Standardized High-Performance Liquid Chromatography to Replace Conventional Methods for Determination of Saturate, Aromatic, Resin, and Asphaltene (SARA) Fractions

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ABSTRACT: One of the main approaches for compositional analysis of crude oils is SARA fractionation in which the sample is separated into saturate, aromatic, resin, and asphaltene fractions based on their polarity. A fully automated standardized SARA analysis for bitumen and heavy crudes has been developed and optimized using three commercial columns packed with different stationary phases based on the combination of adsorption and partition chromatography. The system is equipped with automated six-, eight-, and ten-port switching valves that control the flow direction. In this analytical technique, a bitumen (or heavy oil) sample diluted in toluene is swept through the column by pentane as the primary carrier phase. The sample is separated into four fractions by selective retention through interactions with the solvent mobile phases and the column stationary phases. The poly(tetrafluoroethylene) (PTFE) column filters asphaltenes, ZORBAX CN absorbs resins, and ZORBAX RX-SIL retains aromatics. Three samples of bitumen and heavy oils were fractionated to their SARA fractions by the developed method. Consistent results were obtained, proving the applicability of the new analytical technique to a wide range of crude oil samples. In addition, the performance of the developed SARA high-performance liquid chromatography (HPLC) method was compared with the conventional method, which demonstrates that it is more efficient, cost-effective, and consistent.

INTRODUCTION

The molecular structures of heavy oils and bitumen are highly complex. These complexities make the quantification of each compound very difficult, time-consuming, and expensive. The hydrocarbon-group-type characterization is generally used for the analysis of the chemical composition of crude oils. Liquid chromatography (LC) is one of the main analytical techniques for the analysis of crude oils into subfractions based on the solubility behavior. This method is also known as SARA analysis, in which crude oils are separated into saturate, aromatic, resin and asphaltene (SARA) fractions. Furthermore, SARA analysis would help estimate compatibility for crude oil blending, asphalting stability and fouling tendency, coking propensity, and product stability of crude oils.

The saturate fraction is an oily liquid at room temperature and mostly contains nonpolar hydrocarbons that have linear or branched chains and aliphatic cyclic paraffins. The aromatic fraction is also an oily liquid that has a reddish color and contains molecules that include at least one aromatic ring. This fraction consists of aromatic hydrocarbons with different degrees of condensation, alkyl substitution, and heteroatom content. The resin fraction is dark brown semisolid that contains a higher degree of condensation and heteroatom content compared to the aromatic fraction. Therefore, the resin fraction is often referred to as the polar fraction of the "polars". Asphaltenes contain polycondensed aromatic rings and lateral aliphatic chains. Asphaltenes also can be defined by their solubility range since they are soluble in toluene but precipitated by adding excess n-heptane or n-pentane.

Different methods have been developed and used for SARA analysis of crude oils. The three main methods are (i) gravimetric adsorption chromatography, including ASTM D4124 (standard test method for separation of asphalt into four fractions), ASTM D3279 (standard test method for n-heptane insolubles), ASTM D6560 (standard test method for determination of asphaltenes in crude petroleum and petroleum products), and ASTM D2007 (standard test method for characteristic groups in rubber extender and processing oils and other petroleum-derived oils by the clay-gel absorption chromatographic method); (ii) high-pressure liquid
Several studies have claimed and proved the significant deviations between SARA results generated by ASTM, HPLC, or TLC−FID methods. The results of these different methods can be affected by the eluant nature and molecular weight of the solvents. Gravimetric adsorption chromatography is the most used method for SARA analysis, and we will review this method and its drawbacks in the following.

The original and common approach used for SARA separation is gravimetric adsorption chromatography. The first step of this method is the separation of the asphaltene fraction by adding an excess of an alkane solvent, including n-pentane, n-hexane, or n-heptane. The fraction dissolved in the alkane solvent after deasphalting is called maltenes. This fraction is passed through two columns (i.e., a clay-packed column and a silica-gel column) to retain resins and aromatics, respectively. A saturate is the fraction that is not absorbed by these columns. Desorbing and recovering these fractions can be conducted by applying organic solvents such as toluene or benzene. ASTM D4124, ASTM D3279, ASTM D6560, and ASTM D2007 are described typical approaches for this analysis. In this analysis method, some volatile components of samples may be lost in the evaporation procedure for removing solvents from fractions. Also, this method has been extensively criticized due to the requirement of excessive time and resources, poor reproducibility, and automation issues.

As a part of developing our HPLC technique for SARA analysis, three external commercial laboratories were tasked to perform SARA analysis on identical oil samples (Sample A) with a MW of 513.3 g/mol and a specific gravity of 1.004 (water = 1.0) to demonstrate the shortcoming of the conventional method (i.e., gravimetric adsorption chromatography). Figure 1 shows the results of the SARA analysis conducted by these labs using the conventional method with identical procedures. As Figure 1 illustrates, the results deviate significantly. The results show the average deviations of ±0.96, ±4.37, ±5.81, and ±0.26% for saturates, aromatics, resins, and asphaltenes, respectively. While saturates and asphaltenes have been reproduced adequately, the deviations are significant for aromatics and resins. As can be seen, the results for resins and aromatics vary significantly. The results of SARA analysis are often used in developing pseudocomponents for phase equilibrium calculations, refining, quality control, and design of hydrocarbon processing units and transportation of petroleum products.

HPLC Method for SARA Analysis. HPLC has been used widely for hydrocarbon type separation and identification, including SARA fractionation. Different methods of HPLC such as normal- or reversed-phase columns, isocratic or gradient elution of solvents, column switching, and several detection systems such as UV−visible, evaporative light scattering (ELSD), dielectric constant detector (DCD), and FID are used to achieve the desired separation with a suitable resolution, rapidity, and precision.

Normal-phase HPLC is the classical mode of chromatography that uses a polar stationary phase with a much less polar (nonpolar) mobile phase to separate components. The normal-phase method has been widely used for the determination of the HPLC hydrocarbon type because of the solubility and compatibility of heavy oil samples with nonpolar solvents such as saturated hydrocarbons used in elution. Also, amino, cyano, silica, or diol-bonded silica columns, which are polar stationary phases, can be applied to separate maltenes into saturates, aromatics, and resins based on polarity.

Crude oils are adequately soluble in conventional low-polarity solvents, including cyclohexane, and could be entirely eluted by common normal-phase HPLC solvents. A single column is normally not adequate for separating the whole range of compound polarities in heavy oils. Therefore, multiple columns, column switching, and solvent gradients are often required to separate heavy oils containing an extensive polarity range. In general, the HPLC method is faster, and it has more potential to be automated than gravimetric adsorption chromatography. Many variations of the SARA analysis have been developed, including several automated or semiautomated methods utilizing high-performance liquid chromatography (HPLC).

In conventional HPLC systems, the main difficulty of SARA analysis is associated with the complexity of the sample like heavy oil and bitumen since they contain thousands of molecules with different sizes and polarities. In the HPLC method, the dissolved fractions (saturates, aromatics, resins, and asphaltenes) in a nonpolar carrier phase (n-pentane) are adsorbed on the stationary phase (column) and subsequently removed from the surface using a polar solvent (THF or toluene) and sent to a detector for quantification. Using an abrupt change of carrier-phase polarity (i.e., increasing toluene fraction from 0 to 100%) results in a gradual elution of the analyte, and a sharp and neat peak cannot be obtained. The detector signal would be near to baseline, resulting in an inaccurate analyte measurement. The sharp adjustment in the carrier phase will originate a peak in the detector interfering with the analyte peak.

In this work, to minimize the effect of the primary carrier phase (n-pentane), we have utilized an evaporation method using ethane injection to sweep the columns and then vacuumed the columns to remove the remaining ethane and n-pentane vapor and minimize the carrier-phase signal in the detector.

The current methods of SARA analysis are not able to provide fast, precise, and reproducible analysis. Recently, we developed an automated SARA high-performance liquid
chromatography (SARA-HPLC) method to improve the efficiency, accuracy, and reproducibility of the group-type characterization of heavy oil and bitumen where poly-(tetrafluoroethylene) (PTFE), silica, and cyano columns were nonstandard preparative (packed manually). However, preparative columns do not allow adequate replication of the developed analytical method by other researchers since the packing procedures may vary. To standardize the developed SARA-HPLC and make it reproducible by other researchers, in this work, we introduce standard commercially available packed columns. The original system was modified in different aspects, including the design and configuration of columns, to provide more efficient separation of fractions. The preparative (manually packed) columns were replaced with commercial columns, and the design of the system was improved. The system is fully automated. Samples can be injected without extensive sample preparation and asphaltene separation.

The rest of this paper is organized as follows: the principle and the design of the system are first presented. Then, the performance of the system for SARA fractionation of three heavy oil and bitumen is demonstrated.

**EXPERIMENTAL PROCEDURES**

In our previous study, the fully automated HPLC system was equipped with three columns that were preparative (manually packed) in our lab with silica, cyano, and PTFE to separate asphaltenes, resins, and aromatics, and the fraction that was not adsorbed by these three columns was quantified as saturates. 

Silica has an active, hydrophilic surface that contains acidic silanol functional groups. The polarity of the silica surface can be transformed selectively by chemically bonding it to its less polar functional groups such as cyanopropylsilyl [CN], n-octylsilyl [C8], and n-octadecylsilyl [C18, ODS] moieties on silica, in order of decreasing polarity. 

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Figure 2. Schematic illustrating the SARA-HPLC setup including columns and multiposition valves (A position and B position).

Figure 3. Schematic of the SARA-HPLC system including columns and carrier-phase switching.
In this work, we aim to replace the previous columns packed with silica and cyano with commercial columns to improve the separation of fractions and establish a method that can provide consistent, repeatable, and accurate SARA fractionations for a wide range of samples. The PTFE column remained the same as in our previous work and it is not commercial; however, a guard column (50 × 7.5 mm, 3 μm, PL 1110-1320) was purchased and added prior to entering the sample into three columns to enhance the asphaltene filtration and have better separation from the resin fraction. The materials used in the guard columns are Agilent HC-C18(2) and TC-C18(2) packings, which provide physical filtration for analytical columns. In addition, the use of commercial columns allows the developed SARA-HPLC method to be readily implemented by other researchers. All of the commercial columns were purchased from Agilent Technologies, Inc. The cyano column was replaced with ZORBAX CN (4.6 × 250 mm, 5-micron, P.N. 880952-705), and the silica column was replaced with ZORBAX RX-SIL (4.6 × 250 mm, 5-micron, P.N. 880975-901). The sample is swept through columns by the primary carrier phase of n-pentane, and both columns of PTFE and guard column filtered asphaltenes, which are precipitated in the extra volume of n-pentane. ZORBAX CN containing cyano will absorb resins due to its unique selectivity for polar organic compounds like resins, and ZORBAX RX-SIL consisting of silica will retain moderately polar organic compounds like aromatics.

In our previous work, we noticed that there is a possibility of asphaltene precipitation in the line prior to entering the PTFE columns. Therefore, the system design and a CLICK PLC (programmable logic controller) were modified to be able to improve the asphaltene separation. Moreover, the guard column was added to separate the asphaltene particle with a small size that might not have been filtered by PTFE columns. The columns are coupled together by automated six-, eight-, and ten-port switching valves that control the flow path of solvents, as shown in Figure 2. As the figure illustrates, each valve has two positions A and B that give us the ability to design SARA-HPLC.

**SARA-HPLC Process.** Figure 3 illustrates the process of SARA analysis by the developed method, including the separation and column switching sequence. Normal pentane as the primary carrier phase with a flow rate of 1.3 mL/min is used to sweep 50 μL of the sample (crude oils dissolved in toluene at various concentrations between 0.04 and 0.1 g/mL) out of the sample loop and sent it into the columns. Therefore, asphaltenes precipitated on the PTFE and guard columns due to an extra volume of n-pentane. Simultaneously, a very high polar compound (resins) was retained on the ZORBAX CN column, and ZORBAX RX-SIL absorbed the rest of the polar compounds (aromatics). The saturate fraction is not absorbed by these columns and sent to waste. Then, ethane gas is streamed to sweep pentane out of the column, and ethane is thoroughly vacuumed afterward. Ethane does not strip any adsorbed component from the columns since it is n-alkane lighter than n-pentane. Furthermore, n-pentane can be removed from columns by evaporation to the vapor phase (ethane-rich phase). In the previous study, we applied propane in this step; however, we cannot use it here since the commercial columns are more densely packed than preparative ones and require higher pressure to sweep the columns. This range of pressure cannot be supplied by a propane tank. As a result, we use ethane that can be flowed through the columns followed by vacuuming to minimize the remaining n-pentane in columns.

**UV–Visible Detector for SARA-HPLC.** For analysis of fractions, UV–vis detectors are appropriate for aromatics and polars, but they are not able to detect saturates under the situations used in conventional HPLC detection. Generally, sample preparation and cleanup are essential for detecting and quantifying specific sample components. However, UV–vis detectors have been used to determine specific components in complex heavy oil samples with no need for extensive sample preparation and cleanup.

In this study, Agilent 1290 high-performance liquid chromatography (HPLC) with a UV detector was applied for the analysis of fractions. Each fractionated group except saturates was then swept out of the column by toluene and sent to the UV detector for quantification. The UV wavelength of the detector is set at 300 nm based on UV–vis spectra of aromatics, resins, and asphaltenes. For brevity, further details of UV–vis spectral results are explained elsewhere.

**Automation: Pump and Valve Programs.** A CLICK PLC (programmable logic controller) supplied by Automationdirect was programmed and utilized; therefore, timing can be set, and the analysis can be performed fully automatically. The complete automation of the SARA-HPLC process, including different steps and timing, is listed in Table 1.

**Table 1. General Automation of the SARA-HPLC System Consists of Programming the Timetable and the Position (A or B) of the Valves**

| steps | time event | duration (min) | valve position |
|-------|------------|----------------|----------------|
| (0) sample loading/ sample injection | t₀ | 5 | A | B | A | A |
| (1) sweeping sample by pentane | t₁ | 20 | A | A | A | A |
| (2) drying column by ethane (vacuuming) | t₂ | 110 | A | B | A | B |
| (3) ethane vacuuming | t₃ | 55 | A | B | A | B |
| (4) sweeping aromatic sample to the UV–vis detector | t₄ | 10 | B | A | B | A |
| (5) sweeping resin sample to the UV–vis detector | t₅ | 10 | B | A | B | A |
| (6) sweeping asphaltene sample to the UV–vis detector | t₆ | 10 | B | A | B | A |
| (7) preparation (saturating column with pentane) | t₇ | 20 | A | A | A | A |

Complete analysis, including system reconditioning, needs about 240 min per run. After each run, the device resets automatically and is ready for the next run. Automation helps to minimize human error and improve the performance of the system in terms of accuracy and consistency.

**RESULTS AND DISCUSSION**

First, an oil sample (Sample A) with a MW of 513.3 g/mol and a specific gravity of 1.004 (water = 1.0) provided by local oil producers in Alberta, Canada was analyzed using the developed SARA-HPLC. Further characterization of the sample is explained in the Supporting Information. Three different concentrations of the sample were prepared by...
dilution in toluene. An aliquot (50 μL) of the solution (sample dissolved in toluene) is injected for each analysis.

Figure 4 shows the chromatogram of the SARA analysis of the sample. The main target is to establish a dilution ratio in which the peak area versus bitumen sample concentration follows a linear trend. As a rule of thumb, the peak height for the UV detector is recommended to be less than 1 AU.24 As Figure 5 illustrates, the relation between the bitumen sample concentration and area of chromatograms for asphaltene, resin, and aromatic fractions is linear, which shows the linearity of the detector response to the injected sample amount. These results illustrate that the developed method is capable of running SARA analysis for a wide range of sample concentrations. The optimum sample concentration was obtained in the range of 0.04-0.1 g/mL.

SARA analysis was repeated three times for sample A at a concentration of 0.06 g/mL, as shown in Figure 6. Also, for measuring the repeatability of the system, the relative standard deviations are calculated and reported as 2.21, 1.68, and 0.60 for asphaltene, resin, and aromatic fractions, respectively, which validate the repeatability of the developed method. Standard fractions for SARA fractionation calibration are not available. Therefore, the current setup was scaled up to obtain asphaltene, resin, and aromatic fractions to obtain calibration suitably. In this setup, we used two preparative columns (12.2″ L × 1.7″ ID) packed with cyano and silica. First, the ASTM D2007 standard was applied to separate the asphaltene fraction. Then, the remaining maltene dissolved in n-pentane was swept through the columns. Resin and aromatic fractions are absorbed by the cyano and silica columns, respectively. Toluene was used to sweep out fractions from preparative columns, similar to the procedure of SARA-HPLC. Calibration was obtained by running three concentrations of asphaltene, resins, and aromatics diluted in toluene. Figure 7 demonstrates the results of calibration. As this figure shows, the relationships between chromatogram peak areas and fraction (i.e., asphaltenes, resins, and aromatics) concentrations are linear, which is favorable in chromatography.

The developed SARA-HPLC method was used to obtain SARA fractionations of three oil samples. The samples were provided from oil producers in Alberta, Canada. These samples are produced in a different location in Alberta, so they are different in terms of properties, as illustrated in Table 2. Specific gravities were obtained by an Anton Paar DMA 5000 densitometer, and the molecular weights were obtained by a vapor pressure osmometer (VPO). More characterization is explained in the Supplementary Information.

Sample A was the sample sent to external laboratories to perform conventional SARA analysis and was also used for generating calibration curves. Table 3 indicates SARA analysis as well as the absolute average deviation for three samples in different concentrations as calculated after calibrating the system. It should be noted that the saturate fraction is obtained by material balance calculations since the UV detector is not able to detect saturates. The results prove that the developed SARA-HPLC system is independent of sample dilution in the...
range of 0.04−0.1 g/mL, demonstrating the reliability of the system.

Figure 8 illustrates the results of three SARA analyses in the different concentrations completed for sample A. As the figure shows, asphaltene and saturate fractions in the SARA-HPLC method for sample A are comparable to the results from commercial laboratories presented in Figure 1. Since the resin and aromatic fractions from these laboratories vary significantly with the average deviations of ±5.81 and ±4.37, respectively, we have no solid reference for comparison. In general, the developed SARA-HPLC shows better repeatability for resin and aromatic fractions, with the average divisions of ±0.9 and ±1.2, respectively, compared to the generated results by the external laboratories using the conventional method. The SARA-HPLC analysis takes 240 min, whereas the conventional method can take 3−5 days, and it also needs less solvent compared to conventional commercial methods. Furthermore, as demonstrated, the developed method can be used for SARA fractionation of diverse crude oils. Additionally, the use of commercial columns in the developed SARA-HPLC method makes it standardize and eliminates the inconsistencies of the conventional SARA fractionation approaches such as ASTM D4124, ASTM D3279, ASTM D6560, and ASTM D2007.

**CONCLUSIONS**

SARA analysis is widely used for the compositional analysis of crude oils. Different methods are available for this analysis; however, these methods are not capable of providing accurate, repeatable, and reliable results. Therefore, a new fully automated standardized SARA-HPLC system equipped with commercial columns and multiposition valves was developed to be able to separate SARA fractions. Since there is a high demand for running fast, accurate, and reliable SARA analysis using commercial columns, our system gives us the ability to further advance the SARA fractionation technique to replace current approaches including ASTM D4124, ASTM D3279, ASTM D6560, and ASTM D2007. Furthermore, the developed method in this work is well-defined, allows consistent and reproducible measurements, and can be implemented and replicated by other researchers.

Table 2. Specific Gravity and Molecular Weight for Three Oil Samples A, B, and C

| sample  | specific gravity at 20 °C | molecular weight (g/mol) |
|---------|--------------------------|--------------------------|
| sample A | 1.004                    | 513.28                   |
| sample B | 1.021                    | 563.17                   |
| sample C | 0.953                    | 440.34                   |

Table 3. SARA Analysis Results for Three Oil Samples A, B, and C in Different Concentrations

| SARA fractions | sample A | sample B | sample C |
|----------------|----------|----------|----------|
|                | concentration of oil sample diluted in toluene (g/mL) | mean ± δ |
|                |          |         |          |
| asphaltene     | 0.04     | 16.73    | 16.4 ± 0.9 |
|                | 0.06     | 17.50    | 16.81     |
|                | 0.08     | 15.05    | 15.59     |
| resin          | 15.23    | 18.61    | 16.3 ± 0.9 |
|                | 15.88    | 21.03    | 19.69     |
|                | 17.68    | 21.92    | 21.92     |
| aromatic       | 36.72    | 38.86    | 38.8 ± 1.2 |
|                | 38.99    | 34.04    | 32.51     |
|                | 39.90    | 36.72    | 36.72     |
| saturate       | 31.31    | 38.86    | 38.8 ± 1.2 |
|                | 31.87    | 34.04    | 32.51     |
|                | 32.78    | 36.72    | 36.72     |

Average deviation: $\delta = \frac{1}{n} \sum |(x_i - \mu)|$. 

Figure 7. Calibration curve of (a) asphaltenes, (b) aromatics, and (c) resins.

Figure 8. Results of SARA analysis for sample A repeated three times in different concentrations.
**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01880.

Additional characterization details for oil samples including molecular weight distributions of three oil samples A, B, and C (PDF)

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**Notes**
The authors declare no competing financial interest.

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