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Characterization of DOE Reference Oil Shale: Tipton Member, Green River Formation Oil Shale From Wyoming

Topical Report

F. P. Miknis

August 1988

Work Performed Under Cooperative Agreement: DE-FC21-86MC11076

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Western Research Institute
Laramie, Wyoming

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

SUMMARY

Measurements have been made of the chemical and physical properties of a Tipton Member Green River Formation oil shale from Wyoming. This shale has been designated as a western reference shale by the Department of Energy. Material balance Fischer assays, carbon aromaticities, thermal properties, and bulk mineralogic properties have been determined for the oil shale. Kerogen concentrates were also prepared. Most of the measured properties of the Tipton shale are comparable to results from previous studies of similar shales.

The apparent carbon aromaticity of the Tipton Member raw shale was 0.33, and the hydrogen-to-carbon ratio of the kerogen concentrate was 1.35. Sixty-two percent of the raw shale organic carbon was converted to oil carbon during Fischer assay. By combining NMR and Fischer assay conversion data, it was estimated that as much as 21% of the raw shale aliphatic carbon aromatizes during Fischer assay.

Chemical and physical properties have been determined for the shale oil. ASTM distillation data were used in conjunction with API correlations to calculate molecular weights and viscosities. There was poor agreement between measured and calculated molecular weights for the total shale oil produced from each shale. However, measured and calculated molecular weights agreed reasonably well for true boiling point distillate fractions in the temperature range of 450 - 762 ^{0}F (232 - 406 ^{0}C). Similarly, measured and calculated viscosities of the total shale oil were in disagreement, though good agreement was obtained on distillate fractions for a limited boiling range.

INTRODUCTION

In 1984, the Department of Energy (DOE) made an assessment of its oil shale program based on information from industry, the Fossil Energy Research Working Group, a National Research Council review of safety issues related to synthetic fuels development, a review of available oil shale data, and an examination of the existing DOE oil shale program. This led to a restructuring of the DOE oil shale program. An integral part of the restructured program involves the measurement of fundamental chemical and physical properties of reference oil shales.

The DOE reference oil shale program began in October 1985, when Terra Tek, Inc. of Salt Lake City, Utah was awarded a DOE contract for the establishment and maintenance of an oil shale sample bank. Work sponsored by DOE on oil shales is to be conducted on oil shales in the reference shale program, because data obtained from different research programs on the reference shales will be more consistent and more readily correlated with other oil shale data.

Under the DOE reference shale program, two oil shales per year are to be acquired; five will be from the western United States deposits, and five will be from deposits in the eastern United States. The selected shales will be as representative as possible of deposits chosen for future oil shale development.

During fiscal year 1988 (FY88), two additional reference oil shales were acquired by the DOE. Only one of these, the Tipton Member western reference shale was acquired early enough for chemical and physical properties measurements to be made in FY88. The second eastern reference shale, a New Albany shale from southern Indiana, was acquired during the last quarter of FY88. Property measurements were not made on this shale; however, it is expected that such measurements would yield results comparable to the New Albany reference shale previously studied (Miknis and Robertson 1987).

PROPERTIES OF ORGANIC MATTER

Oil Shale Sample

The second western reference shale is a Tipton Member Green River Formation oil shale obtained from an outcrop near Rock Springs, Wyoming. Details about the site selection and sample acquisition have been reported by Owen (1987). The oil shale that was received from Terra Tek had a top size of approximately 3/4 inch. The material was reduced in size by grinding, and was then riffled to obtain representative sample material for the property measurements.

Material Balance Fischer Assay

Probably the single most important piece of information about an oil shale is its potential to produce oil during heating. The Fischer assay (American Society for Testing and Materials, Method D-3904-80) is the traditional method for determining the oil potential of an oil shale. In brief, the Fischer assay consists of heating a 100-g sample of oil shale to 932 °F (500 °C) at a rate of 21.6 °F (12 °C)/min and maintaining this temperature for another 40 minutes. The hydrocarbon vapors that distill from the sample condense to form a shale oil. This oil is collected, its volume and weight recorded, and specific gravity determined. From these measurements, the oil potential is reported in either weight percent or gallons of oil per ton of shale. In the material balance Fischer assay (MBFA), the elemental compositions of the products are determined as well.

MBFA results for the Tipton Member reference shale are reported in Table 1. Gas composition is listed in Table 2. The conversion of organic matter to gas, oil, and residue products can be determined from these data (Table 3). The high conversion of organic carbon to oil for the western reference shale is typical of Green River Formation oil shales.

Carbon Aromaticity Measurements

Modern analytical techniques make it possible to determine some of the chemical structural features of the kerogen. The most significant techniques are cross polarization (CP), magic-angle spinning (MAS) ^{13}C nuclear magnetic resonance (NMR) techniques (Miknis et al. 1979). The CP/MAS ^{13}C techniques provide a direct, nondestructive measurement of the organic carbon distribution in oil shales. In particular, the fractions of aromatic and aliphatic carbons can be determined. These carbon types represent the major carbon fractions in oil shales, and their relative amounts largely determine the conversion behavior of oil shales. Highly aliphatic oil shales have high conversions to oil (Miknis et al. 1982a), whereas highly aromatic oil shales produce greater residue carbon (Miknis et al. 1982b).

Solid-state ^{13}C NMR measurements were made on the Tipton Member reference shale, and liquid-state ^{13}C NMR measurements were made on the MBFA shale oil (Table 4). The carbon aromaticity value of the shale is compatible with the conversion data in Table 3. In addition, the shale oil aromaticity values are similar to results of previous work on similar shales (Netzel and Miknis 1982; Miknis et al. 1986).

The combined solid- and liquid-state ^{13}C NMR data, in conjunction with the MBFA conversion data, allow some inferences to be made about the extent of aromatization reactions during Fischer assay. This approach is illustrated in Figure 1, where the carbon data are normalized on the basis of 100 carbon atoms (Herschkowitz et al. 1983). The distribution of aliphatic and aromatic carbons in the raw shale is determined by solid-state ^{13}C NMR measurements. However, in such measurements, the carbonyl and carboxylate carbon functionalities are not well resolved, and partially overlap the aromatic carbon region of the spectrum. The carbons evolving as CO and CO_2 in the MBFA product gas are assumed to originate from carbonyl and carboxylate functionalities in the raw shale. To obtain a more accurate assessment of the carbon aromaticity, the number of carbon atoms in CO and CO_2 computed is from the MBFA gas data and subtracted from the aromatic carbons. Thus, for the Tipton Member reference shale, the distribution of 100 carbons is represented as 63 aliphatic, 33 aromatic and 4 carbonyl/carboxylate carbons.

Table 1. Material Balance Fischer Assay Results for Tipton Member Western Reference Shale

Product	wt %	Gal/ton	% Ash	Mineral Carbon wt %	C wt %	H wt %	N wt %	S wt %	O wt %
Oil	8.84	22.03	-	-	81.6	10.9	2.1	0.5	2.3*
Gas	2.09	-	-	-	42.9	9.1	-	0.1	47.9
Spent shale	85.96	-	81.33	3.7	7.7	0.3	0.5	0.4	43.2*
Water	3.15	7.56	-	-	-	11.1	-	-	88.9
Raw shale	100.00	-	71.23	3.4	14.97	1.4	0.6	0.4	40.3*
% Recovery	100.04	-	98.15	93.50	98.40	129.0	102.60	97.50	102.97

* Determined by neutron activation analysis.

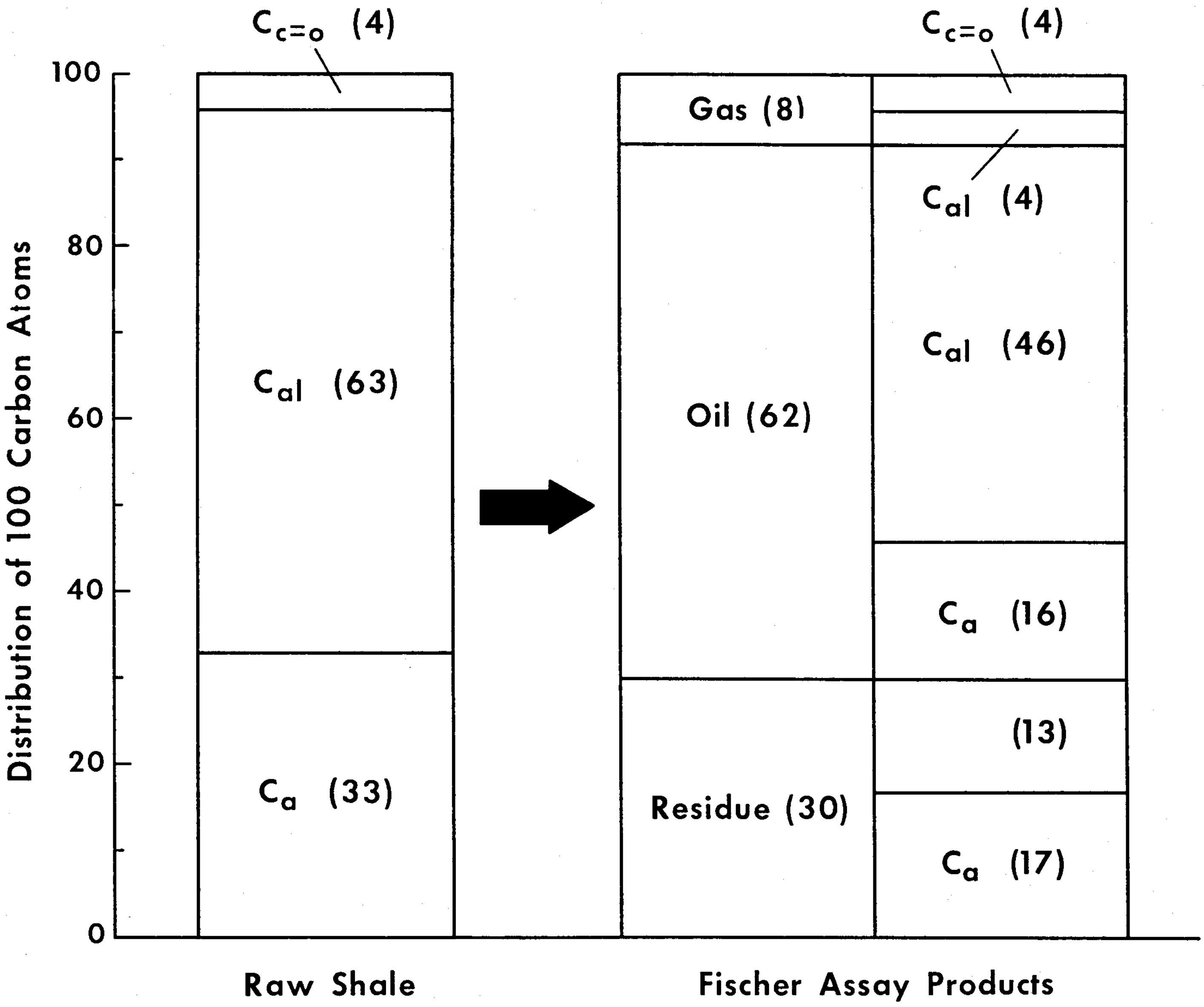

Figure 1. Distribution of Carbon Functionalities in Tipton Member Oil Shale and Fischer Assay Products

Table 2. Material Balance Fischer Assay Gas Analyses of Tipton Member Western Reference Shale

Component	wt %
H_2	0.069
CO	0.172
CH_4	0.204
CO_2	1.242
C_2H_4	0.047
C_2H_6	0.140
H_2S	0.002
C_3H_6	0.088
C_3H_8	0.081
C_4+	0.044

Table 3. Organic Carbon Conversion in Tipton Member Reference Shale

Product	% Conversion
Oil	62.4
Gas	7.8
Residue	29.8

The total number of carbon atoms in the gas, oil, and residue products are determined from the carbon conversion during MBFA (Table 3). The partitioning of carbon atoms in the gas is determined from GC analysis of the gas composition and that in the oil by liquid-state ^{13}C NMR. Attempts to partition the aromatic and aliphatic carbons in the residue using solid-state ^{13}C NMR were not successful because of poor signal-to-noise ratios and broadened signals exhibited by the spent shale spectra. If all of the residue carbon were assumed to be aromatic carbon, then 21% of the raw shale aliphatic carbon aromatizes during Fischer assay. However, because all of the residue carbon may not be aromatic carbon, this amount represents a maximum.

Table 4. Other Properties of Tipton Member Oil Shale and Shale Oil

Property	Value
Heating Value, Btu/lb	
Raw shale	1,730
Spent shale	140
Shale oil[a]	17,630
Molecular Weight--Shale Oil[b]	290
Carbon Aromaticity	
Raw shale	0.330
Shale oil	0.259
Proton Aromaticity	
Shale oil	0.062

[a] Calculated from the Boie equation,
H_g (Btu/lb) = 151.2 (%C) + 499.7 (%H) + 27 (%N) + 45 (%S) - 47.7 (%O)

[b] VPO in toluene

Oxygen Determination by Neutron Activation Analysis

Samples of raw shale, MBFA spent shale, and MBFA shale oils were sent to an outside laboratory (IRT Corporation, San Diego, CA) for direct oxygen determination by neutron activation analysis. Each sample, along with an oxygen standard, was irradiated with 14 MeV neutrons, and counted for ^{16}N induced activity on a single pulse-height analyzer using a pair of 5-in. x 5-in. NaI(Tl) scintillation crystals. The oxygen concentration was determined by comparing the intensity of the 6.13 MeV gamma-ray photopeak of ^{16}N in the sample with that of the oxygen standard.

Oxygen determinations were made in triplicate for the raw and spent shales, and single determinations were made on the shale oil (Table 1). The reported values are for total oxygen and include contributions from organic and inorganic sources. For the raw and spent shales, it is not possible to determine the amount of organic oxygen. However, the oxygen values for the shale oils are organic oxygen values. These organic values can be compared with the values obtained by subtracting the sum of the carbon, hydrogen, sulfur and nitrogen wt % values in each oil (Table 1) from 100%, i.e. using oxygen by difference. The agreement between the direct and by difference oxygen values for the Tipton Member reference shale oil is fair.

Kerogen Concentrates

Kerogen concentrates were prepared to better approximate the atomic hydrogen-to-carbon (H/C) ratio of the organic matter in the Tipton Member shale (Table 5). The procedure involved removal of the bitumen, decomposition of the carbonates using 6N HCl, and removal of silicate minerals using a mixture of 49% HF and 12N HCl (Durand and Nicaise 1980). The procedures used for these steps are fairly straightforward and are based on work by Durand and Nicaise (1980) and Orr (1986). Pyrite removal requires drastic chemical treatment (Orr 1986). In general, pyrite is concentrated with the organic matter when acid digestion procedures are used to concentrate the organic matter.

Yields of kerogen concentrate for the HCl and HCl/HF steps in the procedures are fairly reproducible. The average H/C ratio is 1.35 for the HCl/HF concentrate. This is lower than the value of 1.53 obtained for the Parachute Creek Member western reference shale (Miknis and Robertson 1987), suggesting that there are some differences in the kerogen structure in the two Green River Formation oil shales.

Thermal Properties

Heating Values

Gross heating values were determined on the Tipton Member reference shale using a standard ASTM procedure (D3286). The results are reported in Table 4. Measurements were made on the raw shales and the spent shales from the MBFA tests. The heating value for the shale oil was calculated using the Boie equation (Ringen et al. 1979). The gross heating value of the Tipton Member shale is slightly less than the value of Green River Formation oil shales from Colorado that have similar Fischer assays (Stanfield 1951).

Specific Heats

The specific heats of the raw shale and spent shale from the MBFA were determined for the reference shale. A specially designed ballistic calorimeter was used to measure the enthalpic changes that occur when heating oil shales from ambient temperature to 932 ^{0}F (500 ^{0}C). The design of the calorimeter was patterned after one by Mraw and Kewshan (1984). Data obtained from the dropping calorimeter are listed in Table 6.

The specific heat measurements for the Tipton Member shale agree with those reported by others for shales of comparable richness (Mraw and Kewshan 1986; Cook 1970). The spent shale specific heat measurements are also in good agreement with other studies (Cook 1970; Johnson et al. 1979).

Table 5. **Yields and Elemental Analyses of Oil Shale Concentrates from Tipton Member Western Reference Shale**

Sample	Treatment	Yield, wt % of Starting Shale	Mineral C, wt %	Total C, wt %	H wt %	N wt %	S wt %
Raw shale		100.0	3.4	15.0	1.4	0.6	0.4
1	HCl	60.9	<0.1	16.1	1.9	1.0	0.4
2	HCl	63.6	<0.1	17.2	2.4	0.9	0.5
1	HCl/HF	16.4	<0.1	55.1	6.2	2.0	1.3
2	HCl/HF	15.2	<0.1	59.1	6.4	2.0	1.2

Table 6. Heat of Retorting Tipton Member Reference Oil Shale at 500°C

	Enthalpy of Retorting for 475 °C Temperature Change, cal/g	Enthalpy in Specific Heat*, Cal/g-°C
Western		
Raw	176	0.37 ± 0.01
Spent	123	0.23 ± 0.01

* Arithmetic mean based on four determinations.

Mineralogic Properties

Mineralogic Characterization of Reference Shales

The bulk and clay mineralogies of the raw and retorted reference shales were determined by X-ray diffraction (XRD). Because this technique is qualitative rather than quantitative, peak height data provided in this report should be used as estimates of the relative abundance of minerals within a given sample. Minerals present in minor amounts may be difficult to identify due to mineralogic complexity of oil shales and to the presence of one or more dominant mineral phases. To minimize problems related to sample complexity, slow scans were used to improve accuracy, and multiple runs were performed to increase precision (Miknis and Robertson 1987).

Minerals identified in Tipton Member western reference shale are listed in order of decreasing abundance:

Mineral	Composition
dolomite	$(Ca, Mg, Fe)(CO_3)_2$
analcime	$NaAlSi_2O_6 \cdot H_2O$
K-feldspar	$KAlSi_3O_8$
Mg-siderite	$(Fe, Mg)CO_3$
Na-feldspar	$NaAlSi_3O_8$
illite	$KAl_2(Si_3Al_{10})(OH)_2$
calcite (trace)	$CaCO_3$
pyrite (trace)	FeS_2

The same minerals were identified in the MBFA spent shale. Pyrrhotite ($Fe_{1-x}S$), that formed from thermal reactions of pyrite, was also identified.

Major and Minor Trace Elements

The fate of major and minor trace elements during oil shale retorting is an important consideration when developing short term (e.g. air and water quality) and long term (spent shale leaching) environmental mitigation strategies. The spent shales and shale oils generated from the MBFA, along with the raw oil shales, were analyzed for major and minor trace elements (Table 7) to establish their baseline distribution during oil shale retorting. Two instruments were used for this purpose: (1) a Jarrell-Ash 1100 Series inductively coupled plasma (ICP) spectrometer equipped with a Digital PDP M/23 computer; and (2) a Perkin Elmer 5000 atomic heated graphite atomizer (AA), a Perkin Elmer AS-40 autosampler, and a Perkin Elmer 3600 data station.

Table 7. Major and Minor Trace Elemental Distributions in Tipton Member Western Reference Shale

Element	Raw	Spent	Oil
Major, (%)			
Al	5.48	6.29	
Ca	5.91	6.64	
Fe	3.07	3.45	NM*
K	3.12	3.56	<480.0 ppm
Mg	3.36	3.78	
Mn	0.05	0.05	<4.4 ppm
Na	1.33	1.51	
Sr	0.07	0.07	<0.4 ppm
Minor, (ppm)			
As	20.0	10.0	7.0
Ba	41.4	111.0	<1.0
Be	<4.0	<3.6	<1.0
Cd	<2.0	<2.0	<2.0
Co	14.0	16.0	<1.0
Cr	57.5	67.7	8.9
Cu	87.0	85.8	<1.0
Hg	<0.1	<0.1	<0.1
Li	150.0	159.0	<1.0
Mo	7.2	6.5	<1.0
Ni	31.0	35.0	4.9
Pb	28.0	45.0	2.3
Se	<0.2	<0.2	<0.2
V	132.0	151.0	1.0
Zn	92.4	98.8	NM

*NM = not measured

EPA quality control reference solutions were analyzed after all instrument calibrations to verify the accuracy of the calibrations and the performance of the instrument. Standard Reference Materials, obtained from the National Bureau of Standards, were prepared and, whenever possible, analyzed with each batch of sample to evaluate the accuracy of the analytical procedures being used.

Three methods of sample preparation were used in this work. A multi-acid digestion procedure, developed by WRI, was used to prepare the raw and spent shale samples and shale oils for major and trace element determinations by ICP and AA. A nitric acid and hydrogen peroxide method, also developed by WRI, was used to prepare the raw and spent shales for trace element determinations by AA. The Parr bomb combustion method (Nadkarni 1981) followed by AA analysis was used for trace elements in the shale oils.

The trace element data (Table 7) reaffirm previous observations that the elements of interest remain in the spent shale (e.g., Johnson 1986). The major trace element data also reflect the mineralogy. For example, the high calcium and magnesium values of the western shale reflect its carbonate mineralogy.

PROPERTIES OF REFERENCE SHALE OILS

The chemical and physical properties of shale oils differ considerably from the properties of conventional petroleum sources. Shale oils usually have a lower H/C ratio and higher heteroatom content than other petroleum sources. In addition, the higher temperature processes used to generate shale liquids produce olefins as a result of thermal cracking of the kerogen and bitumen. In order to best use synthetic fuels derived from oil shales, it is important to characterize their chemical and physical properties, at least to the extent of determining distillation properties.

Shale oil was produced from the reference shale using a laboratory reactor that simulates the indirect Paraho Process. The oil was demulsified as described by Robertson (1983).

ASTM D86, D1160, and true boiling point (TBP) distillations were performed on the Tipton Member reference shale oil. In addition, a simulated distillation by gas chromatography was performed. The distillation results are reported in Tables 8 and 9. During the D86 distillation a small amount (<1%) of water in the sample caused severe foaming and spattering. This forced a slower than normal distillation rate which gave erroneously low vapor temperatures. As a result, the D86 distillation was discarded for purposes of characterizing the shale oil.

A 2-L charge was used for the TBP distillation, but due to the small water content, exact cuts at +5 and +10 volume percent were not obtained. The TBP procedures consisted of an atmospheric pressure distillation using a 5:1 reflux ratio, until a 550 °F (288 °C) kettle temperature was reached (394 °F [201 °C] overhead). The apparatus was then cooled, re-started under vacuum, and fractions were collected up to

Table 8. True Boiling Point Distillation Results for Tipton Member Reference Shale Oil

Cut No.	Temp. Range, °F at 1 ATM	Weight	Wt %	Cum. Wt %	Specific Gravity	API 60/60	Volume (mL)	Vol %	Cum. Vol %
58534-A	180(IBP)-347	67.4	3.68	3.68	0.7932	46.9	85.0	4.29	4.29
58534-B	347-394	81.4	4.44	8.12	0.8222	40.6	99.0	5.00	9.29
58534-C	394-450	88.1	4.81	12.93	0.8393	37.1	105.0	5.30	14.59
58534-D	450-487	84.8	4.63	17.56	0.8565	33.7	99.0	5.00	19.59
58534-E	487-522	86.7	4.73	22.29	0.8745	30.3	99.1	5.00	24.59
58534-F	522-560	87.9	4.79	27.08	0.8888	27.7	98.9	4.99	29.58
58534-G	560-596	89.0	4.85	31.93	0.9001	25.7	98.9	4.99	34.57
58534-H	596-625	90.5	4.49	36.87	0.9106	23.9	99.4	5.02	39.59
58534-I	625-661	92.5	5.05	41.92	0.9218	22.0	100.2	5.07	44.66
58534-J	661-690	93.6	5.11	47.03	0.9297	20.7	100.7	5.08	49.74
58534-K	690-762	191.6	10.45	57.48	0.9443	18.4	202.9	10.24	59.98
58534-L	762-835	188.3	10.27	67.75	0.9522	17.1	197.8	9.98	69.96
58534-M	835-905	188.4	10.28	78.03	0.9619	15.6	195.9	9.89	79.85
58534-N	905-995	183.6	10.01	88.04	0.9692	14.5	189.4	9.56	89.41
58534-O	995 +	212.9	11.61	99.65	1.0313	5.7	206.4	10.42	99.83

Table 9. ASTM D1160 and Simulated Distillation Results For Tipton Member Reference Shale Oil

ASTM D1160 Distillation		Simulated Distillation	
Vol %	Temperature, °F	Wt %	Temperature, °F
5	386	-	to 100
10	440	0.1	101-200
20	591	0.7	201-300
30	592	7.2	301-400
40	653	18.5	401-500
50	712	32.4	501-600
60	765	48.0	601-700
70	825	63.1	701-800
80	886	78.9	801-900
90	960	88.6	901-1000

a 590 °F (310 °C) kettle temperature (690 °F [366 °C] overhead, atmospheric equivalent temperature). The residue was moved to a 1-plate (D1160 type) apparatus for the final fractions, up to a 995 °F (535 °C) cut point. The apparatus was shut down just before a 1,000 °F (538 °C) cut temperature because of vacuum deterioration that indicated the onset of thermal cracking. Fractions collected on the TBP still were approximately 5 vol % of the charge, whereas the 1-plate fractions were approximately 10 vol % of the charge, giving a total of 15 fractions. All data in Table 8 are reported on a dry basis.

The TBP and D1160 results are plotted in Figure 2. The D1160 results agree reasonably well with the TBP results. However, the temperature curve for the D1160 is higher than the TBP curve for the first 60 vol % and lower than the TBP curve for the latter portion. This is the expected result for D1160/TBP comparisons on petroleum samples.

A comparison of the TBP and simulated distillation results is shown in Figure 3. These results are plotted on a weight percent, rather than volume percent, basis in deference to the manner in which simulated distillation data are reported. There is very good correlation between the two distillation procedures for the Tipton shale oil.

Physical Property Calculations

The majority of oil physical property correlations available today have been developed for normal paraffinic crude oils. Shale oil properties can differ greatly from petroleum properties, and therefore, the use of correlations designed for petroleum may give erroneous results. Comparison of some measured properties with correlation results can help determine how valid these correlations are for shale oils.

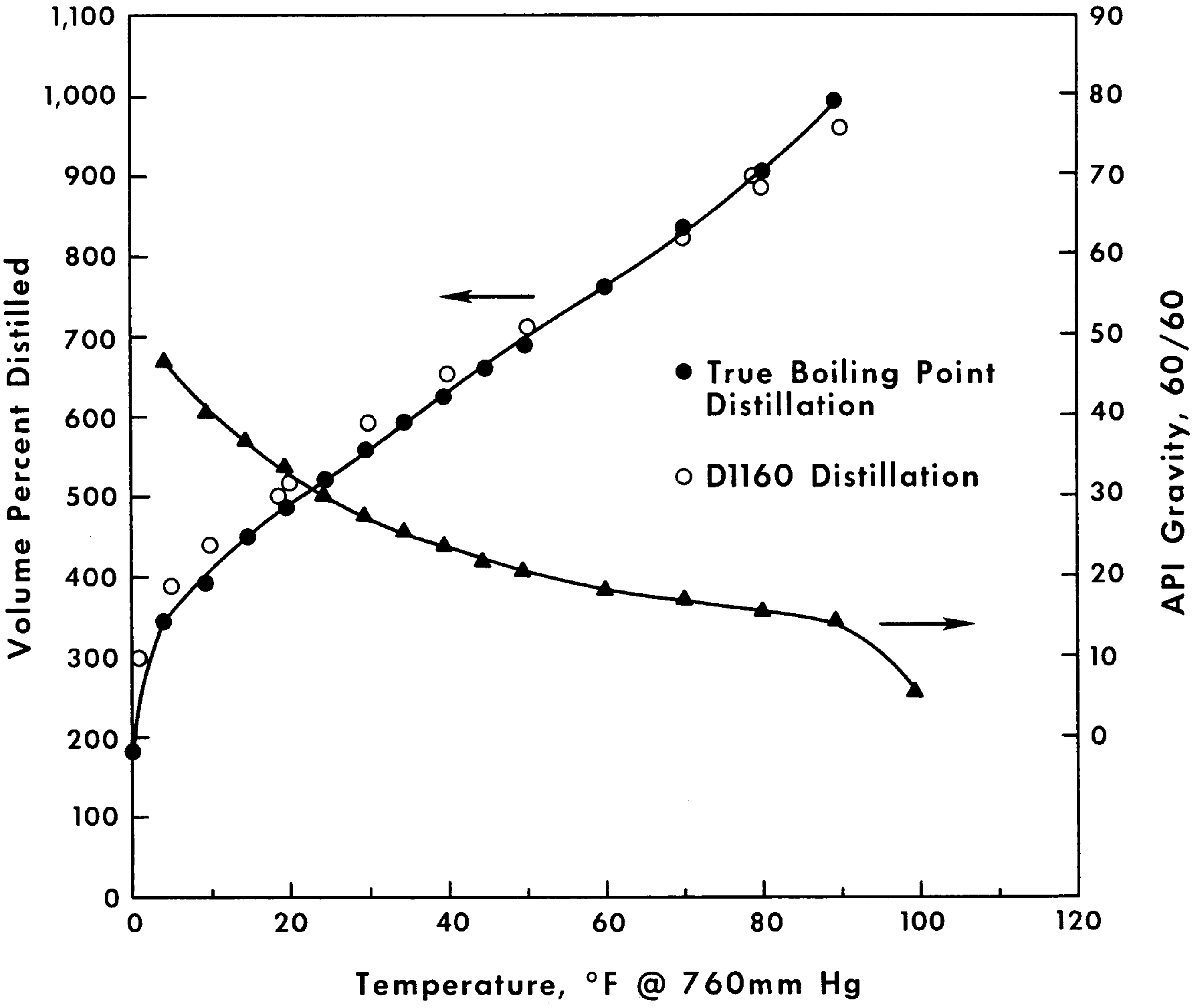

Figure 2. Distillation Curves for Tipton Member Shale Oil

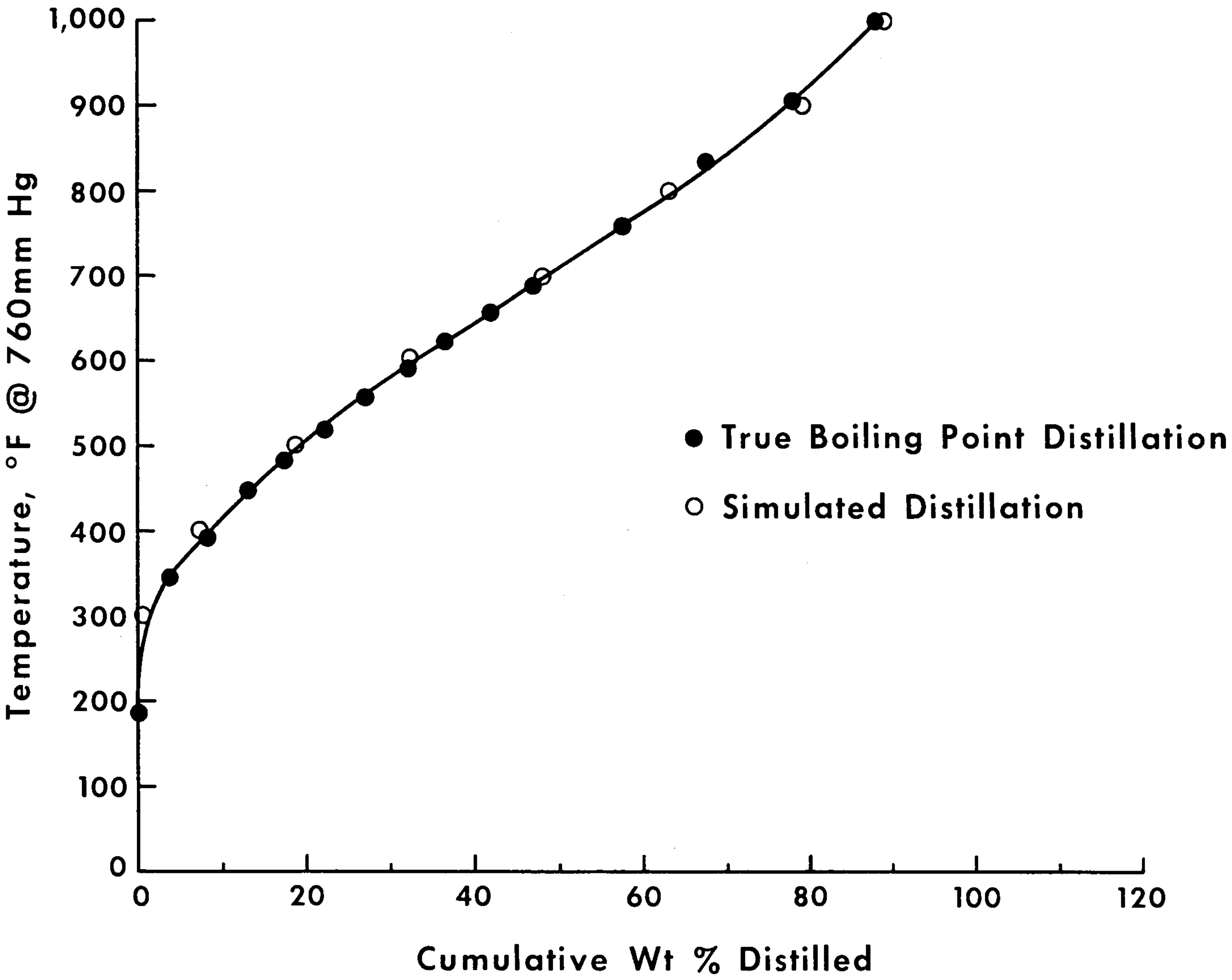

Figure 3. Simulated and True Boiling Point Distillation Curves for Tipton Member Shale Oil

Many of the correlation procedures require specific gravity and average boiling points for input (Miknis and Robertson 1987). The TBP distillation results were used to approximate an ASTM D-86 distillation that allows the determination of the volumetric, mean, molal and cubic average boiling points. Properties are then calculated using these parameters.

Elemental analyses (Table 10) and molecular weights and viscosities (Table 11) were obtained on the whole oil and fractions from the TBP distillation. Molecular weights and viscosities were also calculated for the whole oil and fractions using procedures developed for petroleum (Miknis and Robertson 1987). The calculated molecular weights (Riazi and Daubert 1980; Kesler and Lee 1976; API 1978) agree reasonably well with each other and with the measured values in the temperature range of 450 - 762 ^{o}F (232 - 406 ^{o}C) (Table 11). The procedure of Kesler and Lee (1976) gave the best value for the shale oil.

Viscosities calculated from API correlations (API 1978) agree reasonably well up to average distillation temperatures of 541 ^{o}F (283 ^{o}C) and 676 ^{o}F (358 ^{o}C) for 100 - 210 ^{o}F (38 - 99 ^{o}C) viscosity determinations, respectively. However, the curves for measured and calculated values are similar in shape so that the correlation may be improved by modifying the input parameters.

The molecular weight and viscosity correlations indicate that correlations derived for petroleum are useful over a limited boiling range for shale oils. However, there is poor agreement for whole oil properties. Correlations suitable for predicting physical properties probably can be derived, but such derivations were beyond the scope of this study.

Field Ionization Mass Spectrometric Analysis of Tipton Member and Western Reference Shale Oil

Field ionization mass spectrometry was used in the analysis of the western shale oil. Field ionization is a soft ionization technique that mainly produces molecular ions. The shale oil was thermally vaporized under high-vacuum conditions within the mass spectrometer. A variable heating rate from 86 - 932 ^{o}F (30 - 500 ^{o}C) was used. The multiple spectra acquired during the vaporization of the shale oil were averaged to produce a molecular weight profile (Figure 4). The data can be manipulated to give number average, weight average, or any other average molecular weight value. This method, like any method dependent upon volatility, is limited by the point at which cracking, rather than volatilization, occurs. The cracking temperature is easily detected by the appearance of new lower molecular weight species in the mass spectrum. The number and weight average molecular weights are 316 and 362. The vapor phase osmometry molecular weight, which is a number average value, is 290 amu.

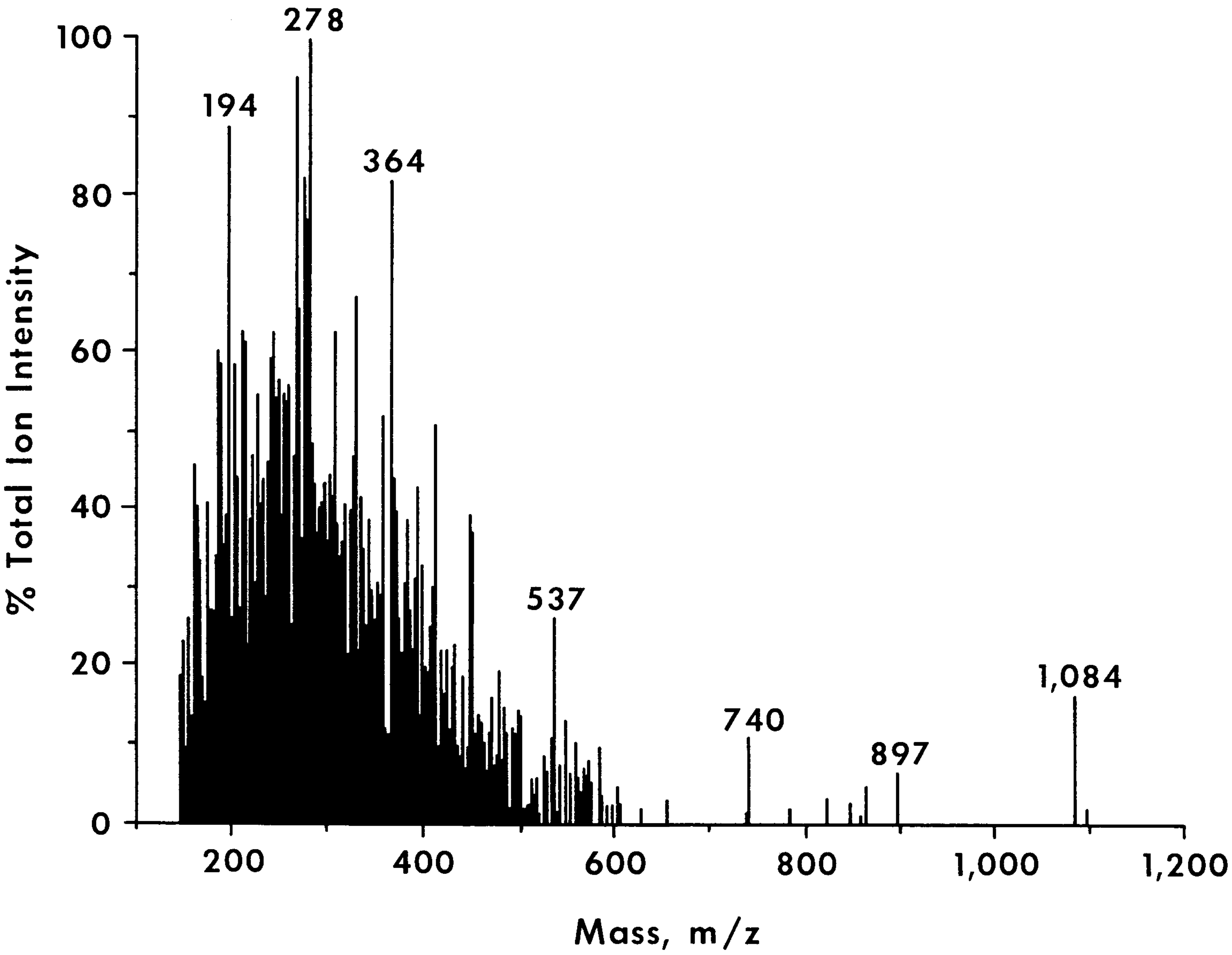

Figure 4. Field Ionization Mass Spectrum of Tipton Member Shale Oil

Table 10. Measured and Calculated Values of Molecular Weight and Viscosity for True Boiling Point Distillate Fractions of Tipton Member Reference Shale Oil.

TBP	Molecular Weight				Viscosity			
					100 °F		210 °F	
Fraction, °F	Measured	Calc.[a]	Calc.[b]	Calc.[c]	Measured	Calc.[c]	Measured	Calc.[c]
180-347	-	110	116	122	1.5	0.6	-	0.3
347-394	-	144	153	153	2.0	1.0	-	0.5
394-450	200	161	172	170	2.5	1.5	-	0.7
450-487	200	176	191	187	3.1	2.0	-	0.9
487-522	200	188	206	200	4.0	2.7	1.3	1.1
522-560	210	200	221	214	5.3	3.7	2.0	1.4
560-596	230	214	239	231	7.5	5.2	2.5	1.7
596-625	230	226	255	246	10.4	7.1	2.9	2.1
625-661	250	239	271	262	15.8	10.1	3.5	2.6
661-690	260	252	288	280	24.9	14.6	4.3	3.2
690-762	310	273	315	309	70.6	27.7	6.8	4.4
762-835	330	309	360	362	155.5	76.3	9.7	7.3
835-905	380	345	405	421	579	259	16.8	12.3
905-995	430	389	460	503	3065	2006	31.1	23.5
995+	810	-	-	-	-	-	1416	-
Whole Oil	290	227	280	248	19.3	-	-	-

[a] Riazi and Daubert, 1980

[b] Kesler and Lee, 1976

[c] API, 1978

Table 11. Elemental Compositions of True Boiling Point Distillate Fractions of Tipton Member Reference Shale Oil

Sample No.	Dist. Cut, ^{o}F, 1 atm	Elemental Analysis, wt %			
		C	H	N	S
58534-A	180-347	81.2	13.2	1.0	0.73
58534-B	347-394	81.2	13.0	1.3	0.63
58534-C	394-450	82.4	13.1	1.2	0.69
58534-D	450-487	83.7	12.9	1.3	0.63
58534-E	487-522	83.2	12.7	1.5	0.64
58534-F	522-560	83.9	12.4	1.8	0.58
58534-G	560-596	83.4	12.4	1.8	0.61
58534-H	596-625	83.2	12.2	2.1	0.60
58534-I	625-661	83.7	11.9	2.1	0.57
58534-J	661-690	82.7	11.8	2.0	0.60
58534-K	690-762	84.2	11.5	2.3	0.61
58534-L	762-835	83.9	11.2	2.9	0.59
58534-M	835-905	85.1	11.2	3.1	0.59
58534-N	905-995	84.4	11.0	3.0	0.59
58534-O	995+	82.9	10.2	2.7	0.59
Whole Oil	-	82.5	11.4	2.8	0.60

Chromatographic Separation of Shale Oils

The reference shale oil generated by Fischer assay was further characterized using techniques of elution chromatography (Miknis and Robertson 1987). The asphaltenes are first removed with pentane. The petrolenes of the crude shale oil are then passed through anion and cation resins to remove strong and weak acids and strong and weak bases which are then recovered from the resins. The material that passes through the resins is chromatographed on grade 12 silica gel with elution by pentane (saturates/olefins), benzene (aromatics), and 2:1 (v/v) benzene-methanol (neutral heteroatomic compounds). The saturate/olefin fraction is separated by chromatograph on silver nitrate treated silica gel into a saturate fraction (pentane) and an olefin fraction (1:3 [v/v]; benzene-pentane). The results of the chromatographic separations are listed in Table 12. The previously reported results for the interim and first reference shale oil (Miknis et al. 1986; Miknis and Robertson 1987) are also listed for comparison.

There are noticeable differences among the compound class distribution of the western reference shale oils, particularly between oil derived from a Wyoming oil shale and the two oils derived from Colorado oil shales. The two Colorado oils were produced from oil shale taken at different locations in the Piceance Creek basin and they have similar compound class distributions. The compound class distribution of the Wyoming shale oil differs markedly.

Table 12. Chromatographic Analyses of Western Reference Shale Oils*

Sample	Asphaltenes	Strong Acids	Strong Bases	Weak Acids	Weak Bases	Saturates	Olefins	Aromatics	Neutral Hetero-Compounds
Second (Tipton)	1.6	11.8	25.9	11.9	9.9	6.5	10.1	7.5	7.5
Interim (Anvil Points Mine)	0.7	14.0	19.5	5.6	4.9	19.2	15.0	19.1	2.7
First (Exxon Colony Mine)	1.4	21.8	19.4	6.6	5.6	14.8	17.5	13.3	1.0

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* All values are wt % of total starting material.

CONCLUSIONS

The properties of the Tipton Member western reference shale are generally comparable to the properties of other western oil shales. Western oil shales from the Green River Formation typically have high conversions to oil because of their low carbon aromaticities and hydrogen richness. The Tipton Member western reference shale had an organic carbon conversion to oil of 62%.

An assessment of the coking tendency was made using NMR and Fischer assay results. Using this approach, we estimate 21% of the carbon in the Tipton Member oil shale may form residue carbon during Fischer assay.

Kerogen concentrates were prepared from the Tipton Member raw shale. The hydrogen-to-carbon ratio of the concentrates were 1.35. This value is lower than those of kerogen concentrates from oil shales in the Parachute Creek Member, Piceance Creek Basin, Colorado, suggesting some structural differences between the two types of kerogen from the Green River Formation.

Carbon-containing minerals dominate the mineralogy of the Tipton Member oil shale. These minerals are indicative of the lacustrine depositional environment of the western shales.

Thermal properties of the reference oil shales and shale oils are in good agreement with other published values.

Standard API and other published correlations do not adequately predict properties of shale oils over the true boiling point distillation range.

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DISCLAIMER

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