The Use of HPLC to Determine The Saturate Content of Heavy Petroleum Products

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THE USE OF HPLC TO DETERMINE THE SATURATE CONTENT OF HEAVY PETROLEUM PRODUCTS

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ABSTRACT

The refractive index response factors for several pure saturate fractions isolated from heavy petroleum products were determined using a μ-Bondapak aminopropylmethylsilyl bonded amorphous silica HPLC column. The response factors for saturates obtained from asphalts had an average refractive index response factor of 1.06 ± 0.096 V/g and the saturates obtained from industrial supercritical fractions had an average refractive index response factor of 1.13 ± 0.048 V/g. The difference between these two values can probably be attributed to the fact that different researchers prepared the pure saturates. Based on this assumption, it was possible to obtain an overall response factor for saturates from high boiling petroleum materials. The overall average response factor for the saturates from these heavy petroleum products was determined to be 1.10 ± 0.079 V/g. The data collected in this study indicate that petroleum jelly, with a response factor of 1.05 V/g, may be used as an adequate saturate calibration standard for asphalt and asphalt related materials.

INTRODUCTION

Much effort has been expended in determining the chemical composition of asphalt and other heavy petroleum products. Composition data are required by refiners who wish to upgrade their residues. Residue upgrading by catalytic cracking requires that the metals (especially Ni and V) content of the feed be as low as possible so that the catalyst deactivation is minimized. It is widely known that the metals concentrate in the most highly condensed, most polar molecules (asphaltenes) in petroleum residues.[1,2,3] If the content of this highly polar fraction is too high, catalytic cracking may not be economical. In addition, chemical or group-type composition information is necessary, because many residue processing parameters have been determined empirically based on the aromatic and paraffinic contents of the feedstock, in order to maximize yield of high value products.

The chemical composition of petroleum residues is also important to the scientist, especially the asphalt chemist who is interested in correlating asphalt behavior to chemical composition. At least one method for determining composition based on chemical reactivity[4] is routinely used. Generally, these chemical reactivity classification methods only allow for empirical correlations, since the fractionated components are irreversibly altered in the separation process.[5] Although the fractions from such separations can be analyzed individually, the properties determined from individual analyses are undoubtedly not representative of their properties in the unfractionated asphalt.

To eliminate the irreversible changes that the chemical reactivity separation methods produce, several chromatographic techniques for asphalt group-type fractionation have been proposed over the past several decades. Many of the group-type fractionation methods, including the method of Rostler and Sternberg,[4] entail performing a binary fractionation of the material based on solubility in some arbitrary solvent. The solvents of choice typically have been paraffinic hydrocarbons. The insoluble fraction, if present, is separated by filtration and is referred to as the asphaltene fraction, or simply asphaltenes. The paraffin-soluble fraction is called maltenes or petrolenes. It is widely known that the quantity of asphaltenes increases with decreasing carbon number and increased branching in paraffinic solvents. As discussed previously, the asphaltene fraction contains most of the metal-bearing species. The asphaltenes have been shown to be responsible for the highly viscous nature of asphalts.[6,7]

More complicated separations focus on further separation of the maltene fraction. The most well known of these is the column chromatography method of Corbett.[8] This method has since been adapted by the American Society for Testing and Materials (ASTM D4124) as the standard method for determining asphalt composition. In the standard method, the asphaltenes are separated by

precipitation from a 100:1 (vol% n-C_7:wt% sample) solution and the maltenes are then separated into saturates, naphthene aromatics, and polar aromatics by elution chromatography using an open column containing activated alumina. The maltenes are loaded onto the column and solvents of increasing solvent strength are used to elute the various fractions. N-heptane is added to the column, followed by toluene, a mixture of 50:50 (vol%:vol%) toluene:methanol, and finally trichloroethylene.

The saturate-like molecules, having little affinity for the alumina, are eluted first with n-C_7 up to the elution of the n-C_7/Toluene solvent front. The polar aromatics, which are highly retained on the alumina, concentrate at the TCE/Toluene:MeOH solvent front and elute last. The naphthene aromatics elute between the saturates and the polar aromatics. The difficulty of this separation arises from the fact that the solvent fronts are not distinct. In fact, the solvent fronts rarely, if ever, travel down the column uniformly. This is crucial as the separation cut-points are determined by visual inspection and can be highly subjective.

In the mid 1970s to early 1980s, petroleum chemists began to use the relatively new analytical technique of high performance liquid chromatography (HPLC) for group-type analyses of petroleum and coal derived materials.[9-15] One primary advantage of HPLC is the elimination of cut-point subjectivity. Low solvent volume (80 mL vs. 1500 mL), low solvent toxicity (n-C_6 vs. Toluene and TCE), and much shorter analysis times (10-40 min. vs. several days) are additional benefits of using HPLC.

Suatoni and Swab utilized a μ-Porasil packing to perform group-type analyses on several high boiling compounds in one of their earlier works.[9] They concluded that the saturate fractions from different materials with similar boiling points possessed nearly the same refractive index (RI) response factor (RF_s) regardless of crude source. Furthermore, they analyzed several compounds with a wide range of boiling points and they showed that the RF_s was a function of residue boiling point range. In essence, they were able to construct a calibration factor correlation based on sample boiling point.

This is explained by inspecting Figure 1 which shows the refractive index of n-alkanes as a function of carbon number,[16] which is intimately related to boiling point. It has been noted elsewhere that unlike the data of Suatoni and Swab, the data presented in Figure 1 suggest that the refractive index may approach a limiting value.[17]

In a later experiment, Gayla and Suatoni reported data that indicated that the RF_s values for saturates obtained from coal liquids with widely varying boiling points were *identical* for three out of the four materials studied.[15]
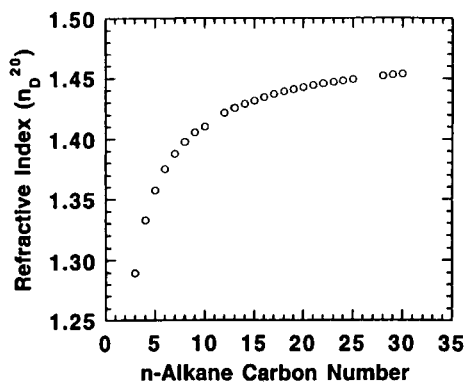
Figure 1. Refractive index of n-alkanes up to C_{30} as a function of n-alkane carbon number. Data taken from Ref. 16.

Dark and McGough performed separation of asphalts using a μ-Bondapak column and multiple solvents to produce 9 separate fractions.[14] They used RF_s values determined from crude oils rather than the RF_s values from the asphalts they investigated to quantify the various fractions. They indicated that the RF_s values were in error, but they concluded that relative comparisons could be made. The reason for this error is evident from Figure 1. Two different crude oils may have widely different average boiling points (average n-alkane carbon numbers), and thus, have widely different RF_s values. Furthermore, the average boiling point of a crude oil is significantly different from the average boiling point of its own residue.

In a later work, Dark concluded that the best agreement between HPLC crude oil saturate content and open column saturate content was obtained when the HPLC saturate content was determined by difference, rather than by direct methods.[18] This work is commonly cited in more recent publications and, as a result, most of the subsequent HPLC studies have focused on determining the content of the aromatic components using various detectors and obtaining the saturate content by difference.[19-22]

In fact, some researchers have abandoned the use of detector calibration altogether, and have instead relied on gravimetric methods.[23] Lundanes and Greibrokk were able to obtain calibration factors for saturates obtained from crude oil residues, but only after GPC fractionation was performed to narrow the molecular weight range (ie. boiling point range) of the sample.[17]

This work is an attempt to determine if accurate quantitation of the saturate content in asphalt and asphalt related materials can be accomplished using refractive index response factors. Because most refiners typically operate their vacuum distillation towers at similar conditions, it is natural to assume that the highest boiling residues (asphalts) should all have similar RF_s values, as demonstrated by Suatoni and Swab. Furthermore, if the RF_s values for high boiling residues are similar, it may be possible to isolate a *suitable* standard saturate calibration material.

MATERIALS

This experiment involved the analysis of industrial supercritical fractions (ISCF) obtained from a number of different refiners, and asphalts obtained from the Strategic Highway Research Program (SHRP) materials reference library (MRL). The other material analyzed in this study is petroleum jelly obtained from a local supermarket.

Supercritical fractions were analyzed because they are typically products of residue upgrading. They are also of interest due to their potential for use as either asphalt additives or asphalt recycling agents. Most currently available recycling agents are by-products of lube oil manufacture.

To minimize the aromatic content in lube oils, the process conditions are typically quite conservative, resulting in recycling agents with high saturate contents. It is recommended, that recycling agents contain no more than 30% saturates in order to produce good quality recycled asphalt mixtures.[24] This is because saturates and asphaltenes are inherently incompatible.

Supercritical fractionation is one potential industrial method for controlling the saturate content in recycling agents. Thus, it is essential to be able to accurately quantify the saturate content in ISCFs. In this work, the ISCFs have been given arbitrary designations to protect the identities of the companies supplying material.

Several "standard" asphalts were obtained from the SHRP MRL. These SHRP asphalts have been studied extensively throughout the world and a large data base of chemical and physical properties exists for these asphalts. The SHRP reference included at the end of this paper is by no means an exhaustive compilation of available data.[25]

METHODS

HPLC Standards Preparation

To perform quantitation of the saturate content in the heavy petroleum products, it was necessary to obtain standard materials. Because it is not possible to purchase "saturates" from chemical suppliers, it was necessary to perform preparative column chromatography to isolate saturate fractions from various petroleum products. Several variations of the Corbett procedure were utilized. Initially, the "pure" saturates were prepared according to the procedure outlined in ASTM D4124. As the experiment continued, this procedure was modified first by substituting n-hexane for n-heptane and then by performing prefractionation according to the "giant Corbett" procedure described by Peterson et al.[26] in order to produce larger quantities of the pure fractions.

The paraffin fraction from the "giant Corbett" procedure was then fractionated following the method in ASTM D4124 to produce a pure saturate fraction and a slightly saturate-contaminated light naphthene fraction. Using these methods, pure saturate fractions were obtained for eight ISCF materials and four core SHRP asphalts.

Instrumentation and Sample Preparation

A WATERS 600E multisolvent delivery system was utilized for gel permeation chromatography (GPC) and HPLC analyses of the petroleum products investigated in this study. Injection was accomplished with a Waters 700 WISP autoinjector. A WATERS 410 differential refractometer (RI) was utilized for sample detection. Data acquisition and processing were performed using Baseline 810 software.

For GPC analyses, helium-sparged HPLC grade tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1 mL/min. Three columns of decreasing pore size of 1000, 100, and 50 Å were utilized in series to accomplish separation.

The 1000 and 100 Å columns are 7.8 mm ID x 300 mm long and are packed with 7 μm ultrastyragel particles. The 50 Å column is 7.8 mm ID × 600 mm long and is packed with 5 μm PLGel particles. Samples were prepared by dissolving 0.2 ± 0.01 g of sample in 10 mL of THF. The samples were then filtered through 0.45 μm PTFE membrane syringe filters and 100 μL aliquots were injected onto the columns. Molecular weight was determined from calibration with polystyrene standards. The columns and detector were operated isothermally at 313.2 K.

For HPLC analyses, helium-sparged HPLC grade n-hexane was utilized as the mobile phase. The flow rate was controlled at 2 mL/min. A single column 7.8 mm ID × 300 mm long packed with 10 μm μ-Bondapak aminopropylmethylsilyl bonded amorphous silica was used for the analyses. The column was backflushed fifteen minutes after injection to speed the elution of the polar aromatics and shorten the analysis time. Samples were prepared by dissolving 0.20 ± 0.01 g of sample in 10 mL n-hexane. The "pure" saturate samples were prepared by dissolving 0.100 ± 0.005 g in 10 mL n-hexane due to the limited quantity of material. Even so, several of the "pure" saturate fractions were exhausted in this study. After the samples were filtered through preweighed 0.45 μm PTFE membrane syringe filters, 20 μL aliquots of the maltene fraction were injected onto the column. Sample elution was monitored by both the RI detector and a UV detector (WATERS 486 Tunable Absorbance Detector). The UV detector was utilized to monitor the purity of the saturate fractions and was operated at a wavelength of 254 nm. The columns and detectors were operated isothermally at 308.2 K. The saturate content was determined from the pure saturate refractive index RF_s, as described in the results and discussion section.

Response Factor Determination

A representative asphalt RI chromatogram is shown in Figure 2. Three peaks are evident. The first, sharp peak signifies elution of the saturates. The second, broader peak is produced by elution of the (naphthene) aromatics. The final peak, which elutes approximately 30 minutes after injection indicates elution of the polars (aromatics). The resolution between the saturates and aromatics, in general, is not sufficient to allow an accurate determination of the saturate peak area. As a result, the peak height is used rather than the peak area for quantitation purposes. The RF_s is calculated by dividing the peak height by the mass of the pure saturate fraction weighed into the scintillation vial.

RESULTS AND DISCUSSION

Pure Saturates

The RF_s values and molecular weights for pure saturates obtained from the 12 different petroleum materials and the petroleum jelly are listed in Table 1. Average RF_s values for asphalt saturates, ISCF saturates, all of the heavy petroleum product saturates studied in this work, and the petroleum jelly are listed in Table 2. It is immediately obvious from the data in Table 2 that the
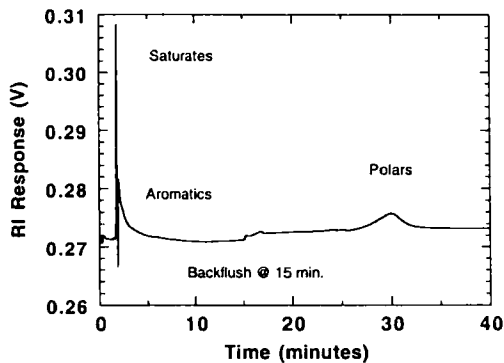
Figure 2. Refractive index chromatogram of SHRP AAC-1 separated on a 7.8 mm by 300 mm μBondapak aminopropylmethylsilylbonded amorphous silica HPLC column using n-hexane as the mobile phase at a flow rate of 2 mL/min.

Table 1

GPC Molecular Weights and HPLC Refractive Index Response Factors for 13 Saturate Fractions

Saturate Source Material	M_n	M_w	RF_s (V/g)
AAA-1	611	842	1.10
AAD-1	515	706	1.02
AAF-1	914	1142	1.24
AAM-1	1576	2285	1.03[a]
ISCF A	970	1328	1.16
ISCF B	934	1322	1.11
ISCF C	1157	1529	1.18
ISCF D	1215	1635	1.19
ISCF E	952	1220	1.09
ISCF F	906	1325	1.11
ISCF G	816	1218	1.13
ISCF H	901	1188	1.05
Petroleum Jelly	800	1164	1.05

[a] Three different "pure" saturate samples analyzed.

Table 2

Average Refractive Index Response Factors for Saturate Groups

Group	RF_s (V/g)
Asphalt saturates[a]	1.06 ± 0.096
ISCF saturates[a]	1.13 ± 0.048
All saturates analyzed	1.10 ± 0.079
Petroleum Jelly	1.05

[a] pure asphalt saturate fractions and pure ISCF saturate fractions isolated by different researchers at different times

saturates from industrial supercritical fractions have a slightly higher overall RF_s than the asphalt saturates. Even though this is expected based on the slightly higher molecular weights of the ISCF saturates, this difference in average RF_s may be attributed to the fact that the ISCF saturates were produced nearly a year after the asphalt saturates and the fact that the two different groups were isolated by different researchers.

Furthermore, the saturate fraction obtained from asphalt AAM-1 has the highest molecular weights of all samples analyzed but has one of the lowest response factors. Therefore, it is natural to conclude, that the variations in RF_s values are due mainly to operator subjectivity (one of the main problems associated with the open column method) and are not indicative of any real difference between the saturates.

This argument may naturally be extended to say that petroleum jelly is similar enough to the asphalt and ISCF saturate fractions that it has the potential for use as a "standard" saturate for the HPLC determination of saturate content in heavy petroleum products such as asphalts. Even if the petroleum jelly does not have *exactly* the same RF_s as the materials examined in this study, it may still be a suitable calibration standard. The petroleum jelly not only has approximately the same RF_s value as the asphalt and ISCF saturate fractions but it is also of similar molecular weight. It should be noted that the molecular weight values reported in Table 1 represent alkanes with carbon numbers between 37 and 112. The molecular weights reported in Table 1 may seem high, but they match values for saturate fractions obtained from both vapor pressure osmometry and field ionization mass spectrometry.[27] The UV chromatograms of all of the saturate fractions analyzed indicated approximately the same amount of UV active species in each fraction, including the petroleum jelly.

Asphalt Saturate Contents

Once it was determined that the saturates from the different asphalts, supercritical fractions, and the petroleum jelly were all similar, it was possible to determine the saturate contents of any unknown sample. This was done by injecting an unknown sample onto the columns and determining the peak height for the saturate fraction. The saturate content in the sample was determined by dividing the sample peak height by the appropriate RF_s and then dividing by the sample mass used and multiplying by 100 to obtain saturate content in terms of weight percent (wt%).

The saturate contents, in wt%, of the eight SHRP core asphalts are listed in Table 3. This table shows the saturate contents of the asphalts determined using the asphalts own saturate RF_s, the average asphalt RF_s, the overall average RF_s, and the RF_s of the petroleum jelly in comparison with values obtained from the literature [Appendix A, Ref. 25]. The values obtained from HPLC calibration using the various response factors are remarkably similar to each other but are, in general, not the same as those obtained from the literature. Upon closer investigation it is evident that the saturate contents determined by HPLC for all of the asphalts except AAD-1 are higher than the literature values. However, this does not mean that the HPLC values are incorrect. In fact, the HPLC saturate contents are probably much more accurate. The differences between the HPLC determined saturate contents and the saturate contents determined by the traditional method can be attributed to the use of different stationary phases for the different analyses. The aminopropylmethylsilyl bonded phase in the HPLC column retains the naphthene aromatics better than the naked alumina in the open column. The increased retention of the naphthene aromatics results in more saturates eluting before the naphthene aromatics elute in the HPLC separation. Data published by Dark support this belief and indicate that even more efficient separation of the saturates and (naphthene) aromatics may be possible using naked silica as the stationary phase.[18] However, using silica as the stationary phase may cause irreversible adsorption of the polar (aromatic) fraction.[9]

The increased retention of the naphthene aromatics and large deviation from the literature saturate value is most evident for asphalt AAM-1. While the use of an average RF_s or the petroleum jelly RF_s might possibly result in a large deviation from the "true" value, it is unlikely that the use of the RF_s for the saturates from AAM-1 would cause the deviations evident in Table 3. That is, using the RF_s for the saturates from a given asphalt should result in accurate saturate contents for that given asphalt. Further support for the inaccuracy of the data obtained from the open column techniques can be seen in the variability of the literature values themselves. The literature saturate contents reported in Table 3 [Appendix A, Ref. 25] differ from other values reported in the same reference [Table 3, Ref. 25].

Table 3

**Saturate Content of SHRP Core Asphalts
Using Various Calibration Standards**

Asphalt	MRL %S	HPLC %S Asphalt's Own RF_s	HPLC %S Asphalt Ave. RF_s	HPLC %S Overall Ave. RF_s	HPLC %S Petroleum Jelly RF_s
AAA-1	10.6	10.8	11.1	10.8	11.2
AAB-1	8.6	--	12.4	12.1	12.5
AAC-1	12.9	--	17.3	16.8	17.5
AAD-1	8.6	7.6	7.3	7.1	7.4
AAF-1	9.6	10.7	12.5	12.1	12.6
AAG-1	8.5	--	9.6	9.3	9.7
AAK-1	5.1	--	6.0	5.8	6.0
AAM-1	1.9	12.0	11.6	11.2	11.7

This only substantiates the statement that the cut-points for the traditional open column technique are subjective, sometimes highly subjective. HPLC techniques eliminate most, if not all, operator subjectivity if a suitable calibration standard is used. The data collected in this study indicate that petroleum jelly may be a suitable standard.

CONCLUSIONS

All of the previous work on HPLC calibration has relied on the tacit assumption that the saturate data from the standard open column separation methods are correct and that the HPLC saturate contents must be determined in such a way as to minimize the difference between the two values even if this requires obtaining the saturate content by difference. This belief that the open column saturate contents represent the true saturate contents has undoubtedly hindered development of HPLC as an analytical tool in characterization of heavy petroleum products even though it has been known for over ten years that bonded phase HPLC provides better separation of the naphthene aromatics from the saturates.

A natural consequence of this is that the saturate contents determined by HPLC should be more representative of the "true" saturate content. Even with improved and/or complete resolution of the saturate and naphthenic fractions, accurate quantitation of the saturate *character* in the asphalt may never

be possible as a molecule containing a benzene ring with an aliphatic side chain with thirty carbon atoms will be grouped as a naphthene aromatic even though it probably exhibits entirely saturate-like behavior in the material.

It has been shown in this study that the refractive index response factors for saturates obtained from heavy petroleum products are similar to each other and to the response factor for petroleum jelly. Therefore, petroleum jelly, with a response factor of 1.05 V/g, may be an *adequate* saturate calibration standard for asphalt and asphalt related materials.

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