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Normal phase high performance liquid chromatography for fractionation of organic acid mixtures extracted from crude oils

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Abstract

Crude oil contains such an extensive range of compounds that a complete analysis is impossible. Fractionation by chemical properties is often used to simplify analytical handling. This work presents a high performance liquid chromatography (HPLC) method using normal phase chromatography on a cyano-bonded phase column to separate acid extracts from crude oils into four fractions; non-polar compounds, saturated carboxylic acids, phenols and polyfunctional acids. The method has been developed both in analytical scale for characterisation of acid extracts, and in preparative scale to provide sufficient sample amounts for further analysis by complementary methods.

Keywords: HPLC; Cyano column; Normal phase; Crude oil; Petroleum acids; SPE

1. Introduction

Crude oil is formed by the slow thermal cracking of organic matter incorporated in sedimentary rocks [1], and therefore contains such an extensive range of compounds and molecular species that a complete chemical analysis is impossible to achieve. The components include a wide range of functionalised compounds in addition to the bulk hydrocarbons, and analysis of these fractions is even more challenging than for the hydrocarbons [2]. Gas chromatography (GC) is normally the chosen method when analysing crude oil. GC chromatograms often show a large hump, termed unresolved complex mixture (UCM), which makes the analysis very difficult. Sutton et al. [3] have estimated 250,000 unidentified compounds in the UCM of a biodegraded crude oil. Analysis of crude oils for specific compound types is thus a considerable challenge.

The characterisation of acidic compounds in petroleum is most often undertaken to explain a physical or technical property of the oils, like corrosion [4], emulsion stability [5] or wettability change of solid surfaces by adsorption [6,7]. The traditionally used measure of the acid content in petroleum samples is non-aqueous titration which gives a "Total Acid Number" (TAN) [8]. However, this value contains no information on the composition of the acids, and does not correlate well with, e.g. the degree of corrosion caused by oils of different acidities [9], so more detailed analyses are needed to correlate with the physical effects of the acids. At the other extreme of precision, recently developed methods that analyse very complex mixtures directly with no pre-treatment have been applied to petroleum acids. Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) has been applied to heterocompounds in coal extracts [10] and naphthenic acids analysis [11], and gives a detailed overview of the distribution of acids in the sample, based on the molecular masses. These methods have a great capacity for determination of molecular compositions of such complex mixtures, but the challenge of relating the analytical data to the chemical properties of the components remains, and fractionation that separates the samples into fractions containing uniform chemical structures is still required for testing in the specific contexts. Thus, extensive work-up schemes are still needed for separating the sample into sub-fractions with similar chemical compositions.

Column chromatography (CC) and high performance liquid chromatography (HPLC) are useful techniques for this purpose. They are often used in normal phase mode to separate the hydrocarbon phase from the more polar fractions of the oil, e.g. in saturates–aromatics–resins–asphaltenes fractionation (SARA) [12]. In petroleum analysis, a silica stationary phase is

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often used for normal phase CC and HPLC separation, using a sequence of solvents with increasing polarity to elute the hydrocarbons and functionalised compounds as separate fractions [13,14]. However, the use of silica is limited by its very polar properties and tendency to irreversible adsorption of polar compounds, and recovery factors as low as 50% are considered acceptable [14,15]. The acid extracts analysed in this work contain compounds with high polarity, including the microbially produced biosurfactants that are of special interest due to their very strong surface active properties. A review of group separation of petroleum products by HPLC is published by Kamiński et al. [16]. However, the methods focus on fractionation of the hydrocarbons, and acidic compounds are addressed to a limited degree.

In previous investigations, ion pair HPLC has been used for separation of crude oil acids by acid strength [17]. This method uses a dynamic equilibrium on silica to control the retention of acidic compounds on the column, which makes it difficult to acquire stable retention time values and gives a long equilibrium time. Ion exchange chromatography has been used by Jones et al. [18], in the form of non-aqueous SPE ion exchange (SAX quaternary amine) for selective extraction of the carboxylic acids from crude oils. This procedure does not include sub-fractionation of the acids.

Reversed phase liquid chromatography using a silica column modified with C18 alkyl chains is often used to separate polar compounds. Lee et al. [19] have used non-aqueous reversed phase HPLC for separation of lipids. We have tested this method for analysis of the acids extracted from crude oil. Different solvents based on the gradient profile from Lee et al. were tested on a C18 column. The chromatogram showed that the sample components were separated to some degree, but no baseline separation of groups was obtained. In addition, non-polar compounds can probably be irreversible attached to the non-polar column material. Thus, the C18 column is not well suited for the samples we want to analyse.

As an intermediate polarity between the silica and the C18 column, a column material consisting of silica modified with cyanopropyl groups (cyano column) can be used. Such sorbents have been used in geochemical and petroleum analysis for group type fractionation [20] to avoid irreversible adsorption of asphaltenes and other polar oil components. This type of column is evaluated to be more suitable than silica for the analysis of the acids extracted from crude oil. Amino modified silica is also used for fractionation of polar petroleum constituents [21], but is not considered optimal for the acid fraction due to the added complexity of retention behaviour that can result from possible ion exchange behaviour on the amine groups.

The aim of this work is to develop an HPLC method to characterise the distribution of acidic organic compounds in crude oils, and to prepare fractions suitable for further analysis at molecular levels and also for testing of physical properties. This work presents an HPLC method using normal phase chromatography on a cyano-bonded phase column which provides a stable and fast separation of organic acids from crude oils into four well-defined fractions that correspond to the main types of acidic compounds; weak acids with no acidic protons, saturated carboxylic acids, phenols and polyfunctional acids. The method is developed both in analytical scale for characterisation of acid extracts, and in preparative scale to provide sufficient sample amounts for further analysis by complementary methods. The method is applied on a sample set of acid extracts from crude oils from the Norwegian continental shelf. These oils include both biodegraded and non-biodegraded oils.

The solvent programmes are modified from the solvent combinations conventionally used in petroleum group type separations [13,14,20], but they have been adjusted to give a slow, gradual increase in polarity to ensure good separation of the different acid types.

Two detectors are used: an evaporative light scattering detector (ELSD), which detects all compounds except low-boiling compounds that evaporate together with the solvent, e.g. certain phenolic compounds, and a UV detector that detects all molecules with suitable chromophores.

2. Experimental

2.1. Standards and samples

The standards used are of p.a. quality. This includes a commercial standard of naphthenic acids (technical purity, Aldrich) and a commercial biosurfactant, surfactin (purity approx. 98%, Sigma). Surfactin is a lipopeptide, and contains a seven-membered ring made up of four different amino acid units (leucine, glycine, valine and aspartic acid), linked with a hydroxy fatty acid. The biosurfactant rhamnolipid (0.25% in water) was provided by Professor I. Banat, University of Ulster [22]. Rhamnolipid is a glycolipid, and consists of the sugar structure rhamnose and hydroxy fatty acids. The solvents are all of HPLC or p.a. quality.

Acids are extracted from a sample set of eight crude oils, spanning from heavy biodegraded oils enriched in asphaltenes to light non-biodegraded oils. The oils originate from the Norwegian continental shelf and are supplied by Norsk Hydro ASA (seven oils) and Statoil ASA (one oil). The oils are marked with letters, B for biodegraded oils and S for sweet, non-biodegraded oils, followed by a number indicating production field and a letter denoting different wells or different batches within one field.

Two methods of acid extraction are used: an ion exchange method described by Mediaas et al. [23] and a liquid–liquid extraction described by Constantinides and Arich [24] and others [25,26]. These extraction procedures are also presented in a recent paper by Borgund et al. [27].

2.2. HPLC procedure

A P680 HPLC Pump (Dionex, California, USA) and a Rheodyne 7725 manual injector (Rheodyne, California, USA) with a 20 μl (analytical column) or 100 μl (semi-preparative column) loop are used for the analysis. Two types of detectors are used: a light scattering detector (ELSD, Sedex 55 Light Scattering Detector, France; operation temperature, 40 °C; nebulizing gas, nitrogen) and a UV detector (UVD340U Dionex, diode-array