

## ISOLATION OF ORGANIC MATTER BY THE NAOH-HCL METHOD FROM TWO MARINE OIL SHALES USING OVEN AND SEALED AUTOCLAVE TECHNIQUES

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**Abstract.** *Organic matter (OM) was isolated from two marine oil shales, El-Lajjun and Julia Creek, using NaOH-HCl and humin and humic acid fractions separated. Two treatments were required to reduce humin ash yield to below 11 wt% db. The humin yield of the autoclave method was 80 wt% of OM (dry mineral-matter-free, dmmf), compared to only 20–60 wt% dmmf for the oven method, possibly due to the increased NaOH solution strength and some oxidation. Oven and autoclave methods both gave humin similar in chemical structure to shale OM, regardless of yield. This similarity has implications as to shale OM structure.*

**Keywords:** *marine oil shale, organic matter, NaOH-HCl treatment, oven and autoclave methods, humin and humic acid.*

### 1. Introduction

Oil shale is a sedimentary rock which contains a wide range of minerals and an appreciable amount of organic matter (OM) [1, 2], which can be used to generate electrical energy or produce higher value fuels [3, 4]. The composition of the inorganic matter varies considerably. The large fraction of inorganics makes it difficult to study the organic fraction in detail, so that there has, for a long time, been considerable interest in treating the oil shale to obtain an organic matter-rich fraction. Lengthy physical procedures, which have the advantage of not changing the structure of the organic material, have been used, such as sink-float [5], making up a slurry of oil shale in a mixture of *n*-cetane and water and separating the aqueous phase

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which become charged with mineral matter [6], and froth flotation [7], often combined with mild acid treatment to remove carbonates and other mineral species.

The most common of the chemical procedures that have been used involves hydrofluoric acid, usually in combination with hydrochloric acid, which removes the carbonates, oxides etc. [8–11]. Fluoride-containing material is often removed after reaction using boric acid [10–12]. However, the OM isolated by this treatment is not identical in chemical structure to that in the original oil shale. Some nitrogen is lost [13], chlorine [13, 14] and fluorine [13] are incorporated and there are changes in the oxygen-containing groups detectable by  $^{13}\text{C}$  NMR [13, 15]. Another disadvantage is that there is no simple way of separating the OM isolated into a small number of classes, which often assists analysis of a complex system. The so-called bitumens are often extracted by an organic solvent [16] before acid treatment [15], but this is not a well-defined fraction, because an additional solvent extraction after washing with dilute HCl will give a high yield of extract [11]. Further, in some countries, such as Australia, HF is considered to be so dangerous that Government authorities urge that its use be avoided if possible [17].

The treatment with strong alkali followed by an acid wash is an alternative chemical treatment [18, 19] that could, unlike many of the other treatments, be universally applicable. One advantage of such methods is that the OM is divided into distinct fractions which are amenable to further study. These are humin, insoluble in alkali and acid, humic acid, soluble in alkali but insoluble in acid, and fulvic acid, soluble in alkali and acid. This definition of solubility fractions has been used for OM from recent sediments [20], OM from coal [21] and OM from oil shale [22]. The alkali-acid method of extraction has been extensively applied to coal [23] and soil [24].

A detailed procedure was developed by McCollum and Wolff [18] and Wolff and McCollum [25] for Colorado oil shale. A possible problem with their procedure is that the yield of humin (alkali- and acid-insoluble material), which was the only fraction quantified and studied, showed marked variations. The results of one series of experiments in closed (not sealed) vessels in an oven imply humin yield varying between 11 and 57 wt% dry mineral-matter-free (dmmf) for the same oil shale [25]. A second series gave humin yields of 78–80 wt% dmmf for a single NaOH-HCl treatment in oven experiments, rising to over 95 wt% dmmf for a 4 h treatment in a sealed autoclave [18]. The humin ash yield for the second series was always relatively low (8–18 wt% dry basis, db) but the variations in humin yield over both series call into question how representative the humin structure would be of the organic structure of the original oil shale. McCollum and Wolff [18] found that humins from the second series of experiments had the same Fischer assay (wt% dmmf) and N/C atomic ratio as the original oil shale, though there was some oxidation and aromatization, but more detailed comparisons would be desirable.

Notwithstanding these limitations, the NaOH-HCl method appears to be useful in studying the organic structure of Colorado oil shale, a lacustrine shale [4]. An earlier study indicated that this method was also useful in studying the organic structure of marine oil shales [13]. OM isolated from two marine oil shales, El-Lajjun (Jordan) [4] and Julia Creek (Queensland, Australia) [4], using HF-HCl was compared with the humin fraction of the OM isolated from the same oil shales by the NaOH-HCl method under one set of conditions. The two isolated fractions from each shale were not identical in chemical structure to each other or to the OM in the original shale, but the change from the original OM was small for both isolation methods [13]. Thus the NaOH-HCl method is a useful alternative to the HCl-HF method. It was therefore of interest to investigate how yields and chemical structures for the products isolated by the NaOH-HCl method, in closed (not sealed) oven and sealed autoclave variants varied with treatment conditions and how closely their chemical structure resembled that of the oil shale OM. The same two marine oil shales used in the earlier experiments were studied. The fact that the NaOH-HCl method divides the OM of the oil shale into distinct fractions defined by their acid and alkali solubility may facilitate investigation of the structure of the oil shale OM in ways that have not been applied previously. Such investigations on low-rank coal have been fruitful [26, 27].

## 2. Experimental

### 2.1. Materials

The oil shale from the El-Lajjun deposit in the Karak region in Jordan was provided by Jordan Energy and Mining and the oil shale from the Julia Creek deposit, Queensland, Australia was supplied by Extract Oil (Global Oil Shale).

N<sub>2</sub> was purchased from Air Liquide. Analytical grade sodium hydroxide was purchased from Merck and analytical grade 32% hydrochloric acid was provided by Ajax Finechem Pty Ltd. Deionized water was used in washing steps.

### 2.2. Organic matter isolation

#### 2.2.1. NaOH-HCl treatment using the oven method

100 g of ground oil shale sample (– 180 μm) was heated with 310 g of an aqueous solution of (50% w/w) NaOH at 160 °C in a flow of N<sub>2</sub> in a 2 L stainless steel beaker partially covered with a watch glass. The treatment time was 16 h with occasional agitation in order to mix the shale with the NaOH solution. During the treatment, much of the water evaporated. After cooling, the NaOH-treated shale was washed with water several times and the filtrate was kept for humic acid determination. The solid was then treated

with 1 L of 2M HCl, stirred for 1 h at room temperature and filtered by vacuum filtration. The humin was washed with water several times until the pH was 5–6, to remove traces of acid. The sample was then dried at 70 °C under N<sub>2</sub> for a few hours [18].

#### 2.2.2. NaOH-HCl treatment using the sealed autoclave method

10 g of ground oil shale sample (– 180 µm) was mixed thoroughly with 31 g of an aqueous solution of 50% w/w NaOH in a 100 mL autoclave. The autoclave was filled with 3 MPa (cold) N<sub>2</sub> and heated at 160 °C for 16 h without stirring, cooled and then the treatment products were recovered by deionized water. The solution was filtered, washed with water and the filtrate was kept for humic acid determination. The solid was stirred with 1 L of 2M HCl for 1 h at room temperature and then washed with water several times until the pH was 5–6, then dried at 70 °C under N<sub>2</sub> for a few hours.

#### 2.2.3. Humic acid determination

The NaOH filtrate solution was collected and acidified using dilute HCl until the pH of the solution was around 1. The solution was kept overnight for precipitation and then the precipitate was collected, dried at 105 °C under N<sub>2</sub>, weighed and kept in a sealed container for further characterization.

### 2.3. Humin and humic acid characterization

The NaOH-HCl treatment was repeated for both the oven and autoclave methods until low ash yields were obtained (< 12 wt% db). The ashing was done at 490 °C so that the obtained ash yields represented approximately the inorganic matter content of the humin and humic acid fractions [28].

Elemental analysis for C, H, N and S for the humins and humic acids was carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand. The analyses were converted to wt% dry mineral-matter-free basis by using the ash yield of the humins and humic acids and organic oxygen amount was calculated by difference. There will be a small error in the calculated oxygen amount due to neglect of the Cl (and F) contents [13]. The original oil shales were washed with dilute HCl to remove inorganic C and acid-soluble S. The resulting HCl-insoluble oil shales were analysed for C, H, N and S and the analyses converted from wt% dry basis to wt% dmmf as for the humins and humic acids and organic O was calculated by difference. Knowledge of the loss in weight on washing with dilute HCl permitted calculation of C, H, N, S and O for the original oil shale on a wt% dmmf basis. Corrections were made for O and H in minerals where necessary. The S included pyritic and organic S.

Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) analysis for the humins and humic acids was carried out as described by Qi et al. [29] on a Chemical Data Systems (CDS) Pyroprobe 5200 connected to a GC-MS (Agilent 6850 GC and 5790 MSD). A 0.20–0.25 mg (for ash content < 10%)

or 0.50–0.60 mg (for ash content > 50%) sample was used. The pyrolysates were compared with regard to their boiling point distributions by dividing the total ion chromatogram (TIC) into three retention time ranges, corresponding roughly to three boiling point ranges. The first range was from the retention time for  $n\text{-C}_6\text{H}_{14}$  to that for  $n\text{-C}_{11}\text{H}_{24}$ , corresponding approximately to the boiling point range for gasoline [30]. The second range was from above the retention time for  $n\text{-C}_{11}\text{H}_{24}$  to the retention time for  $n\text{-C}_{17}\text{H}_{36}$ , corresponding approximately to the boiling point range for kerosene [31]. The third range was above the retention time for  $n\text{-C}_{17}\text{H}_{36}$ , and the peaks in this range were assigned to heavier oil. The percentage of the total peak area in each of these retention time ranges (gasoline, kerosene and heavier oil) was calculated. A similar division of the pyrolysate TIC was used by Fei et al. [32].

### 3. Results and discussion

#### 3.1. Humin and humic acid yields

The humin and humic acid yields obtained from NaOH-HCl treatments of El-Lajjun and Julia Creek shales using oven and autoclave methods are given in Table 1. The extraction by each method had to be repeated twice to obtain low ash humin. The relatively slow removal of inorganic material by NaOH-HCl can be understood in terms of the principal mechanism of the process in coal and oil shale. It is thought that the NaOH converts silica and acid-insoluble silicates to sodium silicates, insoluble in alkali, but dissolved by HCl along with the carbonates and other acid-soluble minerals. The hypothesis of conversion to sodium silicates by the NaOH is supported by X-ray diffraction (XRD) studies of the product after NaOH treatment [25, 33] and experiments in which clay or silica alone was reacted with NaOH under the conditions of the NaOH treatment [34]. Analogy with the Bayer process has also been taken as evidence for the formation of sodium silicates [33, 34]. It is reasonable that the rate of sodium silicate formation will depend on the structure of the silicates present and how easily the solution can diffuse into the particles, so that it will vary with the oil shale, as observed, and also that the rate will be relatively slow in all cases because of the nature of the reaction.

McCollum and Wolff [18] noted lower humin yields in the oven than in autoclave experiments for Colorado oil shale, and the same effect was observed in this work for marine oil shales (Table 1). The humic acid yields (not determined by McCollum and Wolff) were, in contrast, higher for oven experiments. There are two main differences between the autoclave and oven environments that, on the basis of earlier studies, could contribute to the higher humic acid yields in the oven. The first is the possible presence in the oven atmosphere of oxygen from the air; exposure to oxygen has been reported to increase the humic acid yield from, for example, oil shale [35],

**Table 1. Humin and humic acid yields after the treatment of El-Lajjun and Julia Creek oil shales with NaOH/HCl using oven and autoclave methods\***

		El-Lajjun oil shale		Julia Creek oil shale	
		Oven method	Autoclave method	Oven method	Autoclave method
First treatment	Humin, wt% dmmf	75.0±8.3	98.9±0.1	78.3±4.7	98.6±2.5
	Humin ash, wt% db	45.9±10.2	30.0±2.9	30.2±7.3	39.1±2.6
Second treatment	Humin, wt% dmmf	25.4±6.0	80.1±1.6	40.2±1.1	75.5±0.2
	Humin ash, wt% db	4.9±1.8	4.7±0.5	11.0±1.0	5.2±2.9
	Humic acid, wt% dmmf	53.0±6.6	11.6±1.6	21.1±3.4	2.7±1.2
	NaOH-soluble, HCl-soluble fraction + Loss on evaporation, wt% dmmf (by difference)	21.6±0.5	8.4±2.7	38.7±1.9	21.8±3.3

\* The errors are standard deviations based on the results for duplicate runs.

low rank coals [36] and sub-bituminous coals [37]. The second is the higher NaOH concentration in the oven experiments due to water evaporation. Higher NaOH concentration has been found to increase the humic acid yield from low-rank coals in some circumstances [38].

The treatment conditions used in the oven method had an important effect on the humin yield, even with a constant ratio of oil shale to NaOH solution weights and the same container volume. Higher humin yields were obtained when less shale weight was used in the NaOH-HCl treatment (see Table 2). The mixing frequency and the power of agitation were probably important factors in this effect of starting weight. Variation in the amount treated may have also been partially responsible for the variation in yield reported by Wolff and McCollum [25].

**Table 2. The effect of shale starting weight on the humin yield for El-Lajjun oil shale treatment with NaOH-HCl using the oven method**

Shale starting weight, g	Humin yield, wt% dmmf
20	62.2
40	33.2
60	25.4
100	22.9

The effect of evaporation on humin yields at the humin drying temperature (70 °C) and treatment temperature (160 °C) was studied by drying the humins obtained by the oven and autoclave methods in the oven at these two temperatures and the loss on drying was calculated as the difference of humin weight before and after drying (Table 3). Drying the humins at 70 °C had no effect on humin yield, but a small loss of the humin weight of less than 4.4% was observed at 160 °C. The small loss suggests that the low humin yield was mainly due to the formation of humic acids and also fulvic acids (alkali-soluble and acid-soluble) rather than to evaporation.

**Table 3. The loss of humin weight by evaporation at different oven drying temperatures, wt% db**

Loss on drying, wt% db					
		El-Lajjun humin		Julia Creek humin	
Drying temperature, °C	Time, h	Oven humin	Autoclave humin	Oven humin	Autoclave humin
70	0–24	< 0.05	< 0.05	< 0.05	< 0.05
	24–48	< 0.05	< 0.05	< 0.05	< 0.05
160	0–24	2.60	1.94	1.00	1.00
	24–48	1.75	1.40	1.30	0.98

In order to study the effect of treatment temperature on humin yields, the El-Lajjun oil shale was treated twice at room temperature with NaOH-HCl and the results were compared to those obtained at 160 °C. The sample was mixed with 50% w/w NaOH and the mixture was stirred for 16 h at room temperature. After that, the sample was washed with water and treated with HCl as described in section 2.2. After the two treatments, the humin yield was high (almost 98 wt% dmmf) but with high ash yield (about 45 wt% db) compared with 4.9 wt% after two treatments at 160 °C. This experiment suggests that the high temperature is necessary to convert silica and silicate minerals to sodium silicates which are then acid-soluble.

### 3.2. Humin and humic acid characterization

#### 3.2.1. Elemental analysis

Table 4 gives the C, H, N, S and O results for the humins and humic acids (expressed as wt% dmmf) obtained from the NaOH-HCl treatments of El-Lajjun and Julia Creek shales using the oven and autoclave methods. The yield of humic acid from the autoclave treatment of Julia Creek oil shale was too small for elemental analysis. The organic elemental analysis of the humins obtained by the two methods was almost the same and similar to that of the original oil shale. The lower sulfur content of Julia Creek humins compared to the original oil shale is probably due to the fact that many of the

sulfur compounds in the Julia Creek oil shale are inorganic [13] and so were removed by the NaOH-HCl treatment [13, 39]. The high oxygen content of the humic acids for both shales indicated that the OM was oxidized during NaOH treatment at high temperature. This increased the solubility of OM in the NaOH solution, and part, but not all, of this was precipitated as humic acid in the acidic media.

**Table 4. Elemental analysis of humins and humic acids obtained by the oven and autoclave methods, wt% dmmf\***

Sample	C	H	N	S	O (by difference)	Atomic H/C ratio
El-Lajjun raw shale	69.9±1.0	8.5±0.1	1.58±0.04	11.00±0.10	9.10±1.20	1.45±0.03
El-Lajjun humin oven	71.9±0.2	9.1±0.1	1.13±0.01	12.46±0.19	4.65±0.47	1.50±0.02
El-Lajjun humic acid oven	60.9±0.4	7.0±0.02	1.58±0.04	9.38±0.16	21.18±0.58	1.36±0.02
El-Lajjun humin autoclave	72.9±0.03	9.1±0.01	1.56±0.08	13.68±0.01	2.72±0.13	1.47±0.01
El-Lajjun humic acid autoclave	41.0±0.4	4.4±0.03	2.50±0.01	35.92±0.59	16.12±1.05	1.28±0.03
Julia Creek raw shale	72.4±2.4	8.9±0.2	2.8±0.1	12.2±1.9	3.8±4.6	1.46±0.01
Julia Creek humin oven	74.1±0.01	8.1±0.1	2.3±0.02	5.4±0.1	9.7±0.2	1.33±0.01
Julia Creek humic acid oven	58.2±0.1	6.4±0.2	2.0±0.1	6.8±0.1	26.5±0.4	1.31±0.1
Julia Creek humin autoclave	73.3±0.1	7.8±0.01	2.5±0.02	8.4±0.03	8.0±0.1	1.30±0.01

\* The errors for the raw oil shales were based on the errors reported by the commercial laboratory and those for the humins and humic acids were the standard deviations of duplicate measurements.

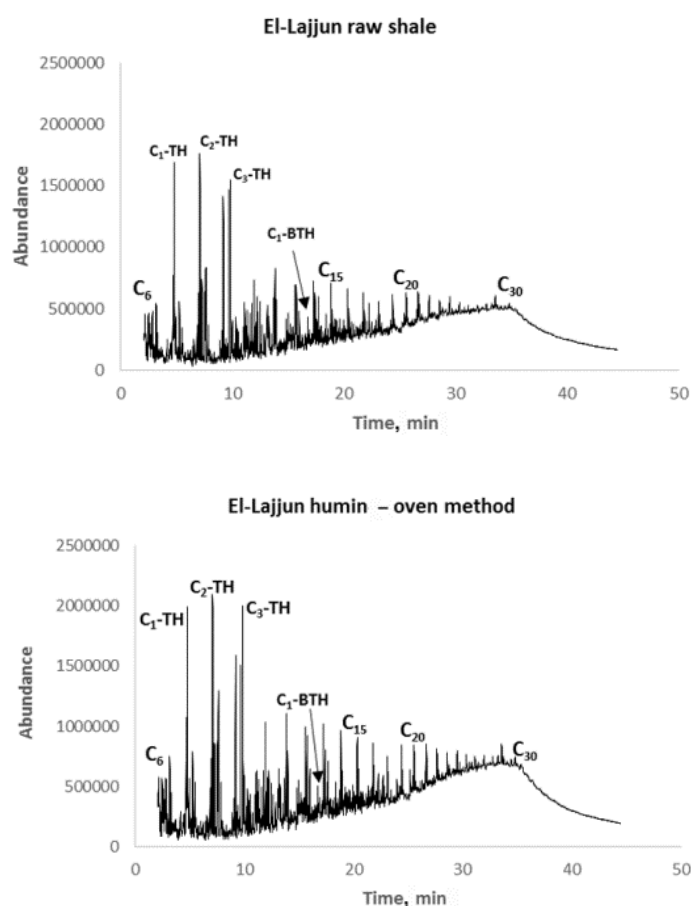
The analysis of the El-Lajjun oven humic acid may be compared with that of the humic acid previously extracted from the El-Lajjun oil shale in open conditions, but at room temperature and with much lower concentrations (0.5 M) of NaOH, hence in much smaller yield (0.013%) [22]. The humic acid obtained under these mild conditions had a lower atomic H/C ratio (1.22) compared to that of the oven humic acid (1.36, Table 4). A similar effect of severity of NaOH treatment has been observed for brown coals; humic acid extracted from a Victorian coal under conditions giving a small yield contained little wax-derived, high-H/C-atomic ratio material compared to the final humin after humic acid extraction, and therefore had a



lower H/C ratio than the humin. However, the composition of the humic acid approached that of the humin as the NaOH extraction conditions became more severe [27].

### 3.2.2. Py-GC-MS

Py-GC-MS TICs of the El-Lajjun and Julia Creek raw shales, humins and humic acids extracted by NaOH-HCl treatment using oven and sealed autoclave methods are shown in Figures 1 and 2. The chromatograms of the raw shales and the two humins extracted by the oven and autoclave methods were similar, with a predominance of aliphatic straight chains. Considerable amounts of sulfur compounds, such as thiophenes, were also observed. The



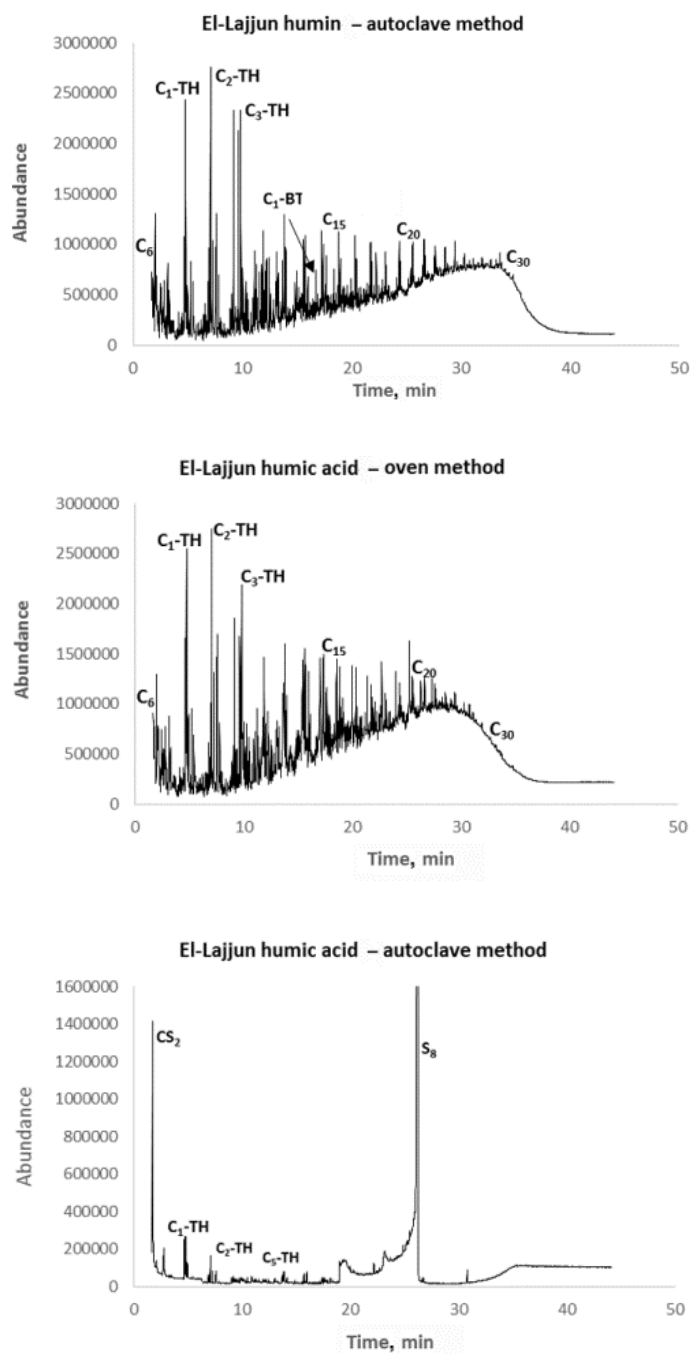
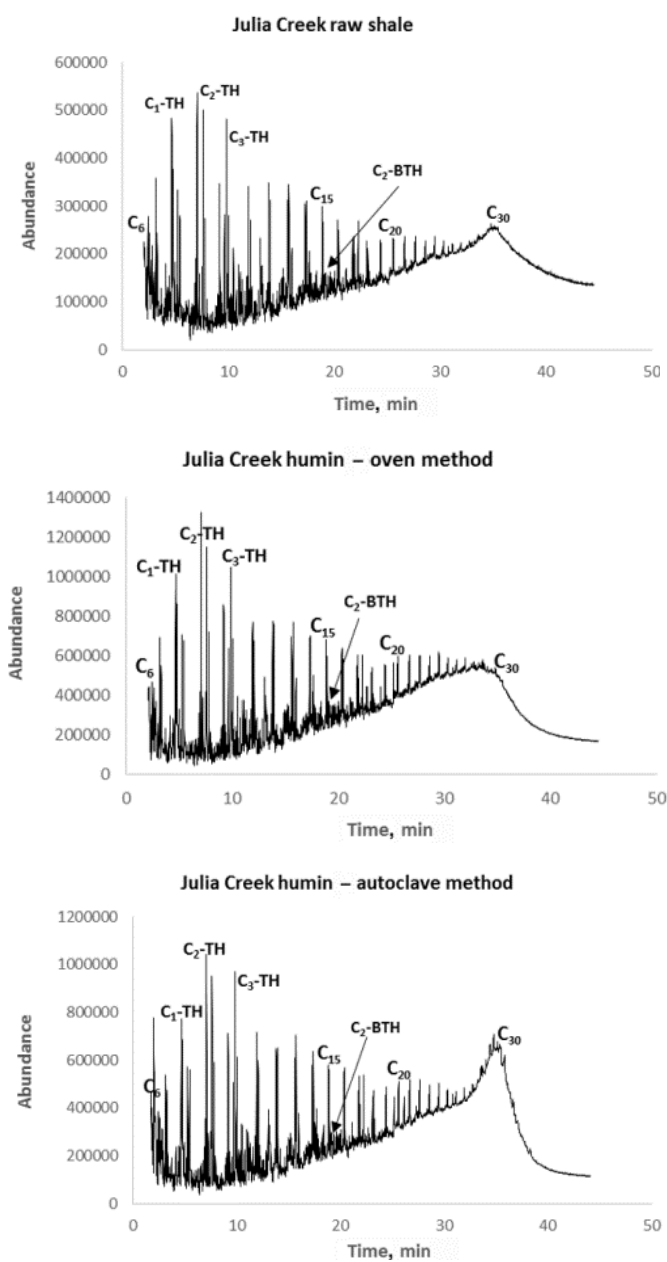


Fig. 1. Total ion chromatograms of Py-GC-MS for humin and humic acid fractions obtained from El-Lajjun oil shale by the NaOH-HCl treatments using oven and autoclave methods. C<sub>n</sub> – alkene/alkane of chain length n, TH – thiophene homologues, BTH – benzothiophene homologues.



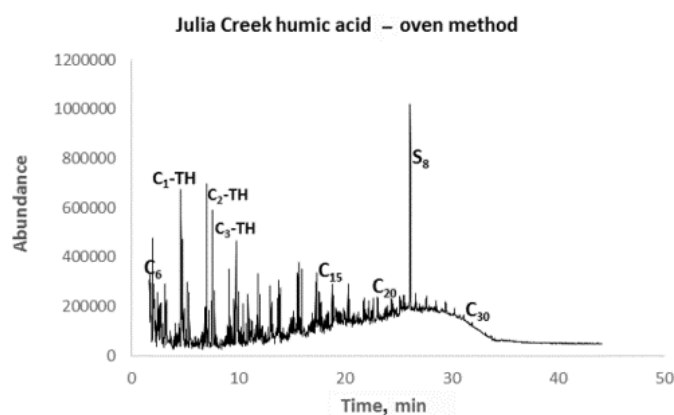


Fig. 2. Total ion chromatograms of Py-GC-MS for humin and humic acid fractions obtained from Julia Creek oil shale by the NaOH-HCl treatments using oven and autoclave methods.  $C_n$  – alkene/alkane of chain length  $n$ , TH – thiophene homologues, BTH – benzothiophene homologues.

chromatograms of the humic acid and the humins produced by the oven method were similar, suggesting that high NaOH concentration and the possible presence of oxygen in the oven treatment produced a humin and a humic acid of similar structure (see section 3.1). The similarity in elemental analysis and TICs between the oven humin and humic acid suggests that a relatively small amount of oxidation and/or depolymerization were sufficient to convert humin into an alkali-soluble form. In contrast, the humic acid produced by the autoclave method was different in that the major pyrolysis products were elemental sulfur ( $S_8$ ) and  $CS_2$ . This must be associated with the high sulfur content of the material (36 wt% dmmf), compared to the much lower values observed for the shale, the humin and the humic acid prepared by the oven method (< 14 wt% dmmf). A significant but much smaller peak for  $S_8$  was present in the TIC of the pyrolysate from the Julia Creek oven humic acid and the pyrolysate from the El-Lajjun oven humic acid. These results indicate that the unchanged NaOH concentration and the absence of oxygen in the autoclave treatment atmosphere decreased the extent of depolymerization, resulting in a greatly reduced level of alkali-soluble materials (see section 3.1).

Table 5 shows that the boiling-point distributions of the fragments produced by flash pyrolysis at 650 °C for the raw shales and the humins produced by the oven method were similar, with most of the fragments being in the range of heavier oil. The oven humic acid fragments included more kerosene and less heavier oil than the corresponding humins. The Julia Creek autoclave humin tended to give higher-boiling-point pyrolysis fragments than the original oil shale. The results for humic acid from the autoclave treatment of Julia Creek oil shale are not given as there was insufficient sample for Py-GC-MS analysis.

**Table 5. Percentage fractions of gasoline, kerosene and heavier oils obtained by Py-GC-MS for El-Lajjun and Julia Creek humins and humic acids (only for El-Lajjun) using oven and autoclave NaOH-HCl demineralization methods**

Sample	% Gasoline (C <sub>6</sub> -C <sub>11</sub> )	% Kerosene (C <sub>11</sub> -C <sub>17</sub> )	% Heavier oil (> C <sub>17</sub> )	Kerosene/heavier oil
El-Lajjun raw shale	20.0	22.7	57.4	0.4
El-Lajjun humin oven	22.3	22.0	55.8	0.4
El-Lajjun humic acid oven	15.4	30.8	53.8	0.6
El-Lajjun humin autoclave	15.7	25.4	58.9	0.4
El-Lajjun humic acid autoclave <sup>a</sup>	–	–	–	–
Julia Creek raw shale	23.2	21.2	55.6	0.4
Julia Creek humin oven	20.1	23.1	56.8	0.4
Julia Creek humic acid oven	21.8	29.5	48.7	0.6
Julia Creek humin autoclave	14.6	19.9	65.5	0.3

<sup>a</sup> Only one clear peak could be distinguished in the Py-GC-MS spectrum (Fig. 1).

It should be noted that the sum of humic acid and humin yields for the oven method was almost the same as the humin yield of the autoclave method (Table 1). This is to be expected since the oven method produced both humin and humic acid with similar characteristics. Also the similarity in the organic structure of both oven and autoclave humins indicated that the two methods produced the same humins but the higher NaOH concentration and the presence of oxygen in the oven method led to bond breaking, resulting in the production of humic acid with a similar structure to the humin, apart from the reaction of S-containing compounds.

The similarity of analytical results for the humins produced by the oven and autoclave methods, despite the difference in yields, may give clues to the nature of the bonds broken by NaOH treatment under the severe conditions of oil shale alkali digestion. The increase in humic acid yield with decrease in coal rank, i.e. with increase in coal oxygen content [40] and with oxidation of oil shale or coal [35–37], and the high oxygen content of the small, soluble, humic acid fragments (Table 4) all suggest that the oxygen groups are important in the NaOH attack on oil shale (or coal) structure. The relatively small oxygen content of the El-Lajjun and Julia Creek oil shales (Table 4) suggests that bonds involving oxygen may not be important in the overall structure of the OM, so that changes in these linkages may break up the polymer without making big changes in the structure of the small organic units which are the principal constituents of the polymer.

For low-rank coals there is also a similarity in structure (elemental analysis and Py-GC-MS) between the coal, humin and even humic acid when the humic acid yield is sufficiently high [27, 41]. This applies even

though the humic acid yield under comparable conditions is much higher for low-rank coals than for oil shale. In the case of coal, this similarity in structure is explained by the mechanism of solubilization in which alkali disrupts hydrogen bonds holding the coal molecules in large aggregates without altering the overall organic structure [41].

#### 4. Conclusions

The NaOH-HCl treatment applied to marine oil shales of different types gives an alkali- and acid-insoluble fraction (humin) of low ash yield, with elemental analysis and molecular characteristics resembling in many respects those of the original oil shale. The autoclave method affords higher yields of humin. The similarity in the analysis and molecular characteristics of humin and humic acid obtained by the oven method suggests that a minor amount of depolymerization and some oxidation are sufficient to solubilize part of the organic material. The results differ from those for low-rank coal for which humic acid produced in low yields differs in structure from humin.

The NaOH-HCl method thus provides a possible alternative for all oil shales, marine and lacustrine, to the HF-HCl method, for extracting the organic fraction from the oil shale in a form that can be studied without interference from the inorganics. It is desirable to control the experimental variables (time, amount treated) to maximize humin yield with minimum ash.

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