Optimization of the preparative separation of petroleum maltenes by liquid adsorption chromatography

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Abstract

Liquid adsorption chromatography on classical adsorbents is most often used for the group analysis of high-boiling petroleum fractions, i.e., their separation into saturated hydrocarbons, mono-, di- and polyaromatics, and polar aromatic compounds. The optimization of a preparative separation of petroleum maltenes into the mentioned hydrocarbon compound classes by liquid adsorption chromatography on dual silica gel-neutral alumina column was performed. Conditions of this separation, i.e., the volume of the mobile phases used, their composition and flow-rate were optimized on the base of detailed analysis of the chromatographic fractions obtained using elemental analysis, UV spectrophotometry, ^{1}H NMR and vapor pressure osmometry. This optimization allows a substantial shortening in time of separation and separated compound class concentrates of a higher purity can be obtained.   © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The elucidation of the compound class composition of high-boiling petroleum fractions and their processing products is a prerequisite for process control work and for obtaining fundamental information on cracking, hydrotreating, blowing and other refining processes.

The multicomponent character of petroleum fractions is increased with their increasing boiling point. This is due to the increasing number of isomers for the given carbon number and the increasing number of heteroatom-containing compounds. For this reason the chromatographic separation of high boiling petroleum fractions into individual components is practically impossible. For practical purposes the sepa-

ration of these fractions into groups of chemically related compounds is performed using individual techniques of liquid chromatography or their suitable combination.

Great attention has been paid to developing appropriate procedures, which meet most of the generally desired capabilities, i.e., separation of saturated hydrocarbons, mono-, di- and polyaromatics and polar compounds. The separation scheme combining liquid chromatography on classical adsorbents, silica gel and neutral alumina, and macroporous ion exchangers developed by US Bureau of Mines (USBM) and American Petroleum Institute (API) represents a fundamental contribution to solving this problem [1,2]. Modifications of this USBM–API separation scheme were proposed by Sawatzky et al. [3] and Jewell and co-workers [4,5]. All these three preparative separation schemes [1–5] are the pro-

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cedures most often used for compound class separation of high-boiling petroleum fractions in original or modified version [6–13]. Wallace et al. [14] studied the separation of high-boiling petroleum fractions on classical adsorbents and ion exchangers and recommended for this sample type separation to use only liquid chromatography on classical adsorbents. Recently, a procedure for the compound class separation of sediment, rock and coal extracts, petroleums and bitumens using silica gel and silica gel modified with HCl and KOH was proposed by Willsch et al. [15]. The separation of fossil fuels and their processing products with the use of extrographic technique was also studied [16,17].

Due to the above-mentioned character of high-boiling petroleum fractions an overlapping of the elution of individual compound classes, i.e., the purity of separated compound class concentrates is the main problem of their separation. In this paper the optimization of the preparative separation of hydrocarbon compound classes present in maltenes, forming a substantial part of petroleum residue, was performed using liquid adsorption chromatography on classical adsorbents – silica gel and neutral alumina. The aim of this optimization was to shorten the time of separation and mainly to obtain compound class concentrates of a higher purity.

2. Experimental

The vacuum residue of West-Siberian petroleum and a blown bitumen prepared by a laboratory oxidation of this residue were used as starting materials for the preparation of maltenes by extraction with pentane. Properties of these materials are introduced in Table 1.

The optimization of preparative separation of petroleum maltenes was studied using a glass column

of 650 mm×26.6 mm I.D. Its lower half was packed with neutral alumina 90, Lachema (Brno, Czech Republic; particle size about 0.1–0.2 mm) which had been activated at 400°C for 8 h. The upper half was packed with silica gel 100, Fluka (particle size 0.063–0.200 mm) purified by Soxhlet extraction with a benzene–diethyl ether–methanol (1:1:3, v/v) mixture. After extraction, the adsorbent was dried at 50°C under vacuum 4.4 kPa for 8 h and then activated at 160°C for 48 h.

The sample of maltenes from the vacuum residue (1–4.3 g) was dissolved in 10 cm^3 of hexane and applied to the adsorbent column prewetted with hexane. The sample was separated into saturated hydrocarbons, mono-, di- and polyaromatics and polar aromatic compounds by a successive elution with series of mobile phases using the modified chromatographic method of Sawatzky et al. [3]. A constant flow-rate of the mobile phase (10–20 cm^3 min^{-1}) was ensured with a pump. In the course of the separation subfractions of 100 cm^3 volume were collected. The chromatographic fractions obtained were then stripped of the mobile phases on a rotary vacuum evaporator and dried in a vacuum dryer at 80°C and a pressure of 4.4 kPa to a constant mass.

2.1. Analytical methods

Carbon and hydrogen contents were determined with a Perkin-Elmer analyzer, Model 240C.

UV spectra were measured in hexane solution on a Shimadzu Model UV 1601 spectrophotometer with a 10 mm thickness of the absorbing layer.

[1]H nuclear magnetic resonance (NMR) spectra were measured on a Bruker Model AM 400 spectrometer at 400 MHz at 50°C using about 0.1 g of sample dissolved in 0.6–0.7 cm^3 of 0.05 *M* solution of chromium acetylacetonate in $CDCl_3$ with the addition of 1% (w/w) of tetramethylsilane.

Table 1
Characteristics of used bitumens

Sample	Softening point R&B[a] (°C)	Penetration at 25°C (0.1 mm)	Asphaltenes content[b] (%, w/w)
Vacuum residue	41	205	12.1
Blown bitumen	88	3	37.7

[a] ASTM D 36.
[b] Separated with pentane.

Relative average molecular mass was determined on a Knauer 11.00 osmometer in benzene at 37°C. Samples were measured at four concentrations and the results obtained were extrapolated to infinite dilution. The osmometer was calibrated with squalane and anthracene.

Selected structural parameters describing the average molecule of fractions from the chromatographic separation of maltenes were calculated according to Williams [18] using elemental analysis, ^{1}H NMR and vapor pressure osmometry data.

3. Results and discussion

The purity of compound class concentrates obtained from the chromatographic separation of high-boiling petroleum fractions by liquid adsorption chromatography represents one of the main problems of this separation. Due to the character of the individual hydrocarbon classes present an overlapping of their elution can be observed in the course of their chromatographic separation.

It was established that during the separation of high-boiling petroleum fractions on dual silica gel-neutral alumina column a part of monoaromatics is eluted commonly with saturated hydrocarbons [19]. This fact is understandable, considering that a mono-aromatic hydrocarbon molecule with an M_r of about 750 is estimated to contain, besides six aromatic carbon atoms, about 48 saturated carbon atoms in substituents on the aromatic ring, and the aromaticity (the relative content of aromatic carbon atoms) of this monoaromatic hydrocarbon is about 0.11. As a result of such a high content of saturated carbon atoms, the effect of the aromatic ring may be weakened to such an extent, that the chromatographic behavior (i.e., the elution volume) of some monoaromatic hydrocarbons may be similar to that of some saturated hydrocarbons present in maltenes.

Similarly, a partial overlapping of aromatic hydrocarbon classes elution can be observed also in the course of separation of mono- and diaromatics and di- and polyaromatics. An extent of this overlapping depends on the average molecular mass of the high-boiling petroleum fraction to be separated. The higher the M_r of this fraction is, the higher is the content of saturated carbon atoms in the mono-, di-

and polyaromatics present, and consequently also the extent of overlapping during their separation.

To optimize the amount of maltenes and a flow-rate of mobile phases for the preparative separation of maltenes by liquid adsorption chromatography on dual silica gel-neutral alumina column a series of chromatographic experiments was performed using an elution order according to the modified method of Sawatzky et al. [3]. The volumes of the mobile phases were the same, but calculated for a size of the chromatographic column used. Because of a previous experience, only the amount of benzene was increased by about 25% to obtain a better separation of the yellow polyaromatic fraction from the brown black fraction of polar aromatic compounds 1. The elution of polar aromatic compounds 2 with methanol was not performed. This eluent partially solved alumina and eluted only a negligible part of maltenes.

Table 2 presents the column loading and mobile phase flow-rate used for the chromatographic experiments performed with maltenes from the vacuum residue. In Table 3 the composition of mobile phases, their volumes used, and the character of separated fractions are introduced. Table 4 summarizes the results obtained, i.e., the contents of separated compound classes. As an example the course of maltenes separation for experiment No. 5 is shown in Fig. 1. Subfractions of 100 cm^3 volume were collected after removing 200 cm^3 of hexane. This corresponded with a sufficient reserve to a death volume of the chromatographic column 275 cm^3, which was estimated as the amount of hexane necessary for a total wetting of the column packed with both adsorbents.

It is evident from the data introduced in Tables 2

Table 2
Column loading and flow-rate used for chromatographic separation of maltenes from vacuum residue

Experiment No.	Mass of maltenes (g)	Mobile phase flow-rate (cm^3 min^{-1})
1	0.9936	10
2	1.3260	10
3	1.5425	10
4	2.1494	10
5	4.2571	10
6	4.2935	20

Table 3
Composition and volumes of mobile phases used

Mobile phase	Volume (cm^3)	Prevailing compounds type
Hexane	1000	Saturated hydrocarbons
Hexane–benzene (19:1, v/v)	1200	Monoaromatics
Hexane–benzene (17:3, v/v)	1200	Diaromatics
Benzene	500	Polyaromatics
Benzene–diethyl ether–methanol (1:1:3, v/v)	500	Polar aromatic compounds 1
Compounds remain on adsorbents used	–	Polar aromatic compounds 2

and 4 that no effect of separated maltenes amount on the efficiency of their separation, i.e., on the yields of individual fractions, was found up to the value of 4.3 g. A partial penetration of dark polar aromatic compounds into the column of alumina was observed visually for chromatographed maltene amount higher than 4.5 g. Therefore 4.5 g of maltenes were considered as a maximum loading for the used chromatographic column size. The efficiency of maltenes separation was not affected by a mobile phase flow-rate up to the value of 20 cm^3 min^{-1}. At higher flow-rates of mobile phase the pressure gradient along the column was significantly increased.

The course of the elution of saturated hydrocarbons and monoaromatics was evaluated using UV spectrophotometry. UV spectra of subfractions eluted with hexane and the mixture hexane–benzene (19:1, v/v) were measured in the region 250–320 nm. Values of an integral absorption coefficient for these subfractions were calculated using measured concentration values and absorbance values determined by a graphic integration. Regarding the course of maltenes elution with hexane–benzene (19:1, v/v,

see Fig. 1), only monoaromatics should be eluted in subfraction No. 13. Therefore the integral absorption coefficient of this subfraction was considered to be the coefficient of monoaromatics present in the sample. Using this coefficient the content of monoaromatic hydrocarbons in other subfractions was determined. It was established that subfraction Nos. 1 and 2 contained only saturated hydrocarbons. Starting from subfraction No. 3 monoaromatics were eluted and their content was increased with an increasing elution volume. From subfraction No. 7 this type of aromatic hydrocarbons prevailed.

To evaluate the course of maltenes separation, subfractions forming a chromatographic peak of corresponding compounds type and subfractions eluted in the valley between two chromatographic peaks were always combined (see Fig. 1 and Table 5). The separation of maltenes with the described fraction combining was repeated some times to obtain a sufficient amount of collected fractions enabling their detailed analysis.

Elemental analysis data and the average molecular mass values for subfractions from 1 to 37 are presented in Table 5. Table 6 summarizes the

Table 4
Results of chromatographic separations of maltenes from vacuum residue

Experiment No.	Fractional composition[a] (%, w/w)					
	Saturated hydrocarbons	Monoaromatics	Diaromatics	Polyaromatics	Polar aromatic compounds	
					1	2[b]
1	9.2	9.9	9.1	16.5	47.0	8.3
2	9.6	9.5	8.9	16.7	46.4	8.9
3	9.1	9.4	9.0	15.9	45.8	10.8
4	9.3	9.2	9.1	16.3	46.2	9.9
5	9.6	9.4	9.2	16.2	46.9	8.7
6	9.9	10.1	8.9	17.1	45.2	8.8

[a] Relative to the amount of separated maltenes.
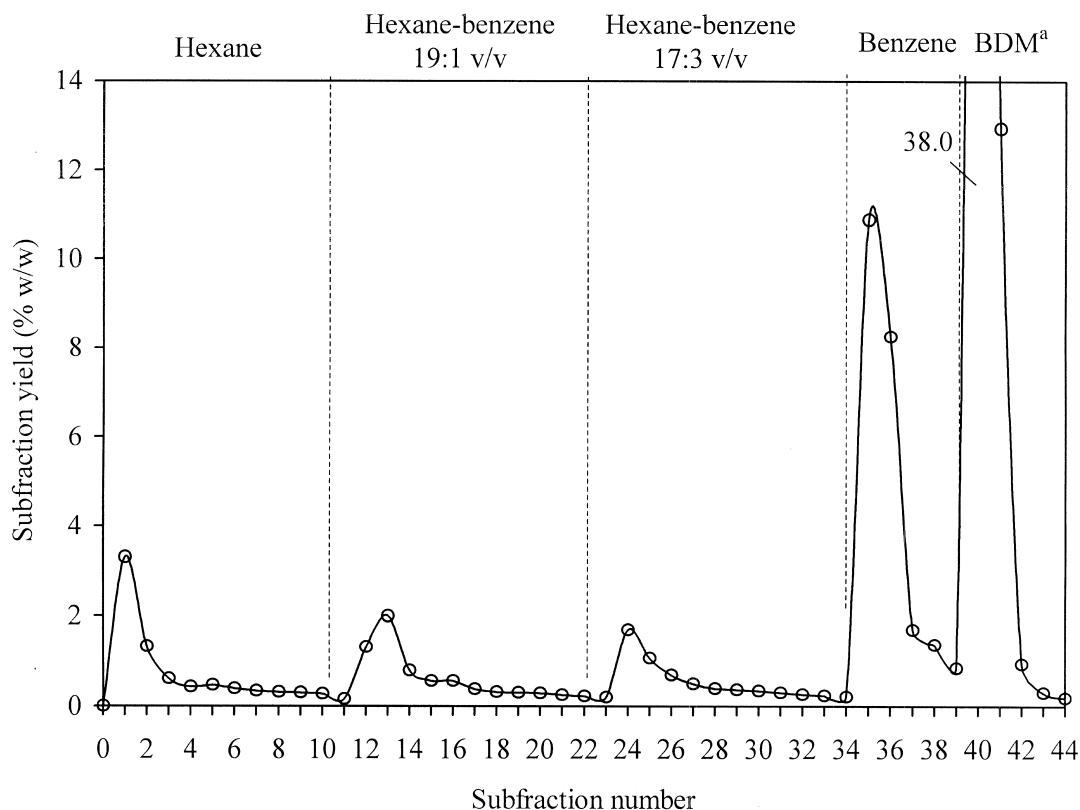[b] Calculated by difference.

Fig. 1. Course of maltenes separation for experiment No. 5 ([a]benzene–diethyl ether–methanol, 1:1:3, v/v).

relative abundance of the individual types of hydrogen. The values of structural parameters describing an average molecule of the aromatic fractions calculated according to Williams [18] are introduced in Table 7. Only the number of aromatic rings in the average molecule (parameter R_A) of mono- and

Table 5
Elemental composition and relative average molecular mass for hydrocarbon subfractions from chromatographic separation of maltenes from vacuum residue

Subfraction No.	C (%, w/w)	H (%, w/w)	$(H/C)_{at}$	M_r
1–6	85.7	13.9	1.93	725
7–12	86.3	13.2	1.82	720
13–15	86.0	12.7	1.76	740
16–19	85.2	12.0	1.68	735
20–22	85.1	11.9	1.68	725
23–26	85.5	11.8	1.65	720
27–30	85.4	10.8	1.51	750
31–34	85.4	10.5	1.47	770
35–37	85.7	10.2	1.41	820

Table 6
Relative abundance of hydrogen atom types for hydrocarbon subfractions from chromatographic separation of maltenes from vacuum residue

Subfraction No.	H_1 [a]	H_2	H_3	H_4
1–6	0.000	0.761	0.239	0.000
7–12	0.056	0.717	0.200	0.027
13–15	0.076	0.697	0.189	0.038
16–19	0.100	0.659	0.186	0.055
20–22	0.105	0.651	0.191	0.053
23–26	0.107	0.645	0.193	0.055
27–30	0.138	0.612	0.176	0.074
31–34	0.132	0.604	0.174	0.090
35–37	0.161	0.576	0.164	0.099

[a] H_1, hydrogen atoms of CH, CH_2 and CH_3 groups in the α-position to aromatic rings (2.0–4.0 ppm); H_2, hydrogen atoms of CH_3 groups in the β-position and CH and CH_2 groups in the β-position and more distant to aromatic rings (1.0–2.0 ppm); H_3, hydrogen atoms of CH_3 groups in the γ-position and more distant to aromatic rings (0.5–1.0 ppm); H_4, aromatic hydrogen atoms (6.0–9.0 ppm).

Table 7
Selected structural parameters for aromatic hydrocarbon subfractions from chromatographic separation of maltenes from vacuum residue

Subfraction No.	Structural parameter[a]						
	f_a	n	% AS	C_A^M	C_S^M	R_A	R_S
7–12	0.09	17.2	52	4.7	47	0.8	2.8
13–15	0.14	12.7	50	7.5	46	1.4	3.6
16–19	0.21	9.5	47	10.9	41	2.2	4.4
20–22	0.21	9.0	49	10.9	41	2.2	4.5
23–26	0.22	8.8	49	11.4	40	2.4	4.5
27–30	0.32	6.7	47	16.8	36	3.9	5.5
31–34	0.35	6.9	42	19.0	35	4.7	5.2
35–37	0.39	5.6	46	22.8	36	5.9	6.4

[a] f_a, aromaticity, i.e., relative content of aromatic carbon atoms; n, average number of carbon atoms per saturated substituent of aromatic rings; % AS, percentage of non-bridge aromatic carbon with saturated substituents; C_A^M, number of aromatic carbon atoms in an average molecule; C_S^M, number of saturated carbon atoms in an average molecule; R_A, number of aromatic rings in an average molecule; R_S, number of saturated substituents of aromatic rings in an average molecule.

diaromatics was calculated using the value of the average number of aromatic carbon atoms (parameter C_A^M). The calculation of this parameter according to Williams [18] in the case when 1–2 aromatic rings are present in an average molecule is incorrect.

It is evident from the calculated values of the aromatic carbon atoms number in an average molecule (Table 7, parameter C_A^M) that monoaromatics

are the dominant type of compounds in subfraction Nos. 7–12 and 13–15. Diaromatics prevail in subfraction Nos. 16–19, 20–22 and 23–26, and finally in subfraction Nos. 27–30, 31–34 and 35–37 polyaromatics are eluted. Concerning other structural parameters, the percentage of non-bridge aromatic carbon atoms with a saturated substituent (parameter % AS) lies in the range 42–52%. The average number of carbon atoms per saturated substituent of aromatic rings decreases in the framework of one mobile phase with an increasing elution volume and further also with an increasing average number of aromatic carbon atoms.

Regarding the above mentioned facts, another chromatography of maltenes from the vacuum residue was performed for which the mixtures hexane–benzene with a lower content of benzene (24:1 and 22:3, v/v) were used. The aim was to shift the elution of diaromatics eluted commonly with monoaromatics and the elution of polyaromatics eluted commonly with diaromatics to higher elution volumes and so to improve their separation. Upon the use of hexane–benzene (24:1, v/v), the separation of mono- and diaromatics was the same as when hexane–benzene (19:1, v/v) was used. In the case of the separation of di- and polyaromatics, the shift of the polyaromatics elution to higher elution volumes by about 200 cm³ was found using hexane–benzene (22:3, v/v).

Table 8
Optimized composition and volumes of mobile phases for preparative separation of petroleum maltenes on used chromatographic column

Mobile phase	Volume (cm³)	Prevailing compounds type
Hexane	600	Saturated hydrocarbons
Hexane–benzene (24:1, v/v)	500	Monoaromatics
Hexane–benzene (22:3, v/v)	500	Diaromatics
Benzene	500	Polyaromatics
Benzene–diethyl ether–methanol (1:1:3, v/v)	500	Polar aromatic compounds 1

Table 9
Fractional composition of maltenes from vacuum residue (VR) and blown bitumen (BB)

Sample	Fractional composition (%, w/w)					
	Saturated hydrocarbons	Monoaromatics	Diaromatics	Polyaromatics	Polar aromatic compounds	
					1	2[a]
VR	8.4	7.7	8.0	21.1	47.0	7.8
BB	12.9	9.1	6.5	20.9	42.2	8.4

[a] Calculated by difference.

Table 10
Elemental composition and relative average molecular mass for fractions from chromatographic separation of maltenes from vacuum residue (VR) and blown bitumen (BB)

	Fraction[a]	C (%, w/w)	H (%, w/w)	$(H/C)_{at}$	M_r
VR	SH	85.5	13.8	1.92	740
	MA	86.6	13.0	1.79	730
	DA	85.4	11.8	1.65	720
	PA	85.2	10.4	1.45	770
	APC 1	83.4	9.9	1.42	990
BB	SH	85.7	13.8	1.92	740
	MA	86.4	13.0	1.79	760
	DA	85.5	11.9	1.66	750
	PA	85.0	10.6	1.48	800
	APC 1	83.7	10.3	1.46	950

[a] SH, saturated hydrocarbons; MA, monoaromatics; DA, diaromatics; PA, polyaromatics; APC 1, aromatic polar compounds 1.

Table 11
Relative abundance of hydrogen atom types for fractions from chromatographic separation of maltenes from vacuum residue (VR) and blown bitumen (BB)

	Fraction	H_1	H_2	H_3	H_4
VR	SH	0.005	0.760	0.232	0.003
	MA	0.073	0.700	0.199	0.028
	DA	0.109	0.657	0.188	0.046
	PA	0.157	0.586	0.160	0.097
	APC 1	0.165	0.592	0.167	0.076
BB	SH	0.005	0.767	0.227	0.003
	MA	0.075	0.725	0.169	0.031
	DA	0.114	0.650	0.188	0.048
	PA	0.159	0.587	0.171	0.083
	APC 1	0.144	0.601	0.178	0.077

With respect to this finding and to the courses of maltenes separation discussed above the volumes of mobile phases necessary for the elution of individual compound classes were adjusted. The composition of mobile phases and their volumes proposed for the used chromatographic column size are summarized in Table 8.

These optimized conditions of the studied preparative separation of petroleum maltenes were verified using maltenes separated from a blown bitumen prepared by a laboratory oxidation of West-Siberian petroleum vacuum residue. The same procedure as in the case of maltenes separated from the above mentioned vacuum residue was used. Obtained results confirmed the proposed volumes of mobile phases and their composition introduced in Table 8. The both maltenes were separated using these optimized conditions. Their fractional composition determined by this separation is introduced in Table 9. The elemental composition, relative average molecular mass, relative abundance of individual hydrogen atom types and values of selected structural parameters for the individual compound class concentrates separated from the both maltenes are summarized in Tables 10–12.

4. Conclusions

Conditions of the preparative separation of hydrocarbon compound classes present in petroleum maltenes were optimized by liquid adsorption chromatography on dual silica gel-neutral alumina column.

Table 12
Selected structural parameters for fractions from chromatographic separation of maltenes from vacuum residue (VR) and blown bitumen (BB)

	Fraction	Structural parameter						
		f_a	n	% AS	C_A^M	C_S^M	R_A	R_S
VR	MA	0.12	13.3	57	6.2	46	1.0	3.5
	DA	0.22	8.8	54	11.3	40	2.3	4.6
	PA	0.37	5.8	44	20	35	4.2	6.0
	APC 1	0.37	5.6	51	25	43	6.2	7.7
BB	MA	0.13	12.9	55	6.5	45	1.1	3.5
	DA	0.22	8.4	54	11.4	41	2.3	4.9
	PA	0.35	5.8	48	19	37	4.1	6.4
	APC 1	0.34	6.4	47	23	43	5.2	6.7

Optimized conditions of this separation, i.e., the volumes of mobile phases, their composition and flow-rate allow a substantial shortening in time of separation and separated compound class concentrates of a higher purity can be obtained.

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