Chromatographic Isolation of Sulphur Compounds from Oil with the Use of Tin Tetrachloride

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(Received May 24, 2004)

Abstract

Using sweet and sulphurous oils of West Siberia as an example, the regularities in chromatographic isolation and separation of sulphur compounds (SC) with the use of tin tetrachloride have been studied for the first time. It has been demonstrated that the efficiency of SC separation depends on the content of total sulphur in oil. The high extent of decontamination of the studied oils from SC is achieved: 72–95 % with respect to total sulphur and 68–95 % with respect to sulphide sulphur. Most part of SC is isolated with benzene chromatographic fraction irrespective of sulphur content of oil, of Pr/Ph ratio, and of geological confines of a reservoir. Sulphur compounds of the studied oils are presented by thiophenes and sulphides. Oils with 0.22–0.68 mass % of the total sulphur are dominated by alkyl-substituted thiacycloalkanes among sulphides and by alkyl-substituted dibenzothiophenes among thiophenic compounds. Oils with 0.94–1.14 mass % of the total sulphur are dominated by alkylbenzothiacycloalkanes and alkylnaphthenodibenzothiophenes.

INTRODUCTION

One of the major problems in comprehensive oil processing is isolation and qualified use of its heteroatomic components. Sulphur compounds (SC) are the constituents of practically all oils and oil products. Compounds of sulphur that are present in an oil stock considerably complicate oil refining technology, deteriorate the quality of oil products, speed up a corrosive wear of the process equipment, and cause an adverse environmental impact because of formation of sulphur oxides in the process of fuel combustion. The mentioned reasons are responsible for more and more severe constraints regarding the content of sulphur, which are placed on the hydrocarbon raw that is delivered to processors, as well as on oil products.

Current commercial methods for refining oil and its fractions are centred for the most part on destruction of SCs and their removal from combustibles. In oil refineries, the decontamination of oil products is made in units for hydrodecontamination, which has the effect that hydrogen sulphide is formed. This circumstance rules out the possibility of using the natural SC. Meanwhile, organic compounds of sulphur can be extracted from oil products in the form of concentrates and they can be applied in various branches of national economy.

In the context of the preceding, of interest are the investigations on isolating of organic compounds of sulphur from the oil stock, on obtaining the low-sulphur and sulphur products, and on their qualified use.

Previously [1], we have investigated the regularities of SC isolation from high-sulphur distillate fraction with the range of boiling 200–350 °C (content of total sulphur S_{tot} and sulphide sulphur S_s comprise 2.83 and 1.46 mass %, respectively) in the form of complexes with cobalt, nickel, zinc, iron, aluminium, titanium,

and tin chlorides. It has been demonstrated that tin tetrachloride represents the effective chelating agent for chromatographic isolation of oil SC in the form of soluble and insoluble complexes in the hydrocarbon medium. In the process, the high decontamination degree of the initial oil fraction from SC (85 %) can be achieved. Sulphur compounds of sulphide nature are concentrated in benzene fraction, and thiophenic compounds are in alcohol-chloroform fraction.

By the example of sweet and sulphurous oils of West Siberia, we have studied for the first time the regularities of chromatographic isolation and separation of SC with the use of tin tetrachloride.

EXPERIMENTAL

The samples of sweet (content of $S_{tot} < 0.50$ mass %) and sulphurous (content of $S_{tot} > 0.50$ mass %) oils from upper Jurassic depositions in West Siberia (Table 1) were taken as mother substance.

Eluents, specifically, *n*-hexane, benzene, chloroform, and ethanol, that represented the reagents of "pure" (ch.) qualification, were desiccated and refined by distillation. Tin tetrachloride $SnCl_4$ (pure) was used without any additional purification.

The content of total sulphur S_{tot} was determined by the procedure described in [2] and that of sulphide sulphur S_s, by potentiometric titration [3]. The analysis of structural-group composition of SC was conducted by the mass spectrometry method [4].

Sulphur compounds were isolated from oil with the use of the procedure given in [5].

RESULTS AND DISCUSSION

Table 1 presents data about the quantitative content of SC in the studied oils. Fields of the studied oils are located in the territory of Vasyugan and Kaymysov oil-and-gas bearing fields within the limits of Kaymysov anticline, Pudino megaswell, Nyurol'ka and Ust'-Tym valley. Oil source depositions of the studied oils lie in a depth interval of 2482–2808 m. They are characterized by various conditions of accumulation of initial organic matter, as witnessed by the magnitudes of the pristane/phytane ratio (Pr/Ph) [6].

In sweet oils, the content of S_{tot} varies from 0.22 to 0.42 mass % and S_s does from 0.016 to 0.140 mass %. The average content of sulphides comprises 31 rel. %. The Pr/Ph ratio varies from 1.6 to 2.8. Sulphurous oils are characterized by a large content of S_{tot} (0.57–1.14 mass %) and S_s (0.24–0.45 %). The average

TABLE 1

The characteristics of upper Jurassic oils of West Siberia

Deposit, well	Perforation interval, m	Pr/Ph*	Content, mass %	
			S_s**	S_{tot}
		Sweet oils		
Tungol'skoye, R-1	2603–2610	2.8	0.22/19	0.04
Ostaninskoye, 418	2484–2488	1.6	0.28/36	0.02
Chkalovskoye, 10	2560–2567	2.0	0.35/37	0.13
Zapadno-Ostaninskoye, 447	2535–2575	1.6	0.42/33	0.14
		Sulphurous oils		
Nizhnetabaganskoye, 8	2617–2625	0.7	0.57/25	0.14
Katyl'ginskoye, 105	2482–2487	0.9	0.59/29	0.17
Chvorovoye, 1	2765–2772	1.1	0.68/35	0.24
Zapadno-Katyl'ginskoye	2565–2571	1.0	0.94/48	0.45
Karayskoye, 3	2784–2808	0.9	1.14/35	0.40

* Pristane/phytane ratio.

** The first value is content (mass %); the second is rel. %.

TABLE 2

Results of isolation of sulphur compounds from oils by method of liquid adsorption chromatography of complexes with tin tetrachloride

Fraction characteristics	Sweet				Sulphurous oils				
	Tungol'skaya	Ostaninskaya	Chkalovskaya	Zapadno-Ostaninskaya	Nizhne-tabaganskaya	Katyl'ginskaya	Chvorovaya	Zapadno-Katyl'ginskaya	Karayskaya
HF									
Yield, %	63.8	61.6	63.4	69.0	45.8	56.8	44.9	57.5	38.6
Content in a sample*, %:									
S_{tot}	0.07/20	0.11/24	0.13/24	0.17/28	0.16/13	0.16/15	0.16/11	0.27/9	0.14/5
S_s	0.02/32	0.05/26	0.06/29	0.05/25	0.03/10	0.04/13	0.03/6	0.07/9	0.05/5
BF									
Yield, %	7.9	11.2	10.1	9.2	18.3	16.9	24.3	12.3	22.6
Content in a sample*, %:									
S_{tot}	0.73/26	0.81/32	1.15/33	1.35/30	0.87/28	1.46/42	1.22/44	2.41/32	2.77/55
S_s	0.15/30	0.33/31	0.38/30	0.39/26	0.37/48	0.35/35	0.43/44	1.19/33	0.89/50
ACF									
Yield, %	1.3	1.5	1.2	2.1	3.6	2.9	2.8	2.5	4.8
Content in a sample*, %:									
S_{tot}	1.89/11	1.97/11	2.32/8	2.28/11	1.92/12	3.52/17	4.50/19	4.33/12	3.42/14
S_s	0.09/3	0.71/9	0.68/6	0.62/11	0.43/11	0.64/11	0.69/8	1.55/9	0.78/9
IC									
Yield, %	3.4	6.1	2.6	4.0	10.8	9.8	11.0	9.0	10.3
Content in a sample*, %:									
S_{tot}	1.80/28	1.18/26	2.86/21	2.24/21	1.70/32	1.60/26	1.59/26	3.17/30	1.86/17
S_s	0.18/15	0.52/26	1.12/22	0.80/23	0.23/18	0.33/19	0.48/22	1.20/24	0.67/17

* The first value is an absolute content; the second is a relative content.

content of sulphides in oils comprises 34 rel. %. The Pr/Ph ratio varies from 0.7 to 1.3. Among SC of both sweet and sulphurous oils, the proportion of thiophenic compounds is higher than usual, by an average of 69 and 66 rel. %, respectively.

The results of chromatographic isolation of SC from oil crude with the use of $SnCl_4$ (Table 2) demonstrate that the hexane fraction (HF) is the most representative one. The yield of HF comprises 61.6–69.0 and 38.6–57.5 mass % for sweet and sulphurous oils, respectively. The yield of benzene fractions (BF) from sulphurous oils is higher than from sweet oils and it comprises 12.3–24.3 and 7.9–11.2 mass %, respectively. The total yield of alcohol and chloroform fraction (ACF) and the total yield of complexes indissoluble in the hydrocarbon medium (IC) is less for sweet oils than for sulphurous oils (3.8–7.5 and 11.5–15.1 mass %, respectively).

A correlation can be noticed between the total sulphur content and the SC distribution in the various chromatographic fractions extracted from oils with the reduction-oxidation conditions for accumulation of the initial organic matter.

As suggested by evidence from Table 2, HF isolates 20–28 rel. % S_{tot} and 25–32 rel. % S_s for the sweet oils, which are characterized by the higher than usual values of Pr/Ph ratio (>1.6). The most part of SC is extracted into BF: both with respect to S_{tot} (26–33 rel. %) and to S_s (26–31 rel. %). ACF isolates 8–11 rel. % of sulphur compounds and 3–9 rel. % of sulphides. The isolation degree of SC in the form of IC comprises 21–28 rel. % as to S_{tot} and 15–26 rel. % as to S_s.

The isolation degree of SC from sulphurous oils (Pr/Ph < 1.6) into HF does not exceed 17 rel. % with respect to S_{tot} and 13 rel. % with respect to S_s, and into BF, 28–55 rel. % with respect to S_{tot} and 33–50 rel. % with respect to S_s. ACF extracts 12–19 rel. % of sulphur compounds and 8–11 rel. % of sulphides. The isolation degree of SC in the form of IC comprises 17–32 rel. % with respect to S_{tot} and 17–24 rel. % with respect to S_s.

The comparison of data as regards the SC content of alcohol-chloroform and benzene fractions (see Table 2) demonstrates that the chromatographic fractions extracted from sulphurous oils, as compared to the same fractions from sweet oils, are characterized by a greater concentrating extent of the sulphur-containing compounds, both with respect to S_{tot} and S_s.

It should be noted that the chromatographic fractions, which were extracted from sweet and sulphurous oils, differ as to an average cumulative content of sulphur compounds and sulphides (Fig. 1). The extraction degree of combined SC into hexane eluate is higher from sweet (24 rel. %) than from sulphurous (11 rel. %) oils. A proportion of sulphides with the

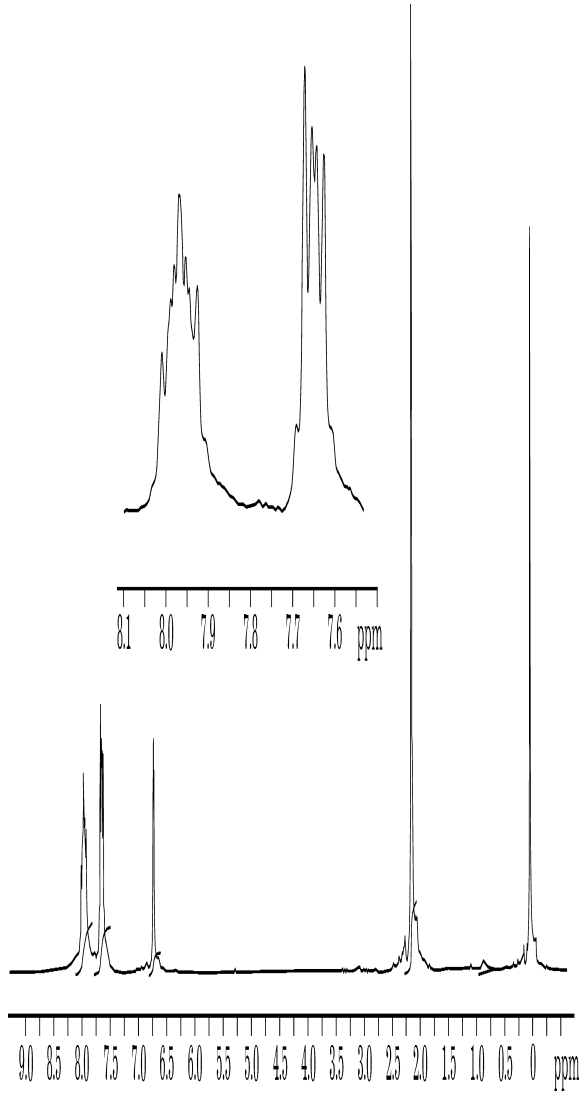

Fig. 1. Total content of sulphur compounds S_{tot} (*a*) and sulphides S_s (*b*) in the chromatographic fractions, which were extracted from sweet and sulphurous oils.

developed alkyl substitution in sweet oils is higher than in sulphurous oils (by an average of 28.0 and 8.6 rel. %, respectively). The isolation degree of SC into benzene fraction from oils that belong to sulphurous ones is more than from sweet oils (an average of 40 and 28 rel. % by the total sulphur, and 42 and 29 rel. % by the sulphide sulphur, respectively). The alcohol-chloroform fraction isolates an average of 10 rel. % of SC from sweet oils and 15 rel. % from sulphurous oils. The isolation degree into ACF for sulphides comprises 7 and 10 rel. %, respectively. The extraction into IC is on average 25 rel. % of SC irrespective of sulphur content of oil; the fraction of sulphides in IC comprises 20–22 rel. %. It should be noted that thiophenic compounds prevail in the composition of SC from chromatographic fractions, except for the benzene fractions, which were extracted from sulphurous oils, wherein SC are represented by sulphides with the percentage of 42 rel. %.

Total isolation degree of SC into polar fractions (without taking into account HF) is practically unaffected by confines of a reservoir as regards the geologic pattern. Accordingly, for the oils lying within the limits of pool roof and valleys, the average degree is 88.0 and 85.4 rel. %, respectively. This parameter is somewhat lower (74.0 rel. %) for the oils that are confined to the Pudino megaswell. Karayskaya oil from the Nyurol'ka valley is characterized by the highest isolation degree of SC, both with respect to S_{tot} and to S_s (95 rel. %). It is most sulphurous oil from the series of the studied oils.

From the data acquired, it is apparent (see Table 2) that the most part of SC is extracted into BF irrespective of sulphur content of oil, of the accumulation conditions for initial organic matter, and of geological confines of the reservoir.

We have investigated the structural-group composition of sulphur compounds from BF, which were extracted from oils with various value of total SC.

The major types of sulphides of this fraction are the compounds, whose composition is expressed by empirical formulae $C_nH_{2n-z}S$ ($z = 2$, 8) and $C_nH_{2n-z}S$ ($z = 8$, 14). The

TABLE 3

Structural-group composition of sulphur-containing compounds of sweet and sulphurous oils from upper Jurassic depositions in the various fields of Western Siberia, rel. %

Compound	z	M_r of the first representative in the series	Content				
			Tungol'skoye	Nizhnye-tabaganskoye	Chvorovoye	Zapadno-Katylrginskoye	Karayskoye
			Sulphides				
Thiabicycloalkanes	2	128	6.1	14.6	11.5	6.8	5.6
Thiatricycloalkanes	4	154	10.1	17.0	13.8	11.1	10.9
Benzothiacycloalkanes	8	136	7.8	6.9	8.4	22.5	16.9
Naphthothiacycloalkanes	14	186	1.5	0	1.6	2.4	2.7
			Thiophenes				
Trinaphthenothiophenes	10	176	15.0	9.9	2.9	7.3	9.3
Benzothiophenes	10	134	12.1	9.1	8.1	7.7	8.8
Naphthenobenzothiophenes	12	174	14.5	5.3	8.0	6.5	6.5
Dinaphthenobenzothiophenes	14	200	4.6	7.0	3.0	2.0	3.2
Dibenzothiophenes	16	184	10.7	17.9	19.0	9.0	13.8
Naphthenobenzothiophenes	18	224	7.1	8.2	5.4	16.5	14.8
Dinaphthenonaphthothiophenes	20	236	7.5	3.3	5.8	5.2	5.2
Naphthobenzothiophenes	22	234	3.1	0.7	2.5	2.2	2.1

Notes. 1. M_r is molecular mass; z is a degree of hydrogen unsaturation in $C_nH_{2n-z}S$. 2. Content of total sulphur (S_{tot}) in oils comprises for the fields, mass %: Tungol'skoye – 0.22, Nizhnyetabaganskoye – 0.57, Chvorovoye – 0.68, Zapadno-Katyl'ginskoye – 0.94, Karaiskoye – 1.10.

proportion of these compounds in the oils of Tungol'skoye, Nizhnyetabaganskoye, Chvorovoye, Zapadno-Katyl'ginskoye, and Karayskoye fields comprises 35.5, 38.5, 35.3, 42.3, and 36.1 rel. % from total SC, respectively. Among the specified types of compounds of sulphide nature, thiacycloalkanes dominate in oils with content of S_{tot} 0.22, 0.57, and 0.68 mass %, the content of these compounds being less in more sulphurous oils. Oils with content of S_{tot} of 0.94 and 1.14 mass % are characterized by an increased content of benzothiacycloalkanes. The proportion of structures with z being equal to 4 and 8 is higher in all oils.

It is evident from data of Table 3 that as the sulphur content of oil increases, the proportion of tri- and tetracyclic aromatic SC rises and accordingly, the proportion of dicyclic compounds is reduced. In BF that was isolated from sweet oil, the proportion of benzothiophenes is higher than that of dibenzo- and naphthobenzothiophenes. In sulphurous oils, the proportion of dibenzo- and naphthobenzothiophenes is higher than the proportion of benzothiophenes.

The structures of sulphides and thiophenes are characterized most likely by the existence of 1–4 short alkyl (methyl and ethyl) substituents.

CONCLUSIONS

Thus, the regularities of chromatographic isolation and separation of SC with the use of tin tetrachloride have been studied for the first time by the example of sweet and sulphurous oils of West Siberia. It has been demonstrated that the liquid adsorption chromatography with the use of $SnCl_4$ is more effective to isolate SC of sulphurous oils. The high decontamination extent of the studied oils from SC is achieved: 72–95 % with respect to S_{tot} and 68–95 % to S_s. The total isolation degree of SC into polar fractions from sweet oils averages 64 and 58 rel. % as to the total and sulphide sulphur, and from sulphurous oils, 81 and 72 rel. %, respectively. The most part of SC is extracted into BF irrespective of sulphur content of oil, of the Pr/Ph ratio, and of geological confines of a reservoir. Thiophenic compounds dominate within the composition of SC from chromatographic fractions. It has been demonstrated that thiophenes and sulphides represent SCs from the studied oils. In oils with mass fraction of the total sulphur being 0.22–0.68 %, alkyl-substituted thiacycloalkanes prevail among sulphides, and alkyl-substituted dibenzothiophenes do among thiophenic compounds. Oils with content of the total sulphur being 0.94–1.14 mass % are dominated by alkylbenzothiacycloalkanes and alkylnaphthenodibenzothiophenes.

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