimp-type caps lined with Teflon. These caps are designed to permit puncture and withdrawal of vapor samples from the outage with a hypodermic syringe. For this purpose each cap is drilled in the center to produce a small hole, and the cap is lined with a Teflon liner. Each bottle is placed in a steel mesh container and then heated for 16 hours in an oil bath held at 93.3° C. Cool the assembly and the bottles. Determine the oxygen in the ullage of each by gas chromatography. Open the bottles and analyze the aged fuel for gums and residue.

Analyzing Aged Fuel

The fuel-insoluble gum and inorganic residue are separated from the fuel by filtration. Soluble gum is determined on the filtered fuel by ASTM Method D 381. Insoluble gum is dissolved in gum solvent and measured by evaporation of solvent. Inorganic residue is determined by weighing the filter.

Materials and Apparatus

Glass reservoir, with air-pressure connection and an approximately 9-mm-OD delivery tube.

Size 9 neoprene stopper, bored to accept delivery tube.

Gooch low-form filtering crucible: Pyrex, fritted disk, 30 ml, fine porosity.

Crucible holder.

Eight ASTM D381 air-jet gum beakers.

Stirring rod with policeman.

Gum solvent (1:1:1 acetone-toluene-methanol).

n-Heptane.

D 381 gum bath; analytical balance; 93.3° C oven; desiccator without desiccant.

Determining Soluble Gum

Weigh a filtering crucible (hereafter called "filter") and eight gum beakers. Assemble the reservoir-stopper-filter-holder arrangement for filtration. With gentle air pressure, pass the aged fuel from bottle A through the filter and collect the filtrate. Set aside. Pass the fuel from bottle B through the same filter, collecting in a separate container. Make duplicate determinations of all jet gum in each filtrate. Report their average as soluble gum, mg/100 ml.

Determining Insoluble Gum

Place a container beneath the filter. Rinse each bottle and the filter free from fuel by adding three successive 50-ml portions of heptane into each bottle by gently swirling, and pass rinsings through filter. Discard rinsings.

Place a weighed gum beaker beneath filter. Rinse and police bottle A with 15 ml of gum solvent, then pass the solution through filter into beaker. Repeat twice with 15- to 20-ml portions of solvent for a total of not more than 50 ml of solution in gum beaker.

Place another gum beaker beneath filter and carry out the gum solvent steps on bottle B.

Run gum method on the two solutions.

$$\text{Insoluble gum, mg/100 ml} = \frac{\text{residue A, mg} + \text{residue B, mg}}{4.56^{2}}$$

Determining Inorganic Residue

To determine the residue collected on the filter, dry the filter in a 93.3° C oven for 1 hour, cool at least 2 hours, and weigh.

$$\text{Inorganic residue, mg/100 ml} = \frac{\text{residue, mg}}{4.56}$$

To obtain total gum, add the insoluble gum to the soluble gum value.

III. Method for Determining Oxygen in Ullage of Test Bottles

A sample of the vapor is withdrawn from the closed bottle through a septum and injected into a gas chromatograph. This yields an oxygen-argon peak and a nitrogen peak from the air in the ullage. Oxygen content is calculated from the ratio of the peak heights for oxygen and nitrogen from the ullage compared with the ratio of those from air.

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[2] Combined filtered volume from bottles A and B divided by 100.

Materials and Apparatus

A gas chromatograph is equipped with a thermistor detector and a 5-foot by 1/4-inch copper column which is packed with 30- to 60-mesh molecular sieve 13X and conditioned with helium at 204 to 318° C for 6 hours. It is operated at ambient temperature with a helium flowrate of 67 ml/min and 25-ma filament current.

Procedure

Inject an amount of the sample from ullage to produce a nearly full-scale nitrogen peak (50 to 80 μl). Repeat once or twice to get a duplicate pattern. Inject an amount of air to give a nitrogen peak of about the same height, and repeat for a duplicate.

Calculations

Since the chromatographic column does not separate oxygen and argon, the oxygen peak must be corrected for the latter. This is a simple matter, after known quantities of argon have been injected and the sensitivity of the detector to this gas has been established.

Comparison of peak heights is used in the presence of hydrocarbon vapors in the ullage. Calculate oxygen by the following steps:

1. Correct the average oxygen peak height for argon in the air sample.
2. Divide this corrected peak height by the average height of the nitrogen peak. Quotient is R_a.
3. In like manner, figure the oxygen/nitrogen ratio, R_s for the replicate injections of ullage sample.
4. The volume percent of oxygen in air is 1/3.71748 that of nitrogen. Assuming that the ratio of oxygen to nitrogen is constant unless the oxygen is depleted, calculate oxygen by the following formula:

$$\frac{1}{1+3.71748\cdot\frac{R_a}{R_s}} \times 100 = \text{oxygen in air in bottle ullage on argon-free bases, present.}$$

Convert the result to a "whole air" basis by multiplying by 0.99.

IV. Calculation of Predicted 32 Week Gum Levels

The predicted gum levels after 32 weeks of storage are calculated from the data developed during the 16 hour acceleration stability test. The first step is to calculate MF_{16} as follows:

$$MF_{16} = \frac{\text{pct } 0_0 - \text{pct } 0_{16}}{\text{pct } 0_0}$$

Where MF_{16} = multiplying factor

G_0 = quantity of gum obtained prior to the 16 hour test, mg/100 ml

G_{16} = quantity of gum obtained after the 16 hour test, mg/100 ml

0_0 = 21 percent

0_{16} = oxygen in the bottle after the 16 hour test, percent.

The predicted gum after 32 weeks at 43.3° C is:

$$G_{43.3} = m\,(MF_{16}) + G_0 + C$$

Where:

$G_{43.3}$ = gum after 32 weeks at 43.3° C

m = slope of the line relating gum formed in the 16 hour test to amounts formed during 43.3° C storage. For 32 weeks this is 9.15

C = a constant which is 1.2.

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