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SAMPLE MANAGEMENT AND CHEMICAL CHARACTERIZATION OF THE PARAHO/SOHIO/U.S. NAVY CRUDE AND REFINED SHALE OIL SUITE*

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Introduction

The role of the EPA/DOE Fossil Fuels Research Materials Facility (the "Chemical Repository") in this study is to actively support and coordinate the health effects investigations of this oil shale development by acting as a central point for acquisition, cataloging, storage, and distribution of referenceable materials for study. In addition, selected materials are chemically fractionated for bioassay and are characterized in additional detail beyond that of routine stability monitoring. Finally, the Facility is acting as an information transfer agent to insure that the results of the investigations are made available to the oil shale industry and the funding agencies.

This chapter is concerned with the sample management and characterization aspect of the Facility's role in this study.

Sample Acquisition and Inventory

The first concern of the Facility in this investigation was to obtain shale- and petroleum-derived materials relevant for study. Through the cooperation of the U.S. EPA, U.S. DOE, U.S. Navy, and The Standard Oil Company of Ohio (SOHIO), arrangements were made to have samples of the crude shale oil, process materials, and final, finished jet and diesel fuel products collected and sent to the Facility. Lt. Cdr. L. J. Jenkins of the U.S. Navy Medical Research Institute,

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Wright Patterson Air Force Base, Ohio, provided the petroleum-derived jet and diesel fuels which the U.S. Navy is using as a "conventional" reference point in their toxicity studies.

A major objective was to obtain the materials in an uncontaminated state. For this reason, type 304 stainless steel drums were obtained by the Facility, were cleaned, and were shipped to the SOHIO refinery at Toledo, Ohio for direct collection of the shale-derived samples and return shipment. Smaller (5 gal) samples of highly volatile or corrosive process materials were collected in Teflon-lined steel pails, also provided by the Facility. In the case of the petroleum-derived fuels, shipment was made to the Facility in carbon steel drums lined with an epoxy resin which the Navy has found effective for fuel storage. Both sets of samples were received at the Facility in the winter of 1978-1979. They were sampled in the spring of 1979 (see below) and are now being stored at 4°C in the storage Repository of the Facility.

The current inventory of the bulk volumes of these materials is listed in Table 1. The information shown includes the unique identifying Repository Sample Number assigned to each material, the descriptive name of the material, the reference number used by the SOHIO refinery, and the current bulk sample amount stored at the Facility. The suite of materials includes the crude shale oil (No. 4601), six process materials (Nos. 4602-4607), three finished jet fuel and diesel fuel marine products (Nos. 4608-4610), and a byproduct (No. 4612). Included in the suite are four petroleum-derived jet fuels and diesel fuel marine (Nos. 4613-4616) which the U.S. Navy is using as a "conventional fuel" reference point for comparison with the shale-derived fuels. The Petroleum JP-4 (No. 4613) is not currently being studied because of the decision not to produce a shale JP-4, but it is available for future use.

Sample Aliquotting

The sample aliquotting protocol was designed to maximize sample homogenicity, aliquot uniformity, and sample stability, and to minimize the possibility of sample contamination and degradation. The main features of this protocol were as follows:

a) On the day of sampling of a particular material, the drum lid was replaced with a special stainless steel lid fitted with a stainless steel ball valve and an adjustable air leak to allow direct withdrawal of the sample from the drum to minimize contamination in handling.

Table 1. Inventory of Crude and Refined Shale Oils and Petroleum Equivalents

Repository Sample Number	Date	Description	SOHIO Reference Number	Quantity (Gal)
4601	11-03-78[a]	Crude Shale Oil	CSO-556	53
4602	11-29-78[a]	Hydrotreated Shale Oil	C5HTSO-554	53
4603	11-21-78[a]	Weathered Gasoline Feedstock	WGFS-55	4.5
4604	11-22-78[a]	JP-5 Precursor	PREJP5-555	53
4605	11-27-78[a]	JP-8 Precursor	PREJP8-555	53
4606	11-21-78[a]	DFM Precursor	PREDFM-555	53
4607	11-30-78[a]	Hydrotreated Residue	HTR-555	53
4608	1-24-79[a]	JP-5 Product	FINJP5-554	53
4609	11-27-78[a]	JP-8 Product	FINJP8-554	53
4610	2-21-79[a]	DFM Product	FINDFM	53
4612	-[b]	Acid Sludge from DFM Treatment	-	4.5
4613	1-19-79[c]	Petroleum JP-4	-	55
4614	1-10-79[c]	Petroleum JP-5	-	53
4615	1-10-79[c]	Petroleum JP-8	-	53
4616	1-10-79[c]	Petroleum DFM	-	3

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[a] Date of sampling.
[b] Date not supplied.
[c] Date of receipt.

b) The sample and aliquot-to-aliquot uniformity was maximized by solar heating of the drums (accomplished by spraying a 180° sector of the drum exterior with flat-black paint and orienting this painted side of the drum toward the sun) to raise the material to a temperature above its pour point. Thorough mixing was accomplished by rotation of the drum after inserting two six inch lengths of type 304 stainless steel pipe into the drum to facilitate agitation. The lighter, low viscosity materials such as the jet and diesel fuels were sampled in the mornings, while the heavier, more viscous crude and hydrotreated shale oil and hydrotreated residue were sampled in the afternoons to allow longer solar heating periods. These measures were effective for homogenizing most of the samples. However, the drums of Crude Shale Oil, Hydrotreated (HDT) Shale Oil, and HDT Residue all contained a layer of a thick gel material which was not completely dissolved by this treatment. Although the mateiral was not completely homogenized, the sample aliquots appeared to be uniform.

c) To minimize contamination, the samples were withdrawn directly into the sampling containers which had been rinsed with methanol, dried, and pre-rinsed with a portion of the sample material itself. After sampling, the headspace of each container was briefly flushed with argon to exclude oxygen and to provide an inert blanket.

d) To minimize possible photodegradation and sample-container interaction, the sampling containers were foil-covered or amber-colored borosilicate glass bottles of 0.125, 0.5, and 1 l volumes. Borosilicate glass is the preferred[1] container material. Soft glass has been shown[2] to interact with hydrocarbon fuels. For larger sample requirements, uncoated carbon steel drums (5 gal capacity) also were used. These drums were specially ordered to omit the usual rust-inhibitor inner surface coating which could contaminate the sample.

e) The samples were shipped immediately by air express to minimize the delay between aliquotting by the Facility and receipt by the investigators participating in the study.

f) Sample aliquots not immediately distributed were stored in the dark at -30°C to minimize degradation.

Sample Distribution for Matrix-Approach Study

Although the most of the samples were distributed soon after the aliquotting was conducted, additional aliquots have been distributed since then to other investigators. The current distribution of this suite of materials is shown by the study matrix in Table 2, where the materials and studies form adjacent axes, and the investigators (Key to investigators in Table 3) comprise the matrix.

The matrix indicates that a wide variety of investigations and talent from institutions across the country is being focused on a common set of materials. Laboratories of the U. S. government, private industry, and private and public universities are participating. Studies of the materials range from physical and chemical characterization to biological and ecological effects, including toxicity, mutagenesis, and carcinogenesis. Additional investigators will be added as the study continues.

Sample Stability Monitoring

A continuing concern of the Facility is the stability of the materials under storage. In order for data obtained with materials shipped months or years apart to be considered comparable, the stability of the materials must be monitored and characterized to demonstrate minimal change.

A battery of routine stability tests has been set up to characterize several parameters of stability, based on reports[3-6] of changes in the physical and chemical properties of crude and refined synfuels in accelerated aging tests. The battery of tests includes the following:

a) Direct gas chromatographic (GC) profile of the material to detect changes in the major chromatographable organic constituents which would occur with evaporation, degradation, or contamination of the major volatile organic constituents.

b) Infrared spectrum (IR) of the material to detect changes in the organic functionality, particularly in the ~ 1700 cm^{-1} spectral region for absorption by carbonyl groups. Increases in carbonyl absorption band intensities correlate with aging and gum formation.[4,6] Contamination also may be detected if the contaminant has a unique, well-defined spectrum different from that of the sample.

c) Viscosity and density measurements to detect aging. The viscosity increases[3,5,6] upon aging.

Table 2. Study Matrix of the Paraho/SOHIO Crude and Refined Shale Oil Suite[a]

	Test	Chemistry					Biology, Ecology										
Repository Number	Research Material	Comprehensive Analysis	PAH Analysis	Stability Screening	Special Studies	Chemical Class Fractionation	Mouse Skin Carcinogenesis	Bacterial Mutagenesis	Drosophilia Mutagenesis	Acute Oral Toxicity to Mice	Pond Ecosystem Effects	Marine Ecosystem Effects	Combustion Products Mutagenicity	Cilia Toxicity	Mouse Lung Tumorigenicity, Skin & Eye Irritation, Toxicity	Mice Interperitoneal Tumorigenesis	Trout Embryo Larvae Hatching & Morphology
4601	Crude Shale Oil	1	2,5	15	15	16	3-5	5-7	8,9	10	11	—	—	13	17	18	19
4602	HDT Shale Oil	1	2,5	15	15	16	3-5	5-7	8	10	11	—	—	13	17	18	—
4603	Weathered Gas Feedstock	1	—	15	—	16	—	6	8	—	—	—	—	—	—	—	—
4604	JP-5 Precursor	1	—	15	—	16	—	6	8	—	—	—	—	—	—	—	—
4605	JP-8 Precursor	1	—	15	—	16	—	6	8	—	—	—	—	—	—	—	—
4606	DFM Precursor	1	2	15	—	16	3,4	6	8	—	—	—	12	—	—	—	—
4607	HDT Residue	1	2,5	15	15	16	3-5	5,6	8	10	11	—	—	13	17	—	—
4608	JP-5 Product	1	5	15	—	16	3-5	5,6	8,9	—	11	—	—	—	17	—	—
4609	JP-8 Product	1	5	15	—	16	3-5	5,6	8	—	—	—	—	—	17	—	—
4610	DFM Product	1	2,5	15	15	16	3-5	5,6	8	—	11	14	12	13	17	18	—
4612	Acid Sludge	1	—	—	—	16	—	6	8	—	—	—	—	—	—	—	—
4614	Petroleum JP-5	—	5	15	—	16	4,5	5,6	8,9	—	11	—	—	—	17	—	—
4615	Petroleum JP-8	—	5	15	—	16	4,5	5,6	8	—	—	—	—	—	17	—	—
4616	Petroleum DFM	—	5	15	—	16	3	5,6	8	—	11	14	—	13	17	18	—

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[a] Key to investigator number is in Table 3.

Table 3. Key to Investigators[a]

Table 2 Number	Investigator	Institution/Company
1	L. W. Burdett	Union Oil Company[b]
2	S. C. Blum	Exxon Corporation[b]
3	W. Barkley	Kettering Laboratory[b]
4	J. M. Holland	Oak Ridge National Laboratory
5	L. M. Holland	Los Alamos Scientific Laboratory
6	J. L. Epler	Oak Ridge National Laboratory
7	F. T. Hatch	Lawrence Livermore Laboratory
8	S. Zimmering	Brown University
9	M. Legator	University of Texas
10	H. P. Witschi	Oak Ridge National Laboratory
11	J. M. Giddings	Oak Ridge National Laboratory
12	D. L. Coffin	U. S. Environmental Protection Agency
13	J. N. Dumont	Oak Ridge National Laboratory
14	N. Richards	U. S. Environmental Protection Agency
15	W. H. Griest	Oak Ridge National Laboratory
16	B. R. Clark	Oak Ridge National Laboratory
17	L. Smith	Oak Ridge National Laboratory
18	W. Pepelco	U. S. Environmental Protection Agency
19	W. Birge	University of Kentucky

[a] See Table 2

[b] Sponsored by the American Petroleum Institute

d) Simulated distillation to determine any changes in the boiling point distribution of the material which might be induced by loss of volatile constituents.

e) Elemental compositional scan by instrumental neutron activation analysis to detect inorganic contamination of the material by its container.

This battery of tests is being applied not only to the bulk samples in long-term storage in the drums and to aliquots for short-term distribution in borosilicate glassware, but also to aliquots taken in flint glassware and stored under various temperatures. This allows the stability of the materials to be studied under a variety of conditions to determine which is the optimum:

Amber Borosilicate = both room temperature and -30°C
Amber Flint = both room temperature and -30°C
Stainless Steel = 4°C

All of the above are under argon and are kept in the dark.

The results of the physical property measurements for the initial sampling at "time zero" (except where indicated) are shown in Table 4. Repetition of these measurements on the materials after one year of storage under various conditions shows little, if, any detectable change from the values listed (thus, they are not included here), with the possible exception of a 10 to 30 percent increase in the viscosity of the HDT Residue. Interestingly, the viscosity increased more in samples stored in borosilicate than in flint. This same container glass type effect has been observed in the storage of No. 2 burner oils and diesel fuels, and was attributed not to an acceleration of fuel degradation by the borosilicate glass, but rather to an interaction of the soft glass with the fuel which slowed deterioriation. Although the soft glass container would appear to "stabilize" the material, it is probably an interaction with the material (which would partially contaminate it) which lends the apparent "stabilizing" effect.

In the other stability tests, the infrared spectra recorded on a Fourier Transform IR spectrophotometer and the gas chromatograms generated on a 3 m x 3 mm glass column packed with a Dexsil 400 coated support did not show any detectable changes in the samples after one year of storage. This would suggest that no gross changes have occurred.

Stability testing will be continued on the samples at periodic intervals to monitor potential changes and follow up on the observations made after the first year of storage to determine if a trend is occurring, or if any of the initial year's results are spurrious.

Chemical and Physical Characterization

Part of the bioassay support function of the Facility is to perform chemical and physical measurements which would aid in interpretation of bioassay responses and endpoints. Part of this characterization is obtained in the baseline stability studies. Table 4 indicates, for example, that the Crude Shale Oil, HDT Shale Oil, and HDT Residue are relatively viscous, high-boiling materials separate in properties from the other samples. It is interesting to note that the heavier materials are exhibiting mutagenicity and carcinogenicity in contrast to the renal effects of the refined products. Also, the data in Table 4 suggest that the shale-derived jet and

Table 4. Physical Properties of the Crude, Process, and Refined Product Samples

				Boiling Points (°C) by Simulated Distillation		
Repository Sample No.	Description	Density[a] (g/cm^3)	Viscosity (CS)	Initial	Average	Final
4601	Crude Shale Oil	0.197[b]	50.5[a,b]	20	358	514
4602	Hydrotreated Shale Oil	0.842[b]	7.14[a,b]	158	369	514
4603	Weathered Gasoline Feedstock	-	0.84	17	92	168
4604	JP-5 Precursor	-	1.58	124	201	271
4605	JP-8 Precursor	-	1.64	125	207	272
4606	DFM Precursor	0.835	3.74	152	278	330
4607	Hydrotreated Residue	0.866[b]	20.6[b]	255	401	513
4608	JP-5 Product	0.800	1.66	117	211	274
4609	JP-8 Product	-	1.60	113	206	273
4610	DFM Product	0.829	3.57	135	277	333
4612	Acid Sludge from DFM Treatment	-	130.	-	-	-
4614	Petroleum JP-5	0.805	2.16	60	225	287
4615	Petroleum JP-8	-	1.81	25	205	291
4616	Petroleum DFM	0.838	3.16	96	268	363

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[a] Data from samples stored at -30°C in amber borosilicate glass.
[b] Measurements performed at 38°C; others in same column performed at 25°C.

diesel fuels are very similar to their petroleum equivalents. More detailed physical and chemical data on the shale-derived materials are available in a Union Oil Company report.[7]

Information on the general chemical class nature of the materials is generated in the course of their chemical class fractionation for bioassay. In this procedure, the materials are separated into acid/base fractions,[8] and the neutrals are further subdivided by gel chromatography[9] into various aliphatic and aromatic subfractions. Data averaged from one to four replicates from the bioassay preparation of this suite of material are listed in Table 5. Although these data are derived from a preparative-scale procedure, and not an analytical method, they are useful for defining the general chemical nature of the organic constituents. The material with the greatest mutagnic activity, carcinogenicity, and toxicity is the Crude Shale Oil which contains the greatest percentage of acidic and basic constituents. However, all the materials are seen to be essentially neutral and paraffinic in character, particularly the finished fuels as is the objective of the refining. The relative amounts of the two aromatic fractions in the fuels and their precursors appears to parallel the volatility data in Table 4. The hydrotreating step appears to reduce acidic and basic constituents as might be expected from a partial removal of s- and n-heteroatomic functionality. Similarly, the acid/clay treatment appears to have reduced ether-soluble base constituents, going from the precursors to the products. Some difficulty was experienced in recovering fractions from the lighter, more volatile fuels and their precursors, and probably occurred in the solvent removal steps.

The elemental compositional scans of the stability study are not yet complete. However, the data generated in the baseline "time zero storge" studies a year ago have provided some information on the relative inorganic content of the materials. At least two distinct groupings of the materials can be made by inorganic content. The Crude Shale Oil, HDT Shale Oil, HDT Residue, and the Acid Sludge (the last possibly in a separate group, considering its sulfuric acid matrix) contain the highest concentrations of elements such as Na, K, Al, Mn, Cl, Cr, Fe, Zn, Br, Ag, Au, and La, whereas the jet and diesel fuel precursors and products contain 0.1 to 0.01 the concentrations of such elements. These differences would be expected from the refining.

IR spectra also were taken during the stability tests. Comparison of the IR spectra in Figure 1 for the Crude Shale Oil and HDT Shale Oil also shows the reduction of heteroatomic content by the hydrotreating process, and the similarity of the HDT Residue to the HDT Shale Oil. The spectra also illustrate the essentially hydrocarbon nature of these

Table 5. Chemical Class Fraction Data for Crude, Process, and Refined Product Samples

	Percentage Composition[a]											
Chemical Class Fraction	No. 4601 Crude Shale Oil	No. 4602 HDT Shale Oil	No. 4603 W. Gas Feedstock	No. 4604 JP-5 Precursor	No. 4605 JP-8 Precursor	No. 4606 DFM Precursor	No. 4607 HDT Residue	No. 4608 JP-5 Product	No. 4609 JP-8 Product	No. 4610 DFM Product	No. 4614 Petroleum JP-5	No. 4616 Petroleum DFM
Volatile	0.3	1.2	36.1	1.9	2.1	0.7	0.6	3.8	5.5	0.6	2.3	1.0
Base (Ether Soluble)	3.7	1.3	0.16	2.25	4.1	2.2	0.8	0.1	0.2	<0.02	0.3	0.02
Base (Insoluble)	1.0	0.4	0	0.6	0	0.7	0.7	-	0.2	-	-	-
Acid (Ether Soluble)	0.4	0.2	0.07	0.6	0.3	0.1	0.3	0.5	-	0.07	0.9	0.1
Acid (Insoluble)	1.1	0.3	0	0.5	0	0.5	0.6	-	0	-	-	-
Total Neutrals	93.3	92.2	27.1	89.1	86.1	105	99.4	90.8	90.3	97.9	93.9	97.5
Aliphatic	58.9	51.5	2.2	40.4	50.0	84.8	53.2	37.8	36.4	82.4	59.3	65.0
Mono/Diaromatic	26.4	21.0	0.05	5.2	5.7	12.3	34.2	4.5	5.2	7.2	4.1	17.9
Polyaromatic	2.8	4.1	0.6	0.09	0.2	0.6	10.0	0.1	0.1	0.1	0.1	1.3
Residue	2.1	4.6	-	2.4	1.3	1.8	5.1	1.1	1.8	2.1	2.0	1.3
Total Recovery[b]	97.7	95.3	63.4	48.1	63.7	102	102	47.5	49.4	92.5	68.2	86.7
Number of Replicates	2	4	1	2	2	2	2	2	1	1	2	1

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[a] Percentage of original sample.

[b] Based on neutral fractions.

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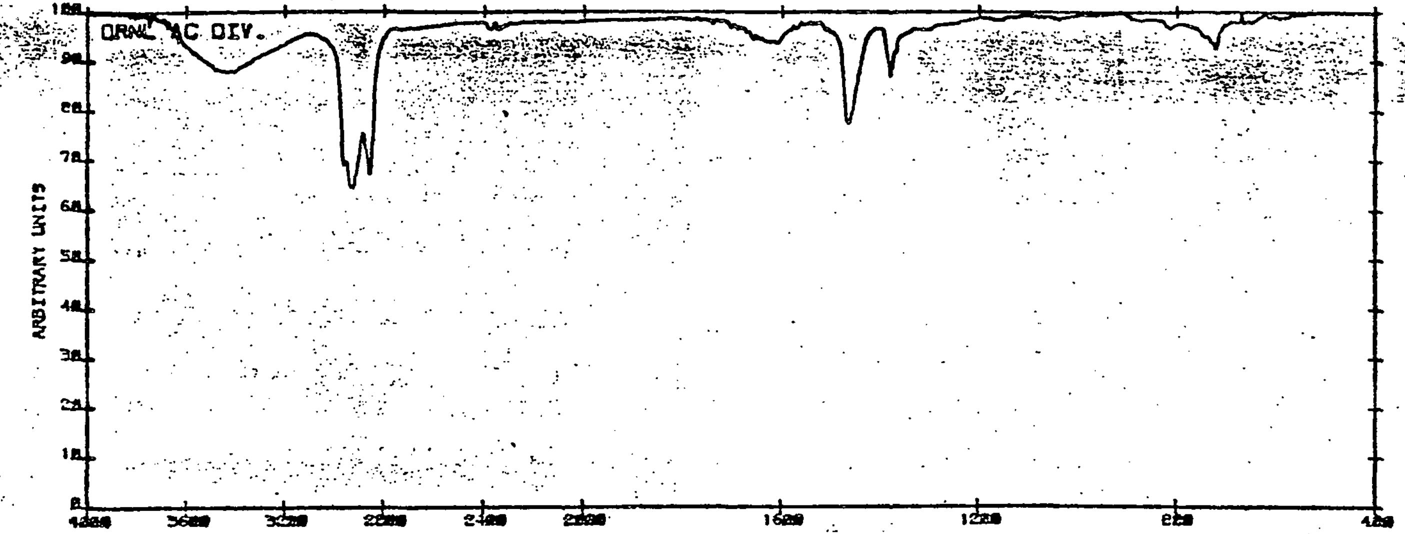
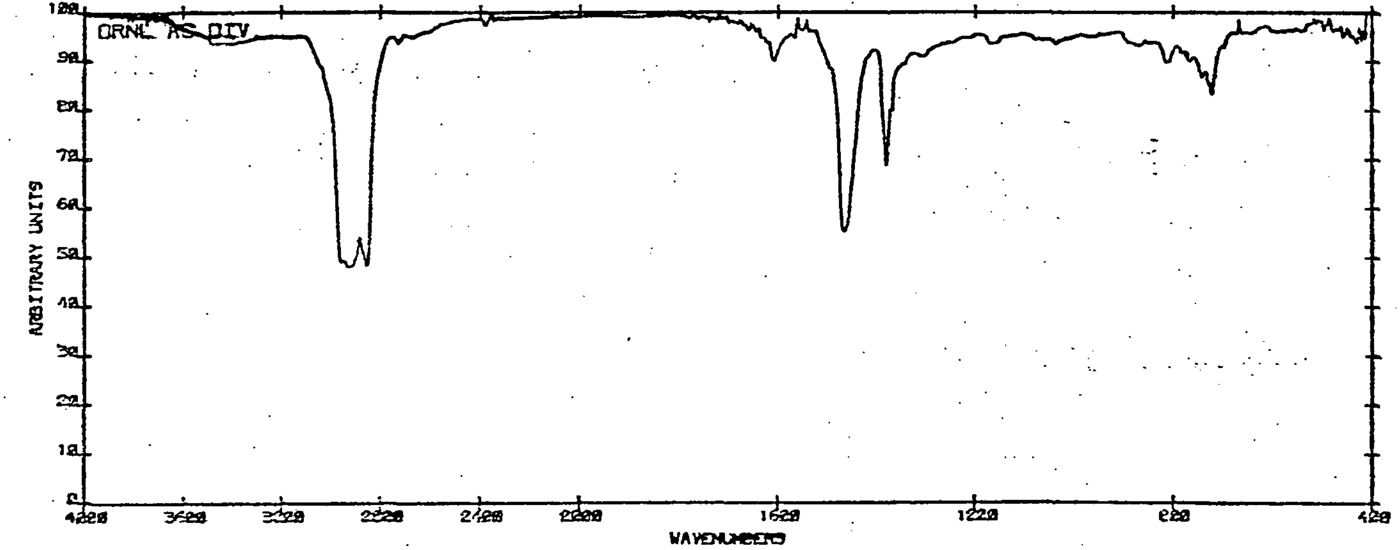
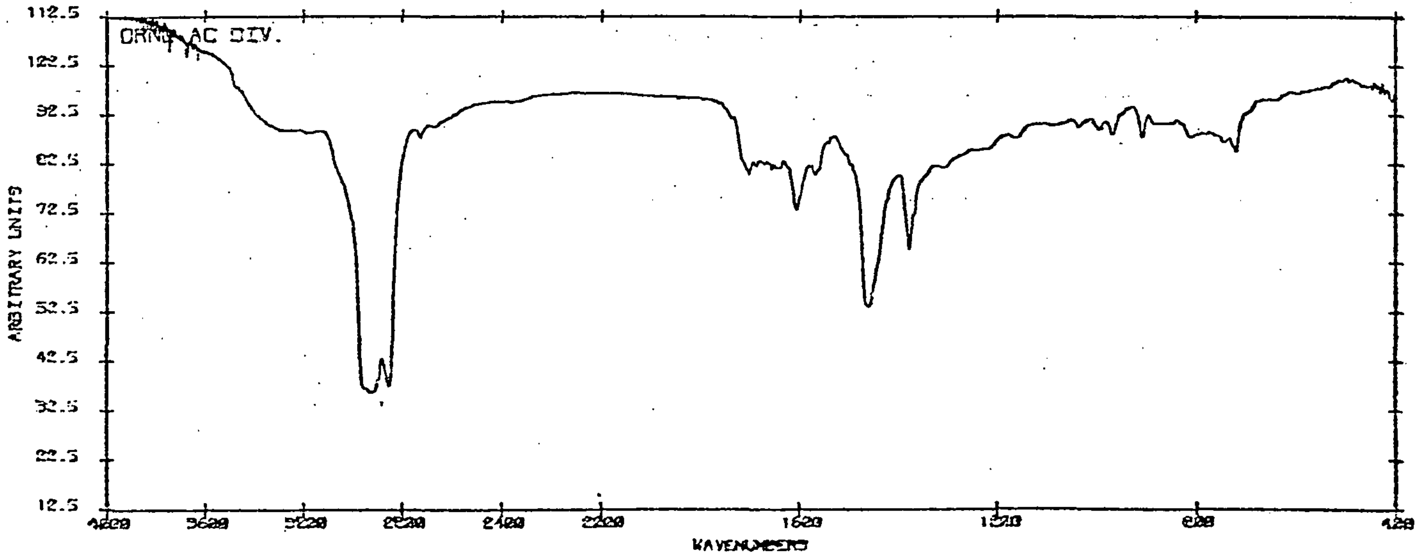


HDT RESIDUE



HDT SHALE OIL



CRUDE SHALE OIL

Figure 1. Infrared Spectra of Crude and HDT Shale Oils and HDT Residue

materials, with the spectra of the other materials being very similar to each other. No differences could be distinguished between the shale- and petroleum-derived products by IR.

Non-routine glass capillary column GC profiles of the diluted materials do show some interesting differences which correlate with the other data. Figure 2 shows the profiles for the Crude Shale Oil, HDT Shale Oil, and the HDT Residue. Hydrotreatment considerably increases the n-paraffin content (see also Table 6) and eliminates the baseline rise and "hump" in the gas chromatogram which would be associated with polar heteroatomic species which are not well resolved on a nonpolar stationary phase. The HDT Residue is seen to lack most of the C_{10}-C_{18} n-paraffins of the previous two samples (as is expected from its fractionation), but these removed species are recovered in the jet and diesel fuel products (see Figure 3 and Table 6).

Table 6. Measurements of Total n-Paraffins in Some Crude, Process, and Refined Samples

No.	Description	Conc., mg/g	Major Species
4601	Crude Shale Oil	27	C_{10}-C_{33}
4602	HDT Shale Oil	102	C_{10}-C_{34}
4607	HDT Residue	65	C_{18}-C_{34}
4608	JP-5 Product	197	C_{10}-C_{13}
4610	DFM Product	155	C_{12}-C_{18}
4606	DFM Precursor	158	C_{12}-C_{18}

Some small, minor differences in the chromatographable constituents of the shale-versus petroleum-derived products are visualized by this capillary GC technique. The glass capillary column GC profiles of diesel fuel marine derived from shale (upper chromatogram) and petroleum (lower chromatogram) in Figure 4 show some minor differences in the relative amounts of some constituents eluting near C_{17} and C_{18}. The petroleum-derived DFM also appears to contain a small percentage of higher paraffins than does the shale-derived DFM. Similar minor differences also were noted between the shale- and petroleum-derived jet fuels. The similarity in bioassay responses observed thus far for the petroleum- and shalederived fuels would suggest, however, that these differences are negligible.

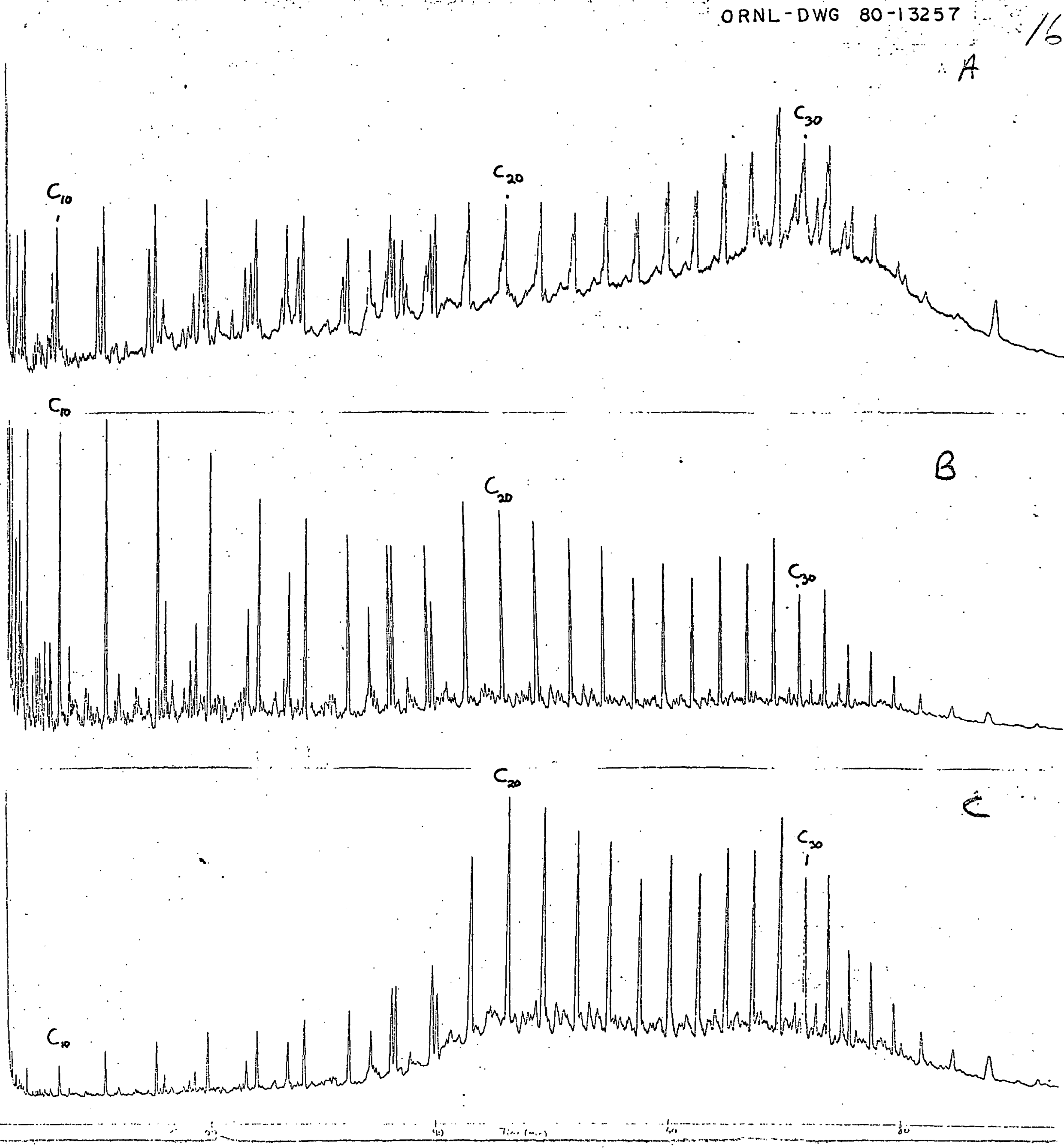


Figure 2. Capillary-Column Gas Chromatograms of (A) Crude Shale Oil, (B) HDT Shale Oil, and (C) HDT Residue

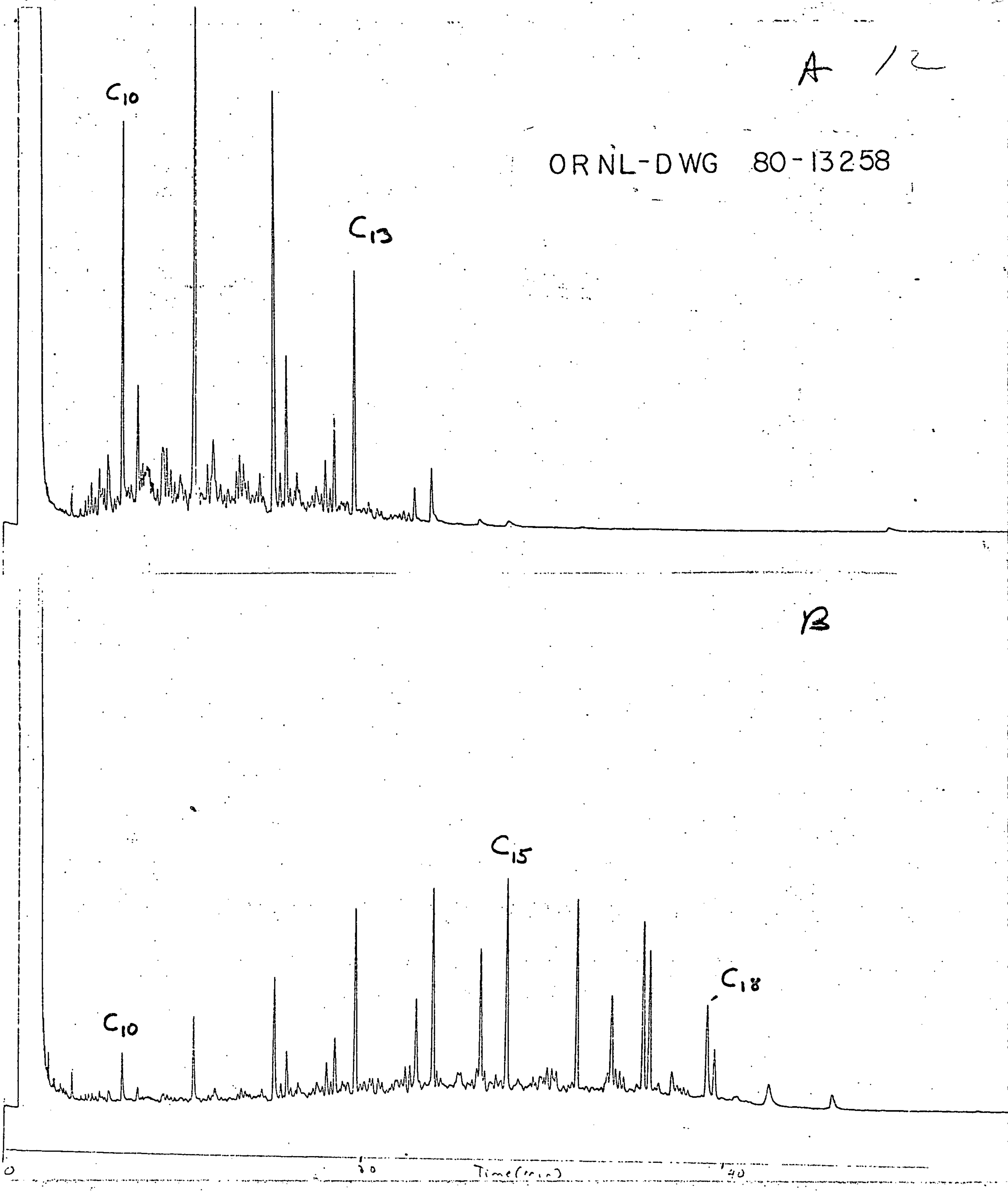


Figure 3. Capillary-Column Gas Chromatograms of
(A) JP-5 Product and (B) DFM Product

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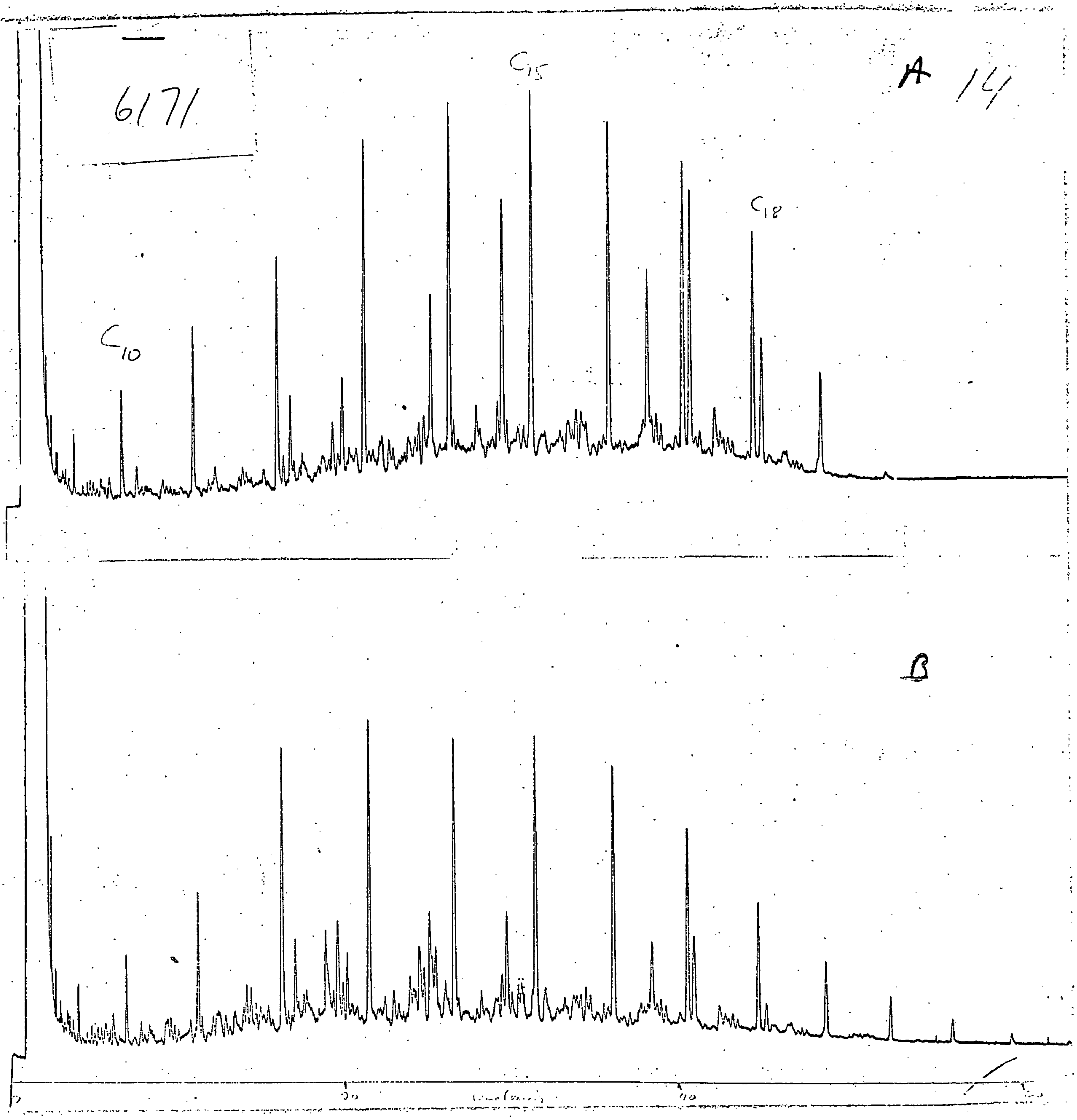

Figure 4. Capillary-Column Gas Chromatograms of
DFM Derived from (A) Shale and (B) Petroleum

Specific bioactive constituents also are being measured in the samples to aid in bioassay response interpretation. Table 7 contains data for measurements of benzo(a)pyrene in selected samples. It may be significant to note that although the benzo(a)pyrene content of the HDT Shale Oil and HDT Residue is equal to or greater than that of the Crude Shale Oil, the toxicity, mutagenicity, and carcinogenicity of the latter is greater than that of the former two. This result suggests that other classes of constituents, possibly those included in the relatively greater percentage of acidic and basic constituents of the Crude Shale Oil (Table 5), may be the determinant bioactive species. In contrast to these heavier materials, the jet and diesel fuels are seen to contain very little benzo(a)pyrene.

Table 7. Measurements of Benzo(a)pyrene in Some Crude, Process, and Refined Samples

No.	Description	Conc., μg/g
4601	Crude Shale Oil	11
4602	HDT Shale Oil	11
4607	HDT Residue	16
4608	JP-5 Product	N.D.[a]
4614	Petroleum JP-5	∿ 0.04
4606	DFM Precursor	0.03
4614	DFM Product	0.04

[a] ND = not detected.

The Facility will continue in its central role of sample management for this health effects investigation. The specific measurement of bioactive constituents will be extended, and the participation of other investigators in the study will be solicited.

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