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DISCLAIMER

Molecular-Weight Distributions for Heavy Fossil Fuels from Gel-Permeation Chromatography and Characterization Data

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ABSTRACT

A correlation is presented for calculating molecular-weight distributions for high-boiling hydrocarbon mixtures from measurements using gel-permeation chromatography (GPC). The correlation uses GPC elution volume, hydrogen-to-carbon ratio from elemental analysis, and hydrogen distribution from proton-NMR spectroscopy. Results for 45 pure hydrocarbons give an average deviation of less than 4 percent. For application to fractions, the procedure is illustrated with results for an Alaskan North-Slope residue. Characterization data are reported for thirteen heavy fossil-fuel fractions, including coal-liquefaction products and crude oils.

Introduction

Design calculations for processing heavy fossil fuels require physical properties of such fuels. To estimate properties, it is necessary to characterize fuels by appropriate experimental methods (Tsonopoulos et al, 1986). A commonly used characterization parameter is the Watson K factor. The advantage of this parameter follows from its simplicity; it is based on relatively simple experimental measurements (boiling point and density). However, Watson's K factor, first proposed more than fifty years ago, is often not adequate, especially for heavy fractions with high aromaticity.

As new methods of chemical analysis became available, new proposals were advanced for characterizing fossil-fuel mixtures; these include group-contribution methods and structural details obtained from sophisticated state-of-the-art analytical techniques (Allen et al, 1984; Charleswork, 1980; Clutter et al, 1972; Petrakis et al, 1983; Poirier and Das, 1984; Scheppele et al, 1981; Schwager and Yen, 1979; Speight, 1970; Thompson et al, 1973). Such methods, however, are too cumbersome for typical engineering work. For engineering purposes, relatively simple characterization procedures have recently been proposed for distillable, high-boiling fossil fuels (Alexander et al, 1985; Creagh, 1985). These procedures use only standard "off-the-shelf" analytical equipment; they can be performed without special expertise. This work discusses an extension of these characterization procedures with particular attention to very heavy non-distillable fossil-fuel fractions. Since it is not easily possible to obtain a boiling point for very heavy fractions, for such fractions it is necessary to measure some other property which closely correlates with boiling point. That property is molecular weight.

Previous work from this laboratory (Alexander et al, 1985; Creagh, 1985) discussed experimental procedures for measuring the following: atomic composition and the molar hydrogen-to-carbon ratio (H/C) as obtained from elemental analysis; hydrogen distribution, from proton-NMR spectroscopy, yielding a measure of aromaticity; the number of methyl groups per molecule, obtained from IR spectroscopy; and number-average molecular weight (MW), obtained from freezing-point depression in nitrobenzene. However, freezing-point depression measurements are inaccurate for very heavy hydrocarbons due to the extremely low concentrations required. For molecular weights of very heavy hydrocarbons, a useful experimental procedure is gel-permeation chromatography (GPC). This work describes a method for measuring molecular-weight distributions of heavy-aromatic fossil fuels using GPC data, coupled with characterization data.

Analytical Procedure

GPC measurements are made with a Waters-Associates Model 6000A liquid chromatograph using flowrates of 1 ml/min. The solvent is tetrahydrofuran (THF). A Waters Model R401 differential refractometer is used as a mass detector. [A Waters Model 440 UV-absorbance detector operating at 254 or 313 nm is also available as a mass detector; its use is discussed later.] A Waters μStyragel® column packing is used to allow separation on the basis of molecular size. Five columns (7.8 mm ID X 30 cm) are used in series. The first column has a nominal pore size of 1000 Å; the pore size of the second column is 500 Å, and the remaining three columns have a pore size of 100 Å. The packing material is a fully porous, highly-crosslinked styrene-divinylbenzene copolymer. Figure 1 shows a schematic of the apparatus.

To remove any suspended matter, samples are filtered through a 0.4 μm filter, using a Sample Clarification Kit supplied by Waters Associates. Samples which are not normally liquid at room temperature are dissolved in a small amount of tetrahydrofuran prior to filtration. For refractive-index (RI) detection, 25-50 μl of the filtered samples are injected into the chromatograph using a syringe.

Preparative vs. Analytical Modes of GPC Operation

To obtain the weight-percent distribution of a fraction, it is necessary to determine the amount of the original residue sample in each molecular-weight range. For this purpose, the GPC must be run in the preparative (large-sample-volume) mode. The filtered sample solution is injected and sub-fractions are collected at even time increments using an automatic sample collector. After evaporating the solvent in a vacuum oven, each sub-fraction is weighed. Thus the RI response can be related to weight percent. However, each time a new residue is characterized, the RI response must be re-determined since different residua have different response characteristics.

Preparative GPC requires large-diameter columns and high-capacity pumps. Preparative GPC equipment is therefore more expensive and generally less common than analytical (small-sample-volume) GPC equipment. However, preparative work can be performed using an analytical GPC by making multiple injections of the same fraction until enough of each sub-fraction has been accumulated for accurate weight measurement. Alternatively, as a reasonable first approximation, the RI area-percent can be assumed to be the same as the weight-percent. This assumption greatly simplifies the characterization by requiring analytical operation only. The accuracy of this assumption is discussed later.

GPC Calibration with Model Compounds

To calibrate the column, 45 model compounds were used; these compounds, shown in Table 1, vary in molecular weight from 84 to 535. Figure 2 shows a plot of GPC elution volume against molecular weight. It is evident that this plot is not sufficient for calibration; GPC elution volume depends not only on molecular weight but also on molecular structure.

A much improved correlation is obtained when appropriate characterization parameters are included in data reduction. Table A-1 of Appendix A gives characterization parameters for the model compounds.

In an effort to relate molecular weight with GPC elution volume and characterization data, several statistical methods were used to derive a correlation and to analyze its stability. The final form of the correlation is:

$$\ln MW = A + B\,V \tag{1}$$

where

$$A = A_0 + A_1\,H/C + A_2\,H_\alpha + A_3\,H_\beta + A_4\,H_\gamma$$

$$B = B_0 + B_1\,H/C + B_2\ln H/C + B_3\,H_\alpha \quad .$$

Here MW = Molecular Weight, g/mole

V = GPC Elution Volume, ml

H/C = Molar Hydrogen-to-Carbon Ratio

H_α = Fraction of hydrogen atoms attached to carbons alpha to an aromatic ring

H_β - Fraction of hydrogen atoms attached to carbons beta or further, but non-terminal, to an aromatic ring

H_γ - Fraction of hydrogen atoms attached to terminal carbons

The H/C ratio is obtained from elemental analysis, while the hydrogen distribution is obtained from proton-nuclear-magnetic-resonance data; these are normalized to include only alpha (1.7-4.0 ppm shift), beta (0.9-1.7 ppm), gamma (0.5-0.9 ppm), and aromatic-type (6.0-9.0 ppm) hydrogen atoms. The 4.0-6.0 ppm shift range, which covers olefinic and phenolic hydrogens, is not taken into account here.

The form of the correlation is similar to that used in calibration functions for molecular-weight determinations of polymers. Linearity with respect to the elution volume is maintained. However, the slope and intercept depend on characterization parameters.

Table 2 gives the calibration coefficients obtained by multiple regression. Figure 3 shows a comparison between correct and calculated MW for the model compounds given in Table A-2 of Appendix A; the average percent deviation is about 3.6 percent. The largest error (about eleven percent) was for saturated cyclic compounds, such as cyclooctane.

To assure that the correlating equation is not overly influenced by any particular compound or compounds, the stability of the correlation was examined using cross-validation, wherein data regression is repeated with exclusion of a different compound each time. The cross-validation procedure indicates that the correlation is stable over the range of model-compound molecular weights. Table A-3 of Appendix A compares the normal regression to the cross-validation results and finds the coefficients to be consistent. The mean cross-validation coefficients are nearly identical to those from the normal regression. The range for most of the cross-validation coefficients is also narrow with respect to the mean values. The two exceptions (coefficients A_2 and B_3) are for terms involving H_α. The minimum and maximum values of these coefficients occur when excluding p-bis-(o-methylstyryl)-benzene and squalene. Both of these compounds have alpha hydrogens which are also olefinic. Reclassification of these "dual" hydrogens for these two compounds is likely to stabilize the range of the H_α term coefficients, but this was not considered here.

Application of the Correlation to Synthetic Mixtures

To test Equation (1), three synthetic mixtures were run on the GPC. The first mixture contained five n-alkanes. The second mixture contained five aromatic compounds. The third mixture contained both n-alkanes as well as aromatics. All compounds in the mixtures had been used previously for calibration. Properties of the three mixtures are given in Table A-4 of Appendix A. Molecular weights estimated by GPC for the three mixtures are within 5-10 percent of the correct values.

The estimated molecular weight for the alkane mixture was higher than the known value (219 compared to 200), while that for the aromatic mixture was exactly correct (178). The estimated molecular weight of the mixture containing both alkanes and aromatics was low (185 compared to 196). These results follow from the simplifying assumption that the RI area-percent is equal to the weight-percent. The assumption would be essentially exact if the refractive index for every compound in the mixture was a constant. Unfortunately, this is not the case, as shown in Table A-5 of Appendix A. Even within groups (alkanes, aromatics) there are large differences. Refractive index generally increases with increasing molecular weight and with increasing aromaticity. The effect of molecular weight on refractive index is more pronounced for alkanes than for aromatics. The higher molecular-weight alkanes have a higher RI than the lower molecular-weight alkanes; therefore, the simplifying assumption over-estimates the n-alkane-mixture molecular weight, since more weight-percent was assigned to the higher molecular-weight alkanes.

Most aromatics have a significantly higher RI than alkanes. Even low molecular-weight aromatics have a higher RI than heavier alkanes. Thus, in a mixture of both aromatics and alkanes, the effect of RI differences within the alkanes tends to be cancelled by the effect of the higher weight-percent given the lower molecular-weight aromatics. Most heavy fossil-fuel fractions are a complex mixture containing many aromatics as well as alkanes. Therefore, because of cancellation of errors, the assumption that the RI area-percent is equal to the weight percent provides a good approximation for mixtures of many types of compounds. While it is difficult to predict exactly the error which follows from this assumption, mixtures containing primarily alkanes are likely to give high molecular-weight estimates. Mixtures containing primarily aromatics are more likely to give correct results because of a lower trend for the RI to increase with increasing molecular weight.

Improved molecular-weight estimates can be made if the weight-percent distribution is determined by preparative GPC operation. For example, for the alkanes mixture, the molecular-weight estimate based on the true weight-percent distribution is much closer to the correct value (205 compared to 200).

Application of the Correlation to a Heavy Fraction

GPC data were obtained for a non-distillable Alaskan North-Slope residue. The measured molecular-weight distribution was compared to results obtained using mass spectrometry.

The GPC was run in both the preparative and analytical modes. In the preparative mode, eight fractions were collected from the GPC following UV detection. Since only analytical-size columns were available, six runs were required to obtain enough material in each fraction for accurate weight measurement and further analysis by mass spectrometry. The solvent was evaporated from the collected fractions and the weight of each fraction was recorded to relate the UV response to the weight percent of the residue. [The H/C ratio and hydrogen distribution of the original residue were used with Equation (1) to calculate the molecular weight of each fraction. In preparative GPC work, the H/C ratio and hydrogen distribution of the eluted fractions should be used, provided there is enough material after solvent removal for their characterization.]

Field-ionization and chemical-ionization mass spectroscopy were used to determine the molecular weight of the original residue as well as of those fractions that contained enough material. A comparison was also made using the equal-RI-response assumption and the analytical mode of operation.

Field ionization uses a powerful electric field to remove an electron from the molecule (Howe et al, 1981; Schlunegger, 1980). Since fragment ions are often completely absent, molecular ions are primarily observed. This so-called "soft" ionization technique provides molecular-weight information directly.

Chemical ionization is based on a charge transfer in an ion-molecule reaction (Scolnick et al, 1976). As in field-ionization, fragment ions are much less likely than molecular ions, which are closely related to the original molecule. Thus, chemical ionization also yields molecular-weight information.

Since THF contains a preservative (butylated hydroxytoluene, MW = 220) which directly interferes with the molecular-weight determination using mass spectroscopy, it is necessary to use distilled THF for mass-spectrometric measurements. Distilled THF must be handled with care since prolonged exposure to air and light can cause formation of explosive peroxides.

Figure 4 shows the field-ionization mass spectograph for the Alaskan North-Slope residue. Comparison shows that the chemical-ionization technique gives molecular weight to within 5 percent of that determined by field-ionization. The weight-average molecular weight is estimated to be 630 by field-ionization mass spectroscopy and 609 by chemical-ionization mass spectroscopy.

Table 3 summarizes calculations using the equal-RI-response assumption to estimate molecular weight from GPC measurements and characterization data. Figure 5 gives the molecular-weight distribution of the Alaskan North-Slope residue, as calculated in Table 3. The GPC weight-average MW estimation (639) is only about 1 percent higher than that obtained by field-ionization mass spectrometry. The GPC technique also provides a good approximation to the "true" molecular-weight distribution as shown by field-ionization mass-spectrometry (Figure 4). The preparative GPC technique gave similar results.

Molecular-Weight Estimates for Thirteen Fractions

Characterization work has been completed for thirteen heavy fossil-fuel fractions, including coal-liquefaction products and crude oils. Results are summarized in Appendix B. All molecular-weight estimates were compared with mass-spectrometry measurements, as shown in Table B-2 of Appendix B. The average deviation for the petroleum liquids is about six percent. The coal-derived liquids have a higher average deviation of about fourteen percent; this larger deviation probably follows from the higher proportion of hetero-atoms. Heteroatomaticity has not been included in the correlation.

Several molecular-weight estimates are lower than those expected from the nominal boiling-point ranges given by the suppliers. However, the GPC results are consistent with mass-spectrometric measurements. Since the molecular-weight measurements were made long after the nominal boiling-point measurements, it is likely that, with time, there was decomposition of the samples.

Discussion Toward Possible Improvements

Gel-permeation chromatography separates compounds on the basis of molecular size, not molecular weight, as demonstrated by chemical-ionization mass spectroscopy for seven of the eight GPC fractions collected from the Alaskan North-Slope residue. As shown in Table 3, the molecular weights of these fractions were predicted using Equation (1) with the H/C ratio and hydrogen distribution taken as those for the overall residue. Mass spectra for the seven fractions indicate that they do not have distinctly different molecular weights. Thus, while the larger molecules elute first, there is no clear separation of the molecules by molecular weight.

The lack of separation by molecular weight for this residue may be due to the solvent flow rate (1 ml/min) which may be too high for good separation. Another possible cause could be the choice of solvent; hydrogen bonding with the solvent changes the effective "molecular size" of an eluting compound. A third possible cause could be the pore size of the packing; a larger pore size may be necessary for better separation. Nevertheless, Equation (1) provides a good approximation for the overall molecular-weight distribution.

While initial results with GPC are encouraging, further studies may provide additional information using UV detection in addition to RI detection. [For UV-absorbance detection, lower sample concentrations are necessary. Samples are prepared by dissolving a small amount (10-20 mg) of the hydrocarbon in THF. The usual sample concentration is 1-5 g/l. A measured quantity of the filtered solutions, usually 50 μl, is injected into the chromatograph using a syringe.]

UV is well suited for detecting aromatics. Since paraffins are essentially invisible in the UV spectra, UV absorption provides a possible method to measure the aromatics distribution. Since refractive-index detection gives the total mass distribution, the paraffin distribution could be determined by difference. However, aside from the concentration-requirement differences between UV and RI, there are other significant problems. For example, for UV, the extinction coefficients relating absorbance to concentration are much more variable amongst different species than their refractive indices. On the other hand, knowing the aromatic distribution could allow correction of the RI differences between aromatics and alkanes. The use of an internal standard may allow consistent comparison between the UV and RI responses.

A more detailed characterization could be obtained by performing a preliminary solvent extraction, prior to making GPC measurements, as discussed in Appendix C. Preliminary separation by extraction would allow determination of separate molecular-weight distributions according to paraffinic-aromatic classification.

Conclusions

The correlation presented here is useful for obtaining molecular-weight distributions of heavy fossil-fuel residues from gel-permeation chromatography. For such residues, the hydrogen distribution is obtained from proton-NMR spectroscopy and the molar hydrogen-to-carbon ratio from elemental analysis. Characterization data are reported for thirteen heavy fossil-fuel fractions, including coal-liquefaction products and crude oils.

Acknowledgments

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Additional support was provided by the American Petroleum Institute and by the National Science Foundation. Dr. Prange is grateful to the Alexander von Humboldt Stiftung for a Feodor Lynen fellowship. Fossil-fuel samples were provided by Exxon Research and Engineering Co., Chevron Research Co., Air Products and Chemicals Inc., and Syncrude Canada Ltd.

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TABLE 1. MODEL COMPOUNDS FOR GPC CALIBRATION

Compound No.	Name	Compound No.	Name
1	Cyclohexane	24	9,10-Dihydro Phenanthrene
2	Toluene	25	1-Phenyl Octane
3	Ethyl Benzene	26	Tetradecane
4	m-Xylene	27	Pyrene
5	Ethyl Cyclohexane	28	1-Phenyl Decane
6	Cyclooctane	29	Hexadecane
7	2,2,4-Trimethyl Pentane	30	p-Terphenyl
8	n-Propyl Benzene	31	Heptadecane
9	Cumene	32	Octadecane
10	1,2,4-Trimethyl Benzene	33	1-Phenyl Tridecane
11	Naphthalene	34	Eicosane
12	n-Butyl Benzene	35	Coronene
13	iso-Butyl Benzene	36	p-bis-(o-Methylstyryl)-Benzene
14	tert-Butyl Benzene	37	9,10-Diphenyl Anthracene
15	2-Methyl Naphthalene	38	1,1,4,4-Tetraphenyl-1,3-Butadiene
16	Biphenyl	39	1,2,3,4-Tetraphenyl-1,3-Cyclopentadiene
17	2-Ethyl Naphthalene	40	m-Quinquephenyl
18	1-Phenyl Hexane	41	Octacosane
19	Bicyclohexyl	42	Squalene
20	Diphenyl Methane	43	Decacyclene
21	Dodecane	44	Rubrene
22	Anthracene	45	Hexaphenyl Benzene
23	Phenanthrene		

TABLE 2. COEFFICIENTS FOR GPC CORRELATION

A_0	1.177e+1
A_1	-1.650e+0
A_2	-1.834e+0
A_3	1.056e+0
A_4	8.792e-1
B_0	-1.787e-1
B_1	5.805e-2
B_2	-6.184e-2
B_3	5.987e-2
R^2	0.9903
Avg % Deviation	3.6
Max % Deviation	11.9

R^2 = proportion of the total variance accounted for by the correlation, also known as the correlation coefficient.

$$\text{Avg \% Deviation} = 100 \sum_i \frac{|(\text{calc. MW} - \text{correct MW})|}{\text{correct MW}} \Big/ \sum i$$

$$\text{Max \% Deviation} = 100 \max_i \frac{|(\text{calc. MW} - \text{correct MW})|}{\text{correct MW}}$$

TABLE 3. CALCULATION OF MOLECULAR WEIGHT FROM GPC MEASUREMENTS

1	2	3	4	5
V, ml	RI Area %	MW (a)	Col 2/Col 3	Col 2 * Col 3
25	0.68	1196	0.000569	813.28
26	4.25	1076	0.003950	4573.00
27	7.18	968	0.007417	6950.24
28	8.44	870	0.009701	7342.80
29	9.44	783	0.012056	7391.52
30	11.48	704	0.016307	8081.92
31	12.38	633	0.019558	7836.54
32	11.38	570	0.019965	6486.60
33	9.35	512	0.018262	4787.20
34	7.20	461	0.015618	3319.20
35	5.42	415	0.013060	2249.30
36	4.01	373	0.010751	1495.73
37	2.97	335	0.008866	994.95
38	2.21	302	0.007318	667.42
39	1.64	271	0.006052	444.44
40	1.16	244	0.004754	283.04
41	0.81	219	0.003699	177.39
TOTALS	100.00		0.177903	63894.57

$$\overline{MW}_N = \sum \text{Col } 2 / \sum \text{Col } 4 = 100/0.177903 = 562 \quad \text{(b)}$$

$$\overline{MW}_W = \sum \text{Col } 5 / \sum \text{Col } 2 = 63894.57/100 = 639 \quad \text{(c)}$$

(a) Molecular Weight calculated using Equation (1) with the following characterization parameters :

$H/C = 1.492, \quad H_\alpha = 0.181, \quad H_\beta = 0.561, \quad H_\gamma = 0.195$

(b) Number-Average MW compares to 700 (±105) from freezing-point-depression measurements.

(c) Weight-Average MW compares to 630 and 609 from field-ionization and chemical-ionization mass spectroscopy, respectively.

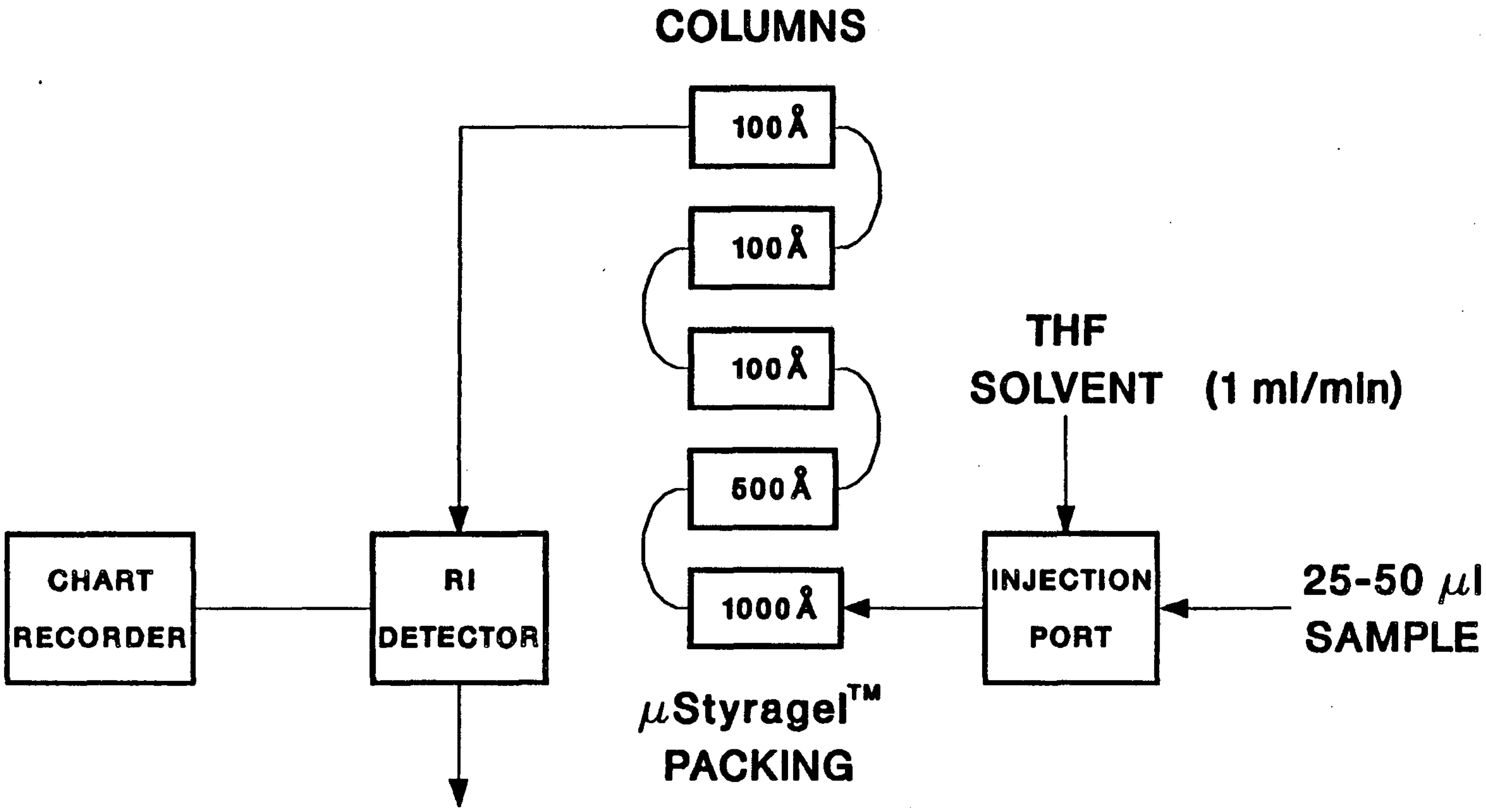

FIGURE 1. Schematic of Gel-Permeation Chromatograph

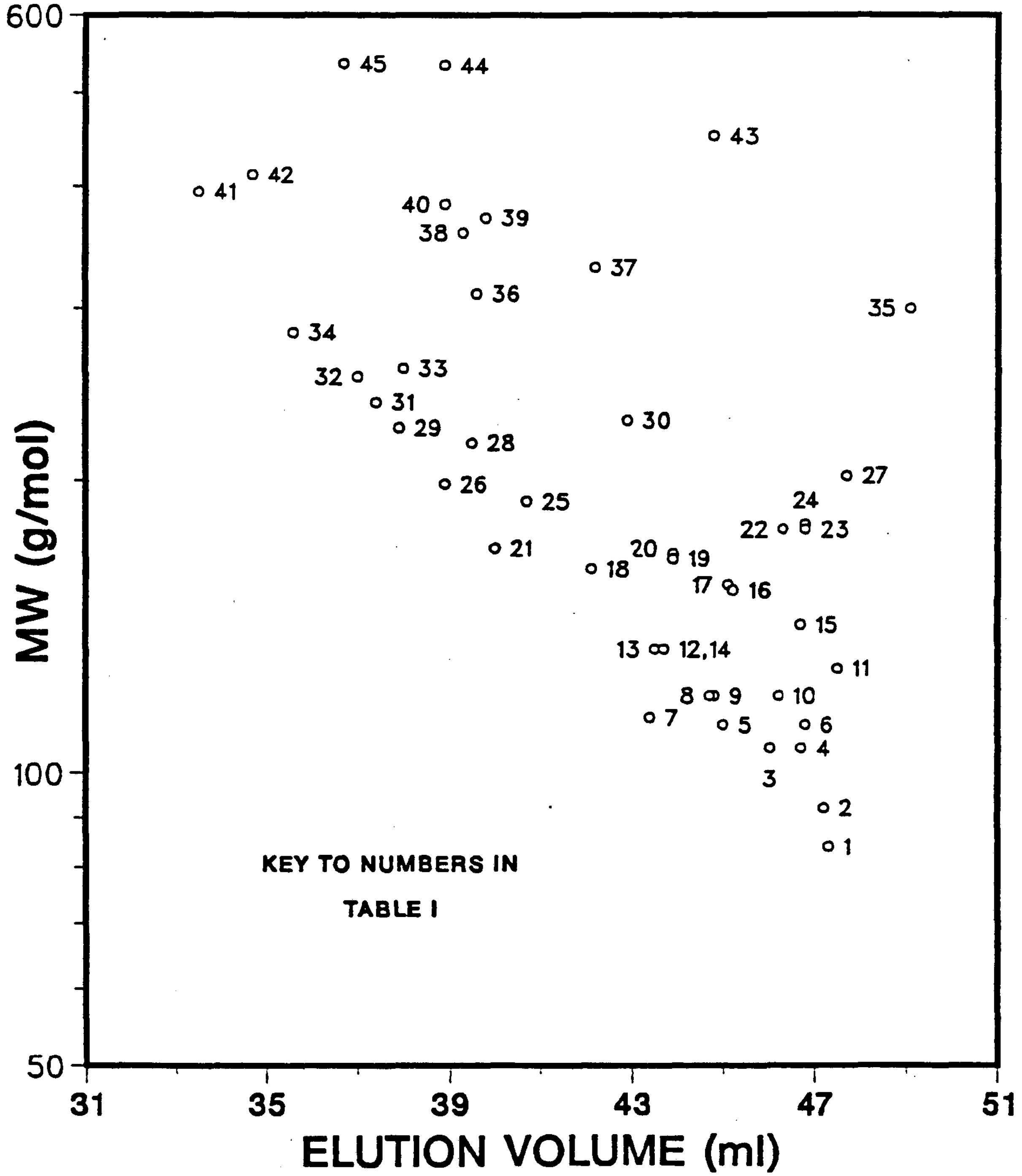

FIGURE 2. Elution Volumes of Pure Hydrocarbons Do Not Correlate with Molecular Weight Alone

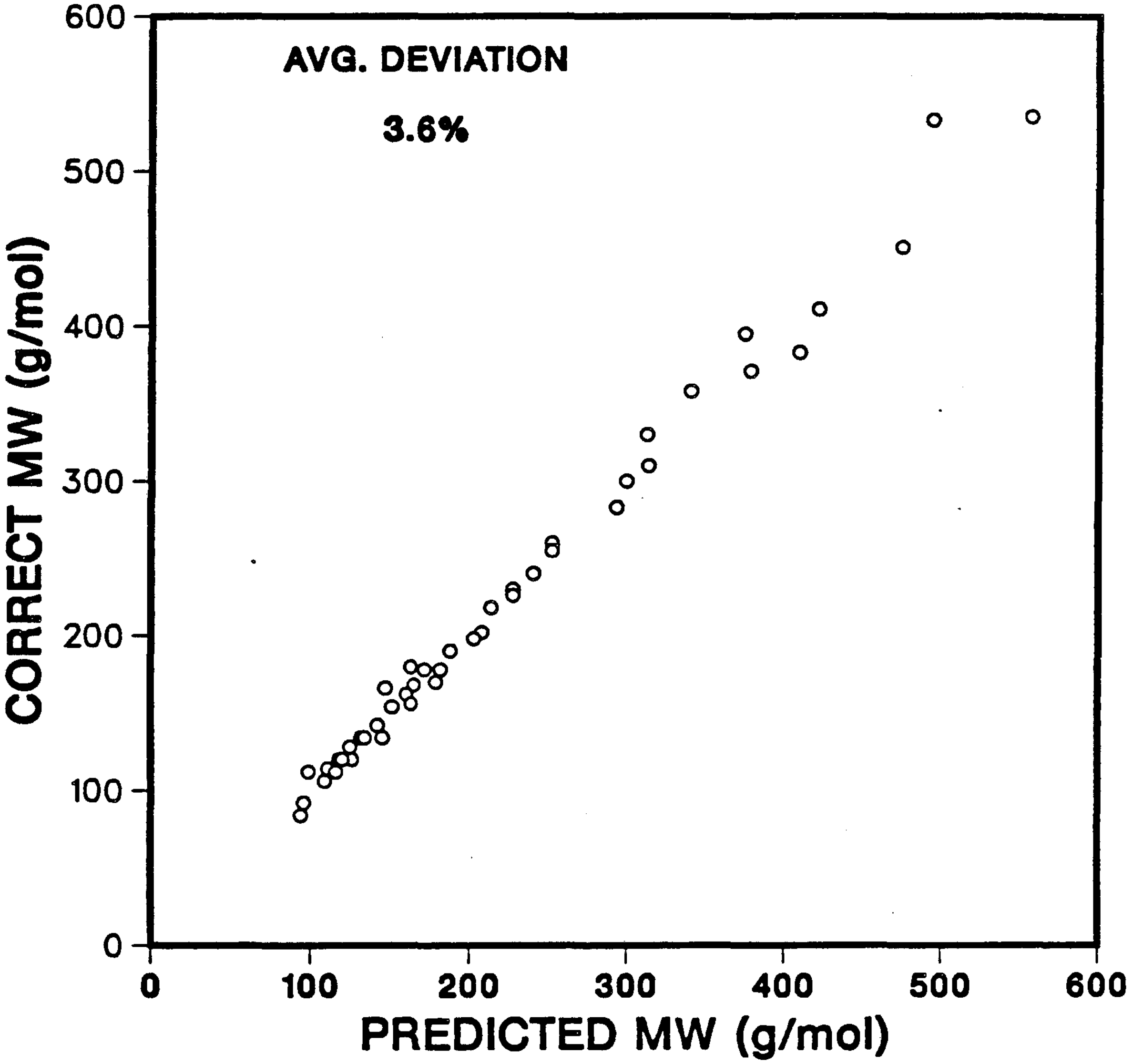

FIGURE 3. Molecular Weights for Pure Hydrocarbons from GPC Measurements and Characterization Data

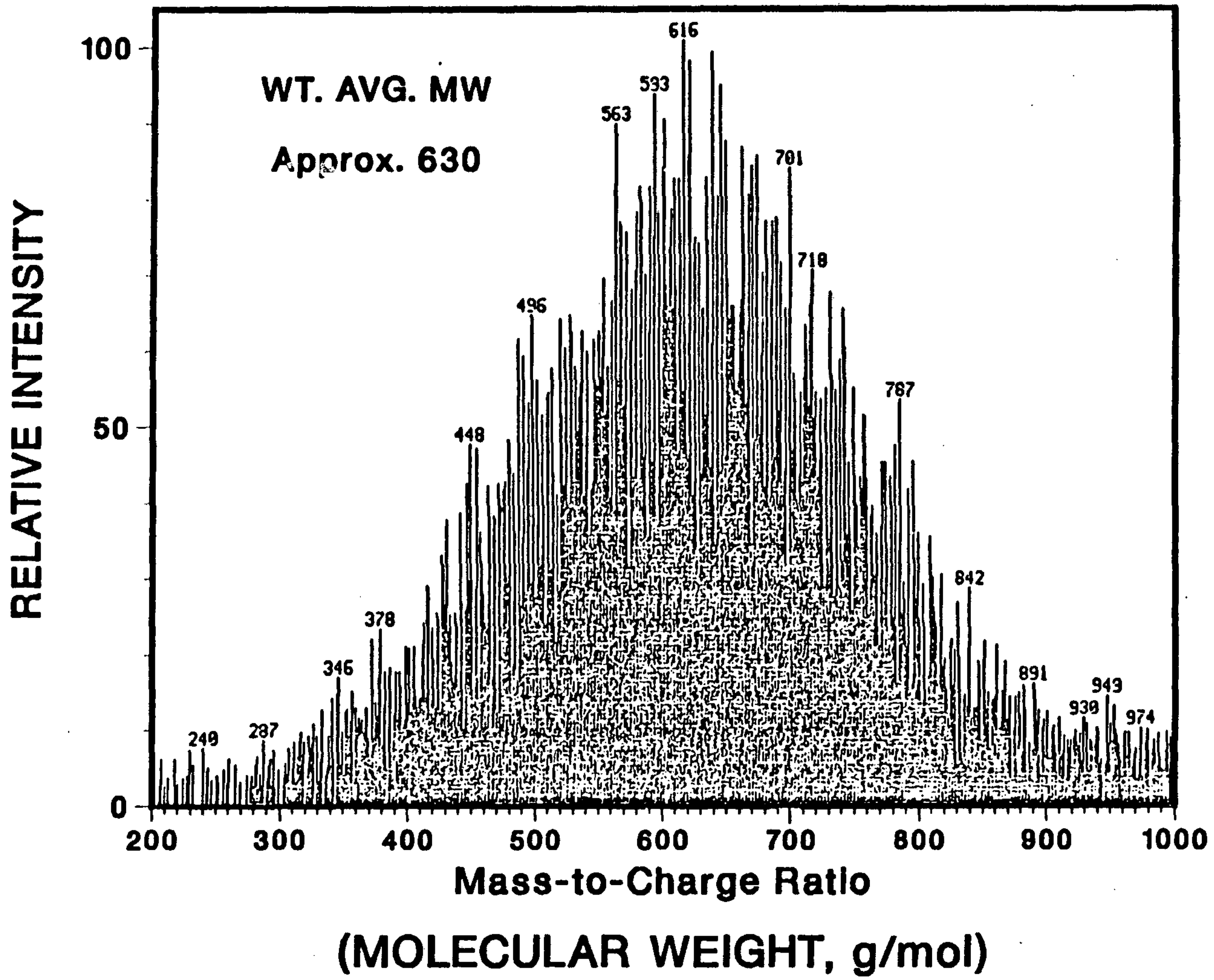

FIGURE 4. Field-Ionization Mass Spectrum of an Alaskan North-Slope Residue

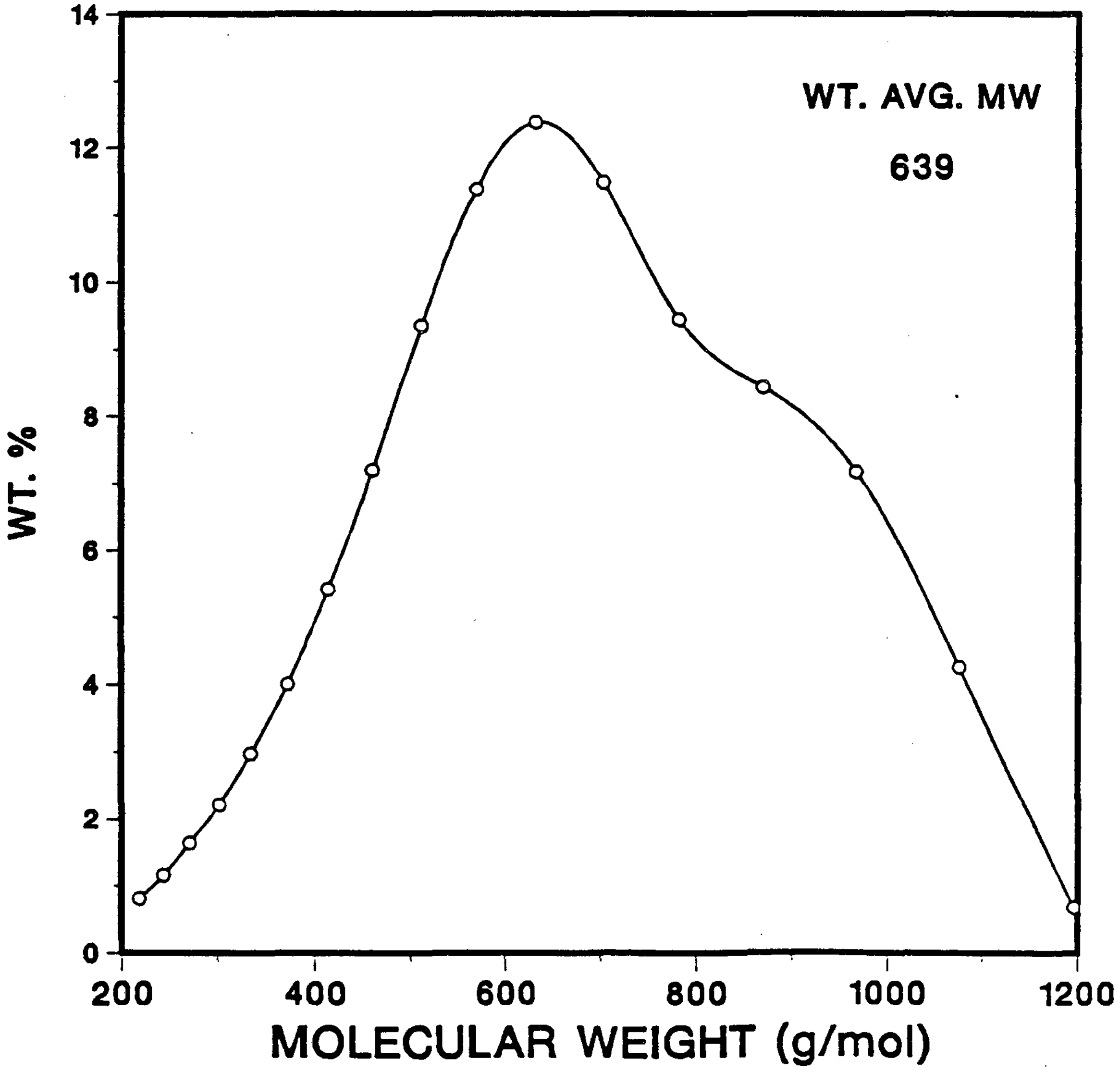

FIGURE 5. Molecular-Weight Distribution of an Alaskan North-Slope Residue from GPC Measurements and Characterization Data

APPENDIX A

SUPPLEMENTARY INFORMATION FOR GPC CALIBRATION

Appendix A gives additional information concerning the calibration of the GPC columns with pure hydrocarbons.

Table A-1 summarizes characterization parameters for the calibration compounds. Parameters reported are: molecular weight, GPC elution volume, molar hydrogen-to-carbon ratio, and the distribution of alpha, beta, and gamma-type hydrogen atoms. A list of the compounds is given in Table 1.

Table A-2 shows a comparison of correct and GPC-measured molecular weights for the calibration compounds. The average deviation is about 3.6 percent.

Table A-3 summarizes the GPC correlation stability analysis using cross-validation. All coefficients are shown to be stable, with only A_2 and B_3 affected by two compounds having alpha hydrogens that are also olefinic.

Table A-4 gives properties of three synthetic mixtures used to verify the GPC correlation. The H/C ratio and hydrogen distribution is calculated by adding the moles of carbon atoms, hydrogen atoms, and alpha-, beta-, and gamma-type hydrogen atoms for each compound in the mixture.

Table A-5 presents refractive indices of typical hydrocarbons. Refractive index (RI) is shown generally to increase with rising molecular weight and rising aromaticity. Aromatic compounds have significantly higher RI than alkanes, but there is less tendency for the RI of aromatics to increase with molecular weight.

TABLE A-1

CHARACTERIZATION PARAMETERS FOR MODEL COMPOUNDS

Compound No.	MW	V	H/C	H_α	H_β	H_γ
1	84	47.3	2.000	0.000	1.000	0.000
2	92	47.2	1.143	0.375	0.000	0.000
3	106	46.0	1.250	0.200	0.300	0.000
4	106	46.7	1.250	0.600	0.000	0.000
5	112	45.0	2.000	0.000	0.833	0.188
6	112	46.8	2.000	0.000	1.000	0.000
7	114	43.4	2.250	0.000	0.167	0.833
8	120	44.7	1.333	0.167	0.167	0.250
9	120	44.8	1.333	0.083	0.500	0.000
10	120	46.2	1.333	0.750	0.000	0.000
11	128	47.5	0.800	0.000	0.000	0.000
12	134	43.7	1.400	0.143	0.286	0.214
13	134	43.5	1.400	0.143	0.071	0.429
14	134	43.7	1.400	0.000	0.643	0.000
15	142	46.7	0.909	0.300	0.000	0.000
16	154	45.2	0.833	0.000	0.000	0.000
17	156	45.1	1.000	0.167	0.250	0.000
18	162	42.1	1.500	0.111	0.444	0.167
19	166	43.9	1.833	0.000	1.000	0.000
20	168	43.9	0.923	0.167	0.000	0.000
21	170	40.0	2.167	0.000	0.769	0.231
22	178	46.3	0.714	0.000	0.000	0.000
23	178	46.8	0.714	0.000	0.000	0.000
24	180	46.8	0.857	0.333	0.000	0.000
25	190	40.7	1.571	0.091	0.546	0.136
26	198	38.9	2.143	0.000	0.800	0.200
27	202	47.7	0.625	0.000	0.000	0.000
28	218	39.5	1.625	0.077	0.615	0.115
29	226	37.9	2.125	0.000	0.824	0.177
30	230	42.9	0.778	0.000	0.000	0.000
31	240	37.4	2.118	0.000	0.833	0.167
32	255	37.0	2.111	0.000	0.842	0.158
33	260	38.0	1.684	0.063	0.688	0.094
34	283	35.6	2.100	0.000	0.857	0.143
35	300	49.1	0.500	0.000	0.000	0.000
36	310	39.6	0.917	0.455	0.000	0.000
37	330	42.2	0.692	0.000	0.000	0.000
38	358	39.3	0.786	0.000	0.000	0.000
39	371	39.8	0.759	0.000	0.091	0.000
40	383	38.9	0.733	0.000	0.000	0.000
41	395	33.5	2.071	0.000	0.897	0.103
42	411	34.7	1.667	0.000	0.455	0.546
43	451	44.8	0.500	0.000	0.000	0.000
44	533	38.9	0.667	0.000	0.000	0.000
45	535	36.7	0.714	0.000	0.000	0.000

TABLE A-2

CORRECT AND GPC-MEASURED MOLECULAR WEIGHTS FOR PURE HYDROCARBONS

Compound No.	Correct MW	Meas. MW	% Dev.	Compound No.	Correct MW	Meas. MW	% Dev.
1	84	94	11.9	24	180	163	-9.4
2	92	96	4.3	25	190	188	-1.1
3	106	109	2.8	26	198	203	2.5
4	106	109	2.8	27	202	208	3.0
5	112	116	3.6	28	218	214	-1.8
6	112	99	-11.6	29	226	228	0.9
7	114	111	-2.6	30	230	228	-0.9
8	120	120	0.0	31	240	241	0.4
9	120	126	5.0	32	255	253	-0.8
10	120	118	-1.7	33	260	253	-2.7
11	128	125	-2.3	34	283	294	3.9
12	134	134	0.0	35	300	300	0.0
13	134	132	-1.5	36	310	314	1.3
14	134	145	8.2	37	330	313	-5.2
15	142	142	0.0	38	358	341	-4.7
16	154	151	-1.9	39	371	379	2.2
17	156	163	4.5	40	383	410	7.0
18	162	160	-1.2	41	395	375	-5.1
19	166	147	-11.4	42	411	422	2.7
20	168	165	-1.8	43	451	475	5.3
21	170	179	5.3	44	533	494	-7.3
22	178	182	2.2	45	535	557	4.1
23	178	172	-3.4				

TABLE A-3

GPC CORRELATION STABILITY COMPARISON (a)

Assessment		Coefficients				
		A_0	A_1	A_2	A_3	A_4
Normal Regression		11.77	-1.650	-1.834	1.056	0.8792
Cross-Validation	Mean	11.77	-1.650	-1.810	1.057	0.8795
	Min.	11.61	-1.792	-2.041	0.976	0.8333
	Max.	11.90	-1.507	-0.381	1.109	0.9576
	(b) Range, %	1.2	8.6	45.9	6.3	7.1

Assessment		Coefficients			
		B_0	B_1	B_2	B_3
Normal Regression		-0.1787	0.05805	-0.06183	0.05987
Cross-Validation	Mean	-0.1787	0.05805	-0.06185	0.05936
	Min.	-0.1828	0.05348	-0.06374	0.02867
	Max.	-0.1744	0.06257	-0.06051	0.06512
	Range, %	2.3	7.8	2.6	30.7

Assessment		R^2	Avg % Dev	Max % Dev
Normal Regression		0.9903	3.6	11.9
Cross-Validation	Mean	0.9904	3.6	12.0
	Min.	0.9895	3.2	9.8
	Max.	0.9921	3.7	14.4

(a) Cross-Validation for 45 regressions excluding a different model compound each time.

(b) Range = $100 \left| \frac{(\text{max. value} - \text{min. value})/\text{mean value}}{2} \right|$

TABLE A-4

PROPERTIES OF THREE SYNTHETIC MIXTURES USED FOR CALIBRATION VERIFICATION

Alkane Mixture

Compound	MW	grams	Wt. %	10^3 Mol
Decane	142.3	1.3327	18.9	9.366
Dodecane	170.3	1.3405	18.9	7.870
Tetradecane	198.4	1.4113	19.9	7.114
Hexadecane	226.5	1.4356	20.3	6.340
Octadecane	254.5	1.5584	22.0	6.123

H/C = 2.147 H_α = 0.000 H_β = 0.794 H_γ = 0.206

Wt.-Avg. MW = 200.5 Predicted MW = 219

Aromatic Mixture

Compound	MW	grams	Wt. %	10^3 Mol
Naphthalene	128.2	0.4600	20.0	3.589
Biphenyl	154.2	0.4637	20.1	3.007
Anthracene	178.2	0.4812	20.9	2.700
Pyrene	202.2	0.4522	19.6	2.236
p-Terphenyl	230.3	0.4458	19.4	1.936

H/C = 0.750 H_α = 0.000 H_β = 0.000 H_γ = 0.000

Wt.-Avg. MW = 178.2 Predicted MW = 178

Combined Mixture

Compound	MW	grams	Wt. %	10^3 Mol
1-Phenyl Hexane	162.3	1.5490	20.6	9.545
Dodecane	170.3	1.4424	19.2	8.468
1-Phenyl Octane	190.3	1.5608	20.8	8.200
Tetradecane	198.4	1.4744	19.6	7.432
1-Phenyl Tridecane	260.5	1.4898	19.8	5.720

H/C = 1.800 H_α = 0.048 H_β = 0.663 H_γ = 0.169

Wt.-Avg. MW = 196.2 Predicted MW = 185

TABLE A-5

REFRACTIVE INDICES OF SOME PURE HYDROCARBONS

	Mol. Wt.	Refractive Index
Solvent		
Tetrahydrofuran	72	1.4070
Alkanes		
n-Decane	142	1.4102
n-Pentadecane	212	1.4315
n-Eicosane	283	1.4425
n-Pentacosane	353	1.4491
Aromatics		
Toluene	92	1.4961
m-Xylene	106	1.4972
1,2,4-Trimethyl Benzene	120	1.5048
Ethyl Benzene	106	1.4959
n-Propyl Benzene	120	1.4920
n-Butyl Benzene	134	1.4898
Biphenyl	154	1.4750
2-Methyl Naphthalene	142	1.6015
Phenanthrene	178	1.5943

APPENDIX B

CHARACTERIZATION OF THIRTEEN FOSSIL FUELS

Appendix B presents characterization data for thirteen fossil fuels using the procedures described in this paper and in previous work.

Table B-1 gives molar hydrogen-to-carbon ratios and hydrogen-distribution data for thirteen fossil fuels.

Table B-2 compares the GPC-measured, weight-average molecular weight to that obtained from mass spectrometry. Average deviation for the petroleum liquids is about 6 percent. Coal-derived liquids have a higher average deviation of about 14 percent; this larger deviation probably follows from the higher proportion of hetero-atoms. Heteroatomaticity has not been included in the correlation.

Table B-3 gives the elemental analysis. Table B-4 shows the concentrations for hydroxyl, primary amine, secondary amine, and methyl functional-groups. Values are reported as number of groups per molecule.

TABLE B-1

MOLAR H/C RATIO AND HYDROGEN-DISTRIBUTION DATA FOR THIRTEEN FOSSIL FUELS

Source	H/C	H_α	H_β	H_γ
Exxon A-1	1.703	0.089	0.568	0.220
Exxon A-3	1.665	0.110	0.556	0.223
Exxon A-5	1.649	0.057	0.487	0.197
Exxon B-1	1.633	0.144	0.448	0.289
Exxon B-3	1.585	0.139	0.466	0.263
Exxon B-4	1.548	0.151	0.446	0.208
SRC II Middle	1.231	0.283	0.222	0.099
SRC II Heavy	0.953	0.263	0.174	0.071
WCLP 4	1.401	0.220	0.333	0.151
WCLP 5	1.434	0.213	0.398	0.183
WCLP 7	1.432	0.205	0.432	0.154
WCLP 8	1.375	0.223	0.429	0.140
ANS Resid	1.492	0.181	0.561	0.195

H/C - Molar Hydrogen-to-Carbon Ratio

H_α - Fraction of hydrogen atoms attached to carbons alpha to an aromatic ring

H_β - Fraction of hydrogen atoms attached to carbons beta or further, but non-terminal, to an aromatic ring

H_γ - Fraction of hydrogen atoms attached to terminal carbons

TABLE B-2

WEIGHT-AVERAGE MOLECULAR WEIGHT OF THIRTEEN FOSSIL FUELS

Source	Nominal Boiling-Point Range, °F	GPC Measured Mol. Wt.	Std. Dev.	Mass Spectrometry Mol. Wt.
Exxon A-1	700-725	224	76	228
Exxon A-3	750-775	257	83	265
Exxon A-5	800-825	248	80	274
Exxon B-1	650-700	199	59	201
Exxon B-3	750-800	221	73	248
Exxon B-4	800-850	232	77	269
SRC II	Middle	148	34	153
SRC II	Heavy	210	70	202
WCLP 4	425-450	153	30	122
WCLP 5	450-500	159	41	140
WCLP 7	600-650	163	53	209
WCLP 8	650-700	185	71	215
ANS	Resid	639	213	630

SRC II - Solvent Refined Coal Process

WCLP - Wilsonville (Ala.) Coal Liquefaction Pilot Plant Process

ANS - Alaskan North Slope Crude

TABLE B-3

ELEMENTAL ANALYSIS OF THIRTEEN FOSSIL FUELS

	Weight Percent				
Source	C	H	N	S	O (a)
Exxon A-1	84.87	12.13	0.44	2.56	—
Exxon A-3	85.81	11.99	0.39	1.76	0.05
Exxon A-5	85.03	11.77	0.29	2.91	—
Exxon B-1	85.91	11.78	0.10	2.21	—
Exxon B-3	85.27	11.34	0.28	3.05	0.06
Exxon B-4	84.99	11.04	0.18	3.12	0.37
SRC II Middle	85.89	8.87	1.10	0.23	3.91
SRC II Heavy	89.90	7.19	1.20	0.32	1.39
WCLP 4	82.84	9.74	0.43	0.11	6.88
WCLP 5	85.15	10.25	0.33	0.20	4.07
WCLP 7	88.52	10.64	0.39	0.09	0.36
WCLP 8	88.99	10.27	0.48	0.04	0.22
ANS Resid	85.56	10.71	0.70	2.07	0.96

(a) calculated by difference

— denotes less than 0.01 %

TABLE B-4

FUNCTIONAL-GROUP CONCENTRATIONS OF THIRTEEN FOSSIL FUELS

	Number of groups per molecule			
Source	OH	NH_2	NH	CH_3
Exxon A-1	—	—	—	3.2
Exxon A-3	—	—	—	3.5
Exxon A-5	—	—	0.06	3.8
Exxon B-1	—	—	—	3.0
Exxon B-3	—	—	—	3.4
Exxon B-4	—	—	—	3.5
SRC II Middle	0.05	—	—	1.4
SRC II Heavy	0.02	—	0.01	1.9
WCLP 4	0.07	0.01	—	1.7
WCLP 5	0.03	—	—	1.5
WCLP 7	—	—	—	1.5
WCLP 8	0.01	—	—	1.7
ANS Resid	0.02	—	0.06	9.2

— denotes less than 0.01 %

APPENDIX C

PRELIMINARY SOLVENT EXTRACTION

A more detailed characterization can be obtained by performing a preliminary solvent extraction on the original residue material, prior to all other measurements. Extraction separates the fraction into chemical types.

The original residue is solvent extracted first with n-heptane, next with toluene, and finally with pyridine. The first solvent removes the saturated hydrocarbons, some unsaturated hydrocarbons and light aromatics; the second removes heavy aromatics; and the last removes most very heavy organic residua, including some heteroatomic hydrocarbon derivatives. Material not dissolved by any of these solvents is probably primarily inorganic matter.

For preparative GPC work, the original residue material is run and the RI-response/weight-percent relationship is determined. The solvent-extracted fractions can then be run separately on the GPC in the analytical mode using the same RI-response/weight-percent relationship as that used for the original residue. For best results, the H/C ratio and hydrogen distribution used in Equation (1) should be determined for each of the solvent-extracted fractions.

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