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SEPARATION OF KETONES AND ACIDS FROM CRUDE OILS

E. Strelnikova, L. Stakhina, O. Serebrennikova

Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, 3, Academichesky Ave., 634021 Tomsk, Russia

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Abstract

The method intended to separate ketones and acids from crude oils and petroleum products was based on chromatography with silica gel modified with 10 % potassium silicate as precolumn and ordinary silica gel as the main column using a mixture of hexane, dichloromethane, methanol and formic acids as a mobile phase. Separation efficiency was tested using standard compounds. The method was applied to separate ketones and acids from West Siberian oils.

Key words: silica gel, modification, potassium silicate, crude oils, ketones, acids.

Introduction

Oxygen compounds (along with nitrogen- and sulphur-containing compounds) are considered as a significant component of fossil fuels. Oxygen compounds are mainly distributed among resins and asphaltenes. In oils oxygen compounds are mainly presented by phenols, furan derivatives and carbonyl compounds (carboxylic acids, ketones and esters) and also by the compounds containing two and more heteroatoms including oxygen. Carbonyl compounds constitute the major portion of petroleum oxygen-containing compounds. In spite of quantitative and qualitative varieties our knowledge about petroleum oxygen compounds is still scanty. It is mainly caused by the lack of reliable analytical methods for their characterization in fossil fuels. In recent years, however, the role of oxygen-, nitrogen- and sulphur-containing compounds in geochemical processes has attracted increasing interest and their practical application in petroleum geochemistry has been recognized as promising.

Separation and analysis of petroleum oxygen compounds is a very difficult task.

Acidic compounds are traditionally separated from oils and oil fractions via extraction by aqueous or alcoholic solutions of alkalis either at the room temperature or at heating. Since the method is based on reaction of neutralization and substantially depends on acid-base balance of the system, the positive effect is reached only for strong petroleum acids. Besides this procedure is marginally successful because of low results reproducibility.

The use of adsorption chromatography on silica gel modified by potassium hydroxide to separate acidic components from oils is worthy of special attention[1]. It should be noted, that alongside with potassium silicate free alkali may also be presented on the surface of silica gel modified by alkali. As a result it can promote side reactions and thereby distort the results.

Separation of acids and phenols from hydrocarbons blends via chromatographic separation on a silica gel modified by potassium silicate[2] having basic character is considered to be the most promising. A high degree of separation of acidic compounds at minimal change of their native structures is the advantage of the method.

To separate ketones from oils and hydrocarbon blends one obtained their derivatives using reagents Girard-T (trimethylammonium acetohydrazide chloride) and Girard-P (pyridinium acetohydrazide chloride)[3-5]. The obtained products are water- and alcohol-soluble and are easily separated from a hydrocarbon phase. A low degree (20-35 %) of ketones separation and insufficient reproducibility are the disadvantages of this method.

Liquid-adsorption chromatography (LAC) is considered to be a more promising method, where polar acidic and basic components are consecutively removed from the oil, then several fractions are separated from a neutral part by adsorption on silica gel or on the mixed sorbent - silica gel-aluminum oxide[6-8]; and ketones are concentrated in one of them.

Thus to separate ketones from source rock extracts[6] one used a double-layered sorbent (silica gel above alumina) and the following series of the solvents: petroleum ether, the mixture of petroleum ether and dichloromethane (4:1), the mixture of petroleum ether and dichloromethane (1:4), dichloromethane, dichloromethane and methanol (1:1), respectively. Ketones were concentrated in the fraction, which was eluted with petroleum ether: dichloromethane at a ratio of 1:4. However, there are references, that ketones are concentrated in more polar fractions, i.e. dichloromethane: chloroform (9:1)[7] and chloroform [8].

Based on the foregoing we suppose that liquid-adsorption chromatography (LAC) involving ordinary silica gel or silica gel modified with potassium silicate is the most promising method. Using this method one can simultaneously and independently separate carboxylic acids and ketones with a high degree of desired product extraction.

Experimental

Model compounds were eluted using a glass column 10 mm in diameter and 500 mm in length. The column was packed with silica gel (particle size 0.2 mm) at a weight ratio of 1:30 to a sample, and silica gel modified with potassium silicate was applied on top at a weight ratio of 1:10 to a sample.

Hexane, mixtures of hexane and dichloromethane at ratios of 4:1 and 1:4, mixture of dichloromethane and methanol at a ratio of 1:1 and 3 % formic acid mixed with dichloromethane and methanol (1:1) were used as mobile phases (Figure 1).

Fractions obtained were evaporated to small volumes. Thus, the following oil fractions were obtained:

K-1 – eluted by hexane;
K-2 – eluted by hexane and dichloromethane mixture (4:1);
K-3 –eluted by hexane and dichloromethane mixture (1:4);
K-4 – eluted by dichloromethane and methanol mixture (1:1);
K-5 – eluted by 3 % formic acid mixed with dichloromethane and methanol.

The content of ketones in oils was determined by electronic spectroscopy of carbonyl derivatives with 2,4-dinitrophenylgidrazine by the intensity of absorption bands in the visible spectrum (430-490 nm) using spectrophotometer UVIKON 943 (France)[9] .

The content of acids in oils was determined by potentiometric titration using an alcohol solution of potassium hydroxide as a titrant[10].

Subsequent isolation of acid concentrates was carried out using an express method based on gradient-elution chromatography in combination with chemical modification[11]. The isolated acids were treated with diazomethane to prepare methyl ethers.

Methyl ethers of the acids were analyzed by gas-liquid chromatography using chromatograph Tsvet-500M. One used a quartz column 25 m in length, fixed phase – phenylmethylsilicone (SE-54) and flame-ionization detector; temperature was increased from 80^0C to 280 ^{0}C at a gradient of 4 ^{0}C min^{-1}. The n-acids were identified by a method of internal standard.

Gas chromatography-mass spectroscopy (GC-MS) of ketone fraction was carried out using device Hewlett-Packard 6890/5973 under the conditions of temperature programming. One used a capillary column (35 m in length and 0.25-0.35 mm in diameter) coated with HP-1. The temperature was increased from 50 ^{0}C to 310 ^{0}C at a gradient of 3 ^{0}C min^{-1}. Ketones were identified comparing GC-MS data obtained for oil concentrate under study with the database using processing system DS-2130.

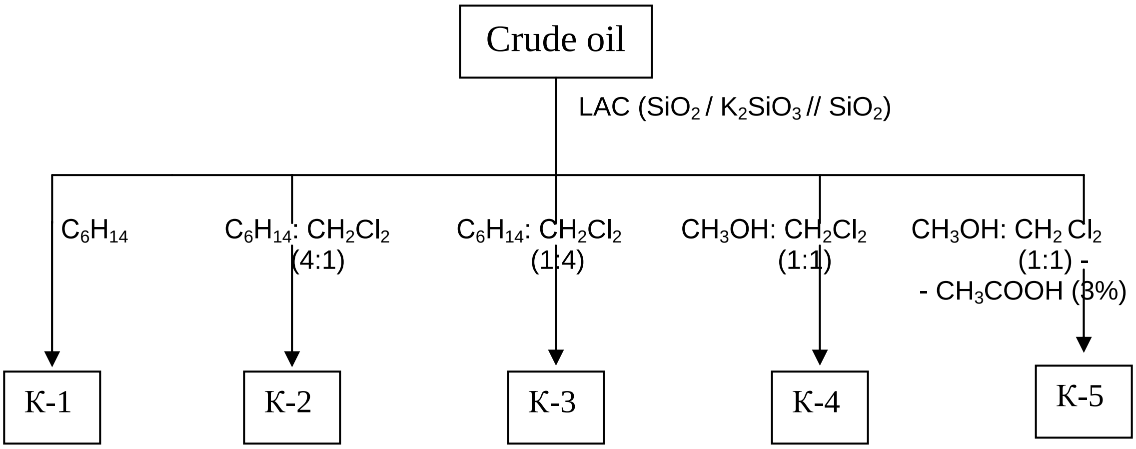

Figure 1. Analytical procedure.

Results and Discussion

Chromatographic behavior of model compounds. The given scheme was preliminary approved on a mixture of model compounds. Since aliphatic and aromatic ketones[6,12-15]] , were earlier identified in oils so 8-pentadecanone, fluoren-9-one, indane-1-one and xantone were used as model compounds. Based on our data[15] saturated aliphatic acids of normal structure (*n*-acids) C_{10}–C_{30}, among which even homologues containing up to 20 carbon atoms predominated, were found to prevail in Jurassic oils of West Siberia. As far as palmitic (C_{16}) and stearic (C_{18}) acids predominated therefore they were used as model compounds.

The results obtained on separation of model compounds are presented in Figure 2.

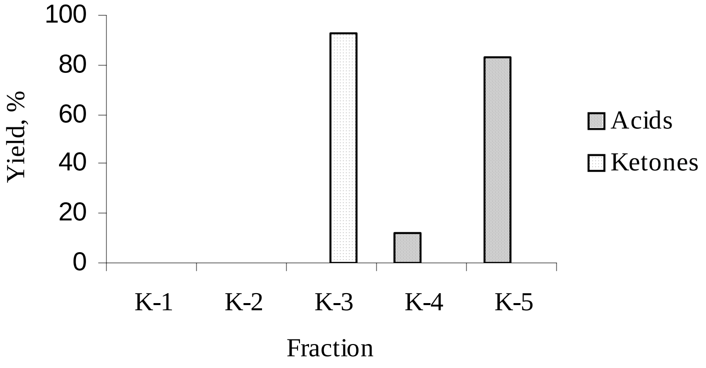

Figure 2. The results of model compounds separation

Thus, as a result of model compounds separation by the given scheme ketones were completely concentrated in fraction K-3, which was eluted with a mixture of petroleum ether: dichloromethane (1:4), and 83.1 % of acids were concentrated in fraction K-5, which was eluted with 3 % solution of formic acid mixed with dichloromethane:methanol (1:1).

Separation of ketones and acids from crude oils. Three West Siberian oils differing in their characteristics were used as the objects of research. The characteristics of these objects are presented in Table 1. As is seen from the presented data all thee oils are characterized by different contents of hydrocarbons (HC), resins and asphaltenes (R+A), sulfur, nitrogen and oxygen.

Table 1. General characteristics of oils.

Deposit	Depth of sediment, m	Content, % wt.				
		HC	R+A	S	N	O
Tungolskoye	2603-2610	94.2	5.8	0.22	0.10	0.68
Gerasimovskoye	2742-2750	88.0	9.8	0.88	0.10	1.05
Pikhtovoye	2906-2927	82.4	17.5	0.82	0.15	0.99

The results of chromatographic separation of oils into fractions and the contents of acids and ketones are presented in Table 2.

Table 2. The results of chromatographic separation of oils.

Sample	Fraction	Yield, %.	Group content, % wt.		Degree of separation, %	
			CO	COOH	Ketones	Acids
Pikhtovoye	Crude oil	-	0.29	0.02	-	-
	K-1	70.7	0.00	0.00	0.0	0.0
	K-2	5.1	0.45	0.00	7.9	0.0
	K-3	16.7	0.93	0.00	53.6	0.0
	K-4	2.6	0.47	0.21	4.2	27.3
	K-5	4.9	0.00	0.28	0.0	68.6
	Total:	100	-	-	65.7	95.9
Gerasimovskoye	Crude oil	-	0.37	0.00	-	-
	K-1	78.2	0.00	0.00	0.0	0.0
	K-2	5.3	0.58	0.00	8.3	0.0
	K-3	10.7	1.75	0.00	50.6	0.0
	K-4	2.7	0.62	0.10	4.5	27.0
	K-5	3.1	0.00	0.23	0.0	70.2
	Total:	100.0	-	-	62.4	97.2
Tungolskoye	Crude oil	-	0.23	0.004	-	-
	K-1	85.1	0.00	0.000	0.0	0.0
	K-2	3.8	0.69	0.000	11.4	0.0
	K-3	7.5	1.61	0.000	52.6	0.0
	K-4	0.9	0.72	0.090	2.8	20.3
	K-5	2.7	0.00	0.110	0.0	74.3
	Total:	100	-	-	66.8	94.6

In accordance with the data presented in Table 2 the greatest contents of ketones (51-54 %) were observed in fraction K-3, which was eluted by the mixture of petroleum ether: dichloromethane (1:4). The greatest contents of acids (69-74 %) were observed in fraction K-5, which was eluted by 3 % formic acid in a mixture of dichloromethane: methanol (1:1).

According to the data obtained on GC analysis of methyl ethers of the separated acids saturated carboxylic acids of normal structure (*n*-acids) C_{12}–C_{26} with even/odd prevalence were found to predominate in Gerasimovskaya oil. Palmitic (C_{16}) and stearic (C_{18}) were dominating acids (Figure 3).

According to the data of GC–MS analysis a homologous series of alkylketones (*n*-alkane-2-ones) of structure C_8–C_{28} was found in ketones concentrate without prevalence of either even or odd compounds. The content of n-alkane-2-ones C_{10} and C_{16} was maximal.

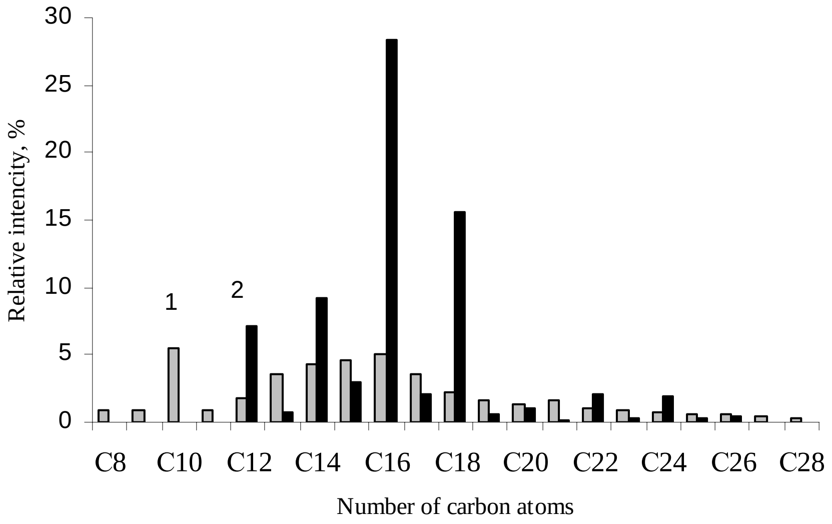

Figure 3. Distribution of n-alkane-2-ones (1) and n-acids (2) in oil recovered from Gerasimovskoye oil field.

Conclusion

Chromatography on the mixed sorbent (silica gel modified with 10% potassium silicate/silica gel) with specially chosen set of solvents is an effective tool for separation of ketones and acids from crude oils. It was proved by testing the elution behavior of model compounds and by separation of ketones and acids from three West Siberian oils.

Using this method for the analysis of crude oils a degree of separation amounted to 51-54 % for ketones, and 69-74 % for acids.

It has been determined that saturated alkylketones and fatty carboxylic acids (n-alkane-2-ones and n-acids accordingly) predominate in ketones and acids concentrates obtained from West Siberian oils using the given method.

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