

<https://doi.org/10.3176/chem.1984.3.04>

УДК 662.736 : 543.51'423

*Eda GRÜNER, J. ARRO, Silvia RANG,  
A.-M. MÜÜRSEPP*

**INVESTIGATION OF NEUTRAL OXYGEN COMPOUNDS  
OF HEAVY SEMICOKING OIL OF KUKERSITE SHALE BY MASS  
SPECTROMETRY AND LOW TEMPERATURE  
PHOSPHORESCENCE SPECTROSCOPY**

*(Presented by O. Eisen)*

The distillation residue of the semicoking oil of kukersite shale (boiling above 300°C) contains about 50% of neutral oxygen compounds (NOC) which are unextractable with alkaline solutions and have a molecular mass of over 400. We have shown earlier [1] that by thin-layer chromatography (TLC) NOC can be separated into groups of compounds differing in hydrocarbon structure, but having the same functional groups (the carbonyl and hydroxyl mainly). These fractions are still too complex to enable us to identify any individual compound by luminescence or mass spectrometry. In this work the Huang-Minlon modification of Wolff—Kishner's method was used [2] to reduce ketones in NOC to hydrocarbons prior to TLC separation, mass spectrometric and low temperature phosphorescence spectroscopic examination.

Only 12% of NOC were reduced. The hydrocarbons formed were separated and divided into fractions by TLC on aluminium oxide (Brockmann II, neutral), *n*-hexane serving as an eluting agent (Table).

Electron impact mass spectra were recorded on an MH-1320 instrument at 14 and 70 eV ionization energies using a direct sample introduction. The phosphorescence spectra recorded at the Institute of Geochemistry and Analytical Chemistry of the USSR Academy of Sciences were taken at liquid nitrogen temperature (77 K) in *n*-hexane.\*

The 70 eV mass spectra exhibit low-mass fragmentation series with  $m/z$  29, 43, 57..., indicating the presence of saturated aliphatic hydrocarbon chains (groups) in parent molecules, whereas the series with  $m/z$  77, 91, 105... arise from aromatics. The series with  $m/z$  27, 41, 55, 69... refer to the presence of olefinic or naphthenic groups.

The existence of aromatic or conjugated double-bonded compounds follows also from the intensive phosphorescence of all the reduced NOC fractions. The phosphorescence spectra of fractions 4—6 have a characteristic fine structure (Fig. 1), not excluding the presence of naphthalene derivatives. Fractions 1 and 2 seem to contain mixtures of unreacted oxygen compounds. Their mass and phosphorescence spectra are complex and will not be discussed here.

In 14 eV mass spectra of fractions 3—5 some major homologous series of molecular ions appear (Fig. 2). In fraction 4 such a series

\* The authors express their gratitude to N. Lebedeva and T. Sorokina for their kind help in recording phosphorescence spectra.

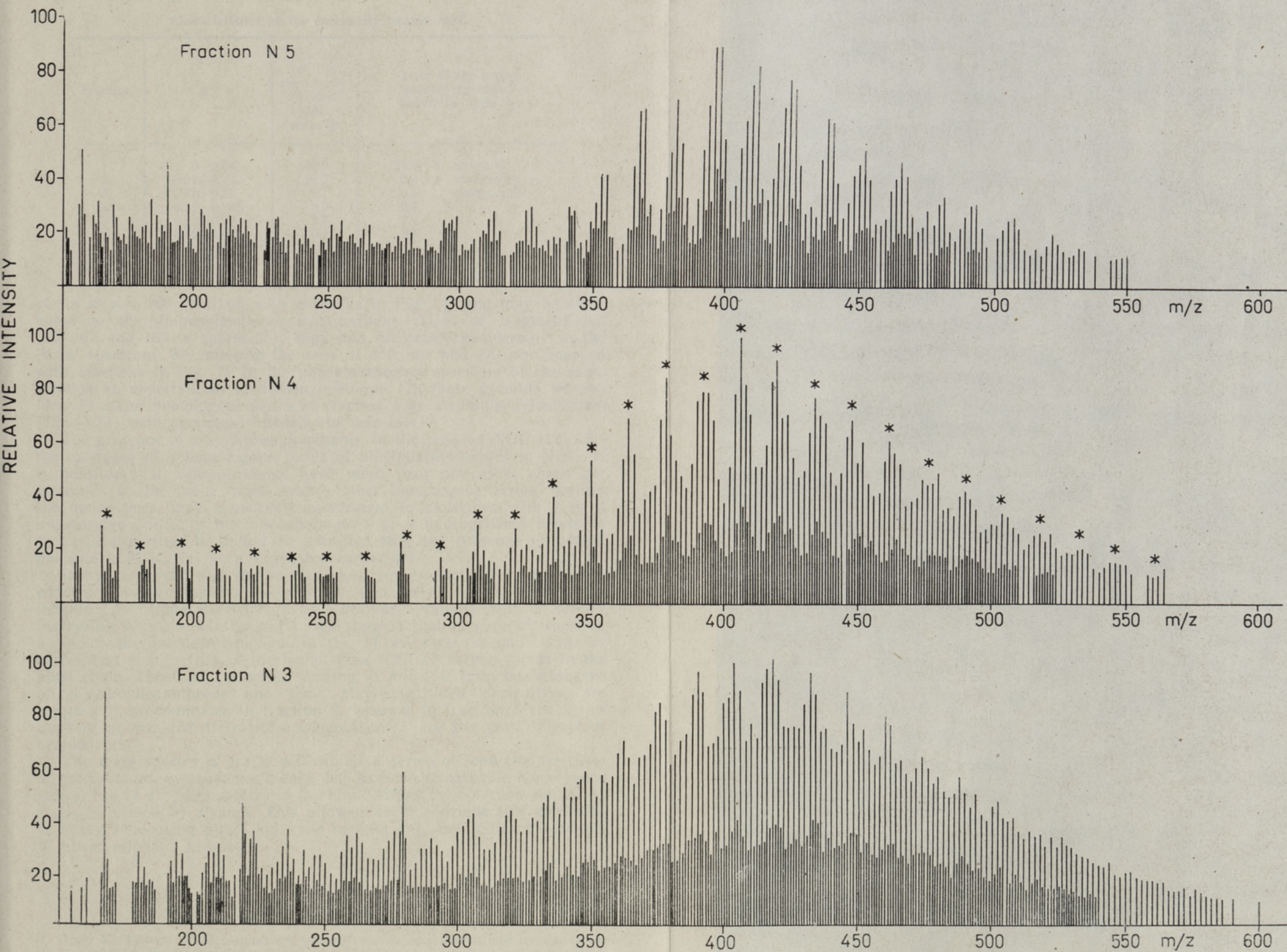


Fig. 2. 14 eV mass-spectra of fractions of the reduced NOC.

RELATIVE INTENSITY



Fig. 1. Phosphorescence spectra recordings of fractions of the reduced NOC; 1 fr. 4, 2 fr. 5, 3 fr. 6.

## Characteristics of the chemically treated NOC

Fraction	$R_f$	Fraction of the chemically treated NOC, mass %	Yield of the heavy semicoking oil of kukersite, mass %
1	0—0.04	60.9	24.6
2	0.04—0.12	23.2	9.4
3	0.12—0.31	1.1	0.4
4	0.31—0.52	6.0	2.4
5	0.52—0.79	2.7	1.1
6	0.79—1.00	6.1	2.4

} oxygen-containing compounds

starts at  $m/z$  168 (marked with asterisks in Fig. 2), and may be attributed to the diphenylmethane hydrocarbons. Yield of fragment-ions  $m/z$  167 and 169 is appreciably high and increases considerably in the 70 eV spectrum. We interpret the lines at 440, 464 and 473 nm (marked with asterisks in Fig. 1) in the phosphorescence spectrum of the same fraction as appertaining to diphenylmethane. On these grounds we can identify major homologous series of fraction 4 as alkyldiphenylmethanes ( $168+n14$ ) with maximum intensity in case  $n=17$ .

The presence of alkyldiphenylmethanes in the reduced NOC indicates the existence of a homologous series of alkylbenzophenones in NOC. It is possible that benzophenones have more than one alkyl chain per molecule. In the same mass spectra other homologous series, besides the major ones, may supposedly correspond to molecules with 1 or 2 unsaturated bonds in the side chain or 1 or 2 hydrogenated bonds in the aromatic ring. It should be admitted that the presence of benzophenone in NOC has been suggested earlier [3].

It was observed that in the decomposition products of kukersite the concentration of alkylated compounds, with an alkyl chain up to  $C_{17}$  included, is comparatively high and decreases rapidly with a further increasing of molecular mass [4]. We suggest that in case of fractions 3 and 5 the intensity maxima in the 14 eV mass spectra (Fig. 2) correspond also to that of the homologues with 17 carbon atoms in the alkyl chain. The  $C_nH_{2n-16}$  series starting at  $m/z$  180 (dihydroanthracene or dihydrophenanthrene and their alkyl-substituted derivatives are suggested) predominates in fraction 3, whereas in fraction 5 the series starting at  $m/z$  158 (tetrahydroacenaphthenes) are the most important components.

The mass spectra of fraction 6 exhibit a series of ions characteristic of cycloalkanes, cycloalkenes/dienes, but have no remarkable homologous series. The 14 eV mass spectra of fraction 6 shows no molecular ion series  $C_nH_{2n+2}$  formed by alkanes. This allowed us to conclude that the NOC of heavy semicoking oil of kukersite contain only insignificant amounts of linear aliphatic ketones.

## REFERENCES

1. Арро Я., Грюнер Э. Исследование тяжелой смолы полукоксования сланца-кукерсита. 4. Разделение нейтральных кислородных соединений на группы. — Изв. АН ЭССР. Хим., 1984, 33, № 1, 22—27.
2. Huang-Minton. A simple modification of the Wolff—Kishner reduction. — J. Amer. Chem. Soc., 1946, 68, N 12, 2487—2488.

3. *Файнберг В. С.* Исследование в области химии и технологии сланцевой смолы. Автореф. докт. дис. Таллин, 1974, 49.
4. *Клесмент И. Р.* Состав алифатических соединений тяжелой смолы полукоксования эстонского сланца-кукерсита. — Хим. тверд. топл., 1975, вып. 4, 122—127.

*Academy of Sciences of the Estonian SSR,  
Institute of Chemistry*

Received  
Nov. 17, 1983

*Eda GRÜNER, J. ARRO, Silvia RANG,  
A.-M. MÜURISEPP*

#### **KUKERSIIDI RASKUTTEÕLI NEUTRAALSETE HAPNIKU- ÜHENDITE MASSISPEKTROMEETRILINE JA MADALA- TEMPERATUURILINE FOSFORESTSENTSSPEKTROSKOOPILINE UURIMINE**

Massispektromeetria ja madalatemperatuurilise fosforestsentsspektroskoopia abil on uuritud süsivesinikke, mis tekivad üle 300°C juures keeva utteõli neutraalsete hapnikuühendite hüdrasiiniga töötlemisel. Ühes kitsa fraktsiooni massispektris on leitud molekulaarsete ionide seeria, mis vastab alküüldifenüülmetaani reale. Seda kinnitab ka sama fraktsiooni madalatemperatuuriline fosforestsentsspekter. Mainitud süsivesinikud said tekkida alküülbensofenooni taandamisel.

*Эда ГРЮНЕР, Я. АРРО, Сильвия РАНГ,  
А.-М. МЮРИСЕПП*

#### **ИССЛЕДОВАНИЕ НЕЙТРАЛЬНЫХ КИСЛОРОДНЫХ СОЕДИНЕНИЙ ТЯЖЕЛОЙ СМОЛЫ ПОЛУКОКСОВАНИЯ КУКЕРСИТА С ПОМОЩЬЮ МАСС-СПЕКТРОМЕТРИИ И НИЗКОТЕМПЕРАТУРНОЙ ФОСФОРЕСЦЕНЦИИ**

Исследовались углеводороды, которые образовались при обработке гидразином нейтральных кислородных соединений тяжелой сланцевой смолы, кипящей выше 300°C. В масс-спектре одной узкой фракции углеводородов обнаружена серия молекулярных ионов, которая соответствует ряду алкилдифенилметана. Правомерность этого подтверждает и низкотемпературный спектр фосфоресценции той же фракции. Указанные углеводороды могли образоваться при восстановлении алкилбензофенонов.