Systematically structural identification of nitric compounds in crude oil with chemometric resolution

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Abstract: Aimed at the problem of classification of non-hydrocarbons of crude oil, the theoretical standpoint that the polarity of a compound depends on the whole structure and composition of molecule instead of a kind of heteroatom or its functional group was presented. A method was established for the systematically structural identification of nitric compounds in crude oil. The pre-fractionation of a crude oil sample into 7 fractions was performed by di-adsorption column chromatography with neutral aluminum oxide and silica gel. Subsequently, the individual components were obtained by using capillary column gas chromatography, and the types of compounds were detected by a mass spectrometer. In combination with a chemometric resolution, the compounds of fraction were further identified. This method can relieve the difficulty of classical analysis in identifying those species with very low contents or without being completely separated. The structures of 168 nitric compounds in a crude oil sample were determined by this method.

Key words: column chromatography; chromatography-mass spectrometry; chemometric resolution; structural identification; non-hydrocarbon compound; crude oil; nitric

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1 INTRODUCTION

Because of its significance in environmental chemistry, organic geo-chemistry, processing and refining of petroleum, etc, the structural identification of individual non-hydrocarbon compound in crude oil, especially the identification of nitric compound, has increasingly received attention. Due to the complexity of crude oil sample, the pre-fractionation of composition is very necessary before the analysis of individual compound. The methods for separating and analyzing compositions in crude oils were summarized by Mansfield et al. The column chromatography technology for separating and analyzing the compositions is widely used because of its advantages. However, on applying this method, there are still some problems. For example, all the process of pre-separation, presented in literatures on the separation of non-hydrocarbon into nitrogen-, sulfur- and oxygen-containing fractions, etc, ignores the existence of multifarious-heteroatom compounds which mainly exist in the forms of non-hydrocarbon compounds. In addition, because of the complexity of the non-hydrocarbons in respect of components, structures, kinds and amounts, etc, any optimum separation conditions are unable to separate completely all individual non-hydrocarbon compound in every oil sample. Consequently, the identifying mistakes will occur if experimental data are not treated with chemometric resolution, sometimes, the identification analysis is actually unable to be carried out. Therefore, the improvement of the existing method is necessary.

2 EXPERIMENTAL

2.1 Main apparatus and reagents

The main apparatus are as follows: gas chromatograph (Hewlett Packard 5890 Series, American); mass selective detector (Hewlett Packard 5972 Series, American); fluorophotometer (Model 930, Shanghai Analytical Instrument Factory, China); rotation evaporimeter (Model AAA R-201, Shanghai Shensheng Ltd of Science and Technology, China); cycle aqua vacuum pump (Model SHZ-D(III), Yingyuyuhua Instrument Factory, China); ultrasonic generator (Model SB2200, Shanghai Branson, China); electrothermal blast cabinet (Model 101A-1, Shanghai Total Factory of Experimental Instruments, China); chromatography column (acid burret of 25 mL).

Chloroform, hexane, benzene, anhydrous ethanol, dichloromethane, tetrahydrofuran, neu-
2.2 Column chromatography separation of fractions in crude oil sample

Crude oil samples were from Shengli Oil Field, China. A two-step separation method with neutral alumina and silica gel filling in the adsorption chromatography column was employed to separate the non-hydrocarbons in the sample into 7 fractions ($D_1, D_2, D_3, D_4, D_5, D_6$ and $D_7$), the flowchart of separation is shown in Fig. 1.

About 0.75 g of crude oil was dissolved into 2.0 mL of chloroform in a titration bottle (300 mL) with a stopper. After the solvent volatilized completely in a gentle stream of dry nitrogen gas at ambient temperature, 300 mL of hexane was gradually added into the bottle being continuously rocked. The mixture was shocked by ultrasonic for about 30 min, then was stillled for 24 h, the asphaltene was filtered by a funnel with pledget in its neck. The filtrate was received with other titration bottle (300 mL), and the titration bottle containing asphaltene was washed with hexane till the achromatous filtrate emerges. The filtrate was placed in water bath (40 °C) and concentrated by a rotation evaporimeter (the rate of evaporation was lower than 120 drop/min) to about 3 mL for subsequent chromatographic separation.

32 g of neutral alumina were added into a chromatography column with pledget at its bottom. At the same time, the external wall of the column was gently knocked for uniform filling, and 30 mL of hexane was immediately added into the column for soaking the immovable phase, and the chromatography column was installed in a fume cupboard at 15–40 °C. The above concentrated filtrate was adsorbed onto the neutral alumina, and then its fractions were eluted in turn with the following solvents: 300 mL of hexane for aliphatic hydrocarbon fraction $A_1$, 150 mL of mixture solvent consisting of dichloromethane and hexane (2:1 in a volume ratio) for aromatic hydrocarbon fraction $A_2$, 200 mL of benzene for non-hydrocarbon fraction $D_1$, 250 mL of chloroform containing 0.75% (in volume fraction) ethanol for non-hydrocarbon fraction $D_2$, 100 mL tetrahydrofuran containing 10% ethanol for non-hydrocarbon fraction $D_3$.

With 30 g of the silica gel, a chromatographic column of silica gel was made in the same way as the column of neutral alumina. The fraction $D_4$ was also concentrated to about 3 mL similarly by the rotation evaporimeter, and transferred into the silica gel column. And then, its fractions were eluted in turn with the following solvents: 150 mL of the mixture of hexane and benzene (1:1 in volume ratio) for non-hydrocarbon fraction $D_5$, 100 mL of benzene for non-hydrocarbon fraction $D_6$, 120 mL of the mixed solvent of benzene and anhydrous ether (1:1 in volume fraction) for non-hydrocarbon fraction $D_7$, 100 mL of tetrahydrofuran containing 10% ethanol for non-hydrocarbon fraction $D_8$. During the elution of the fraction $D_7$, the rate of elution might be increased by increasing the difference in pressure.

![Fig. 1 Flowchart of fractionation of crude oil samples by two-step column chromatography](image-url)