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Insight into unresolved complex mixtures of aromatic hydrocarbons in heavy oil via two-dimensional gas chromatography coupled with time-of-flight mass spectrometry analysis

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ABSTRACT

The aromatic hydrocarbon fractions of five crude oils representing a natural sequence of increasing degree of biodegradation from the Liaohe Basin, NE, China, were analyzed using conventional gas chromatography–mass spectrometry (GC–MS) and comprehensive two-dimensional gas chromatography (GC × GC). Because of the limited peak capability and low resolution, compounds in the aromatic fraction of a heavily biodegraded crude oil that were analyzed by GC–MS appeared as unresolved complex mixtures (UCMs) or GC "humps". They could be separated based on their polarity by GC × GC. UCMs are composed mainly of aromatic biomarkers and aromatic hydrocarbons with branched alkanes or cycloalkanes substituents. The quantitative results achieved by GC × GC-FID were shown that monoaromatic hydrocarbons account for the largest number and mass of UCMs in the aromatic hydrocarbon fraction of heavily biodegraded crude oil, at 45% by mass. The number and mass of diaromatic hydrocarbons ranks second at 33% by mass, followed by the aromatic biomarker compounds, triaromatic, tetraaromatic, and pentaaromatic hydrocarbons, that account for 10%, 6%, 1.5%, and 0.01% of all aromatic compounds by mass, respectively. In the heavily biodegraded oil, compounds with monocyclic cycloalkane substituents account for the largest proportion of mono- and diaromatic hydrocarbons, respectively. The C_4-substituted compounds account for the largest proportion of naphthalenes and the C_3-substituted compounds account for the largest proportion of phenanthrenes, which is very different from non-biodegraded, slightly biodegraded, and moderately biodegraded crude oil. It is inferred that compounds of monoaromatic, diaromatic and triaromatic hydrocarbons are affected by biodegradation, that compounds with C_1-, C_2-substituents are affected by the increase in degree of biodegradation, and that their relative content decreased, whereas compounds with C_3-substituents or more were affected slightly or unaffected, and their relative content also increased. The varying regularity of relative content of substituted compounds may be used to reflect the degree of degradation of heavy oil. Moreover, biomarkers for the aromatic hydrocarbons of heavily biodegraded crude oil are mainly aromatic steranes, aromatic secohopanes, aromatic pentacyclotriterpanes, and benzohopanes. According to resultant data, aromatic secohopanes could be used as a specific marker because of their relatively high concentration. This aromatic compound analysis of a series of biodegraded crude oil is useful for future research on the quantitative characterization of the degree of biodegradation of heavy oil, unconventional oil maturity evaluation, oil source correlation, depositional environment, and any other geochemical problems.

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1. Introduction

Heavy oil has attracted increased attention because of its large reserves, intensive resources, and advancing oil development techniques [1]. Based on genesis, heavy oil can be divided into original and secondary heavy oil. Original heavy oil accounts for only a limited proportion of the total heavy oil, whereas most heavy oil is secondary heavy oil [2]. Most secondary heavy oil has been subjected to biodegradation. Hunt estimated that approximately 10% of all the world's petroleum reserves have been lost to biodegradation and an additional 10% altered [3,4]. Compounds with different chemical structures in crude oil can be biodegraded selectively, thus the heavy oil composition changes significantly [3]. This variation makes genesis discrimination, maturity evaluation or even the prediction of heavy oil resources more difficult. The physical properties of the heavy oil are easy to know. Nevertheless, given the current analytical conditions, the chemical composition of the heavy oil when compared to the crude oil is still not well identified and requires further investigation. Understanding the chemical composition of heavy oil is of great importance for the qualitative and quantitative determination of the chemical composition of heavy oil, oil source correlation analysis, evaluation of the degree of biodegradation, geochemical problems such as genesis discrimination, heavy oil developing and refining, and solving environment problems such as oil spills.

Gas chromatography (GC) is the most conventionally used tool for normal crude oil sample analysis. Because of the limited peak capability and low resolution ratio in GC analysis of heavy oil samples, compounds with the same boiling point and different polarities are co-eluted, which results in a rise of the chromatogram baseline (the so-called "humps"). Since it is difficult to identify compounds in the "humps", they are termed unresolved complex mixtures (UCMs) [5,6]. The high-concentration compounds produce discernible peaks in UCMs, but even these peaks are likely to consist of multiple overlapping compounds. The low-concentration compounds can hardly be detected because they are covered by the rising baseline [7]. As the "humps" become more obvious with increased degree of biodegradation, fewer compounds in the UCMs can be identified. Although tandem quadrupole mass spectrometry (MS) can assist with compound identification in the UCMs to some extent, this technique cannot provide pure mass spectra of the target compounds, and offers strong evidence for unknown compound identification because of the interference of co-eluting peaks and the baseline [8].

To explore the chemical composition of the UCMs, a number of analytical methods such as molecular sieve, urea complexation, and chemical oxidation have been used to separate the UCM petroleum compounds into distinct chemical fractions or groups, which were further analyzed with GC–MS [9–14]. Some researchers have used combined apparatus to identify UCM constituents [15–21]. However, these methods can only identify some of the UCMs, whereas some complex compound mixtures cannot be resolved and the nature of the compounds that form these UCMs remains unclear [9].

Comprehensive two-dimensional chromatography (GC × GC) originated in the 1990s and is a new technology for complex compound analysis. The GC × GC column system consists of two independent columns with a distinct separation mechanism, and a modulator that connects two columns in series [22–24]. Because of the powerful orthogonal separation capacity of GC × GC, compounds with similar boiling points that cannot be separated in the first column can be separated in the second column, according to different polarities [25]. With the development of GC × GC coupled with time-of-flight mass spectrometry (GC × GC-TOFMS), the mass spectra of UCM compounds can be acquired. The data processing system has a deconvolution function, which can provide an effective basis for compound identification. GC × GC-TOFMS has been applied to UCM analysis by an increasing number of researchers [26–28]. Currently, many previous studies reported the constituents of UCMs in aromatic hydrocarbons focus mainly on toxic contaminants in marine organisms [29–31]. In geological sample, more reports have been paid to the analysis of UCMs of saturated hydrocarbons, known aromatic compounds, or heterocyclic compounds such as sulfur and nitrogen containing compounds [32–38]. Other compounds found in aromatic UCMs, on the other hand, are still lacking sufficient attention.

The purpose of this work is to identify feature compounds in the UCMs. A statistical method based on GC × GC-TOFMS and GC × GC-FID has therefore been developed to analyze for aromatic hydrocarbons in the UCMs of a series of crude oil with different biodegradation degrees. It is expected that this developed method can provide a reference for further research on aromatic hydrocarbon UCMs.

2. Experimental

2.1. Equipment and materials

The comprehensive two-dimensional GC × GC-TOFMS system (LECO Corporation, San Jose, CA, USA) is composed of an Agilent 7890A gas chromatography with flame ionization detector and a Pegasus 4D time-of-flight mass spectrometry (LECO Corporation, San Jose, CA, USA). The Agilent 7890A GC is equipped with a liquid nitrogen-cooled pulse jet modulator. All data were processed using the Chroma TOF software (LECO Corporation, San Jose, CA, USA). DSQII single stage quadrupole GC–MS (Thermo Scientific Corporation, Waltham, Massachusetts, USA) and GC columns (Agilent Technologies, Santa Clara, CA, USA) were used. *n*-Hexane (analytical reagent grade, redistilled), dichloromethane (DCM, analytical reagent grade, redistilled) and silica gel (100–200 mesh, activated at 200 °C for 4 h) were used for the sample retreatment. D_{10}-anthracene was selected as internal standard.

2.2. Sample preparation

The sample suite comprises five progressively biodegraded crude oils were from the Ciyutuo oilfield in the north eastern Depression of the Liaohe Basin, northeast China, and the information of samples is shown in Table 1. Oil biodegradation level was based from scale of Wenger et al. [19].

The protocol of aromatic hydrocarbons extraction is as follows. (1) Approximately 60 mg crude oil was dissolved in an appropriate amount of *n*-hexane. (2) Silica gel packed in a glass column was washed using *n*-hexane, and the oil sample was loaded onto the glass column. (3) As soon as the fluid eluted out the column, 10 mL *n*-hexane was added into the glass column to wash the column three times, and the saturated fraction was collected. Then, 20 mL DCM was used to wash the silica gel six times to collect the aromatic fraction. Ultraviolet light was used to observe the column and control solvent addition. The collected aromatic fraction was

Table 1
Oils analyzed in this study.

No.	Sample	Biodegradation level
1	CI 50–85	None
2	CI 54–82	Slight
3	CI 11	Moderate
4	CI 20–138	Heavy
5	CI 8–340	Heavy