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Quantitative Measurement of Mass and Aromaticity Distributions for Heavy Distillates 1. Capabilities of the HPLC-2 System

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Abstract

This is the first in a series of papers describing a high-performance liquid chromatography (HPLC) system for quantitative measurement of the distribution of both aromatic carbon and mass in heavy distillates. Unique detector algorithms are applied to quantitate the aromaticity and mass of six groups (saturates, 1–4 ring aromatics, and polars) separated from oils using solvent gradients on coupled columns. Separation efficiencies (ring purities) are verified by alternate separations and mass spectra, the aromaticities derived from ultraviolet spectra are validated with ^{13}C-nuclear magnetic resonance, and the evaporative mass detector results are verified by weighing isolated fractions from multiple runs. Both single- and interlaboratory precision are established at ~10% (1σ relative standard deviation). Several examples are provided to illustrate the utility of HPLC-2 data in refining heavy distillates.

Introduction

Modern refineries convert and separate the molecules in heavy distillates into more valuable products. Processes such as hydrogenation, catalytic cracking, lubes extraction, and coking can be optimized by molecular-based compositional analysis of feed and products. In recent years, sophisticated mass spectrometry (MS) and nuclear magnetic resonance (NMR) techniques have been developed to understand the structural transformations and fate of the multi-ring aromatics that are affected by these processes. Because these sophisticated techniques do not lend themselves to routine refinery operation, most processes are controlled with minimal molecular level input.

This is the first in a series of papers describing a high performance liquid chromatography (HPLC) system for quantitative measurement of the distribution of both aromatic carbon and mass in heavy distillates. A fully automated version of the system, designated HPLC-2, has been widely applied to refinery process streams. This HPLC-2 system combines the separation of two columns with the quantitative measurement from two detectors in a system suitable for operation in a refinery setting. Whereas our patents and subsequent papers will detail the separation and measurement techniques (1–5), this paper aims to introduce the overall system, illustrate its application to refinery heavy distillate problems, and discuss the verification of its results with alternate techniques.

The fractionation of heavy distillates from fossil fuels into various classes is well known, but quantitative results have been limited to off-line measurements. No single column is completely adequate for separating the entire range of polarity in heavy distillates (6–10), but full-range separations can be achieved using multiple columns, column switching, and solvent gradients (11–15). There has been no universal quantitative detector for HPLC; various ultraviolet (UV) wavelengths or refractive indexes (RI) can be used in specific cases, but both are structure dependent (i.e., are not universal for general unknowns) (16–18). The diode array detector (DAD) has expanded the range of UV measurements for specific aromatics using HPLC (19–21) but is not yet "universal". Adaptations of the flame ionization detector, which may be structure independent, have been limited by artifacts (memory effects, sample volatilization, etc.) in their desolvation systems (22–25). The evaporative mass detector (EMD) can be quantitative when applied to well-shaped peaks over narrow concentration ranges (26–29) but is limited by sample boiling point, color, and possibly class type (3,30–33).

The development of the HPLC-2 system relies on three interdependent advances: the development of an algorithm for conversion of DAD spectra to aromaticity (1,2), a procedure for wide-range calibration of an EMD (3,4), and an efficient separation of heavy fossil fuels into six fractions (saturates {S}, 1- to 4-ring aromatics {1R–4R}, and polars {P}) in a single chromatographic run (1,5). HPLC-2 systems have been applied within Exxon (Annandale, NJ) for over 10 years. During that time, they have been applied to a broad variety of heavy distillate problems in over 20 locations worldwide. The following discussion draws from experiences at those locations.

Experimental

Representative samples of refinery process streams, crude assay fractions, and laboratory experiments were obtained from

various Exxon affiliates. These included atmospheric resids (AR, 650°F and above), vacuum gas oils (VGO, cuts from 650 to 1050°F), heavy vacuum gas oils (HVGO, cuts from 800 to 1050°F), heavy coker gas oils (HKGO, cuts from 800 to 1050°F), vacuum resids (VR, 1050°F and above), and deep distillates obtained by short-path distillation (DISTACT, cuts from 1050 to 1300°F).

Instrumentation

The HPLC-2 system was assembled from commercially available components (Figure 1). The two normal-phase HPLC columns were mounted on separate switching valves that allowed a forward flow of solvent to be directed through both or either of the columns independently. The HP-8451 (Hewlett-Packard, Palo Alto, CA) collected DAD spectra, served as the system controller, performed post-run calculations, and stored data on disks. Spectra were collected over a range of 204–430 nm for maximum coverage of the aromatic π–π absorption. Because this DAD measurement is roughly 10 times more sensitive to aromatics than EMD, a 1-mm Isco flowcell was used to help match the sensitivities of the two detectors. A Kiethley (Cleveland, OH) 195A served as an interface for the raw EMD signal, converting the analog-to-digital values and communicating across HPIB (IEEE-488) cables. The Varian (Palo Alto, CA) 5560 pump, which communicates with the HP-8451 via RS-232 cables, controlled the autosampler and switching valves.

Separation

The separation was carried out using two columns: a propylaminocyano (PAC) column (Whatman, Clifton, NJ) for separating saturates and mono-aromatics and a dinitroanilinopropyl (DNAP) column (ES Industries, Berlin, NJ) for separating the larger rings. The individual DNAP columns vary somewhat in their retentiveness, so model compounds were used for optimization. The retention times for the six fractions were initially set on the basis of the separation of a hexane solution of model compounds. The starting cut points were based on hexadecane (S), nonadecylbenzene (1R), naphthalene (2R), dibenzothiophene (3R), pyrene (4R), and the reported relative retention times (9). The solution also contained fluorene and phenanthrene which elute later in the 2R and 3R fractions, respectively. Typically, the quality control (QC) sample was used to make final adjustments to the valve timing (which dictated the start of 2R) to give a minimal shoulder on the DAD chromatogram. Likewise, some adjustments were made to the solvent program for 4R and P on the basis of the QC results. Finally, to compensate for variations in sample types, the software found and applied the valley between peaks for S and 1R in its calculation rather than using the fixed value determined for the model compounds.

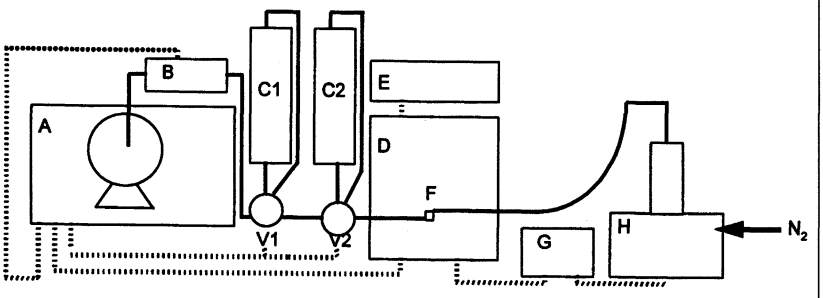


Figure 1. Commercial components assembled into the HPLC-2 system. A, Varian 5560 ternary solvent pump; B, Varian 8055 autosampler; C1, 4.6 x 2500 mm DNAP column; C2, 4.6 x 250 mm PAC column; D, HP 8451 diode array spectrophotometer (DAD); E, HP 9133 dual disk drive; F, Isco 1-mm flowcell; G, Kiethey 195A digital voltmeter; H, Applied Chromatography Systems 750/14 evaporative mass detector; V1 and V2, Rheodyne 7040 six-port switching valves.

Calibration

The DAD response factors for aromaticity were based on the average values determined from the 204–430-nm spectra of over 80 model compounds dissolved in hexane (1,2). Spectra were recorded in 2-nm increments while a steady state flow of sample was pumped through a 1-mm flowcell.

Extinction coefficients for the two peak maxima (210 and 262 nm nonadecylbenzene, TCI America, Portland, OR) were determined in the same 1-mm flowcell. These values were used to determine each system's calibration factors. A 2.00-mg/mL solution was injected and eluted with hexane at 1.5 mL/min. The DAD was programmed to measure the absorbances at 210 and 262 nm. Integration of the absorption at 210 nm across the chromatographic peak was used to calculate a correction specific for each system's deviation from the nominal loop volume and cell path length.

The EMD was calibrated using 15 concentrations from 0.025 to 20 mg/mL under the same conditions. The instantaneous concentration (micrograms per milliliter) at the chromatographic peak maximum (a pseudo-steady-state point) was calculated by applying Beer's Law to the absorbances at 210 and 262 nm. The corresponding peak EMD maximum (millivolts) was also recorded. The fifteen sets of data were then regressed to generate a calibration curve. The two wavelengths were used in order to remain within the Beer's Law linear range over the entire concentration set. EMD calibration data over such a wide range could not be fit with a single function. However, excellent fits can be obtained by regressing the data over two ranges (samples 1–8 and 8–15), which each fit to better than correlation coefficient $r^2 > 0.98$. Using the software, these two regressions were splined at their crossover to generate a calibration algorithm that converted each EMD reading from millivolts to micrograms/milliliter (3,4). The EMD curve for the 2 mg/ml solution was then integrated, and a factor was determined for the residence time in the EMD (i.e., a flow factor).

Data acquisition for heavy distillates

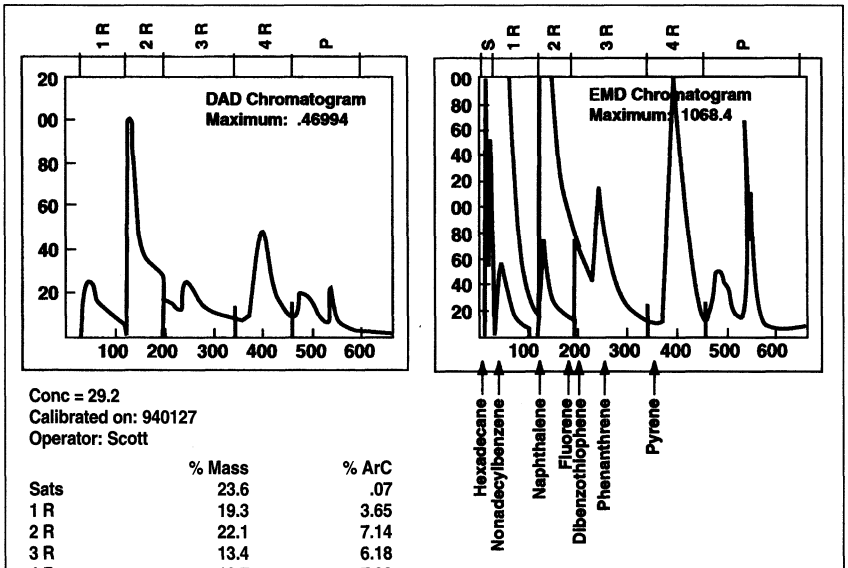
For routine HPLC-2 analyses, 150 mg of heavy distillate was dissolved in 5 mL cyclohexane, filtered (if necessary), placed in vials, and loaded into the autosampler. Samples were then injected and separated using gradient elution with hexane, methylene chloride ($MeCl_2$), and isopropyl alcohol; the pump program is given in Table I. Data collection was complete after 36 min; the remainder of the program regenerated the columns back to an initial "ready" condition. Each set of samples was initiated with a blank to ensure that each analysis started from the same

"ready" condition. This was followed by a quality control sample to establish acceptable system performance before "unknowns" were analyzed.

Data were acquired by the two detectors at 3-s intervals starting after a dead volume delay (3 min) and continuing until the end of run (36 min). During each time interval (i), the system acquired and stored two integrated absorption energies (S1[i] for 204–230 nm and S2[i] for 232–430 nm) from the DAD and a reading (S5[i]) from the EMD. The data array for the complete run was captured in a 3 × 660 data array in random acces memory.

Calculation and reporting

After the raw data had been stored on disk, two chromatograms were plotted (Figure 2). The aromaticity chromatogram plotted the DAD values that would be used in the calculations (i.e., the sum [S1(i)+S2(i)] for data points 0–220 and S2[i] for the remainder of the data points). The raw EMD data were smoothed with a five-point moving average, off-set for the delay between detectors, and baseline corrected before being plotted as the mass chromatogram (Figure 2). The data processed for plotting were then integrated over retention ranges established for the six fractions. The DAD data were used to calculate the aromaticity (%C_a) directly for each fraction by applying aromaticity response factors, system factors (injection volume, flow rate, follicle pathlength, data acquisition rate), and the sample concentration. A small blank correction was made for the spectral contribution of methylene chloride in the last two fractions. The percent mass distribution for each fraction was calculated as a percent of the total mass measured by the EMD. First, the processed EMD data were converted to units micrograms using the EMD calibration functions (19,20). Then, the units micrograms were summed for each fraction, the fractions were added to a total, and their percentage was calculated. The ratio of the total measured mass to the injected mass was reported as percent recovery.



Conc = 29.2
Calibrated on: 940127
Operator: Scott

	% Mass	% ArC
Sats	23.6	.07
1 R	19.3	3.65
2 R	22.1	7.14
3 R	13.4	6.18
4 R	12.7	7.29
P	9.0	3.89
Aromaticity		28.22
Mass Recover		94.9

Figure 2. Annotated HPLC-2 data report.

Table I. HPLC-2 Solvent Program*

Time (min)	n-C_6 (%)	$MeCl_2$ (%)	IPA (%)	Flow (mL/min)	Relays	Comment
0.00	100	0	0	1.5	0	Injection
3.00	100	0	0	1.5	6	S and 1R elute from PAC
9.50	100	0	0	1.5	7	2R elute from DNAP
11.00	100	0	0	1.5	7	End of hexane only for 2R
11.05	95	5	0	1.5	7	Start gradient to chromatofocus 3R
18.00	98	2	0	1.5	7	End 3R gradient
20.00	75	25	0	1.5	7	Steep gradient to move 4R
23.00	80	20	0	1.5	7	End of 4R gradient
26.00	10	90	0	1.5	7	Strong gradient to elute polars
29.00	0	90	10	1.5	7	Introduce IPA to displace strong polars
37.00	0	75	25	1.5	7	Final polarity push to clean column
37.50	0	100	0	2.0	7	Regeneration of DNAP; flush IPA
41.00	0	100	0	2.0	0	Regeneration of both columns
42.00	0	100	0	2.0	0	Brief $MeCl_2$ onto PAC
44.00	100	0	0	2.0	0	Flush residual $MeCl_2$
50.00	100	0	0	2.0	6	Flush DNAP valve bypass loop
52.00	100	0	0	2.0	7	Flush PAC valve bypass loop
54.00	100	0	0	2.0	0	Re-equilibrate system to n-C_6
60.00	100	0	0	2.0	0	Re-equilibrate system to n-C_6
61.00	100	0	0	1.5	0	Re-equilibrate system to n-C_6
75.0(end)	100	0	0	1.5	0	Re-equilibrate system to n-C_6

*Relay 6 bypasses the DNAP column. Relay 7 bypasses the PAC column.

The results were then printed in a standard format (Figure 2).

Validation techniques

Preparative HPLC-2 fractions were obtained by performing multiple automated runs at higher sample concentrations than those used for routine analysis. A modified pump program was used to combine similar fractions with a Gilson 210 fraction collector. ^{13}C-NMR spectra were recorded on a Varian Unity 500-MHz spectrometer to generate aromaticity data. All measurements were carried out in $CDCl_3$ with $Cr(AcAc)_2$ as a relaxation agent. Elemental analyses for carbon (Galbraith, Knoxville, TN) were used to convert the mole percent aromatic carbon to weight percent aromatic carbon. Quantitative MS data for samples and fractions in this work were obtained on Kratos MS-50 instruments. Direct insertion techniques were used for low voltage/high resolution spectra (LV-HR-MS); tungsten emitters were used for field desorption spectra (FD-MS).

Results and Discussion

Separation Conditions

As discussed in detail in the literature (5), the goal of the HPLC-2 separation is to isolate each of the six key molecular fractions in the heavy distillates. Because many previous studies had found that no single column was sufficient to provide the necessary resolution of such a broad range of sample polarities (11–15), a two column approach was developed (5). The DNAP column was chosen because it has excellent aromatic ring selectivity (1) and is relatively insensitive to alkyl substitution, even in gradient elution applications (9). To compensate for its poor resolution of the saturates and mono-aromatics, the DNAP column was coupled with the Whatman PAC column. The latter column provides good saturates/mono-aromatics resolution with hexane elution but is sensitive to substituent effects and difficult to use in the gradient mode (5). In some samples, there was a slight overlap of mono-aromatics into the saturates that was detected by the DAD. The valve-switching/solvent gradient scheme (Table I) was developed to maximize the resolution of the six groups (5). The saw-tooth gradients used for the tri- and tetra-aromatics fractions "chromatofocused" the aromatics types into well-defined peaks that were readily quantitated with HPLC-2 detectors (Figure 2). The final solvent strength was sufficient to complete the elution of polars (5+ ring aromatics, *N*- and *O*-functionalities) without backflush. The regeneration portion of the program was designed to clean any trace residuals on each column and to return the system reproducibly to the same ready status at the start of each analysis. To achieve this "dynamic equilibrium" for each sample, every batch of samples started with a conditioning blank.

The HPLC-2 separation has been validated with several independent techniques. It has been correlated against MS-50 analyses based on a modified clay-gel separation (ASTM D-2007). The data for saturates, total aromatics, and polars agree well with one another (Figure 3). When HPLC-2 was interfaced with a high-resolution MS with a moving belt, carbazoles (3-ring *N*-heterocyclics) were found in both the 4R and P fractions from high nitrogen crudes (35). This observation may help rationalize the weaker HPLC-2/MS-50 correlation for polars. The same liquid chromatography–MS interface has confirmed that the thiophenic rings separate as aromatics (i.e., dibenzothiophenes are included with phenanthrenes) (36). In general, the DNAP retention of thiophene analogs places them in the proper aromatic fraction but slightly ahead of the corresponding aromatic (i.e., dibenzothiophenes in the 3R fraction but ahead of phenanthrenes) (3,4). However, the analogues most weakly retained on DNAP (i.e., the two ring benzothiophenes) have been found in some 1R trapped fractions. When thiophenic rings were treated as aromatics with proprietary software, FDMS analyses of the fractions isolated in preparatory HPLC-2 led to an estimated "ring purity" of nearly 90%.

Aromaticity measurement from DAD spectra

Working from first principles, it has been demonstrated that a UV spectrum can be used to measure the aromaticity of multi-ring aromatics quantitatively (1,2). Studies on more than 80 model compounds have confirmed that there is a nearly constant response per aromatic carbon π–π atomic transition when the spectra are converted to an energy (eV) basis for each wavelength and the absorbance integrated over the range corresponding to 204–430 nm (1,2). Because these integrated absorption energies ("oscillator strengths") include all transitions between a ground state molecule and its excited states, they count the aromatic carbons. In HPLC-2, the spectral data collected by the DAD are split and stored as two values to accommodate the methylene chloride in the solvent program for the last three fractions.

Three response factors are applied to the oscillator strengths

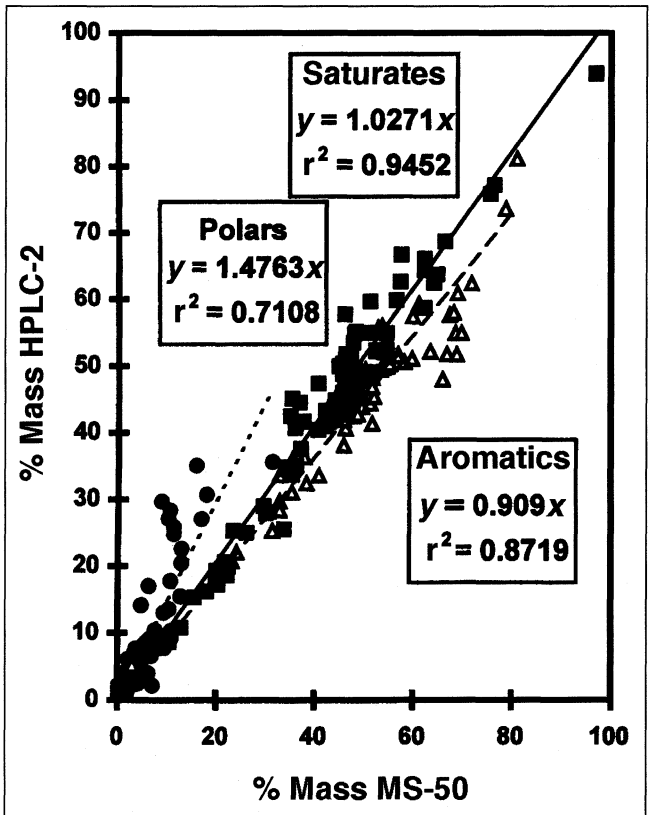


Figure 3. Separation by HPLC-2 and clay-gel MS-50.

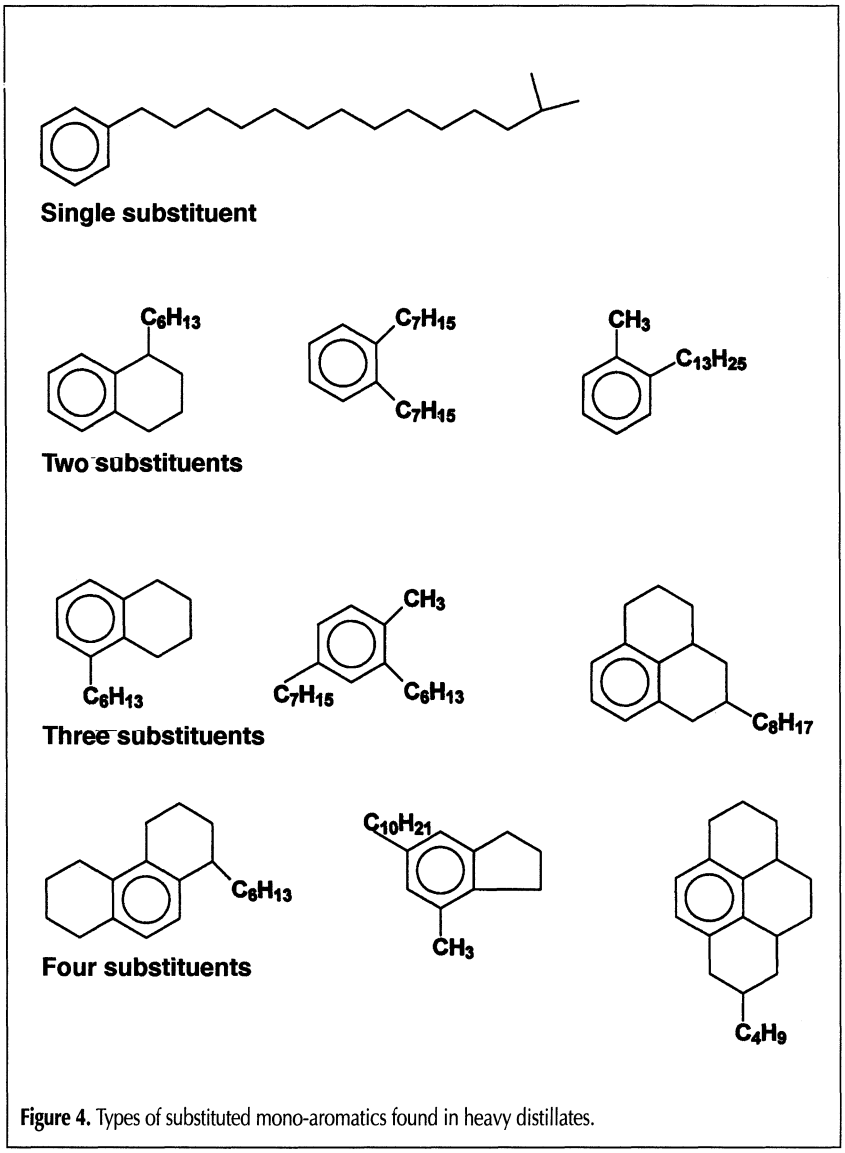


Figure 4. Types of substituted mono-aromatics found in heavy distillates.

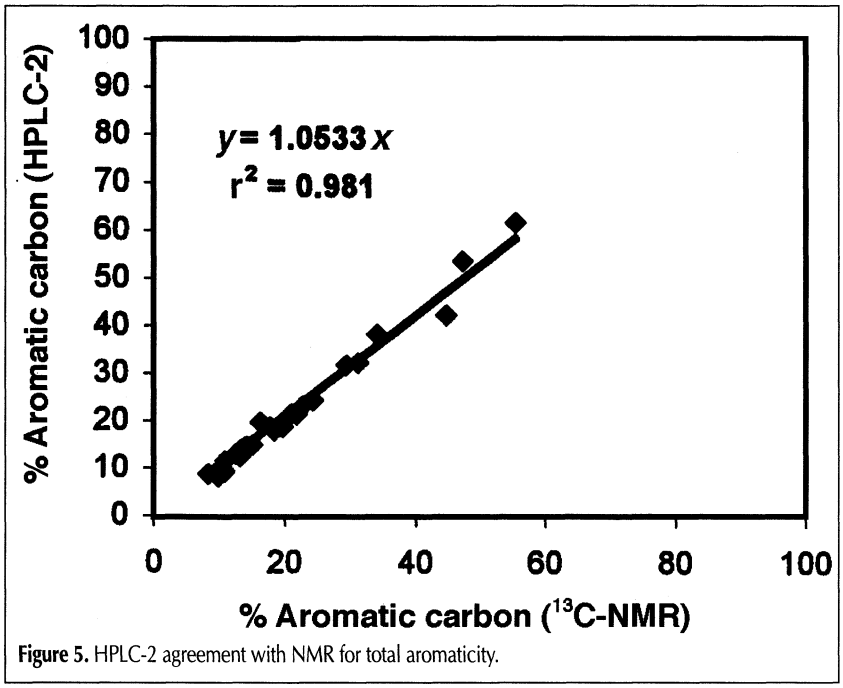


Figure 5. HPLC-2 agreement with NMR for total aromaticity.

obtained from the DAD data for each fraction. One factor is applied to the total (S1 + S2) oscillator strength for the 2-ring aromatics and a second is applied to S2 for the (≥ 3)-ring aromatics in the last three fractions (which exhibit nearly constant response to S2) (1,2). On the other hand, the mono-aromatics in heavy oils can be highly substituted, and the response of the mono-aromatics (S1 + S2) increases with alkyl substitution (Figure 4) (2). When a factor corresponding to mono-aromatics with 3.5 substituents is applied to the sum (S1 + S2), the total $\%C_a$ by HPLC-2 correlates closely with that determined by ^{13}C-NMR (Figure 5). Coincidentally, the response factor for the mono-aromatics (S1+S2) has the same value as that for S2 for the last tree fractions.

When isolated HPLC-2 fractions are redissolved in hexane, the $\%C_a$ can be measured from the full 204–430-nm DAD spectrum using the full-range response factor (Table II). The aromaticities calculated from the spectral data show good agreement with ^{13}C-NMR-derived results for the fractions from both the HVGO and the cat bottoms. These two samples represent major differences in aromatics; the whole HVGO had a low total aromaticity (15.4%) and the unseparated cat bottoms had a high total aromaticity (70%). It should be noted that the "oscillator strengths" measured primarily for available compounds of unknown purity show considerable variability within a class. However, the close correlation of HPLC-2 aromaticity with ^{13}C-NMR values supports the use of average values to the complex mixtures of structural types found in petroleum.

At > 70% aromaticity, HPLC-2 may acquire some spectra where portions of the 204–430 nm range exceed the dynamic range of the DAD, which would lead to low aromaticity results. At the other extreme, spectral noise will limit DAD accuracy below 0.2% per fraction.

The measurement of both the aromaticity and its distribution adds a quantitative dimension previously lacking in HPLC analyses of aromatics. Although DAD spectra are often used to provide qualitative three-dimensional "maps" of the aromatics distributions, only a few attempts have been made at quantitation. Individual polynuclear aromatic hydrocarbons (PAHs) have been speciated and measured in HPLC analyses (25). A technique for estimating PAH ring types by integrating HPLC time slices over selected wavelength regions has been suggested (23). Even these methods have been limited by wavelength dependence of individual aromatics. Integrating the entire aromatic spectral region for each chromatofocused ring class provides a structure-independent quantitative account of the total "aromatic core" in that fraction.

Quantitative mass distribution measurements

The EMD relies on the refractive scattering of light from the spherical particles remaining after desolvation of the droplets created in its nozzle. This makes it particularly effective for the measurement of mixtures that have a boiling point > 650°F, are liquids, and absorb a minimal amount of visible light (i.e., have low color). To a large extent, heavy distillate samples satisfy these conditions.

The operating conditions are optimized individually for each EMD in its HPLC-2 system (3,4). The calibration functions allow quantitative use of the EMD response over an 800-fold concentration range. This accommodates most HPLC-2 peak types (i.e., from tall, narrow S peaks to low, broad P bands). The point-for-point calibration of EMD allows the system to handle the non-linearity of the EMD over a much broader range than possible with peak-height or area calibrations. Previous EMD applications have been limited to quantitation of individual sharp peaks using approximately 15-fold peak-height calibrations to compensate for non-linearity (33,34).

In most cases where only a small portion of the sample (if any) boils below 650°F, HPLC-2 assumes that losses fall equally across all fractions and reports the mass distribution data on a normalized basis. It also reports the actual portion recovered independently. As long as the recovery remains 100 ± 20%, the normalization has only a minor acceptable impact on the mass distribution. Whenever recoveries fall outside of this range, the user is advised by the software that alternate treatments are required.

EMD limitations

Some heavily converted, narrow-boiling samples yield crystalline particulates that reflect light in the EMD, leading to erroneous > 100% mass recovery. For example, a 725–750°F fraction from a high-severity catalytic (cat) cracking experiment gave 145% mass recovery. The narrow-boiling fraction apparently yields "snow-flakes" instead of raindrops in the EMD, leading to an unusually high reflection of light. A similar effect can be used to rationalize the differences observed when the EMD is applied to pure compounds. The crystallinity of each compound may differ sufficiently to create variation in the EMD. Fortunately, most heavy distillates are such complex mixtures that they remain as liquids and behave well in the EMD.

On the other hand, HPLC-2 concentrates colored components largely into the polars. In vacuum resids and asphalts, the mass recoveries may drop when the polars exceed a reported 20% because of the absorption of the light in its refraction path.

HPLC-2 applications are limited by other characteristics of the EMD. The accuracy of the measurements falls off for samples with > 90% in a single peak (tall S peak) or < 2% in a low, flat peak (low P peak). Volatilization losses limit the system to samples with > 80% boiling above 650°F. Samples with > 20% P may suffer low mass measurement from "color quenching" in the EMD. Other sample characteristics can limit the application of HPLC-2. Although most heavy distillates are soluble in cyclohexane, some portions of vacuum resids and highly cracked stocks are not. Likewise, the solvent gradient is sufficient to elute most resid components, but some highly refractory materials with > 30% polars may not be eluted. These deficiencies are generally flagged as having low recovery and require alternate treatments.

EMD mass accuracy and precision

Several techniques have verified the normalized EMD mass distributions: the HPLC-2 data exhibit internal consistency; the saturates/aromatics/polar HPLC-2 data correlate with MS-50 data (Figure 3); and prep HPLC-2 fraction weights compare well with EMD values (Table III).

The performance of HPLC-2 systems is routinely monitored by running a QC sample. Table IV compares the short-term, single-lab precision with the long-term interlaboratory precision for 11 labs. With the exception of the polars, the systems are within 10% 1s relative standard deviation (RSD). The results for the QC sample are charted to detect non-random errors in system performance.

Table II. ^{13}C-NMR and DAD Aromaticities Agree for Preparatory-HPLC-2 Isolated Aromatics Fractions

Sample fraction	HVGO (weight %C_a)*		Cat bottoms (weight %C_a)†	
	DAD	^{13}C-NMR	DAD	^{13}C-NMR
1R	12.6	15.9	36.2	34.2
2R	29.7	29.0	44.0	NA
3R	41.6	37.0	68.9	70.4
4R	52.6	51.8	73.3	75.1

* Aromaticity calculated from DAD spectrum oscillator strength.
† Aromaticity calculated from ^{13}C-NMR (mole % aromatic carbon) and elemental analyses (% carbon).

Table III. Comparison of EMD Mass Distributions with Gravimetric Results

Sample	Lube extract EMD (%)	HVGO Grav* (%)	HKGO EMD (%)	HCCO Grav (%)	EMD (%)	Grav (%)	EMD (%)	Grav (%)
Saturates	24.3	26.6	52.1	53.8	25.3	25.4	17.9	17.6
1-Ring	18.3	15.1	17.3	17.8	10.9	11.5	11.3	12.9
2-Ring	20.8	20.6	11.9	15.0	14.3	15.3	15.6	12.3
3-Ring	13.1	14.8	6.6	8.8	12.1	16.8	17.7	19.0
4-Ring	14.0	11.7	5.6	6.2	14.7	23.1†	26.7	23.8
Polars	9.4	11.0	6.2	1.3	22.5	9.5†	10.9	14.4

* Grav, gravimetric results.
† Non-standard cut point applied for 4-RING/POLARS split.

Table IV. Precision Data for HPLC-2 Quality Assurance Sample

	Single-lab precision*			Interlaboratory precision†		
	Mean weight %	SD‡ (1σ)	%RSD	Mean weight %	SD (1σ)	%RSD
% Aromatic carbon						
S	0.17	0.03	NA	0.08	0.04	NA§
1R	3.24	0.10	3.1	3.39	0.3	8.8
2R	6.02	0.67	11.1	6.76	0.66	9.8
3R	5.43	0.21	3.9	5.62	0.44	7.8
4R	6.73	0.50	7.4	7.19	0.64	8.9
P	4.90	0.32	6.5	4.4	0.58	13.2
Total % carbon	26.53	0.80	3.0	27.48	1.41	5.1
Normalized weight %						
S	24.44	0.19	0.8	23.13	1.08	4.7
1R	20.03	0.50	2.5	19.32	1.23	6.4
2R	21.63	0.87	4.0	20.8	1.1	5.3
3R	13.83	0.39	2.8	13.9	0.38	2.7
4R	12.12	0.19	0.16	13.46	0.41	3.0
P	8.37	0.63	7.5	9.29	1.21	13.0
Recovery	95.90	3.00	3.1	98.92	3.45	3.5

* Precision was based on one month of 20 analyses.
† Precision was based on one year of 1153 analyses in 11 laboratories.
‡ SD, standard deviation.
§ NA, data not available.

Refinery applications

Six refinery applications illustrate the characteristics of HPLC-2 data. The first two show the changes in mass and aromaticity distributions as a function of distillation temperature (Tables V and VI). The remaining four reflect the changes in mass and aromaticity distributions that occur in heavy distillate processes: hydrotreating, cat cracking, coking, and lubes extraction (Table VII). As indicated, the average carbon numbers for each fraction can be estimated from the fraction's aromaticity and mass values. These estimated average carbon numbers serve as an internal consistency check for the HPLC-2 analyses.

Distillation

Whole crudes range widely in total estimated carbon number. Distillates cut from crudes have narrow ranges of carbon numbers that increase with boiling point (as seen for the fractions distilled from HVGO A) (Table V). The lowest boiling fractions provide lower recovery, the saturates gradually decrease, the mono-aromatics rise slowly before the final two fractions, and 4R and P increase throughout. The aromaticity fraction (from overlap of mono-aromatics into the satu-

Table V. HPLC-2 Analyses for Narrow Cuts from HVGO A

	650–700°F	700–750°F	750–800°F	800–850°F	850–900°F	900–950°F	950–1000°F	1000–1050°F	>1050°F	Weighted sum for all cuts	HVGO A initial 100%
Weight % in cut	3.35	1.84	7.32	14.44	24.42	20.31	17.97	6.56	4.19	–	–
% aromatic carbon											
S	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.0	0.0
1R	2.4	2.8	2.8	2.7	2.5	2.2	2.1	1.8	1.4	2.3	2.8
2R	4.9	5.2	4.8	4.4	3.8	3.3	3.2	2.8	2.4	3.7	4.3
3R	2.5	3.1	3.0	2.9	2.5	2.3	2.4	2.2	2.1	2.5	2.9
4R	2.1	2.4	2.6	3.0	3.3	3.5	3.8	4.2	5.0	3.4	3.6
P	3.0	2.5	2.6	2.7	3.0	4.3	3.8	4.4	5.8	3.4	3.3
Total $\%C_a$	14.9	16.0	15.8	15.7	15.1	15.6	15.4	15.5	16.8	15.4	17.0
Normalized weight %											
S	68.7	65.9	60.1	61.9	57.0	51.8	48.4	43.4	35.0	54.3	52.3
1R	10.7	14.4	14.7	16.4	16.5	16.0	16.4	15.8	14.2	15.9	17.1
2R	5.3	8.3	8.9	9.7	10.2	10.5	11.5	11.6	11.8	10.3	11.8
3R	3.2	4.7	6.6	4.5	5.2	6.5	7.1	7.4	8.7	6.0	6.8
4R	4.4	3.0	4.6	3.4	4.5	6.2	7.1	9.1	13.0	5.8	6.7
P	7.7	3.7	5.0	4.0	6.6	9.0	9.5	12.6	17.3	7.9	5.2
Recovery	61.3	77.4	89.3	94.8	101.9	106.6	104.2	104.8	103.4	98.8	97.0
Estimated average carbon number											
1R	23.8	27.3	27.9	32.1	34.8	38.3	41.0	46.0	53.0	35.9	32.8
2R	10.7	15.1	17.3	20.3	24.4	28.7	32.2	36.9	43.6	25.4	24.9
3R	17.4	20.2	28.4	20.6	27.0	35.9	37.5	42.4	51.7	30.8	30.2
4R	34.9	21.9	29.9	20.1	23.6	29.9	31.4	36.0	42.7	28.8	31.1
P	42.2	25.4	32.2	25.4	36.5	34.9	41.1	46.8	48.6	38.3	26.9

rates) becomes reportable in the highest boiling fractions. Acceptable balances are found between the weighted sums of fractions and initial sample for each molecular type. In another example, the carbon numbers for each aromatic type were estimated for the DISTACT distillation fractions of an atmospheric resid (Table VI). For all distillate cuts up to the 1235°F bottoms, the estimated average carbon numbers were reasonable for each ring type and showed a rational increase with boiling point. The poor recovery for the bottoms may be caused by insolubility, incomplete elution, or color quenching in the EMD polars measurement as previously discussed.

Hydrotreating

The objective of hydrotreating is to reduce the coke-forming, large-ring aromatics with little conversion of the heavy distillates to lower boiling fractions. In the hydrotreating example in Table VII, the total $\%C_a$ dropped from 30.9 to 25%, and the saturates mass increased a corresponding 6% in the product. The increased mass in S has been accompanied by an 11% decrease in the combined 3R, 4R, and P mass; the (> 3)-ring $\%C_a$ has dropped nearly 9%, whereas that of the lower aromatics has increased nearly 3%.

Cat cracking

The ability of HPLC-2 to measure the distribution of both mass and aromaticity is also useful for cat-cracking feeds and products. In contrast to hydrotreating, cat cracking converts heavy distillates to lower-boiling high-value products. The strong acid catalysts and high temperature (> 900°F) combine to break bonds, isomerize fragments, and aromatize rings. In the process, feeds with moderate aromaticity ($\%C_a \approx 15\%$) are cracked into valuable light products that are separated from heavy, highly aromatic distillates that boil above 650°F (i.e., heavy cat cycle oil {HCCO} and "cat bottoms") (Table VII). The average carbon number estimated for these heavy distillates demonstrates that few of the long side chains in the feeds survive the cracking process.

Furthermore, the HPLC-2 analyses of samples with such high aromaticity must be carefully evaluated for artifacts. In this case, the HCCO exhibits a total mass recovery > 100% (typical of situations where some fractions produce "snow-flakes" which magnify the scattered light in the EMD). A selective magnification of one fraction distorts the normalized HPLC-2 mass distribution for all. For the HCCO, the system reports low 2R mass (percent mass < $\%C_a$) leading to an unrealistically low average carbon number. From independent knowledge of HCCO composition, the diaromatics may be assumed to be C_4 substituted (i.e., to be light enough to be partially lost in the EMD volatilization). The $\%C_a$ from the DAD are independent of boiling point and can be used to estimate the mass for the diaromatics. Assuming a C_4 substituted naphthalene structure, one can apply a 14:10 ratio to the aromaticity and estimate approximately 11% for the 2R mass.

The cat bottoms contain lower concentrations of S, 1R, and 2R, which pushes the limits of the system. The cat bottoms contain > 50% highly condensed aromatics 4R and P (mostly 5+ ring aromatics and refractory *N*-heterocyclics that are marginally soluble in cyclohexane). The recovery for the cat bot-

Table VI. HPLC-2 Analyses for Distillation Fractions of Resid L

	Atm Resid	650–1090°F	1050–1090°F	1050–1150°F	1050–1200	1050–1235°F	>1235°F
% Aromatic carbon							
Saturates	0.06	0.04	0.1	0.11	0.12	0.12	0.05
1-Rings	2.6	3	2.4	2.1	1.9	1.8	0.2
2-Rings	4.5	5.1	4.2	3.9	3.5	3.4	0.6
3-Rings	4.1	4.5	4.1	4	3.7	3.7	1
4-Rings	5.9	4.9	6.4	6.9	7.1	7.4	5
Polars	6	2.7	4.8	5.6	6	6.6	17
Total $\%C_a$	23.2	20.3	22	22.5	22.3	23	24.2
Normalized % weight							
Saturates	24.5	40.5	26.85	23	19.9	18.8	3.6
1-Rings	18.5	19.1	18.3	17.3	16.1	15.5	3.3
2-Rings	21	16.3	18.4	18.3	18	17.7	4.9
3-Rings	14.1	10	12.8	14.4	14.4	14.2	6.1
4-Rings	14.4	9.4	14.7	18.8	18.8	19.8	24.8
Polars	7.5	4.8	9	12.8	12.8	14	57.4
Recovery	106.8	106.5	109.1	106.1	106.1	107.2	82.1
Estimated total carbon number*							
1-Ring	32.1	33.6	40.1	43.2	44.4	44.9	85.7
2-Ring	30	28.8	39	41.6	45.5	46.1	71.4
3-Ring	31.6	28.7	39.5	41.9	48.7	48.1	75.2
4-Ring	42.8	32.2	38	40.6	43.4	43.9	79.1

* Calculated as $N + N \cdot \left(\frac{\text{mass\%} - \%C_a}{\%C_a} \right) \cdot \frac{12}{14}$ where N = the number of aromatic carbons (6, 10, 14, or 18) for 1R, 2R, 3R and 4R aromatics, respectively.

toms is close to 100%, but the polars may actually be underdetermined. Fresh cyclohexane solutions are clear and bright but develop sediment in the autoinjection vials by the end of a run. If the sample is re-analyzed as a methylene chloride solution, the recovery can increase by as much as 5% with the additional weight exclusively in the polars (methylene chloride solutions are not routinely analyzed because that solvent interferes in the 1R/2R separation). In most cases, the cyclohexane results are acceptable because the correction by the normalization is small. For example, the addition of 5% to the raw polars shifts 4R from 45.1 to 43.0% and P from 30.2 to 33.6% when renormalized. These changes are within the precision of the system.

Coking

The data for coking can be contrasted with that discussed for cat cracking. Coking is a thermal conversion process. It redistributes the carbon and hydrogen in the large molecules of a resid into smaller volatile hydrocarbons and a highly aromatic polymer (coke). The resulting heavy coker gas oil (HKGO) is more aromatic than the vacuum resid feed from which it is derived (Table VII). The average carbon number drops in the HKGO consistent with loss of side chains and an increase in aromaticity of the distillate product.

Lubes extraction

Solvent extraction removes multi-ring aromatics from waxy distillate feeds, leaving raffinates enriched in saturates and highly alkylated mono-aromatics with good lube basestock properties. As illustrated by the data in Table VII, HPLC-2 quantitates the increase in multi-ring aromatics in the extract oil and the corresponding decrease in the raffinate.

Conclusion

HPLC-2 has been developed and widely applied as a fully automated system for measuring the distribution of mass and aromaticy of heavy distillates in six fractions (saturates, 1- to 4-ring aromatics, and polars). Separation conditions have been optimized to generate fractions of high "ring-purity", and algorithms have been developed to provide quantitative measurement of the percent aromatic carbon and mass distributions in these fraction. The separation and measurements have been validated by a variety of techniques. Both short- and long-term repeatability and reproducibility have been established at approximately 10% (1s RSD). Examples from six important refinery processes have been used to illustrate the ability of HPLC-2 to detect changes in molecular composition.

Table VII. Refinery Feed-to-Product Comparisons

	Hydrotreating		Cat cracking				Coking		Lubes extraction		
			Refinery A		Refinery B						
	HVGO feed	Product	Feed	Heavy cycle oil	Feed	Cat bottoms	Vacuum bottoms	Heavy Coker gas oil	Waxy lube distillate	Extact	Dewaxed raffinate
Percent aromatic carbon											
S	0.04	0.08	0.08	0.04	0.03	0.01	0.1	0.1	0.01	0.02	0.03
1R	2.6	4.9	2.9	1.2	2.6	0.3	0.7	2.2	3.7	4.5	2.9
2R	6.7	7.2	4.5	14.8	4.1	2.1	1.6	5.7	8	14	1.2
3R	8.4	5.8	2.7	31.6	2.8	7.4	2.1	7.9	5.3	9.9	0.2
4R	10.7	5.7	2.7	21.6	2.6	32.5	7.1	4.6	2	3.7	0.1
P	2.5	1.3	1.7	2.9	1.2	24.8	13.5	11.4	0.8	1.2	0.2
Total $\%C_a$	30.94	25	14.6	72	13.4	67.2	25.2	42.1	19.9	33.4	4.6
Normalized weight percent											
S	40.3	46.7	55.5	14.6	57.3	10.8	9.3	20.1	45.3	22.8	72.3
1R	13.5	19.5	17.9	2.2	16.4	1.7	6.5	9.9	21.5	20	21.9
2R	12.4	11.7	10.9	8	10.4	2	9.6	10.7	19.9	32.5	5.1
3R	12.4	9.6	6.2	39.2	5.7	10.1	9.9	12.5	8.7	16.2	0
4R	18	9.9	6.4	32.4	5.4	45.1	28	25.9	3.3	5.9	0
P	3.4	2.6	3.2	3.6	4.6	30.2	36.5	21	1.3	2.7	0.7
Recovery											
Estimated average carbon number											
1R	28	21	33	10	33	30	49	24	31	24	40
2R	17	15	22	6	23	10	53	18	23	21	38
3R	20	22	30	17	26	18	59	21	22	22	NA*
4R	29	29	39	26	35	24	63	89	28	27	NA
P	24	33	32	22	62	21	44	31	28	37	NA

* NA, data not available.

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