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Group-type characterization of crude oil and bitumen. Part II: Efficient separation and quantification of normal-paraffins iso-paraffins and naphthenes (PIN)

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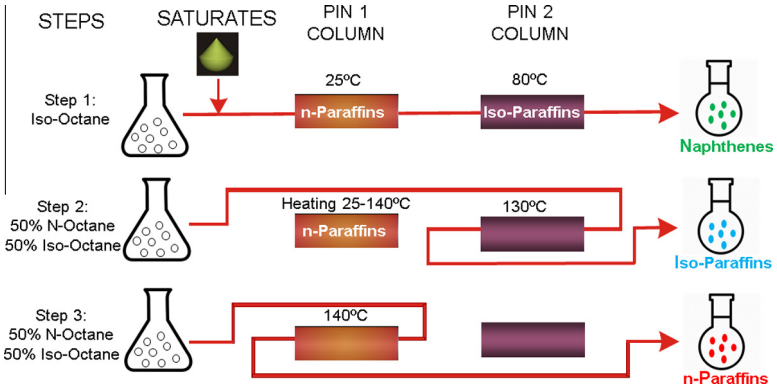
GRAPHICAL ABSTRACT



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ABSTRACT

The SARA (saturates, aromatics, resins, and asphaltenes) separation and quantification have been widely used for characterizing the composition of crude oil and bitumen. The saturate hydrocarbons are the most valuable fraction of the oil industry and contain vital geochemical information for determining the origin and formation of petroleum fluids and for assessing the hydrocarbon potential and sedimentary environment of source rocks. It is therefore necessary to further separate the saturate fraction into normal paraffins, iso-paraffins and naphthenes (PIN fractions). Nevertheless, the convenient approach of PIN separation has never been reported on in the literature. Here, we present an efficient method that allows us to further separate the saturate fraction of crude oil or bitumen into PIN fractions through the automated multi-dimensional high performance liquid chromatography system (AMD-HPLC). In essence, the system is equipped with a "PIN1" column (Silicon: S_{115}) packed with a 5.4 Å molecular sieve and a "PIN2" column (Silicon: 50%S_{115} + 50%S_{130}) packed with a 6.2 Å molecular sieve. Each set of columns is connected in a series via multi-position valves that allow a given column to be inserted "in" or to be by-passed "out" of the flow path of the mobile phase at pre-set times in the process. When use iso-octane and n-octane or their mixture as mobile phases, the system separates the saturate hydrocarbon into PIN fractions simply through three steps under a temperature range of 25–140 °C. An entire PIN analysis cycle takes nearly 60 min, including system re-conditioning. The separated PIN fractions can

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be quantified using either gravimetric method or evaporative light scattering detector (ELSD) technique. Experimental results exhibit excellent qualitative and quantitative capability.

1. Introduction

The compositional analysis of crude oil and bitumen provides important geochemical information for assessing source-rock potential and crude oil provenance in petroleum system analysis projects and for understanding and predicting asphaltene, paraffin, and heavy organics deposition in production, transportation and processing operations. An essential approach of this analysis is the group-type separation of the components of petroleum fluid into saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes (SARA fractions) [1–3]. These separations are necessary to determine the relative concentration of each chemical group and to obtain high purity fractions for subsequent analyses, for example, gas chromatography (GC), gas chromatography mass spectrometry (GC–MS), and isotope-ratio mass spectrometry [4 in press]. The saturate fraction that comprises normal paraffins, iso-paraffins, and naphthenes (PIN) is the most valuable fraction of the oil industry. The relative distribution and abundance of the saturated hydrocarbons have been commonly used to calculate a series of parameters that indicate thermal maturation and hydrocarbon potential of source rocks, for example, the carbon preference index (CPI) [5,6], odd–even predominance (OEP) [7], and naphthene index (NI) [8]. In addition, many of the critical biomarkers occur in the saturate fraction, particularly in the iso-paraffin and naphthene fractions. In petroleum geology and geochemistry, biomarkers have been routinely used to determine the origin and formation of petroleum fluids and the sedimentary environment of source rocks. Although biomarkers present in extremely small quantities in normal crude oil and bitumen, their concentration from the major components is critical if meaningful interpretation of their presence is to be pursued. As a consequence, it is necessary to further separate the saturate fraction into normal paraffins, iso-paraffins, and naphthenes, in other words, PIN fractions.

Traditional methods of group-type separation entail a preliminary "de-asphaltening" with suitable alkane solvents and a subsequent separation of the soluble portion (maltenes) into saturates, aromatics, and resins using open-column elution chromatography or medium-pressure liquid chromatography. However, extensive observations on the effectiveness of these separation procedures have revealed serious inadequacies [9–12]. One of the most significant problems is the extensive cross contamination of the separated SARA fractions as revealed by GC, GC–MS, infra-red spectroscopy (IR), ultraviolet spectroscopy (UV), and most vividly, by re-chromatography of the high performance liquid chromatography (HPLC) of typical SARA fractions derived from the traditional separation methods. To improve the efficiency, accuracy and reproducibility of the group-type characterization of crude oil and bitumen, we recently reported on a novel automated multi-dimensional high performance liquid chromatography (AMD-HPLC) for SARA separation and quantification [4 in press]. This system could fractionate an oil sample of less than 0.1 g into SARA fractions without prior de-asphalteneing. Once a sample is injected, the computer-controlled instrument runs unattended during fractionation and column regeneration. The instrument resets itself and is ready to being the next run. Compared with other methods that commonly require several hours [11,12] or even several days [13–15] per run, an entire analysis cycle of the AMD-HPLC requires nearly 60 min, including system re-conditioning [4 in press].

The further separation of the saturate fraction into individual PIN fractions is even more complex than the SARA separation if traditional methods are used. The first step of these methods often entail urea adduction or molecular sieve occlusion of n-paraffins and subsequent decomposition of the sieve to recover the n-paraffins (Fig. 1). In a strict sense, efficient and convenient approaches for PIN separation and quantification of the saturate fraction have never been reported on in the literature. In addition to SARA separation and quantification, however, the AMD-HPLC system could also provide an excellent approach to characterize the PIN fractions of saturated hydrocarbons in crude oil and bitumen. In this article, therefore, we report on the PIN separation and quantification of the AMD-HPLC method. Similar to the SARA separation, all steps of the PIN separation are controlled by a programmable microprocessor that switches valves and solvents as required by the program. The system is fully automated and completely unattended once an oil sample has been loaded. The technique separates the saturate fraction into pure PIN fractions with extremely good resolution.

2. Method and samples

2.1. Method and procedure

In addition to a cyano column and a silica column for SARA separation [4 in press], the AMD-HPLC system is equipped with a set of two additional proprietary columns for PIN separation based on size-exclusion chromatography. A "PIN1" column (Silicon: S_{115}) is packed with a 5.4 Å molecular sieve, and a "PIN2" column (Silicon: 50%S_{115} + 50%S_{130}) is packed with a 6.2 Å molecular sieve (Fig. 2). Two low thermal mass temperature programmed ovens allow rapid heat-ramping and rapid chilling of the two PIN columns. Each set of PIN columns is connected in a series via multi-position valves that allow a given column to be inserted "in", or to be by-passed "out" of the flow path of the mobile phase at pre-set times in the process. A series of one to six samples can be successively analyzed without extensive sample preparation. Except for the specific solvents and columns, the AMD-HPLC operating procedure for PIN separation is essentially similar to that for SARA separation.

In the PIN process, a pre-weighed sample of saturates is dissolved in 300 µl of iso-octane and "loaded" into a 350 µl loop on the auto-sampling valve. The process proceeds in three steps as depicted in Fig. 2.

In step 1, both the PIN1 and PIN2 columns are inserted into the flow path of the mobile phase. Iso-octane, the first mobile phase, sweeps the sample solution out of the sample loop and "injects" it into the PIN1 column, which, at ~25 °C, will retain the n-paraffins but carry the iso-paraffins and naphthenes forward through the PIN1 column and on into the PIN2 column which, at 80 °C, will retain the iso-paraffins, but allows the naphthenes to pass through to the naphthenes port of the fraction collector.

In step 2, column PIN1 (with the retained n-Paraffins) is bypassed, the temperature of column PIN2 is increased from 80 °C to 130 °C, a new mobile phase is introduced, and the flow direction of the mobile phase through column PIN2 is reversed. The new mobile phase, consisting of a mixture of 50% n-octane (or n-heptane) and 50% iso-octane, is pumped through column PIN2 to allow the new mobile phase to back-flush the