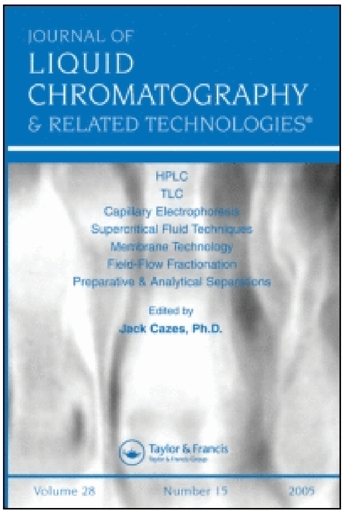

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DETERMINATION OF THE COMPOSITION OF COMMINGLED CRUDE OIL STREAMS BY HPLC-SEC WITH UV AND IR DETECTION

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ABSTRACT

An analytical method utilizing the HPLC-SEC fingerprints of crude oils derived from UV-DAD and IR detectors is presented. It can determine rapidly and accurately the contribution of different crude oils in pipeline mixtures and in commingled production streams.

The method makes use of differences in the distributions of characteristic groups present in the petroleum mixtures throughout the entire molecular weight range to identify and quantify the constituents. An overdetermined system of equations, having as unknowns the mass fractions of the oils in the mixture, is solved iteratively to minimize the error between the signal of the mixture and of the reconstituted.

Case studies are presented to show the successful application of the method in reservoir and production engineering applications.

INTRODUCTION

Efficient management of oil reservoirs produced from commingled layers requires the exact knowledge of the contribution of the individual production streams in the total production. Often, hydrocarbon fluids recovered from different depths of the same reservoir or from adjacent formations have similar geological origins and therefore compositions. Consequently, the conventional compositional characterization methods are not adequate for discriminating the fluids as they exhibit similar physical and chemical properties.

Furthermore, in order to minimize the cost of offshore installations, crude oils from different reservoirs/fields are often driven onshore through the same pipeline. In such cases, the problem of allocating production can be difficult to solve, using solely the physical properties of each individual stream or the gas chromatographic analysis of the effluents.

An analytical method utilizing the HPLC-SEC fingerprints of the crude oils derived from optical detectors could determine characteristic differences in the composition of the constituents to allow discrimination.

THEORY

Gas chromatographic (GC) analysis is until now the most commonly used separation technique for the identification of oils. In this context, chromatographic separations of oils have been used to provide information about the productivity of separate zones in layered reservoirs[1] and the contribution of separate wells in a commingled production stream. Molecular weight distributions (fingerprint analysis) of crude oil samples recovered from different depths can aid in detecting compartmentalization in a reservoir and can contribute towards the determination of compositional gradients.[2,3] This type of information is extremely important for the development and the production planning of the oil fields. Fingerprint analysis of oils has also been used to identify the origin of oil spills found in the environment. Several analytical methods have been employed for this purpose, including GC and GC-MS analysis for the determination of paraffin and isoprenoid distributions,[4] HPLC for the analysis of crudes into functional groups, and HPLC for the determination of the molecular weight distributions.

Optical detectors, such as the fluorescence and the UV, have found wide application as they exhibit high sensitivity in monitoring characteristic chromophore groups. Gray et. al.[5] presented rapid fingerprinting of oils using total scanning fluorescence spectroscopy.

A method for the monitoring of the polyaromatic hydrocarbons in the oils using the same analytical technique was also presented.[6] The UV detector responds to the presence of aromatic and heteroatom compounds in the oils and the recorded absorbance is related mainly to the number of unsaturated bonds. The spectra of the various aromatic groups differ from each other in terms of their intensity and their absorbance range. These differences can be used to determine, quantitatively, the mass percent of the oils present in a mixture, as the absorbance of the mixture at any wavelength is equal to the absorbance of the oils weighted by their mass concentration. The analytical columns used for SEC can achieve separation of the effluent according to the molecular size and offer the opportunity of exploiting differences in the distribution of the chromophore groups contained in the various molecular weight cuts.

Infrared detection can also be used for fingerprinting crude oils as their IR spectra can identify chemical structures and monitor the presence of certain compound classes in the mixture.[7] For hydrocarbons, the vibrations of the C-H bonds occur around 3000 cm^{-1} and the signal of an IR detector connected to an HPLC-SEC system in this region can be counted as selective response of the saturated components which are distributed in the oil.

EXPERIMENTAL

The HPLC system that was used in this study consists of a pump (Waters model 600) and a Diode-Array Detector (Waters model 996) and uses the Millenium software package for data acquisition and analysis. The analytical part of the system consisted of two HPLC-SEC columns, an Ultrastyragel 500 A one from Waters and a Plgel 50 A from Polymer Labs. The mobile phase (chloroform, HPLC grade from Labscan) was filtered through a 20μ membrane filter and degassed with He. The flowrate was set at 0.75 mL/min and the column oven was thermostatically controled at 35°C. The analysis time was 30 minutes. The samples were injected through a 20 μL loop. The ambient temperature in the laboratory changed less than 1°C during the analysis.

It was realized that for oils with strong presence of high molecular weight compounds, such as the oils that were being studied, the procedure for preparing the mixtures and the diluted samples strongly influences the performance of the method. In the beginning, lack of repeatability was observed in the shape of the UV fingerprint between runs of the same fluid. This problem was attributed to the high content of the asphaltenes fraction which has been reported to exhibit self assembly micellar and colloidal behavior.[8] This behavior has been observed to be associated with a critical concentration above which asphaltene monomers coagulate and form larger micelles. The micelles concentration was found to change as they flow through SEC columns due to dilution effects. As a result, the profile of the UV-DAD fingerprint that is produced is not repeatable and its use for identification purposes should be avoided.

To tackle this problem, samples of the oils were recovered from the container to prepare the solutions after the fluid had been subjected to intensive homogenization in an ultrasound bath for 15 min. The solutions were prepared immediately after and were directly injected into the HPLC system.

Experience showed that fingerprints obtained from freshly prepared solutions were different from the ones acquired from the same sample after it had been kept for a long time. These differences were more pronounced in the high molecular weight range and can be interpreted as a result of the formation of colloidal structures that can be created in the solution over time.

Additionally, a series of injections were performed in order to determine the influence of the concentration of the sample on the repeatability of the detector's response. The analysis has shown that a dilution factor of 20 and higher gave repeatable fingerprints.

Three case studies were used to verify the method. The first case was a commingled stream composed from two crude oils produced from reservoirs located 2 miles apart which are considered as belonging to the same basin. The geochemical analysis of the crudes showed that they originated from similar organic matter. The two stock tank oils (STO), (referred to as Oil#1 and #2), were heavy black oils with densities of 870 and 910 Kg/m^3 at 20°C respectively. Their asphaltene content was 4.0 and 7.5 weight percent. Based on the differences of their physical properties (density, sulfur content) the accurate calculation of the mass percent of each oil in the commingled production could not be achieved.

The second case study was a pipeline stream composed from three crude oils (referred to as R#1, #2, #3) not exhibiting apparent similarities in their chemical compositions and which were produced from different reservoirs. Their densities were 767 835 and 860 kg/m^3 and their C12+ mole fractions were 0.08, 0.38 and 0.44 respectively.

The third case consisted of a mixture of crude oils produced from three zones of the same anticline. The fluids in these zones are believed to be isolated from each other by impermeable clays. The three oils (referred to as

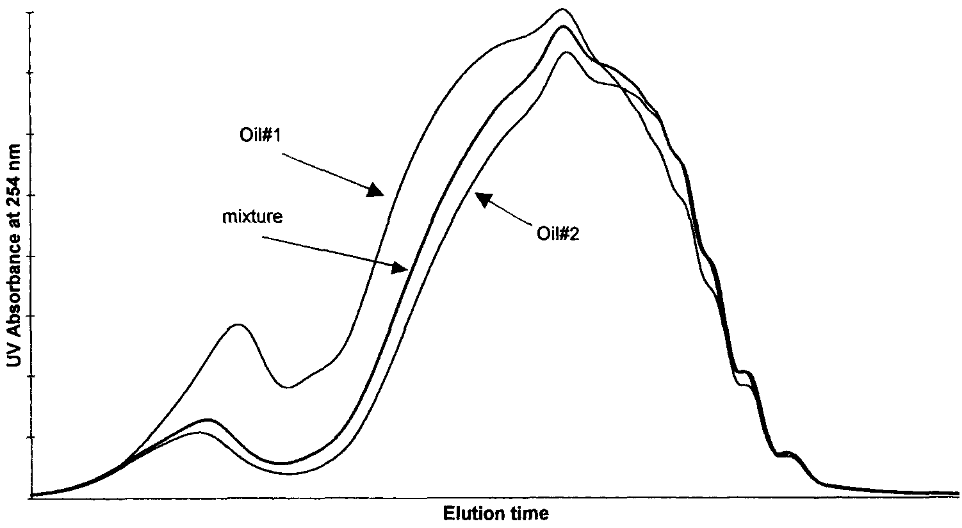

Figure 1. HPLC-SEC UV-DAD fingerprints of the two oils and of one of their mixtures.

Zone#A, #B, #C) had density of 871 kg/m^3. The C7+ molar fractions of the samples were determined by GC to be 0.81, 0.83 and 0.84 respectively. The obtained GC chromatograms had similar shapes and the group type analysis by HPLC gave very similar answers.

Case Study 1

The two oils have a high content of aromatics and heterocompounds and therefore the use of their UV-DAD absorbance was selected for their identification. Three approaches have been investigated.

The first one consisted of exploiting the information of the fingerprints at a given wavelength. Figure 1, presents the UV fingerprints at 254 nm of the two oils and of a mixture prepared from those two. As expected, the molecular distribution of the latter lies between the fingerprints of the constituents. This was also confirmed for the fingerprints recorded at any wavelength between 254 nm and 450 nm.

The signals as they are shown in Figure 1 were transformed into an ASCII file using the time slicing method which contained 100 time values and 100 absorbance values. Subsequently, the absorbance values were corrected

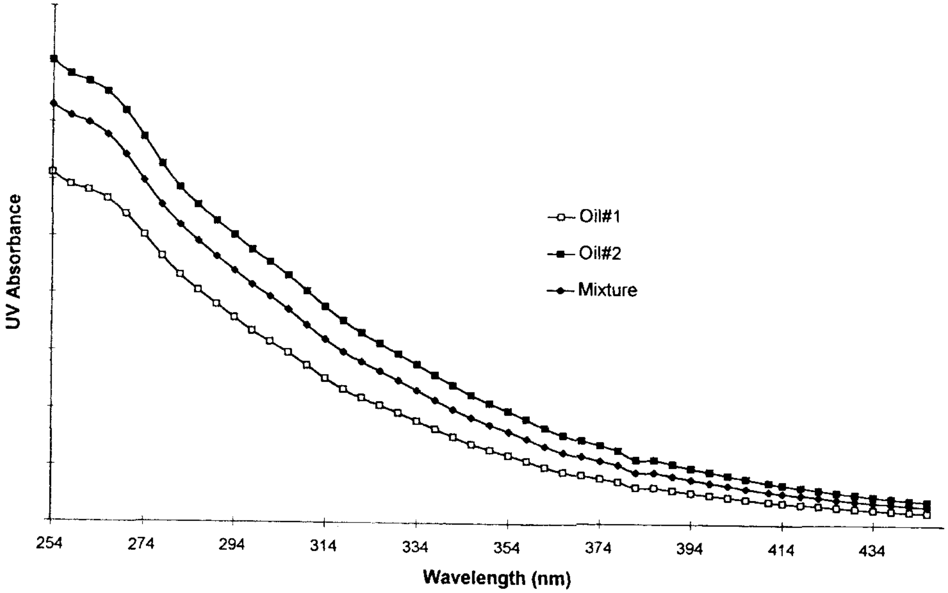

Figure 2. Absorbance of the two oils and of one of their mixtures vs wavelength.

Table 1

Case Study 1 - First Approach

Mixture Composition (% Weight)		Calculated Composition (% Weight)	
Oil #1	**Oil #2**	**Oil #1**	**Oil #2**
29	71	28	72
52	48	50	50
60	40	59	41
69	31	69	31

according to the concentration of the injected solutions for equal injected masses. An overdefined system of 100 equations having as unknowns the mass fractions of the constituents was solved iteratively to minimize the error between the signal of the mixture and that of the reconstituted one. Table 1 presents the results obtained with this method.

Table 2

Case Study 1 - Second Approach

Mixture Composition (% Weight)		Calculated Composition (% Weight)	
Oil #1	**Oil #2**	**Oil #1**	**Oil #2**
93	7	93	7
53	47	54	46
79	21	81	19

Table 3

Case Study 1 - Third Approach

Mixture Composition (% Weight)		Calculated Composition (% Weight)	
Oil #1	**Oil #2**	**Oil #1**	**Oil #2**
70	30	71	29
50	50	48	52
30	70	30	70

The second approach consisted of exploiting the total absorbance of each sample obtained between 254-450 nm with a step of 4 nm (Figure 2). An overdetermined system of 49 equations, having as unknowns the mass fractions of the oils in the mixture, is solved iteratively. The results obtained for this test case are presented in Table 2.

The third approach is a simplified variation of the previous one that can be used with variable wavelength UV detectors. The total absorbance acquired at 265, 285, and 295 nm was calculated for each run after the signals were corrected for equal sample mass injected. Subsequently, the ratios of the areas were determined by two. These values are affected by the presence and concentration of the chromophore groups in the sample. A system of three equations was written having the mass fractions of the constituents as unknowns. Table 3 presents the results obtained using this method.

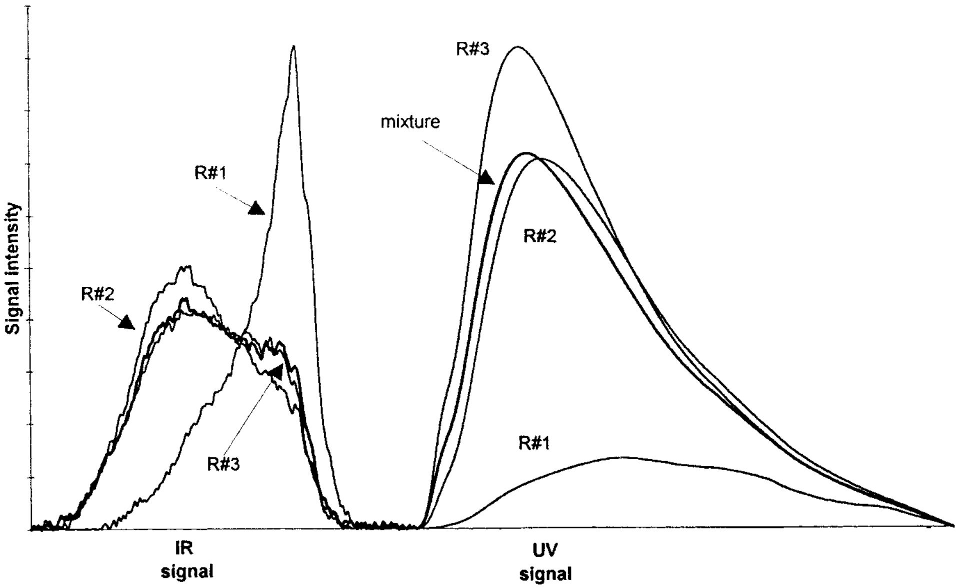

Figure 3. HPLC-SEC IR (2990 cm^{-1}) and UV (290nm) fingerprints of the three STO samples and of one of their mixtures.

Case Study 2

The method described above was applied to the case study of a commingled pipeline mixture comprised of three streams. In this case, the quantitative determination of the composition of the mixture based on the UV fingerprints gave significant inaccuracies. It was decided to implement a second optical detector to generate additional information.

A Foxboro Infrared Detector Miran-1A was connected in series to the UV-DAD detector. Carbon tetrachloride had to be used in this case as a solvent because it is transparent at the 2990 cm^{-1} region where the C-H bond intensively absorbs (stretching).

A third column (Plgel 50 A from Polymer Labs) was also added to improve separation. 290 nm was selected as the wavelength for the monitoring of the UV signal as CCl_4 cuts-off at 265 nm. The analysis was completed in 35 minutes. The samples were prepared at a dilution of 1:50. Figure 3 shows the IR & UV signals of the three oils and of one of their mixtures.

Table 4

Case Study 2

Mixture Composition (% Weight)			Calculated Composition (% Weight)		
R#1	R#2	R#3	R#1	R#2	R#3
20	30	50	19	31	50
11	45	44	9	45	46

The mass fractions of the constituents were determined as the solution of a system comprising of 200 equations which were formed from the two signals using the same time slicing method as above. Table 4 contains results obtained for mixtures of different compositions.

Case Study 3

The developed method was also applied for the quantitative discrimination of a commingled reservoir fluid stream produced through the same production tubing. In this case, the compositions of the three zones were very similar and the differences that their fingerprints exhibited were minute. Figure 4 shows the UV & IR STO fingerprints of the three zones and of one of their mixtures.

The problem could not be solved by solely using any of the two fingerprints as their shapes were very similar. On the contrary, when the two signals were combined in the same system of equations as in Case Study 2 satisfactory results were achieved. Table 5 presents typical results from several mixtures of the crude oils from the three zones.

CONCLUSIONS

HPLC-SEC combined with UV-DAD and IR detection can be a powerful tool in analyzing petroleum mixtures and in identifying and quantifying their crude oil constituents. The data that become available include various information about the presence and concentration of the saturates, unsaturates compound classes and the heteroatoms of the fluids together with their distribution in the molecular weight range. The signals which are obtained

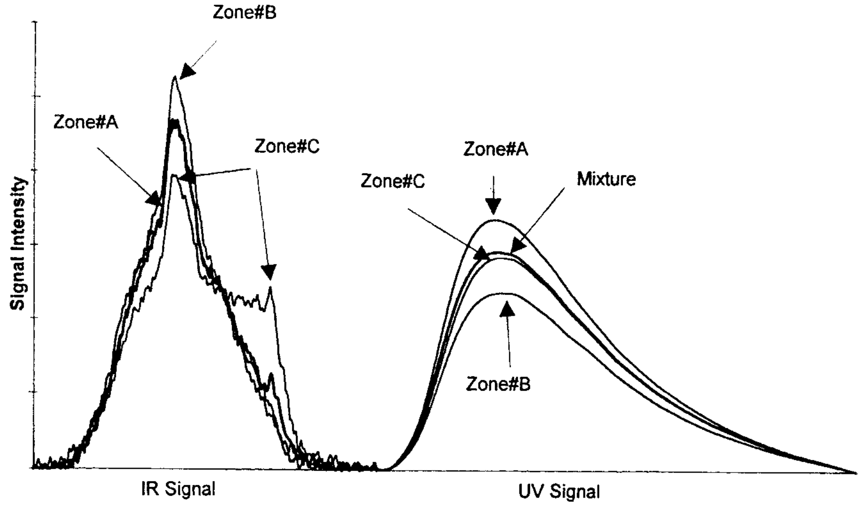

Figure 4. HPLC-SEC IR (2990 cm^{-1}) and UV (290 nm) fingerprints of the STOs from the three reservoir zones and of one of their mixtures.

Table 5

Case Study 3

Mixture Composition (% Weight)			Calculated Composition (% Weight)		
Zone #A	**Zone#B**	**Zone #C**	**Zone #A**	**Zone #B**	**Zone #C**
20	30	50	19	27	54
20	30	50	21	30	49
20	30	50	21	32	47
30	30	40	32	29	38
40	40	20	38	37	25

provide unique fingerprints for each sample. For simple cases where only two constituents are involved, interpretation of any one of the two signals can provide the correct answer. Cases where more than two fluids are involved, even if they exhibit minute compositional differences, can be solved by combining the UV and IR fingerprints.

The method was successfully applied for the determination of the contribution of different crude oils in pipeline oil mixtures and in commingled production streams.

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