

Investigation of oil shale and its pyrolysis tar from the Uvurjargalant deposit in Mongolia

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Abstract. *The yield, properties and composition of soluble and insoluble (kerogen) organic matter (OM) of oil shale (OS) from the Uvurjargalant deposit of Mongolia have been investigated in this study. The study results show that oil shale contains a low amount of moisture and volatile products, while the ash yield is high, 80.43 %, which implies that most parts of oil shale are minerals. The total amount of bitumens in oil shale was very low, 1.24 wt%, whereas the kerogen content was 22.84 wt%, which is relatively high compared to oil shales from other deposits in Mongolia. According to infrared (IR) spectral analysis and the ratio of hydrogen to carbon, the Uvurjargalant oil shale belongs to type I of oil shale. The thermogravimetric analysis (TGA) showed that the organic matter of oil shale decomposed in the temperature range of 300–750 °C and produced gas and liquid products. The pyrolysis tar of Uvurjargalant oil shale was subjected to an air distillation and four fractions were obtained, including one light fraction, two middle fractions and one heavy fraction with the following boiling temperatures: < 180 °C, 180–250 °C, 250–320 °C, > 320 °C, respectively. The yields of each fraction were determined. The silica gel chromatography (SGC) of the first three distilled fractions of oil shale pyrolysis tar with different boiling temperatures shows the greater part of each fraction to be soluble in dichloromethane (M) and the minor part to be soluble in hexane (H). This means that the three fractions are mostly polar compounds. On the basis of the results of gas chromatographic-mass spectrometric (GC/MS) analysis of the distilled light fraction, the fraction distilled at 180–250 °C and the one distilled at 250–320 °C obtained by SGC eluted with hexane, toluene (B) and dichloromethane, respectively. In total, 128 organic compounds soluble in hexane, 83 compounds soluble in toluene and 57 compounds soluble in dichloromethane were identified.*

Keywords: *Mongolian oil shale, pyrolysis, bitumen, thermogravimetry, kerogen.*

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1. Introduction

Oil shale (OS), which is distributed in many places worldwide, is a sedimentary rock containing organic matter (OM) called kerogen and belongs to the group of sapropel solid fuels [1]. Usually, oil shale is utilized by the thermal decomposition (pyrolysis) of its OM [2]. Therefore it is very important to determine OS thermal characteristics. The methods mostly used for determining OS thermal characteristics include techniques such as thermogravimetry (TG), etc. [3].

The geological surveys of coal and oil shale in Mongolia started in 1940. It has been found that significant oil shale resources lie in the central, eastern and southern parts of Mongolia and there are 13 oil shale-bearing basins and more than 40 oil shale deposits. 20% of these oil shale areas comprise an estimated resource of 788 billion tons. In 1980, the first program for studying oil shale in Mongolia was launched, and during this period a number of oil shale deposits, including Khoot, Eedemt, Ovdogkhooloin gashuun, Bayanerkhet, Chagzaliin khudag, Nariin gol, Ulaan tolgoi, Zuun shavartiin ovoo, Beliin jas, Togrog, Bayanjargalan and Sumiin nuur, have been studied more intensively, and some of the selected oil shale samples were sent to Estonia and Japan for more detailed chemical investigations [4, 5].

Located near the Bayanjargalan village of Dundgobi province in the central economic region of Mongolia there are large reserves of brown coal and oil shale, the oil shale deposit found at Khoot is distinguished from the other above-mentioned ones by that it also comprises brown coal. In this deposit, brown coal underlies oil shale. To enable brown coal to be extracted through open cast mining, oil shale is removed and treated as spoil [6–8].

In this study, we have chosen the oil shale of the Uvurjargalant deposit in Mongolia for more detailed investigation on its characteristics, pyrolysis, and the solid residue and condensed liquid products (pyrolysis tar and water) during the pyrolysis.

2. Experimental

2.1. Material

In the study, the oil shale sample of 0.2–0.5 mm granules taken from a depth of 0.8–1.5 m was used. The sample originated from the Uvurjargalant deposit in the Erdenetsant village, which is located 260 km west of Ulaanbaatar in Mongolia. The sample was crushed, sieved and dried at 105 °C.

The analytical samples of Uvurjargalant oil shale were prepared according to Mongolian National Standards (MNS 2719:2001) and their main technical characteristics, including the contents of moisture (MNS 656-79), ash (MNS 652-79) and volatile matter (MNS 654-79), were determined.

The organic elemental composition (C, H, O) of the oil shale sample was determined using the Vario EL III analyser.

Thermogravimetric analysis (TGA) was carried out at heating temperatures from 25 to 1050 °C and a heating rate of 10 °C/min, and continued for 120 min by employing a HITACHI TG/DTA7300 apparatus (Japan) using argon as a purge gas. The experiments were done using about a 10 mg oil shale sample with a size of 0.2 mm in a platinum crucible.

The pyrolysis experiment was performed in a laboratory vertical cylindrical retort made of stainless steel, which may contain 1000 g sample. The retort was placed in an electric furnace (model SNOL) with a maximum temperature of 950 °C. A chrome-alumel thermocouple was immersed in the oil shale bed to measure the actual heating temperature and equipment for temperature control (potentiometer). The retort was connected with an air-cooled iron tube, a water-cooled laboratory glass condenser and a collection vessel for the condensed liquid products (tar and pyrolysis water). The non-condensable gases after the water-cooled condenser left the system through a thin glass tube. The yields of the products, including hard residue (char), tar and pyrolysis water, were determined by weighing in % and the yield of gases by difference.

The liquid condensed products of oil shale pyrolysis form unmixed two layers and can be separated easily in a glass funnel. The upper layer is tar with black brown color and unpleasant smell. The bottom layer is pyrolysis water with bad smell and brown color. The final cleaning of tar from the pyrolysis water usually uses the thermally treated CaCl_2 by mixing and separating (filtering or centrifuging). Such purified pyrolysis tar was subjected to Fourier transform infrared spectroscopy (FTIR) and gas chromatographic-mass spectrometric (GC/MS) analysis.

The FTIR spectra of oil shale and its pyrolysis tar samples were obtained on an Interspec 200-X series of FTIR spectrometers with PIKE Diffusion IR accessories using a KBr disc containing 1% finely ground samples. All the spectra were measured in the frequency range of 4000–400 cm^{-1} , and 32 scans were taken per sample.

The column chromatography (CC) conditions of oil shale pyrolysis tar were the following:

- 5.0 mL glass column; 0.2 g tar sample for each solvent;
- organic solvents used for gas chromatography (GC): hexane (H), benzene (B) and dichloromethane (M), 20.0 mL of each solvent;
- sorbent used: 4.0 g activated silica gel.

The CC was carried out for obtaining the pyrolysis tar fractions soluble in hexane, benzene and dichloromethane. The organic solvent was evaporated from the obtained fraction for the determination of the yield of each fraction.

The conditions of the GC/MS analysis of each fraction were the following:

- the sample of each fraction: 1 ml of each fraction in 1 mL of each solvent;
- the sample for GC/MS analysis: 1 ml of each sample;

- apparatus used: Trace 1310, TSQ8000 GC-MS system and capillary column J W DB-5, 30 m, 0.25 mm I.D., 0.25 μ m (122-5032);
- carrier gas: He;
- the temperature program: 50–320 °C at a heating rate of 10 °C/min; the total run time 46 min;
- library used: the NIST library for the identification of the compounds.

3. Results and discussion

The results of proximate and ultimate analyses of Uvurjargalant oil shale are presented in Table 1.

Table 1. Proximate and ultimate analysis of Uvurjargalant oil shale, wt%

Proximate analysis, %				Ultimate analysis, %						
W ^a	A ^d	V ^d	Q ^{daf} , kcal/kg	C ^{daf}	H ^{daf}	N ^{daf}	O ^{daf}	S _{total}	H/C	O/C
2.66	80.43	19.04	912.00	70.21	9.02	1.50	17.57	1.70	1.54	0.18

Note: a – air-dried, d – dry, daf – dry ash free basis

The results of the main technical characteristics in Table 1 show that the oil shale sample has low moisture and organic volatile matter contents, but a high ash content (80.43 wt%), which implies that most of the oil shale are minerals. Also, the results of the ultimate analysis in Table 1 display the carbon content of oil shale to be lower than that of coal [9].

Thermogravimetric analysis is very important for organic raw materials, including coal and oil shale, and evaluation of their thermal processing, such as coking, pyrolysis, etc.

Thermogravimetric analysis is primarily used to estimate the yields of solid, liquid and gas products from the thermal decomposition carried out at high temperatures and in different gas flows. In the near future, it is important to study in detail the physico-chemical processes that occur during thermal decomposition, depending on impacts such as heating temperature, gas flow and the time of the process. The thermogravimetric (TG) curve was constructed by measuring the mass change of sample using the TG apparatus during the thermal decomposition process under argon gas. The TGA results of the oil shale sample in the form of the TG curve are shown in Figure 1.

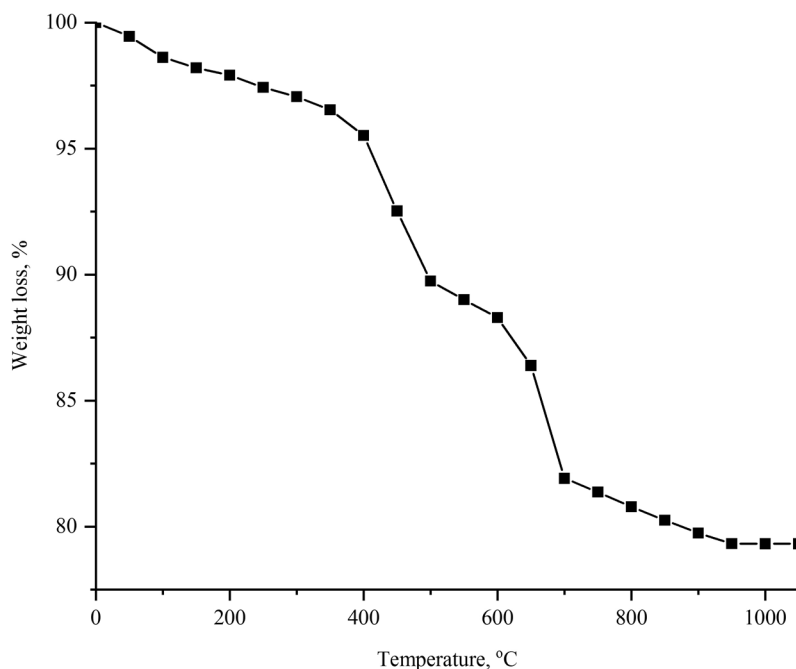


Fig. 1. The TG curve for the weight loss of Uvurjargalant oil shale during the thermal decomposition process.

The TG curve in Figure 1 shows the Uvurjargalant oil shale to go through three main stages of weight loss. In the first stage, the evaporation of moisture, adsorption of gas and decomposition of weak chemical bonds in oil shale molecules occur at temperatures of 20–300 °C. The formation of liquid mass by decomposition of bitumen and kerogen contained in oil shale takes place in the second stage in the temperature range of 300–750 °C. Clay type compounds in oil shale decomposed most intensively. The above analysis shows that the mass loss is up to 26.78% at the temperature of 750 °C. Basically, decomposition is complete at 750–1050 °C, and the residue is formed in the coking process in the third stage. TGA shows the optimal temperature for the decomposition of liquid products from oil shale to be about 750 °C.

Based on its TG curve, the thermal stability indices of the Uvurjargalant analytical oil shale sample were calculated. For example, $T_{5\%} = 350$ °C, $T_{15\%} = 625$ °C and $T_{25\%} = 750$ °C represent the most favourable thermal stability characteristics for the thermal processing of oil shale by pyrolysis.

The thermodynamic (DTA) (Fig. 2) and differential thermogravimetric (DTG) (Fig. 3) curves describe the thermal mechanisms of oil shale and heat effects of the reactions during its thermal decomposition. The DTA curve is constructed by measuring the effects of the heat generated by continuous heating of OS in inert gas.

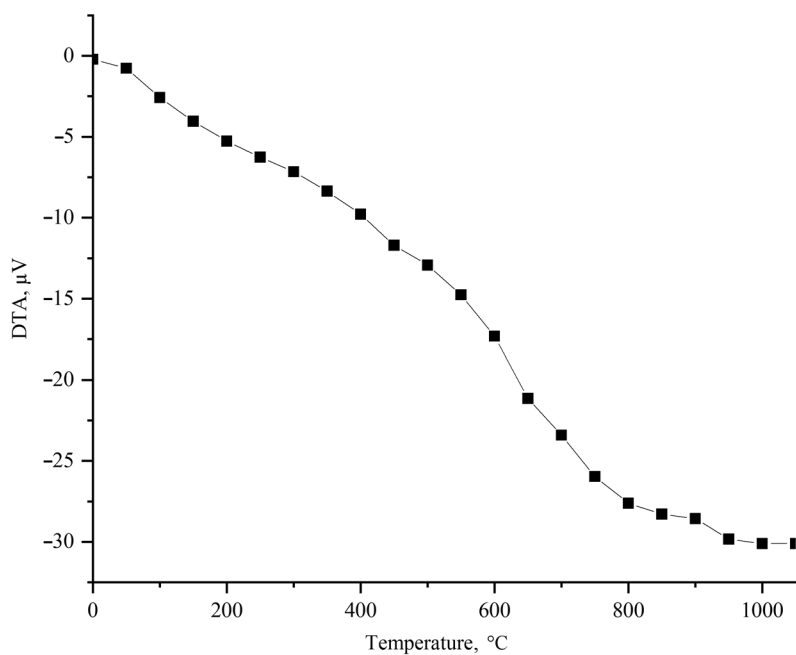


Fig. 2. The DTA curve of Uvurjargalant oil shale.

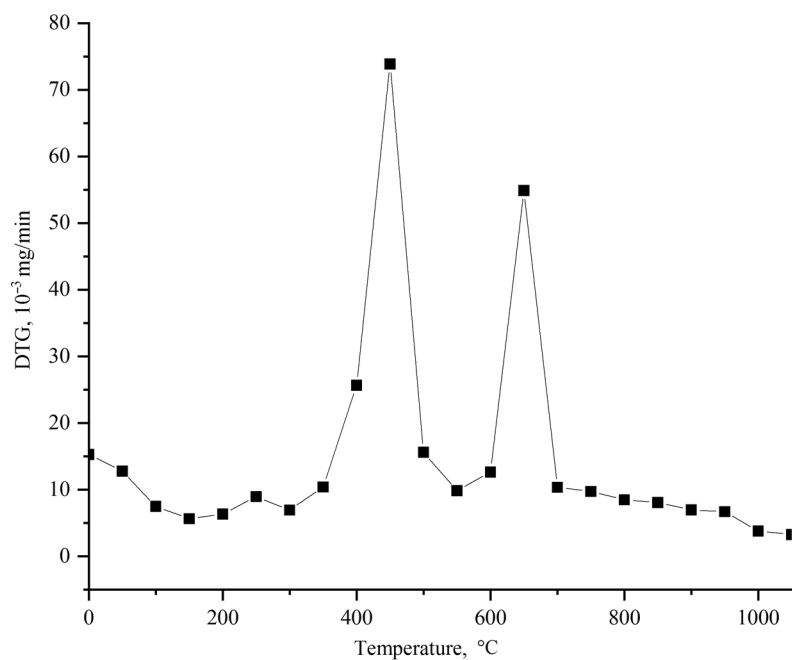


Fig. 3. The DTG curve of Uvurjargalant oil shale.

According to the DTA curve, the thermal decomposition of oil shale is an endothermic reaction and the main stage of decomposition at 300–750 °C is more intense. When the residual polymerization process occurs at 900–1050 °C, the heat absorption process decreases. Various chemical processes, such as decomposition, oxidation and polymerization, take place as a result of thermal decomposition, and the mass change in the processes is expressed as a DTG curve.

According to the TG curve of oil shale, the initial peak is associated with the release of its gas and moisture at temperatures of 20–150 °C, while the major TG peak in the 300–750 °C range corresponds to the release of gas and liquid products. The study has shown the maximum velocity of the decomposition of oil shale organic matter to be at 450 °C.

The structure of the hydrocarbons contained in the Uvurjargalant oil shale was determined by IR spectroscopy, and is shown in Figure 4.

In the FTIR spectrum of Uvurjargalant oil shale (Fig. 4) there are intensive peaks for the aromatic –CH groups at 873 cm^{-1} and 1002 cm^{-1} , a peak for the methyl group C–H and the esteric group –O–CO– connected with aromatic and aliphatic molecules at 1431 cm^{-1} with middle intensity. Also, the spectrum contains peaks with lowest intensities for the ethyl group –OH at 3622 cm^{-1} and for the sulfhydryl group –SH at 2358 cm^{-1} connected with organic and inorganic molecules in oil shale.

The pyrolysis experiments of Uvurjargalant oil shale were carried out in a large-scale pyrolysis retort at 750 °C as foreseen by TGA. The yields of solid residue, tar, pyrolysis water and gas were determined (Table 2).

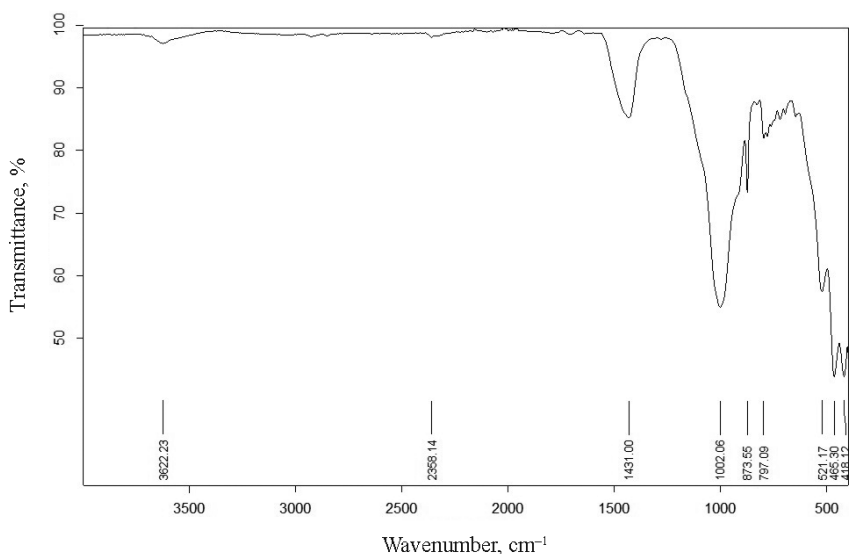


Fig. 4. The FTIR spectrum of Uvurjargalant oil shale.

Table 2. The yields of pyrolysis products of Uvurjargalant oil shale

Oil shale sample	Heating temperature, °C	Tar, %	Pyrolysis water, %	Gas, %	Solid residue, %
Uvurjargalant	750	3.67	2.92	6.90	86.51

Table 2 shows that the yield of char (solid residue) is highest, while those of tar, pyrolysis water and gas are lower. However, the yield of tar is comparatively high at the heating temperature of 750 °C and previously it was discovered that the tar yield decreased by 3.67% at any other heating temperature. The results of proximate analysis of the solid pyrolysis residue of Uvurjargalant oil shale are compared with those of the initial oil sample in Table 3.

Table 3. Proximate analysis of oil shale and solid pyrolysis residue, wt%

Sample	Total moisture, %	Ash, %		Volatile matter, %	
		A ^a	A ^d	V ^a	V ^{daf}
Initial oil shale sample	2.66	78.30	80.43	18.39	96.50
Solid pyrolysis residue	0.45	93.30	93.72	4.60	73.60

Note: a – air-dried, d – dry, daf – dry ash free basis

It can be seen from Table 3 that the yield of volatile matter of solid pyrolysis residue decreased intensively and the yield of ash increased intensively compared to that of the initial oil shale sample after the pyrolysis. It is indicated that oil shale carbonized during pyrolysis. The solid pyrolysis residue can find application as smokeless fuel.

For the characterization of the pyrolysis tar of Uvurjargalant oil shale FTIR analysis was used, the results are shown in Figure 5.

The FTIR spectrum of the Uvurjargalant oil shale pyrolysis tar in Figure 5 shows weak absorption bands for the H of the aromatic –CH group at 1000–1500 cm⁻¹ and 600–800 cm⁻¹ and strong bands for the H of the aliphatic –CH₃, –CH₂ and –CH groups at 2855–2924 cm⁻¹ and also for the H of the –OH, –NH and –NH₂ groups at 3404 cm⁻¹. There are strong bands at 1400–1642 cm⁻¹ for the skeletal C = O groups in ketones, aldehydes, esters and quinines. Therefore, the oil shale tar is a multicomponent mixture mainly consisting of organic substances with aliphatic chains and aromatic structures with oxygen and nitrogen functionalities.

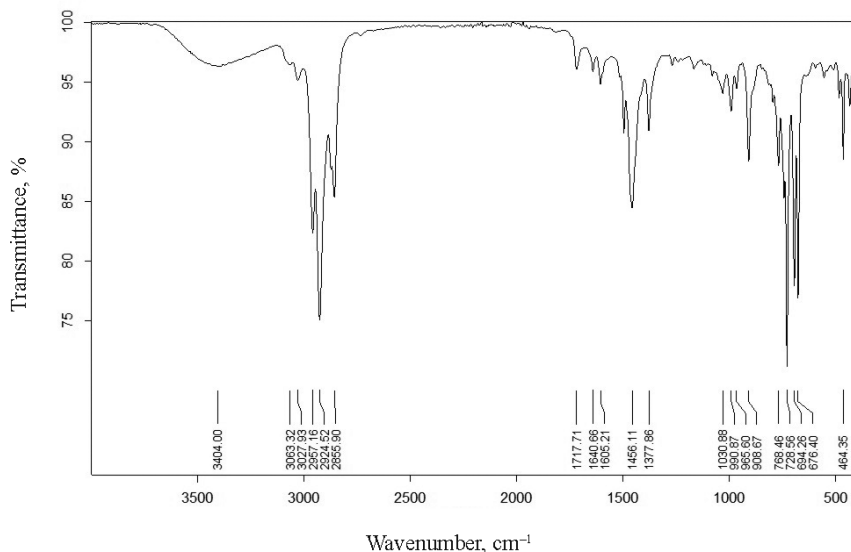


Fig. 5. The FTIR spectrum of the pyrolysis tar of Uvurjargalant oil shale.

The pyrolysis tar of Uvurjargalant oil shale was distilled in the atmosphere, giving several fractions with different boiling temperatures: < 180 °C, 180–250 °C, 250–320 °C, > 320 °C. The yields of the fractions were determined (Table 4).

The distillation of Uvurjargalant oil shale pyrolysis tar gave three fractions, including one light fraction, two middle fractions and one heavy residue. The yields of light and middle fractions are similar, however, the yield of the latter is slightly higher than that of the former. The light and two middle distillates of the oil shale pyrolysis tar were analysed by SGC by elution with different organic solvents, namely hexane, toluene and dichloromethane. By SGC three compound groups soluble in hexane, toluene and dichloromethane were obtained. The yields of each group were determined by weight, the results are presented in Table 5.

Table 4. The yields of distillation fractions of Uvurjargalant oil shale pyrolysis tar with different boiling temperatures

Boiling temperature, °C	Yield of fraction, %	n	Appearance
< 180	15.80	1.4593	Light fraction with yellow white color
180–250	17.82	1.4900	Middle fraction with brown color
250–320	16.18	1.5130	Middle fraction with black brown color
> 320	50.19	–	Heavy fraction (distillation residue) with black color

Note: n – refractive index (index of refraction)

Table 5. The results of SCG of distillation fractions

Boiling temperature, °C	Hexane-soluble fraction (H)	Toluene-soluble fraction (B)	Dichloromethane-soluble fraction (M)	All separated fractions
< 180	1.09	13.72	49.65	64.46
180–250	0.84	3.68	9.69	14.21
250–320	0.74	4.87	28.97	34.58

Table 5 shows that the major part of each fraction is soluble in dichloromethane and its minor part is soluble in hexane. This indicates the three fractions to be mostly polar compounds. The yields of M and B groups were higher in the light fraction than in other fractions. In general, the content of the M group is higher than that of other groups in all fractions. In the case of the H group (aliphatic compounds) the yields of light and middle fractions are similar. Each group of distillation of the three fractions (H, B, M groups) was analysed by GC/MS. The results are given in Tables 6, 7 and 8 and the organic compounds identified are listed in Appendices 1, 2 and 3.

Table 6. The results of GC/MS analysis of the light distillation fraction of pyrolysis tar

Group	Functional group	Content, %	
		GC/MS	Tar
Aliphatic	Alkane C _{9–15}	86.17	0.93
	Alkane C _{16–22}	11.16	0.12
	Alkene	2.67	0.03
Aromatic	Benzene and its derivatives	87.29	11.97
	Naphthalene and its derivatives	4.29	0.56
Polar	Alcohol and phenol and its derivatives	86.99	43.19
	Heteroatomic compounds	4.89	2.42
	Ethers	0.20	0.10
	Ketone and its derivatives	7.92	3.93

The GC/MS analysis of the light distillation fraction identified 38 organic compounds soluble in hexane, 14 compounds soluble in toluene and 13 compounds soluble in dichloromethane (Appendix 1). Each group (H, B, M) of the middle fraction (180–250 °C) of the pyrolysis tar was analysed by GC/MS. The results are presented in Table 7 and the organic compounds identified are listed in Appendix 2.

Table 7. The results of GC/MS analysis of the middle distillation fraction (180–250 °C) of pyrolysis tar

Group	Functional group	Content, %	
		GC/MS	Tar
Aliphatic	Alkane C _{9–15}	77.01	0.64
	Alkane C _{16–22}	19.25	0.16
	Alkene	3.47	0.03
Aromatic	Benzene and its derivatives	91.26	3.36
	Naphthalene and its derivatives	8.74	0.32
Polar	Alcohol and phenol and its derivatives	85.45	8.28
	Heteroatomic compounds	5.42	0.53
	Ethers	0.1	0.01
	Ketone and its derivatives	9.03	0.87

On the basis of the GC/MS analysis (Table 7), 56 organic compounds soluble in hexane, 32 compounds soluble in toluene and 13 compounds soluble in dichloromethane were identified (Appendix 2).

Each group (H, B, M) of the middle fraction (250–320 °C) of the pyrolysis tar was analysed by GC/MS. The results are presented in Table 8 and the organic compounds identified are listed in Appendix 3.

Based on the GC/MS analysis results of the middle fraction distilled at 250–320 °C (Table 8), 34 organic compounds soluble in hexane, 37 compounds soluble in toluene and 31 compounds soluble in dichloromethane were identified (Appendix 3).

In general, the GC/MS analysis of aliphatic compounds (hexane-dissolved fractions) in the light and middle distillation fractions of oil shale pyrolysis tar showed that aliphatic compounds were alkane and alkene C₁₀–C₂₀, and most of them contained hydrocarbons of alkane homology up to C₁₅. It means

Table 8. The results of GC/MS analysis of the middle distillation fraction (250–320 °C) of pyrolysis tar

Group	Functional group	Content, %	
		GC/MS	Tar
Aliphatic	Alkane C ₉₋₁₅	76.87	0.56
	Alkane C ₁₆₋₂₂	19.48	0.14
	Alkene	3.65	0.03
Aromatic	Benzene and its derivatives	93.12	4.53
	Naphthalene and its derivatives	6.88	0.33
Polar	Alcohol and phenol and its derivatives	84.52	24.48
	Heteroatomic compounds	5.63	1.63
	Ethers	0.1	0.02
	Ketone and its derivatives	9.75	2.82

only a small percentage of alkene homology. The alkane homology contained more compounds than alkene homology. This suggests that the hydrogen content of oil shale is high, and hydrogen may have been involved in the reduction reaction with the micro molecules formed from the macromolecules decomposed during pyrolysis. The GC/MS of aromatic compounds (dissolved in toluene) shows most of them to contain benzene and its derivatives. In addition, polar compounds mainly contain phenol and its derivatives, which may be due to the high oxygen content of oil shale.

4. Conclusions

1. The oil shale of the Uvurjargalant deposit contained a low amount of moisture and volatile matter, whereas the ash yield was high (80.43 wt %), which implies that the oil shale consists mostly of minerals. The total content of bitumen in oil shale was very low (1.24 wt%), whereas the content of kerogen (content of insoluble in organic solvent) was 22.84 wt%, which suggests the relatively high kerogen content in it compared to oil shales from other deposits in Mongolia. The infrared spectroscopy data showed aliphatic hydrocarbons to be dominant in oil shale, which can be caused by higher sapropel sources. This suggests that oil shale mainly belongs to the category of kerogen I by the classification of Tisso.

2. The thermogravimetric curve shows the Uvurjargalant oil shale to go through three stages of mass loss during the pyrolysis. The evaporation of moisture, adsorption of gas and decomposition of weak chemical bonds occur in the initial stage at 20–150 °C. The formation of liquid mass by decomposition of bitumen and kerogen present in oil shale takes place in the second stage at temperatures of 150–300 °C. Clay type compounds in oil shale decomposed most intensively. The above analysis shows that the mass loss is up to 26.78% at the temperature of 750 °C. Basically, decomposition is complete at 750–1050 °C, and the residue is formed in the coking process. The study found the ideal temperature range for extracting liquid products from oil shale to be 300–750 °C.
3. The pyrolysis tar of Uvurjargalant oil shale was distilled in the atmosphere and four fractions were obtained: one light fraction, two middle fractions and one heavy fraction. The yield of the heavy fraction was higher than that of other fractions. The infrared spectroscopy and gas chromatography-mass spectrometry showed the light fraction to contain more alkanes and alkenes C₁₀–C₂₀ than the middle fractions. At the same time, the middle fractions contained more benzene and phenol and its derivatives than other fractions.

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Appendix 1. Organic substances determined on the basis of GC/MS of the light distillation fraction obtained by SGC eluted with hexane, toluene and dichloromethane

Hexane-soluble fraction			Toluene-soluble fraction			Dichloromethane-soluble fraction		
RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined
3.13	2.4	3,5-Hexadien-2-ol, 2-methyl-	6.44	2.46	Acetic acid, phenyl-, 3-hexenyl ester	6.05	3.53	Pyridine, 2-ethyl-6-methyl-
3.2	3.92	1-Octene	6.7	4.92	Benzene, (nitro methyl)-	6.46	18.02	Phenol
3.31	3.55	Hexane, 2,4-dimethyl-	6.78	2.01	N-Chloro-2-phenylaziridine	6.55	8.46	2-Octanone
3.39	1.38	3-Octene, (Z)-	7.21	1.07	1,3,5-Cycloheptatriene, 7-ethyl-	6.71	10.78	Pyridine, 2,4,6-trimethyl-
3.68	2.57	1-Methyl-2-methylencyclohexane	7.68	3.12	1H-Indene, 1-chloro-2,3-dihydro-	7.07	3.71	3-Cyclohexen-1-nitrile, 6-methyl-
3.79	1.61	Decanal	7.92	0.66	2H-Indeno[1,2-b]oxirene, octahydro-, (1 $\alpha\alpha$, 1b β , 5 $\alpha\alpha$, 6 $\alpha\alpha$)-	7.85	15.71	Phenol, 2-methyl-
3.98	1.95	Cyclopentene, 3-propyl-	9.72	2.32	1H-Indene, 3-methyl-	8.32	13.01	Phenol, 3-methyl-
4.09	1.92	3-Octen-1-ol, (Z)-	9.84	3.19	Naphthalene, 1,2,3,4-tetrahydro-	8.46	4.79	2-Nonanone
4.25	4.62	Ethylbenzene	10.39	2.16	1H-Indene, 1-methylene-	18.53	0.83	Cyclobutal[dibenzoc[f]cycloheptadiene, 7-oxo-
4.42	8.27	p-Xylene	11.8	1.77	(1-Methylenebut-2-enyl)benzene	19.35	4.11	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans-

Appendix I (continued)

Hexane-soluble fraction			Toluene-soluble fraction			Dichloromethane-soluble fraction		
RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined
4.72	5.28	1-Decene	19.29	6.56	Benzene, 1,1'-(1,2-cyclobutanediyl) bis-, trans-	27.39	2.45	(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-
4.81	7.11	1,3,5-Cyclooctatriene	28.41	59.3	(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-	28.41	12.84	Benzene, 1,1'-[2-methyl-2-(phenylthio)cyclopropylidene]bis-
4.87	3.19	Nonane	28.59	6.76	Benzene, 1,1'-[2-methyl-2-(phenylthio)cyclopropylidene]bis-	28.61	1.76	Thiocarbamic acid, N,N-dimethyl, S-1,3-diphenyl-2-butenyl ester
4.94	1.82	1-Octene, 3,7-dimethyl-	29.52	3.7	α -N-Normethadol			
5.08	1.12	4-Nonene						
5.69	1.6	Cyclopentene,3-(3-methylbutyl)-						
5.85	1.99	1,3,5-Cycloheptatriene, 7-ethyl-						
5.99	3.32	Benzene, 1-ethyl-3-methyl-						
6.31	1.78	2,4-Nonadiyne						
6.53	5.58	1-Octene, 3,7-dimethyl-						

Appendix I (continued)

Hexane-soluble fraction			Toluene-soluble fraction			Dichloromethane-soluble fraction		
RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined
6.67	7.49	Octane, 3,5-dimethyl-						
6.93	1.45	trans-3-Decene						
7.61	2.64	1-Propyne, 3-phenyl-						
7.79	1.29	Tricyclo[3.2.1.0(2,4)]octane, 3-methylene-						
8.42	4.08	1-Decene						
8.58	3.45	Undecane						
10.29	2.73	2-Dodecene, (E)-						
10.44	2.55	Dodecane						
12.08	1.44	1-Octene, 3,7-dimethyl-						
12.22	1.81	Tridecane						
13.79	0.82	3-Dodecene, (Z)-						
13.91	1.37	Pentadecane						
15.4	0.36	6-Tridecene, (Z)-						

Appendix I (continued)

Hexane-soluble fraction			Toluene-soluble fraction			Dichloromethane-soluble fraction		
RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined
15.51	0.93	Hexadecane						
17.03	0.71	Heptadecane						
18.47	0.8	Octadecane						
19.84	0.79	Nonadecane						
21.16	0.35	Eicosane						

Appendix 2. Organic substances determined on the basis of the GC/MS chromatogram of the fraction distilled at 180–250 °C obtained by SGC eluted with hexane, toluene and dichloromethane

Hexane-soluble fraction			Toluene-soluble fraction			Dichloromethane-soluble fraction		
RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined
4.26	0.88	Ethylbenzene	6.48	2.33	Heptanonitrile	3.64	0.66	Acetic acid, butyl ester
4.4	2.24	p-Xylene	6.66	2.59	Benzonitrile	3.75	0.81	Pyridine, 3-methyl-
4.78	3.48	o-Xylene	6.74	2.79	Benzene, 1-ethyl-3-methyl-	4.3	0.63	Ethylbenzene
5.86	0.99	Benzene, propyl-	7.24	1.23	1,3,5-Cycloheptatriene, 7-ethyl-	4.44	2.13	Pyridine, 4-(3-phenylpropyl)-
5.99	1.87	Benzene, 1-ethyl-3-methyl-	7.69	2.96	Benzene, 1-propynyl-	4.68	3.2	Pyridine, 2,6-dimethyl-
6.15	1.41	Benzene, 1,2,3-trimethyl-	8.15	1.78	Benzene, (isocyanomethyl)-	4.91	0.33	2,4-Hexadien-1-ol
6.32	1.97	Benzene, 1-ethyl-2-methyl-	8.32	3.33	Octanenitrile	5.04	0.95	Pyridine, 2-ethyl-
6.52	1.9	1-Decene	8.61	2.68	Benzene, (isocyanomethyl)-	5.52	9.37	Pyridine, 2,4-dimethyl-
6.63	5.18	Benzene, 1-ethyl-4-methyl-	8.87	3.13	Phenol, 2,5-dimethyl-	6.05	4.3	Pyridine, 2-ethyl-6-methyl-
6.76	1.49	Benzene, 2-propenyl-	9.04	1	6,7-Dimethyl-3,5,8,8a-tetrahydro-1H-2-benzopyran	6.2	0.49	2-Norbornyl acetate
7.15	2.06	Benzene, 1,2,4-trimethyl-	9.61	2.57	Naphthalene, 1,2,3,4-tetrahydro-1-methoxy-	6.4	1.52	3-Cyclohexen-1-nitrile, 6-methyl-

Appendix 2 (continued)

Hexane-soluble fraction		Toluene-soluble fraction			Dichloromethane-soluble fraction			
RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined
7.41	1.64	Indane	9.75	4.34	1H-Indene, 3-methyl-	6.49	5.99	Phenol
7.62	3.7	Indene	10.2	2.66	Nonanenitrile	6.64	1.43	Pyridine, 2,4,6-trimethyl-
7.8	2.92	Benzene, 1,4-diethyl-	10.33	5.38	Naphthalene	6.75	2.33	Pyridine, 2,3,5-trimethyl-
7.97	1.22	Benzene, 1-methyl-2-propyl-	10.42	1.07	Hydrocinamic acid, o-[(1,2,3,4-tetrahydro-2-naphthyl)methyl]-	7	2.18	1,2-Dimethyl-5-vinylpyrrole
8.16	1.6	Benzene, 2-ethyl-1,4-dimethyl-	11.75	8.51	Naphthalene, 1,2-dihydro-3-methyl-	7.08	1.2	3-Cyclohexen-1-nitrile, 6-methyl-
8.23	0.8	Benzene, 1-ethyl-2,4-dimethyl-	12.05	2.44	Dodecanenitrile	7.51	1.54	1-(2-Ethyl-3-cyclohexenyl)ethanol
8.43	2.65	1-Undecanol	12.33	4.69	Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene	7.85	6.48	Phenol, 2-methyl-
8.59	2.1	Undecane	12.6	5.43	Benzocycloheptatriene	8.09	4.91	Benzamide, N-methyl-
8.68	1.68	3-Undecene, (E)-	12.85	0.66	9-Methyltricyclo[4.2.1.1(2,5)]deca-3,7-diene-9,10-diol	8.33	10.68	Phenol, 3-methyl-
9.02	1.81	Benzene, 1,2,4,5-tetramethyl-	13.5	0.86	(1-Methylpenta-1,3-dienyl)benzene	8.47	1.56	2-Nonanone

Appendix 2 (continued)

Hexane-soluble fraction		Toluene-soluble fraction			Dichloromethane-soluble fraction			
RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined
9.14	0.93	Benzene, 1-methyl-4-(2-propenyl)-	13.77	3.23	Benzene, (2,4-cyclopentadien-1-ylidene-methyl)-	8.5	1.16	Pyridine, 4-ethyl-2,6-dimethyl-
9.42	1.46	2,4-Dimethylstyrene	14	2.45	5,8,11-Eicosatriynoic acid, methyl ester	9.43	1.02	Phenol, 2,3-dimethyl-
9.62	4.71	Benzene, 1-ethyl-2,3-dimethyl-	14.41	2.41	Naphthalene, 1,7-dimethyl-	9.64	8.43	Phenol, 2,5-dimethyl-
9.75	2.88	Tetraacyclo[5.3.0.0<2,6>.0<3,10>]deca-4,8-diene	15.48	2.85	1-Isopropenyl-naphthalene	9.99	2.29	Phenol, 4-ethyl-
9.84	2.36	Naphthalene, 1,2,3,4-tetrahydro-	17.04	4.27	Fluorene	10.05	6.92	Phenol, 3,4-dimethyl-
10.15	1.07	(1-Methylenebut-2-enyl)benzene	18.5	1.91	(3-Methyl-1,4-diphenylbicyclo[2.2.0]hex-2-yl)methanol	10.34	2.46	2-Decanone
10.36	5.23	Naphthalene	19.27	3.87	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans-	11.26	0.96	Phenol, 3-ethyl-5-methyl-
10.47	2.2	Dodecane	27.37	2.75	(2,3-Diphenylcyclo-propyl)methyl phenyl sulfoxide, trans-	11.39	1.86	Quinoline
10.67	1.5	Octadecane, 6-methyl-	28.26	4.23	Thiocarbamic acid, N,N-dimethyl, S-1,3-diphenyl-2-butenyl ester	11.68	1.55	Phenol, 3-ethyl-5-methyl-

Appendix 2 (continued)

Hexane-soluble fraction		Toluene-soluble fraction		Dichloromethane-soluble fraction	
RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined
11.11	1.08	1,2,4-Metheno-1H-cyclobutal[cd]pentalene-3,5-diol, octahydro-	28.4	7.58	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-
11.58	1.86	Bicyclo[6.4.0]dodeca-9,11-diene	28.59	2.04	Benzene, 1,1'-[2-methyl-2-(phenylthio)cyclopropylidene]bis-
11.65	2.6	Naphthalene, 1,2-dihydro-3-methyl-			Quinoline, 2-methyl-
12.1	1.88	1-Tridecene			1-Naphthalenol, 1,2,3,4-tetrahydro-2,5,8-trimethyl-
12.24	2.41	Tridecane			2-Dodecanone
12.34	2.99	1H-Indene, 1-ethylidene-			Cyclopental[1,3] cyclopropal[1,2] cyclohepten-3(3aH) -one, 1,2,3b,6,7,8- hexahydro-6,6-dimethyl-
12.61	2.9	Benzocycloheptatriene			2-Tridecanone

Appendix 2 (continued)

Hexane-soluble fraction		Toluene-soluble fraction		Dichloromethane-soluble fraction	
RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined
13.79	1.87	1-Hexadecanol	18.51	0.32	(3-Methyl-1,4-diphenylbicyclo[2.2.0]hex-2-yl)methanol
13.93	1.98	Tetradecane	19.28	0.7	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans-
13.99	1.47	Naphthalene, 1-ethyl-	27.39	0.4	(2,3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-
14.2	0.71	Naphthalene, 1,7-dimethyl-	28.27	1.12	Benzene, 1,1'-[2-methyl-2-(phenylthio)cyclopropylidene]bis-
14.41	1.66	Naphthalene, 1,7-dimethyl-	28.42	1.21	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-
15.4	1.28	Cyclopentadecane			
15.52	1.91	Pentadecane			
15.59	0.32	1-Hexadecanol, 2-methyl-			

Appendix 2 (continued)

Hexane-soluble fraction		Toluene-soluble fraction			Dichloromethane-soluble fraction			
RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined
16.92	1.09	Hexadecen-1-ol, trans-9-						
17.03	1.37	Hexadecane						
17.69	0.21	Octadecane, 3-ethyl-5-(2-ethylbutyl)-						
18.37	0.64	1-Nonadecene						
18.46	1.42	Heptadecane						
19.75	0.36	1-Eicosanol						
19.83	0.96	Octadecane						
21.06	0.16	1-Eicosene						
21.14	0.46	Heneicosane						
22.39	0.28	Eicosane						
23.59	0.18	Heptacosane						

Appendix 3. Organic substances determined on the basis of the GC/MS chromatogram of the fraction distilled at 250–320 °C obtained by SGC eluted with hexane, toluene and dichloromethane

Hexane-soluble fraction			Toluene-soluble fraction			Dichloromethane-soluble fraction		
RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined
9.62	2.36	1H-Indene, 1-methyl-	9.84	0.99	Naphthalene, 1,2,3,4-tetrahydro-	7.35	0.74	1-Hexanol, 2-ethyl-
10.34	6.15	Naphthalene	10.38	2.29	1-(2-Methylenecyclohexyl)-3-phenylpropan-1-ol	7.87	1.29	Cyclopentaneacetaldehyde, 2-formyl-3-methyl- α -methylene-
10.45	1.29	Dodecane	12.06	1.52	Dodecanenitrile	8.43	4.88	3,4-Pyridinedimethanol, 6-methyl-
12.34	6.14	1H-Indene, 1-ethylidene-	12.62	1.72	Butanoic acid, 3-[(1-phenylethyl-2-propynyl)oxy]	8.81	0.19	2-[Benzyloxyimino]methyl-3-methyl-1-(1-propanesulfonate)imidazolium
12.61	5.63	Naphthalene, 2-methyl-	13.39	1.38	9-Octadecenoic acid, (2-phenyl-1,3-dioxolan-4-yl) methyl ester, trans-	9.28	0.35	Hexasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl-
13.8	3.2	1-Hexadecanol	13.78	2.99	Dodecanenitrile	9.91	2.49	(E,Z,Z)-2,4,7-Tridecatrienal
13.93	2.52	Tetradecane	14.1	1.65	1H-Indole-3-ethanamine, α -methyl-	10.1	1.83	4-(2,5-Dihydro-3-methoxyphenyl)butylamine
14	3.64	Naphthalene, 1-ethyl-	15.13	3.62	1H,3H-Naphtho[1,8-cd]pyran, 3a,4,5,6-tetrahydro-	10.74	0.28	Endosulfan II
14.19	3.54	Naphthalene, 2,6-dimethyl-	15.42	4.97	Dodecanenitrile	11.71	6.49	4-(2,5-Dihydro-3-methoxyphenyl)butylamine

Appendix 3 (continued)

Hexane-soluble fraction			Toluene-soluble fraction			Dichloromethane-soluble fraction		
RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined
14.41	6.47	Naphthalene, 1,7-dimethyl-	15.59	3.26	1H-Indole, 5,7-dimethyl-	12.14	3.36	Phenol, 3-ethyl-5-methyl-
14.78	2.83	Naphthalene, 1,8-dimethyl-	16.64	4.81	2(3H)-Naphthalenone, 4,4a,5,6,7,8-hexahydro-4a-phenyl-, (R)-	12.25	2.42	2(1H)-Isoquinolinecarboximidamide, 3,4-dihydro-
14.98	2.31	Naphthalene, 1,3-dimethyl-	17.02	11.36	Fluorene	13.23	1.22	Cyclopenta[1,3]cyclopropa[1,2]cyclohepten-3(3aH)-one, 1,2,3b,6,7,8-hexahydro-6,6-dimethyl-
15.41	2.36	Cyclopentadecane	17.28	1.52	9H-Fluorene, 2-methyl-	13.69	2.55	Cyclopenta[1,3]cyclopropa[1,2]cyclohepten-3(3aH)-one, 1,2,3b,6,7,8-hexahydro-6,6-dimethyl-
15.53	4.03	Pentadecane	17.52	0.58	1-tert-Butyl-3-(3-methoxyphenyl)-bicyclo[1.1.1]pentan	14.19	5.24	Pent-3-ene-2-one, 3-phenyl-, oxime
15.79	2.44	3-(2-Methyl-propenyl)-1H-indene	18.1	3.08	Geranyl isovalerate	14.56	5.19	5,7-Dodecadiyn-1,12-bis(carbamic acid, butyloxymethyl ester)
15.87	2.12	Benzyl alcohol, α -isobutyl-2,4,5-trimethyl-	18.45	5.48	Hexadecanenitrile	14.75	6.91	Cyclopenta[1,3]cyclopropa[1,2]cyclohepten-3(3aH)-one, 1,2,3b,6,7,8-hexahydro-6,6-dimethyl-

Appendix 3 (continued)

Hexane-soluble fraction		Toluene-soluble fraction		Dichloromethane-soluble fraction	
RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined
16.93	2.98	Hexadecen-1-ol, trans-9-	18.78	3.61	9H-Fluorene, 2-methyl-
17.04	4.73	Tetradecane, 2,6,10-trimethyl-	19.26	3.03	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans-
18.22	1.49	2(3H)-Naphthalenone, 4,4a,5,6,7,8-hexahydro-4a-phenyl-, (R)-	19.49	2.51	1,7-Dimethyl-3-phenyltricyclo[4.1.0.0(2,7)]hept-3-ene
18.39	2.7	3-Heptadecene, (Z)-	19.86	6.98	Hexadecanenitrile
18.48	5.1	Heptadecane	20.3	2.12	Phenanthrene, 9,10-dihydro-1-methyl-
18.72	1.3	5,8,11,14-Eicosatetraynoic acid	20.41	2.12	Phenanthrene, 9,10-dihydro-1-methyl-
19.76	1.77	1-Hexadecanol, 2-methyl-	20.82	2.18	Piperazine, 1-[5-fluoropentyl]-4-[(3,4-dichlorophenyl)acetyl]-
19.85	3.29	Octadecane	21.2	2.5	Hexadecanenitrile
			15.39	5.58	Bicyclo[4.1.0]heptan-2-ol, 1β-(3-methyl-1,3-butadienyl)-2α,6β-dimethyl-3β-acetoxy-
			15.98	2.37	Bicyclo[4.1.0]heptan-2-ol, 1β-(3-methyl-1,3-butadienyl)-2α,6β-dimethyl-3β-acetoxy-
			16.7	4.66	Bicyclo[4.1.0]heptan-2-ol, 1β-(3-methyl-1,3-butadienyl)-2α,6β-dimethyl-3β-acetoxy-
			16.96	5.45	5,7-Dodecadiyn-1,12-diol
			17.57	14.34	1H-Indole, 4-(3-methyl-2-butenyl)-
			17.71	1.85	Acetic acid, 4-(1H-indol-4-yl)-2-methyl-but-2-enyl ester
			17.84	1.7	1-(2-Nitro-1-phenylethyl)-2-oxocyclopentane-carboxylic acid, methyl ester
			18.15	0.98	1H-Indole, 4-(3-methyl-2-butenyl)-

Appendix 3 (continued)

Hexane-soluble fraction			Toluene-soluble fraction			Dichloromethane-soluble fraction		
RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined	RT min	% of total	Organic substance determined
25.81	1.64	Octacosane	28.26	3.14	Benzene, 1,1'-[2-methyl-2-(phenylthio)cyclopropylidene]bis-			
26.86	0.82	Tetratetracontane	28.4	3.72	Benzene, 1,1'-[2-methyl-2-(phenylthio)cyclopropylidene]bis-			
			28.47	1.26	Benzene, 1,1'-[2-methyl-2-(phenylthio)cyclopropylidene]bis-			
			28.59	1.17	1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-			
			29.54	0.4	α -N-Normethadol			