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## NITRO-CONTAINING COMPOUNDS IN THE CHINESE LIGHT SHALE OILS

### Abstract

Maoming and Fushun shale oils of China were cut into light (<350 °C) and heavy oil (>350 °C) fractions. The light oil was chemically separated into acid, basic and neutral fractions. The neutral oil was subjected to further separation into hydrocarbon, nitrile, ketone and strong polar fraction by open column chromatography. Basic and nitrile fractions were analysed by GC-MS and GC-TSD. Both in Maoming and Fushun light oils, basic nitrogen-containing compounds consist mainly of pyridines, quinolines, acridines and their derivatives characterized by short-chain alkyl substitutions. The *n*-alkanonitriles comprise the major part of the neutral nitrogen compounds.

### Introduction

With the depletion of crude petroleum and natural gas supplies, increased attention is being given to the exploitation of oil shale and coal reserves. The world is very rich in oil shale resources, and its recoverable reserves are estimated to be equivalent to or over the natural petroleum [1]. Oil shale and shale oil will play a more and more important part in the futural energy consumptions. Chinese shale oils are similar in composition to the natural petroleum but more complex and rich in unsaturated and non-hydrocarbons, including nitrogen-, oxygen- and sulfur-containing compounds. In general, fuel products from shale oil are poor in quality owing to the presence of these non-hydrocarbons, especially for the nitrogen-containing compounds.

In petroleum refining industry, nitrogen-containing compounds poison the catalysts in different catalytic processes. They also contribute to stability problems during storage of petroleum products since they induce polymerization processes, which cause an increase in the viscosity and give rise to odour and colour of the oil. A detailed knowledge of the types and concentrations of nitrogen compounds present in shale oil products is clearly valuable in order to optimise methods for their removal and the safe handling of such materials. On the other hand, many useful chemicals can be derived from these non-hydrocarbons after proper treatments, so upgrade the economic aspects of shale oils.

Due to the complex nature of shale oils, some kinds of prefractionation have to be performed prior to further precise analysis. Many different methods have been applied including open column chromatography on silica or alumina with or without modification of the gels, acid/base extraction, derivatization, thin layer chromatography and high performance liquid chromatography using a variety of stationary phase [2-19].

Gas chromatography-mass spectrometry (GC-MS) were considered to be the most successful techniques for the identification of individual compounds. Interference from hydrocarbons with similar elution times has hindered the identification of some nitrogen compounds by GC-MS. Aromatic hydrocarbons give relatively intense M-H ions at odd mass numbers, the intensities of the molecular ions from the nitrogen compounds which are consequently either lost or difficult

to detect unless they are well resolved chromatographically. The interference is particularly severe for aza heterocycles, which are eluted very close to their corresponding aromatic hydrocarbons. Therefore, prior to the GC-MS analysis, nitrogen-containing compound fractions have to be concentrated and separated from other fractions.

This paper presents a simple method for isolation of nitrogen compounds from complex samples by utilizing the combination of open column chromatography; acid/base extraction and focused on the identification and discussion of nitrogen-containing compounds in the shale oil light fractions.

## Experimental

**Sample Preparation.** Shale oils from Fushun and Maoming were separated into light (< 350 °C) and heavy (> 350 °C) oil fractions by vacuum distillation, ASTM standard D-1160. Table 1 lists the main properties of these two shale oils and their distilled fractions.

Table 1. Elemental Composition of the Shale Oils (wt. %)

Sample	C	H	S	N	O	H/C	<i>d</i>	Yield
<b>Maoming</b>								
Crude oil	84.51	10.95	0.84	0.93	2.95	1.55	0.9075	
Light oil	83.85	12.14	0.66	0.87	2.50	1.74		35.4
Heavy oil	85.21	10.53	1.11	1.21	2.87	1.48		64.6
<b>Fushun</b>								
Crude oil	84.58	11.50	0.83	1.27	2.49	1.63	0.8939	
Light oil	82.59	12.03	0.87	0.98	3.53	1.75		36.0
Heavy oil	84.48	10.89	1.11	1.41	2.19	1.55		64.0

10 g light oil was dissolved in 100 ml of *n*-hexane. The *n*-hexane solution was extracted with 3 × 50 ml of 3N NaOH for the separation of the acidic fraction and with 3 × 50 ml of 3N HCl for that of the basic fraction. The aqueous basic and acidic fractions were neutralized with 6N aqueous HCl and solid Na<sub>2</sub>CO<sub>3</sub> respectively, followed with back wash of 4 × 50 ml of CH<sub>2</sub>Cl<sub>2</sub>. The aqueous solutions were discarded and the solvent (CH<sub>2</sub>Cl<sub>2</sub>) was removed by rotary vacuum evaporation to a constant weight in order to leave the acid and basic fractions. The samples were kept under the protection of nitrogen atmosphere for further analyses.

After the removal of acid and basic fractions, an aliquot (1 g) of the neutral fraction was subjected to a combined alumina/silica column separation. The column (120 × 1.5 cm o.d.) is slurry packed with the alumina (neutral, preheated 12 h at 300 °C, 23 g) overlying the silica gel (preheated 12 h at 130 °C, mixed 14 g of 60-80 mesh with 44 g 100-200 mesh), and elutions were performed at a rate of 2 ml min<sup>-1</sup>.

The column chromatography classifies the neutral compounds according to functional group types and elution order. Hydrocarbons including total alkanes, alkenes and aromatics eluted as the first fraction by rinse of 1500 ml of

hexane. The nitrile enriched fraction was then removed as a distinct yellow band with 250 ml of dichloromethane. The third one eluted with chloroform (1000 ml) was the methyl ketone fraction, and the remains in the column were eluted with 250 ml of methanol.

The solvents of all chromatographic fractions were evaporated under reduced pressure to a constant weight, and the solvent-free fractions were reserved under a nitrogen atmosphere for further analyses. Figure 1 presents the schematic diagram of the separation scheme.

**Instrumental Analyses.** Gas chromatographic analyses were carried out on a Varian Model 3700 gas chromatograph equipped with a flame ionization detector (FID), a nitrogen-selective detector (TSD), a SP-4270 integrator and a 25m  $\times$  0.22 mm i.d. silica capillary column wall-coated with SE-30, programmed from 50 to 280  $^{\circ}$ C (hold) at 2  $^{\circ}$ C min $^{-1}$ . The TSD combustion gas flows and bead heating current were adjusted for maximum response and selectivity towards nitrogen compounds; the optimised flows were 4.5 ml min $^{-1}$  for hydrogen and 173 ml min $^{-1}$  for air. A bead heating current of 2.7 A on the arbitrary control box scale was used.

GC-MS analyses were performed on a Finnigan MAT Model TSQ 45B GC/MS/MS/DS instrument fitted with a 25  $\times$  0.22 mm i.d. SE-30 capillary column and programmed from 50 to 280  $^{\circ}$ C (hold) at 2  $^{\circ}$ C min $^{-1}$ . Using 70 eV electron-impact ionization, mass spectra were collected in the mass range of 50-600. The mass spectrometric data was acquired and processed using a Super Incos data system.

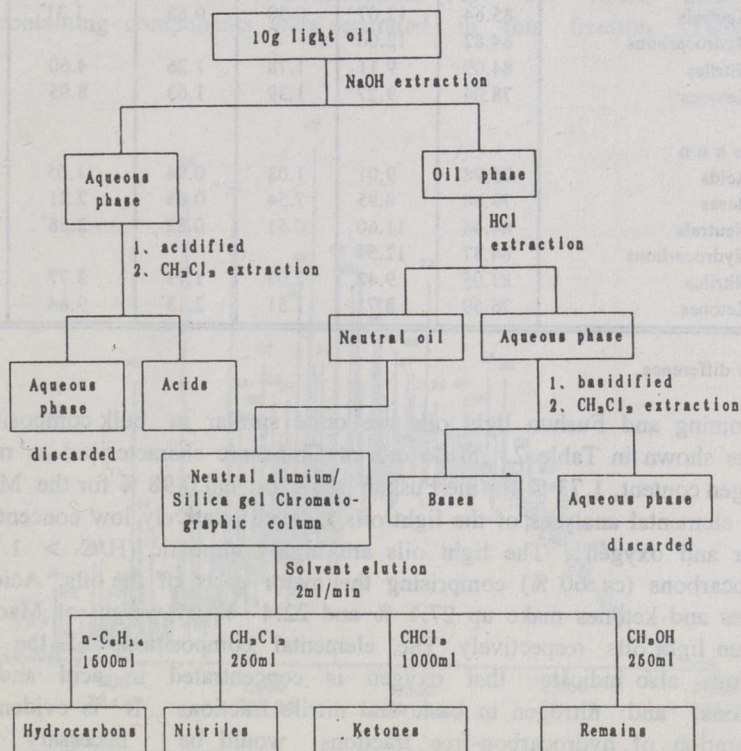


Fig. 1. Schematic diagram for the separation of the light oil

## Results and Discussion

**General Aspects.** Analytical data for acid, basic and chromatographic fractions of Fushun and Maoming light oils are listed in Tables 2 and 3.

Table 2. Gravimetric Results for Light-Oil Fractions (wt. %)

Groups	Maoming	Fushun
Acids	8.5	5.3
Bases	5.1	5.2
Hydrocarbons	60.0	59.5
Nitriles	9.1	7.7
Ketones	4.4	4.2
Remains	3.4	4.0

Table 3. Elemental Composition of the Light-Oil Fractions (wt. %)

Groups	C	H	N	S	O	H/C
<b>Maoming</b>						
Acids	75.36	7.86	1.71	0.85	12.12	1.25
Bases	78.72	8.40	8.15	0.82	3.21	1.28
Neutrals	85.64	12.07	0.30	0.68	1.31*	1.69
Hydrocarbons	84.82	12.00				1.70
Nitriles	84.09	9.11	1.78	1.26	4.60	1.30
Ketones	78.04	9.27	1.39	1.63	8.95	1.43
<b>Fushun</b>						
Acids	75.98	9.01	1.03	0.94	11.05	1.42
Bases	79.48	8.95	7.54	0.86	2.21	1.35
Neutrals	84.48	11.60	0.51	0.83	2.58*	1.65
Hydrocarbons	84.37	12.54				1.78
Nitriles	83.05	9.42	2.03	1.71	3.77	1.36
Ketones	76.59	8.71	1.51	2.18	9.84	1.36

\* = by difference.

Maoming and Fushun light oils are quite similar in bulk composition as the results shown in Table 2. Shale oils of China are characterized as rather high nitrogen content, 1.73 % for the Fushun shale oil and 0.98 % for the Maoming's. The elemental analyses of the light oils indicate relatively low concentrations of sulfur and oxygen. The light oils are highly aliphatic ( $H/C > 1.7$ ), with hydrocarbons (ca 60 %) comprising the major parts of the oils. Acids, bases, nitriles and ketones make up 27.1 % and 22.4 % by weight of Maoming and Fushun light oils respectively. The elemental compositions of the separated fractions also indicate that oxygen is concentrated in acid and ketone fractions, and nitrogen in basic and nitrile fractions. It is evident that the preparation of hydrocarbon-free fractions would be necessary for the satisfactory GC-MS identification of nitrogen and oxygen compounds for these

complex materials, and the most useful fractionation would be a class separation of nitrogen compounds into basic (mostly aza) and neutral species; and the oxygen compounds into acid (mostly phenolic) and neutral species. These separations have made the distinction more easily between isomeric compound types, and facilitated the identification of peaks in the GC-MS chromatogram of the specific fraction examined.

The distribution of nitrogen in the light and heavy oils is shown in Table 4. Nitrogen content in light oils is relatively low, and accounts for 28 % and 33 % of the total nitrogen for Maoming and Fushun respectively.

Table 4. Elemental Nitrogen Distributions  
in the Shale Oils (% of N)

Oil	Maoming	Fushun
light	33	28
heavy	67	72

**Bases.** GC-MS was used for identification of specific compounds in the basic and nitrile fractions. The total ionization current (TIC) chromatogram of Maoming basic fraction is shown in Fig. 2.

GC-MS is known as one of the most successful techniques for the identification of individual compounds, and the complexity of the basic fraction is amply demonstrated by the TIC chromatogram (Fig. 2). More than 100 nitrogen-containing components were separated in this fraction. Table 5

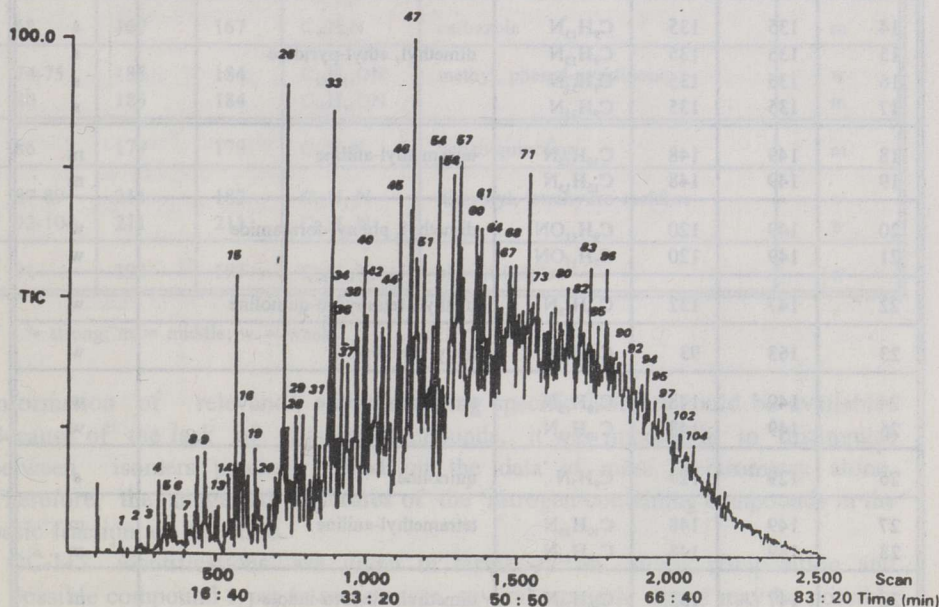


Fig. 2. Total ion chromatogram of basic fraction in Maoming light oil

gives the GC-MS identifications for the numbered peaks in the TIC chromatogram. Some of the peaks contain more than one component, and a number of compound types may be possible for a given atomic composition. In such cases, chemical derivation or other techniques have to be used for further identification. The electronic-impact mass spectra of aromatic nitrogen compounds tend to give intense molecular ions with little fragmentation, and thus little structural

Table 5. Identification of Nitrogen-Containing Compounds in Maoming Basic Fraction

Peak No.	M.W.	Base peak, m/e	Atomic composition	Possible compound type	Intensity*
1	107	107	C <sub>7</sub> H <sub>9</sub> O	ethyl-pyridine	w
2	107	107	C <sub>7</sub> H <sub>9</sub> O	dimethyl-pyridine	w
3	121	120	C <sub>8</sub> H <sub>11</sub> N	methyl, ethyl-pyridine	w
4	121	121	C <sub>8</sub> H <sub>11</sub> N	dimethyl-aniline	m
5	121	121	C <sub>8</sub> H <sub>11</sub> N	trimethyl-pyridine	m
8	135	134	C <sub>9</sub> H <sub>13</sub> N	dimethyl, ethyl-pyridine	m
9	135	135	C <sub>9</sub> H <sub>13</sub> N		m
10	135	135	C <sub>9</sub> H <sub>13</sub> N		m
11	135	135	C <sub>9</sub> H <sub>13</sub> N		m
12	137	118	C <sub>8</sub> H <sub>11</sub> ON	3-pyridine-propanol	w
13	135	134	C <sub>9</sub> H <sub>13</sub> N	trimethyl-aniline	w
14	135	135	C <sub>9</sub> H <sub>13</sub> N	dimethyl, ethyl-pyridine	s
15	135	135	C <sub>9</sub> H <sub>13</sub> N		s
16	135	135	C <sub>9</sub> H <sub>13</sub> N		s
17	135	135	C <sub>9</sub> H <sub>13</sub> N		s
18	149	148	C <sub>10</sub> H <sub>15</sub> N	tetramethyl-aniline	m
19	149	148	C <sub>10</sub> H <sub>15</sub> N		m
20	149	120	C <sub>9</sub> H <sub>11</sub> ON	dimethyl, phenyl-formamide	w
21	149	120	C <sub>9</sub> H <sub>11</sub> ON		w
22	147	132	C <sub>10</sub> H <sub>13</sub> N	methyl, tetrahydro-quinoline	w
23	163	93	C <sub>11</sub> H <sub>17</sub> N	hexyl-pyridine	w
24	149	148	C <sub>10</sub> H <sub>15</sub> N	tetramethyl-aniline	w
25	149	148	C <sub>10</sub> H <sub>15</sub> N		w
26	129	129	C <sub>9</sub> H <sub>7</sub> N	quinoline	s
27	149	148	C <sub>10</sub> H <sub>15</sub> N	tetramethyl-aniline	m
28	149	148	C <sub>10</sub> H <sub>15</sub> N		m
30	147	132	C <sub>10</sub> H <sub>13</sub> N	dimethyl, dihydro-indole	m
31	147	132	C <sub>10</sub> H <sub>13</sub> N		m
32	147	147	C <sub>10</sub> H <sub>13</sub> N	methyl, tetrahydro-quinoline	m

Table 5 (ending)

Peak No.	M.W.	Base peak, m/e	Atomic composition	Possible compound type	Intensity*
33	143	143	C <sub>10</sub> H <sub>9</sub> N	methyl-quinoline	s
34	143	143	C <sub>10</sub> H <sub>9</sub> N		s
36-41	143	143	C <sub>10</sub> H <sub>9</sub> N		m
35	161	146	C <sub>10</sub> H <sub>15</sub> N	trimethyl, dihydro-indole	w
42	157	157	C <sub>11</sub> H <sub>11</sub> N	dimethyl-quinoline	m
44-49	157	157	C <sub>11</sub> H <sub>11</sub> N		s
52-53	157	157	C <sub>11</sub> H <sub>11</sub> N		w
43	175	146	C <sub>12</sub> H <sub>17</sub> N	dimethyl, ethyl-indole	m
54-56	171	171	C <sub>12</sub> H <sub>13</sub> N	propyl-quinoline	s
57-63	171	171	C <sub>12</sub> H <sub>13</sub> N	trimethyl-quinoline	s
64	185	143	C <sub>13</sub> H <sub>15</sub> N	isobutyl-isoquinoline	m
65	186	171	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub>	methyl, tetrahydro-pyridoinole	w
67	186	171	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub>		m
73	186	186	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub>		w
76	186	171	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub>		w
66	185	184	C <sub>12</sub> H <sub>11</sub> ON	methyl, phenoxy-pyridine	s
70-72	185	184	C <sub>12</sub> H <sub>11</sub> ON		s
77	185	168	C <sub>12</sub> H <sub>11</sub> ON		w
68	167	167	C <sub>12</sub> H <sub>9</sub> N	carbazole	m
74-75	185	184	C <sub>12</sub> H <sub>11</sub> ON	methyl, phenyl-pyridinone	w
80	185	184	C <sub>12</sub> H <sub>11</sub> ON		m
86	179	179	C <sub>13</sub> H <sub>9</sub> N	benzo-quinoline	m
87-89	211	182	C <sub>15</sub> H <sub>17</sub> N	dimethyl, tetrahydro-acridine	w
92-104	211	211	C <sub>15</sub> H <sub>17</sub> N		w
91	193	193	C <sub>14</sub> H <sub>11</sub> N	phenyl-indole	w

\* s = strong; m = middle; w = weak.

information of relevance in identifying specific isomers could be available. Because of the lack of standard compounds, it was impossible to distinguish between isomers precisely based on the data of mass spectrometry alone. Therefore, the suggested structures of the nitrogen-containing compounds in the basic fraction are tentative.

GC-MS identifications are given in terms of an atomic composition and a possible compound type; in some cases, several isomeric types may be possible for a given atomic composition, but the absence of neutral nitrogen-containing compounds and hydrocarbons in the basic fraction has removed some ambiguities in the identifications. The preparation of basic fraction has eliminated the

neutral nitrogen compounds, so species such as pyrroles, amides and aliphatic nitriles need not to be considered as possible isomers for compounds identified in terms of an atomic composition by GC-MS.

45% of the nitrogen in the Maoming light oil and 50% in the Fushun's is basic. The basic nitrogen is concentrated in the basic fractions. Very little overlap between the neutral and basic fraction was observed, indicating that acid/base extraction technique was suitable for the light oil. The aqueous acid extraction technique is dependent upon the solubility of the protonated base in the aqueous acid, and it has been noted that such solubilities decrease markedly with increasing molecular weight. Nevertheless, the aqueous acid extraction technique should be satisfactory for these compounds which lie within the normal range of GC (molecular weight 80-300, approximately) [20]. Our separation results and analytical data confirmed that the aqueous acid extraction procedure used for the isolation of the basic fraction was satisfactory for the samples examined, and permitted a more detailed examination of aza heterocycles and other basic nitrogen compounds.

Of the nitrogen-containing compounds identified in Fushun and Maoming basic fractions, the majority contains one nitrogen atom, but a number of more complex (NO and NN) heteroatomic compounds have been found. As expected, the major class in the basic fraction of Maoming and Fushun light oils comprises alkyl-substituted pyridines, quinolines and benzoquinolines (acridine types). Substituted pyridines were first isolated from shale oil in 1855 [21], and pyridines with up to 12 carbons in side-chains have been reported [22, 23]. In this work, substitution by a maximum of six carbons (as side-chains) has been observed. The most abundant pyridines are substituted with three- and four-carbon side-chains. Lacking of the long chain substituted pyridines in light oils implies that the amount of alkyl-substituted pyridines in the heavy oil would be much smaller, so that they may no longer constitute the major part of the nitrogen bases. Methyl phenoxy pyridines and methyl phenylpyridinones have also been found.

Quinolines and its homologues have been detected in several shale oils and derivative of shale oils [23-27], but were less abundant than pyridines. It was found that quinoline or isoquinolines are abundant in the Maoming and Fushun light oil (peak 26 in Fig. 2). Quinoline with its methyl and dimethyl derivatives are the major components of the bases, but derivatives with side-chains longer than three carbons has been identified. A methyl tetrahydroquinoline was also detected. Quinoline together with pyridine homologues comprised the majority of the basic nitrogen compounds both in the Maoming and Fushun light shale oils.

Small amounts of benzoquinolines, principally acridine and methylacridines, have been reported in the polar fraction of shale oil [17, 22, 27, 28]. Benzoquinoline (or benzoisoquinoline) and dimethyl-tetrahydro-acridines have been detected in the basic fraction of both light oils, but not in large quantities. The boiling points of benzoquinolines, benzoisoquinolines and their derivatives are higher than 350 °C; so they could not present significantly in the light oils.

Generally, anilines have scarcely been found in shale oil although their presence in a hydrotreated shale oil has been reported [26, 27, 29]. In the Maoming and Fushun basic fraction, minor amounts of dimethyl- and trimethyl-anilines have been detected. Bett et al. [30] had also found small amounts of anilines in Rundle shale oil. They may be resulted from the ring opening of carbazole type structures during acid extraction [31]. Small quantities



of trimethyl-dihydro-indole, dimethyl-ethyl-indole, methyl-tetrahydro-pyridoinole and phenylindole have also been detected.

**Nitriles.** The nitrile fractions constitute 9.1 % and 7.7 % by weight of Maoming and Fushun light oil, and contain 16.4 % and 20.4 % of the total mass of nitrogen respectively. GC-TSD and GC-MS identification of the nitrile fraction (Figs 3 and 4; Table 6) revealed that they consisted mainly of a homologous series of linear alkanonitriles. Aliphatic nitriles range from C<sub>9</sub> to C<sub>19</sub> in Maoming light oil and from C<sub>7</sub> to C<sub>22</sub> in Fushun's. The carbon chain length distribution patterns are similar to that of the *n*-alkanes. The main GS-TSD peaks are flanked by smaller peaks whose MS fragmentation patterns are suggestive of unsaturated linear aliphatic nitriles.

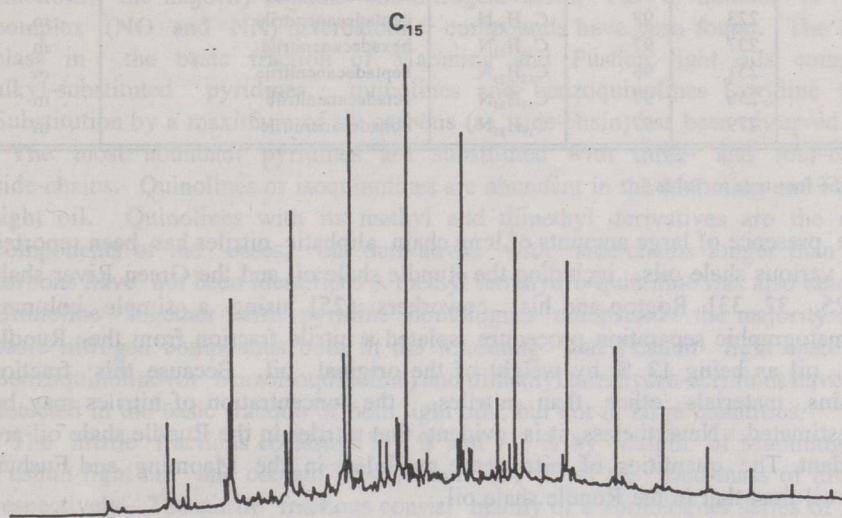


Fig. 3. GC/TSD chromatogram of the nitrile fraction in Maoming light oil

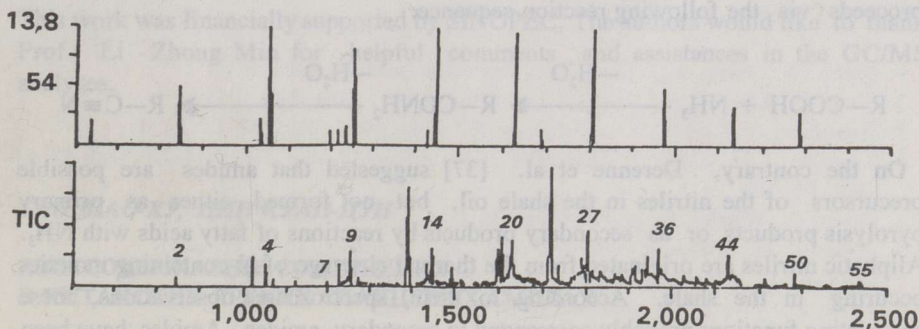


Fig. 4. GC/MS single-ion and TIC chromatogram of the nitrile fraction in Maoming light oil

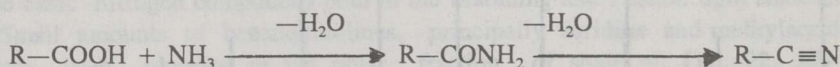
Table 6. Identification of Aliphatic Nitriles in the Maoming Nitrile

Peak No.	M.W.	Base peak, m/e	Atomic composition	Possible compound type	Intensity*
1	139	41	C <sub>9</sub> H <sub>11</sub> N	nonanenitrile	w
2	153	41	C <sub>10</sub> H <sub>19</sub> N	decanenitrile	w
4	167	41	C <sub>11</sub> H <sub>21</sub> N	undecanenitrile	m
7	153	153	C <sub>11</sub> H <sub>7</sub> N	naphthalenecarbonitrile	w
9	181	97	C <sub>12</sub> H <sub>23</sub> N	dodecanenitrile	m
14	195	96	C <sub>13</sub> H <sub>25</sub> N	tridecanenitrile	m
20	209	96	C <sub>14</sub> H <sub>27</sub> N	tetradecanenitrile	m
27	223	97	C <sub>15</sub> H <sub>29</sub> N	pentadecanenitrile	m
36	237	97	C <sub>16</sub> H <sub>31</sub> N	hexadecanenitrile	m
44	251	96	C <sub>17</sub> H <sub>33</sub> N	heptadecanenitrile	m
50	256	97	C <sub>18</sub> H <sub>35</sub> N	octadecanenitrile	m
55	279	97	C <sub>19</sub> H <sub>37</sub> N	nonadecanenitrile	m

\* See the foot-note to Table 5.

The presence of large amounts of long chain aliphatic nitriles has been reported from various shale oils, including the Rundle shale oil and the Green River shale oil [25, 32, 33]. Rogtop and his coworkers [25] using a simple column chromatographic separation procedure isolated a nitrile fraction from the Rundle shale oil as being 13 % by weight of the original oil. Because this fraction contains materials other than nitriles, the concentration of nitriles may be overestimated. Nevertheless, it is evident that nitriles in the Rundle shale oil are abundant. The quantities of nitriles are much less in the Maoming and Fushun shale oil than that in the Rundle shale oil.

Although nitriles have been detected in shale oils, their origin is obscure. The nitrile group has high thermodynamic stability, bond enthalpy of C≡N equals to 2.5 times of C—C bond [34], and could be derived from the degradation of amides [35]. Evans et al. [36] suggested that nitriles are formed during pyrolysis by the reaction of carboxylic acids and/or esters with ammonia which is given off by minerals such as ammonium feldspars when they are present in the shale, and the possible conversion of fatty acids into nitriles during retorting most likely proceeds via the following reaction sequence:



On the contrary, Derenne et al. [37] suggested that amides are possible precursors of the nitriles in the shale oil, but not formed either as primary pyrolysis products or as secondary products by reactions of fatty acids with NH<sub>3</sub>. Aliphatic nitriles are originated from the thermal cleavage of N-containing moieties occurring in the shale. According to their spectroscopic observations, these preexisting functions probably correspond to secondary amides. Amides have been identified in the Rundle retort oils [25] and solvent extracts of the Rundle shale [38]. They are readily dehydrated by pyrolysis to give nitriles without disruption of the carbon skeleton [35].

Maoming and Fushun light oils are similar in composition and distribution of the nitrogen-containing compounds.

## Conclusions

Maoming and Fushun light shale oils are highly aliphatic ( $H/C > 1.7$ ), with hydrocarbons (ca. 60 %) comprising the major parts of the oils. Acids, bases, nitriles and ketones make up 27.1 % and 22.4 % by weight of Maoming and Fushun light oils respectively.

45 % of the nitrogen in the Maoming light oil is basic and 50 % in the Fushun's. Of the nitrogen-containing compounds identified in Maoming and Fushun basic fractions, the majority contains one nitrogen atom, but a number of more complex (NO and NN) heteroatomic compounds have been found. The major class in the basic fraction of Maoming and Fushun light oils comprises alkyl-substituted pyridines, quinolines and benzoquinolines (acridine type). Substitution by a maximum of six carbons (as side-chain) has been observed.

The most abundant pyridines are substituted with three- and four-carbon side-chains. Quinolines or isoquinolines are abundant in the Maoming and Fushun light oil. Quinolines with its methyl and dimethyl derivatives are the major components of the bases, but derivatives with side-chains longer than three carbons have not been identified. A methyl tetrahydro-quinoline was also detected. Quinoline together with pyridine homologues comprised the majority of the basic nitrogen compounds both in the Maoming and Fushun light shale oils. Benzoquinoline (or benzoisoquinoline) and dimethyl tetrahydro-acridines have been detected in the basic fraction of both light oils, but not in large quantities.

The nitrile fractions constitute 9.1 % and 7.7 % by weight of Maoming and Fushun light oil, and contain 16.4 % and 20.4 % of the total mass of nitrogen respectively. The nitrile fractions consist mainly of a homologues series of linear alkanonitriles. Aliphatic nitriles range from  $C_9$  to  $C_{19}$  in Maoming light oil and from  $C_7$  to  $C_{22}$  in Fushun's. The carbon chain length distribution patterns are similar to that of the *n*-alkanes. GC-TSD and MS identification suggest the presence of unsaturated linear aliphatic nitriles.

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ГАО ШАО-ХУ, ЦИН КУАН-ЦУН

АЗОТСОДЕРЖАЩИЕ СОЕДИНЕНИЯ  
В КИТАЙСКИХ ЛЕГКИХ СЛАНЦЕВЫХ СМОЛАХ

Резюме

В связи с истощением запасов сырой нефти и природного газа в мировой практике возрастает интерес к использованию запасов угля и сланца. Сланец и сланцевая смола все больше берутся во внимание при рассмотрении альтернативных источников получения энергии.

Китайская сланцевая смола по своему составу похожа на нефть, но сложнее её и богаче непредельными и неуглеводородными соединениями, куда входят азотистые, кислородные и сернистые соединения. Жидкие топлива, получаемые из сланцевой смолы, относятся в основном к низкокачественным жидким топливам, поскольку содержат неуглеводородные и особенно азотсодержащие соединения, которые отравляют катализаторы в нефтехимической промышленности и тем самым препятствуют использованию каталитических процессов для облагораживания сланцевых смол. Для разработки эффективных методов удаления азотистых соединений из сланцевых смол необходимо знать их состав и содержание в различных фракциях смолы.

Для исследования были взяты суммарные смолы, полученные на сланцеперерабатывающих предприятиях в Маомине и Фушуне (маоминская и фушунская смола). Эти смолы подвергли дистилляции с выделением легкой (<350 °C) и тяжелой (>350 °C) фракций. Выход легкой фракции, или легкой смолы, для маоминской и фушунской нефти составил 35,4 и 36,0 % по массе соответственно. Эта смола имеет в высшей степени алифатический характер ( $N/C > 1,7$ ) и содержит около 60 % углеводородов. Соединения кислотного и основного характера, а также нитрилы и кетоны составляют 27,1 и 22,4 % по массе в легкой фракции соответственно маоминской и фушунской смолы. В суммарной смоле на легкую фракцию маоминской смолы приходится 33, а фушунской смолы - 28 % от общего содержания азота.

Во фракциях обеих смол идентифицированы основные азотсодержащие соединения. Большинство их содержит один атом азота, но они образуют множество комплексов (NO и NN) гетероатомных соединений. Основу легкой фракции как маоминской, так и фушунской смолы составляют алкилзамещенные пиридины, хинолины и бензохинолины (акридинилового типа). Наблюдается замещение шести атомов углерода.

Гомологи хинолина вместе с пиридином составляют большую часть азотных соединений. Бензохинолин (или изобензохинолин) и диметилтетрагидроакридинил обнаружены в легких фракциях в небольших количествах. Нитрильные фракции в легкой смоле маоминской и фушунской смол составляют 9,1 и 7,7 % по массе; на эти фракции азота приходится соответственно 16,4 и 20,4 % от общего его содержания в легкой смоле. В нитрильных фракциях присутствуют в основном гомологи прямоцепочных алканнитрилов. Алифатические нитрилы, содержащиеся в легкой фракции маоминской и фушунской смол, представлены структурами  $C_9-C_{19}$  и  $C_7-C_{22}$  соответственно.

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