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A multi-dimensional high performance liquid chromatographic method for fingerprinting polycyclic aromatic hydrocarbons and their alkyl-homologs in the heavy gas oil fraction of Alaskan North Slope crude

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Abstract

We report an offline multi-dimensional high performance liquid chromatography (HPLC) technique for the group separation and analysis of PAHs in a heavy gas oil fraction (boiling range 287–481 °C). Waxes present in the heavy gas oil fraction were precipitated using cold acetone at −20 °C. Recovery studies showed that the extract contained 93% (±1%; $n = 3$) of the PAHs that were originally present while the wax residue contained only 6% (±0.5%; $n = 3$). PAHs present in the extract were fractionated, based on number of rings, into five fractions using a semi-preparative silica column (normal-phase HPLC). These fractions were analyzed using reverse-phase HPLC (RP-HPLC) coupled to a diode array detector (DAD). The method separated alkyl and un-substituted PAHs on two reverse-phase columns in series using an acetonitrile/water mobile phase. UV spectra of the chromatographic peaks were used to differentiate among PAH groups. Further characterization of PAHs within a given group to determine the substituent alkyl carbon number used retention time matching with a suite of alkyl-PAH standards. Naphthalene, dibenzothiophene, phenanthrene and fluorene and their C1–C4 alkyl isomers were quantified. The concentrations of these compounds obtained using the current method were compared with that of a GC–MS analysis obtained from an independent oil chemistry laboratory.

Keywords: Un-substituted and alkyl-substituted PAH analysis; HPLC; Crude oil; DAD detection

1. Introduction

Determining the chemical constituents of crude oils is of paramount importance for both the oil industry as well as regulatory agencies. Crude oil is a complex mixture of chemical compounds with a wide range of polarities and volatilities, which makes its chemical characterization a challenging task. Generally, analysis of crude oil is done at two different levels of sophistication. The "group-type" analysis involves the separation of compounds into groups, mainly based on polarity, where the groups are classified as Saturates, Aromatics, Resins and Asphaltenes (SARA). For this separation, several liquid chromatographic methods using column liquid chromatography (LC) or high performance liquid chromatography (HPLC) have been developed using polar stationary phases such as silica or alumina [1–8]. Recently, Islas-Flores et al. [1] showed that group-type separation of oil samples using HPLC is simple and effective and yields comparable results to traditional open column liquid chromatography.

SARA analysis of crude oil is relatively quick and finds several applications in the oil industry. Precise knowledge of the group-type composition of crude oil is useful in solving problems during oil drilling and transportation processes [9]. It is also used extensively to guide the process control operations in refineries. Chromatographic procedures that have been developed and validated for SARA analysis have been recently reviewed [10,11]. SARA fractions have been further separated and/or analyzed using chromatographic techniques to characterize the molecular composition of crude oil [12]. Among other compound classes, polycyclic aromatic hydrocarbons (PAHs), which are abundant in the aromatic fraction of crude oil, have been analyzed extensively [13,14]. The type and amount of PAHs present vary widely among different crude oils. PAH profiling finds several applications in oil exploration and also in monitoring environmental pollution. The PAH profile of a given crude oil gives information on its thermal maturity, and several maturity indices have been developed for this purpose [15]. PAHs are also environmental pollutants and PAH profil-

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ing of crude oils is useful in studying and assessing the relative toxicity of crude oils. Standard PAH analysis normally targets un-substituted PAHs, such as the 16 compounds on the United States Environmental Protection Agency (US-EPA) "priority PAH" list. Recent toxicity studies from our group, as well as others, suggest that alkyl-substituted PAH compounds may be more important in characterizing PAH toxicity to early life stages of fish [16–21]. Notably, alkyl-substituted PAHs are significantly more abundant than un-substituted PAHs in crude oil, typically comprising 80–90% of total PAH [22].

For oil spills, the PAH profile of the spilled oil together with the analysis of saturated hydrocarbons and other biomarker compounds has been used successfully to identify the nature and type of oil that was spilled and its weathering status [23,24]. PAH profiling in these studies involved analysis of naphthalene, phenanthrene, fluorene, dibenzothiophene, and chrysene, plus their alkyl-homologs with one to four additional carbon atoms as substituents (C1- to C4-PAHs). The 16 US-EPA priority PAHs were also analyzed [14]. The relative concentrations of these PAHs can give several important clues during an oil spill investigation:

(1) PAH distribution can be used to differentiate the contribution of petrogenic and pyrogenic sources. In general, un-substituted PAHs dominate the pyrogenic sources whereas alkyl-PAHs are found in abundance in a petrogenic source.
(2) PAH distribution patterns of crude oils differ substantially. Therefore, comparing the PAH distribution pattern at a spill site to a crude oil database can identify potential crude oil candidates for further investigation.
(3) The concentration pattern of the C0–C4 PAH can be used as a diagnostic tool to determine the weathering status of the crude oil, as more highly substituted alkyl-PAHs tend to dominate after the oil is weathered (C0 < C1 < C2 < C3 < C4).

Hence, there is a need to develop analytical methods for the analysis of alkyl-substituted PAHs as well as un-substituted PAHs. Several chromatographic methods have been developed for the separation and analysis of PAHs and other petroleum hydrocarbons in crude oil and petroleum products [10]. Among them gas chromatographic (GC) techniques utilizing a flame ionization detector (FID) or a mass spectrometric detector (MS) have been developed and used routinely in oil chemistry laboratories [14,25–27]. However, extensive sample cleanup, including prior group-type fractionation using a liquid chromatographic (LC) method, is often required before the final GC analysis. Recently, Wang and Fingas [26] reviewed the gas chromatographic methods used in oil spill identification.

LC methods have also been used for group-type separation as well as individual PAH analysis in crude oil or oil fractions. LC techniques have a unique advantage of fractionating complex samples into simpler mixture and producing quantities which can be further analyzed using other techniques. Secondly, PAH classes such as alkyl-phenanthrenes and alkyl-anthracenes, alkyl-chrysenes and alkyl-benz[*a*]anthracenes, and even non-substituted isomers of benzofluoranthenes are difficult to distinguish in GC–MS in the absence of authentic standards. These sets of compounds are easily distinguished in HPLC methods with diode-array detection. Moreover, high molecular weight PAHs (>6 aromatic rings) and more polar residues can be easily analyzed, whereas analysis of these compounds could be difficult using GC–MS techniques [28]. Analysis of PAHs using only liquid chromatography can be done with a combination of LC methods. In this approach, PAHs are fractionated based on the number of rings using a normal-phase column, which is followed by separation using a reverse-phase column [29]. Fluorescence detection is a very sensitive method and has been routinely used for quantification of PAHs in standard reference materials [29]. The results obtained using HPLC with fluorescence detection have been found to be in close agreement with GC–MS [30].

McKinney et al. [31] have attempted to analyze PAHs and alkyl-PAHs in five coal liquification process streams using normal-phase HPLC with a diode array detector. The two and three-ring PAHs that have very close diode array spectra could not be resolved and appeared as an un-resolved hump. Sufficient resolution to separate the un-substituted PAHs from their alkyl-homologs was also not obtained. Therefore, it was necessary to collect individual fractions for further analysis using mass spectrometry (MS) to confirm the alkyl-PAHs.

On the other hand, Akhlaq and Gotze [32] used a tiered approach for the characterization of crude oil samples. They used a single-wavelength UV detector for RP-HPLC analysis, and peak assignments were based solely on the retention time of available standards. Although their method can discriminate between different crude oils and diesel fuel, they could not achieve the quantification of PAHs. It should also be noted that the direct determination of PAHs, whether using normal-phase HPLC with diode array detection or the tiered approach with single wavelength UV detection, did not produce detailed PAH fingerprints of crude oil or oil fractions comparable to GC–MS analysis. Based on these observations, we proposed a tiered approach with diode array detection to characterize the PAHs present in the crude oil samples.

Here we report a method for the analysis of un-substituted and alkyl-substituted PAHs in the heavy gas oil fraction (boiling range 287–481 °C) of Alaskan North Slope crude oil using high performance liquid chromatography. The wax materials present in the heavy gas oil fraction were precipitated prior to HPLC fractionation. The PAHs were separated into five fractions based on the number of rings using normal-phase HPLC. These fractions were then analyzed using two reverse-phase columns connected in series and coupled to a diode array detector. The results of PAH analysis using this method were compared to GC–MS results obtained from an independent oil chemistry laboratory.

2. Materials and method

Alaskan North Slope crude (ANSC) oil was fractionated into four fractions using low temperature fractional distillation at Dr. Zhendi Wang's lab at Environment Canada (Ottawa, ON). The