

## Reductive pyrolysis of leonardite humic acids

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*Dedicated to Acad. Dimiter Ivanov on the occasion of his 120<sup>th</sup> birth anniversary*

Leonardite humic acids from Kaz Daglari (Turkey) are studied by reductive pyrolysis. Sample is pyrolysed in a H<sub>2</sub> flow in the temperature range 250°C–950°C. Volatiles are trapped in two ice-cooled Tenax tubes. Atmosphere Pressure-Temperature Programmed Reduction (AP-TPR) technique coupled “off-line” with thermal desorption gas chromatography - mass spectrometry (TD-GC/MS) apparatus is used to specify organic compounds in the pyrolysate. During sample thermal decomposition a broad range of species is produced. Aliphatic compounds, i.e. *n*-alkenes/*n*-alkanes, i.e. *n*C<sub>6</sub>–*n*C<sub>14</sub>; aromatic compounds, i.e. benzene, alkylated benzenes, naphthalenes, biphenyls; oxygen containing compounds, i.e. phenols, methoxy phenols, furans, benzofurans; sulphur containing compounds, i.e. polysulphides, thiophenes and nitrogen compounds, i.e. benzonitriles, indoles and quinolines. Leonardite organic matter is rich in oxygen, where phenolic structures are the most abundant. Compounds are quantitatively interpreted. According to pyrolysis data “average” structural units of leonardite humic acids from Kaz Daglari deposit are mainly composed by 1-2 aromatic cycles, condensed or coupled. Heteroatom compounds are also admitted. Experimental data argue for sample low maturity as rests of lignin building blocks, i.e. methoxy phenols, and carbohydrate degradation products, i.e., 2-methyl-2-cyclopenten-1-one, are still present.

**Key words:** leonardite, humic acids, pyrolysis, structural study

### INTRODUCTION

Leonardite is a concentrated form of humic and fulvic acids and has appearance of coal but it does not reach its compactness. Leonardite is rich in organic matter (50-75%) and its humic acid content could range between 30-80%. Humic acid and other humic compounds stimulate root and shoot development, increase both available plant nutrients and nutrient uptake from soil, and enhance plants resistance to biotic and abiotic stress factors. Effects of humic acid containing fertilizers on plant yield and nutrient uptake depend on humic acid source, concentration, application type, plant species and cultivars. Therefore leonardite humic acids are of special interest in Turkey and Greece, where they are abundant and serve as raw materials for fertilizers industrial production [1-4]. Nowadays there is a tendency for chemical fertilizers to be gradually replaced by natural products, i.e. leonardite and its derivatives. In such circumstances they should be properly characterized.

Pyrolysis techniques have proved their useful application in fossil material study as they supply

detailed information on a molecular level. Janoš [5] in his review on the separation methods in the chemistry of humic substances from different origin stated that pyrolysis – GC/MS, although not ideal, remained the best technique for structural analysis. Different pyrolytic approaches have been used in our previous studies on coal humic acids, i.e. pyrolysis in a stream of water vapor [6], thermochemolysis [7] and reductive pyrolysis [8].

Atmosphere Pressure - Temperature Programmed Reduction (AP-TPR) technique coupled “off-line” with thermal desorption gas chromatography - mass spectrometry (TD-GC/MS) apparatus can be successfully used to specify qualitatively and quantitatively organic functionalities in coal and its derivatives. This pyrolytic technique has been previously developed and successfully applied for the specification of sulphur species in coals [9]. However, it can be used to track qualitatively and quantitatively the volatile organic compounds as well, like hydrocarbons and aromatic species, released during thermal decomposition of the humic acids. In this way information for composition of the non-extractable portion of the organic matter is obtained.

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The aim of the present study is to analyze products of leonardite humic acids reductive pyrolysis by AP-TPR - TD-GC/MS technique and to relate registered volatile components to the sample organic matter composition.

## EXPERIMENTAL

Leonardite from Kaz Daglari (Turkey) is a waxy, brown, shiny, vitreous mineraloid that is easily soluble in alkaline solutions. Its humic acids (HA) are under consideration. HA sample is prepared by 0.1N NaOH extraction and HCl precipitation [10]. Dried sample is milled and sieved < 0.06 mm.

Data for proximate analysis, i.e. moisture, volatile matter (VM), fixed carbon  $C_{\text{fix}}$ , ash content, are acquired by thermo gravimetric analysis using DuPont 951 instrument. The following programme is applied: i) heating with 20°C/min up to 600°C under nitrogen atmosphere; ii) at 600°C isothermal hold of the temperature for 10 min; iii) the atmosphere is switched to oxygen; iv) after 5 min of isothermal period, heating with 20°C/min up to 800°C under oxygen atmosphere. From the thermo gravimetric curves the following information can be obtained: i) moisture content, from ambient temperature up to 150°C; ii) VM content, from 150°C up to 600°C; iii) combustion of  $C_{\text{fix}}$  in oxygen atmosphere at temperature > 600°C; iv) ash content is the residue at 800°C.

Elemental analysis is run with a Thermo Electron Flash EA1113 elemental analyzer. By one measurement C, H, N and S can be determined. The instrument is calibrated with 2,5-bis-(5-tert-butylbenzoxazol-2-yl)thiophene (Thermo Electron). All samples are analyzed in duplicate. The oxygen content is calculated by difference as:  $O\% = 100\% - (C\% + H\% + N\% + S\% + \text{ash}\%)$ .

Pyrolysis is performed in the AP-TPR set-up described previously [11]. Briefly, 40 mg of sample and 20 mg of fumed silica are placed in the reactor under a 100 ml/min flow of pure  $H_2$ . A linear temperature program of 5°C min<sup>-1</sup> from ambient temperature up to 950°C is applied. The outlet of the AP-TPR reactor is connected to a set of two ice-cooled tubes containing Tenax (Sigma-Aldrich), a porous polymer of 2,6-diphenyl-*p*-phenylene oxide, as adsorbent. The volatiles are additionally diluted by adding inert gas to the  $H_2$  flow in ratio 5:1 (v/v) in order to prevent the saturation of the adsorption tube. Volatiles are trapped in two separated temperature ranges: i) 250°C÷550°C for the first tube; ii) 550°C-950°C for the second one. Adsorption tubes are separately desorbed and

analyzed by thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) instrument. The apparatus is used with He as carrier gas at 85 kPa at the following conditions: a) Unity thermal desorber (Marks): primary desorption 20 min at 275°C; Cold trap at - 10°C, heated at maximum heating rate up to 320°C, hold time 15 min; flow path temperature 200°C; b) Trace GC Ultra-Gas chromatography (Thermo Instruments): capillary column 30m ZB 5-MS x 0.25 mm x 0.25 µm Phenomenex; temperature program - 3 min at 30°C, heated 8°C/min to 100 °C, heated 12°C/min to 310°C, hold time 5 min; c) DSQ-Mass spectrometer (Thermo Instruments): EI spectra; Ionization energy - 70 eV; Scan range -  $m/z$  33-480 in 0.4s. Deuterated thiophene,  $d_4$ -thiophene, 3 µg, is applied as a standard. NIST library spectra are used for peak identification. Homologous series are MS tracked by single ion monitoring (SIM) technique.

## RESULTS AND DISCUSSION

The yield of prepared HA is 45 %. Leonardite HA proximate characteristics are the following, in wt. % as received: Ash - 10.20; Moisture - 11.84; VM - 32.23;  $C_{\text{fix}}$  - 45.73. Ultimate analysis is calculated on "dry ash free" basis: C - 63.02; H - 6.12; N - 1.16; S - 4.12;  $O^{\text{diff}}$  - 25.58.

Contents of all compound classes detected in pyrolysate of the leonardite HA subjected to pyrolysis are gathered in Table 1.

**Table 1.** Contents of compound classes.

Compound classes	Content	
	µg	mg/gC <sub>org</sub>
<b>Aliphatic:</b>		
n-Alkenes/n-Alkanes	220.0	11.0
<b>Monoaromatic:</b>		
Benzenes	525.8	26.3
<b>Diaromatic:</b>		
Biphenyls	33.6	1.7
Naphthalenes/Acenaphthylenes	168.4	8.4
<b>Oxygen containing:</b>		
Phenols	206.5	10.3
Methoxy phenols	55.5	2.8
Furans/Benzofurans	6.4	0.3
<b>Sulphur containing:</b>		
Di/Tri Sulphides	24.0	1.2
Thiophenes/Benzothiophenes	27.0	1.4
<b>Nitrogen containing:</b>		
Benzonitriles	1.4	0.1
Indoles	3.4	0.3
Quinolines	4.0	0.2
<b>Total</b>	1276.0	63.8

Their sum represents 6.4% from the organic carbon of the pyrolysed material. Compound classes contents in rel. % are illustrated in Fig. 1. TD-GC/MS chromatograms of 250°C÷550°C and 550°C÷950°C pyrolysates are shown in Fig. 2 and Fig.3, respectively.

The main components in the pyrolysate flue gases of HA destruction in the 250°C-550°C region are benzene and its alkylated homologs, being 26.3 mg/g C<sub>org</sub>, or about 40% of all registered components (Fig.1). Generally, alkylaromatics are considered as a product of the humification of primary plant materials and microbial metabolites that form the skeletons of humic substances. A defined origin of alkyl benzenes could be ascribed only in conjunction with other compounds. Thus, aromatic pyrolysates are ascribed to proteins, and specifically to microbial material, when pyridine and toluene are found simultaneously. A partial microbial origin could be certainly assumed for the HA under study because of the presence of N-containing compounds. However, it should be pointed out that they are in several folds lower amount compared to aromatics (Table 1).

Linear hydrocarbons,  $nC_6$ - $nC_{14}$ , i.e. mono-unsaturated ( $n$ -alkenes) and saturated ( $n$ -alkanes), are registered only in the first tube. These compounds amount up to 17.2 rel. % (Fig.2). Alkylated naphthalenes are abundant in the second tube. The detection of polycyclic aromatic compounds with higher degree of condensation cannot be expected, bearing in mind the immaturity of the sample under study.

With temperature increase, alkylated aromatic compounds are gradually replaced by phenolic structures. Vanillyl phenols, i.e. phenol-2-methoxy and methyl-2-methoxy phenols, are dominant. It is a proof for the presence of rests from conifer lignin arranged in the structural units of the organic matter from leonardite HA. High contents of phenol and its alkylated homologues are an indication for the proceeding of the coalification accompanied by demethoxylation and subsequent phenolic groups rearrangement [12].

During thermal decomposition of leonardite HA a broad range of other species is released as well. Leonardite organic matter is rich in oxygen (~26%), where beside phenolic structures furans and benzofurans are also detected. However the phenolic structures are more abundant compared to the oxygen in cyclic form.

According to the elemental composition of the sample under study, sulphur in leonardite HA is rather high, 4.12%. The relative low ash content of the sample gave us ground to assume that it is more likely distributed in the organic forms. Based on TD-GC/MS data, it is supposed that sulphur is arranged in bridges and cycles. Mass spectrometrically registered sulphur species are linear aliphatic polysulphides (dimethyl disulphide and dimethyl trisulphide), 1.2%, and cyclic sulphur compounds (thiophenes and benzothiophenes), 1.4%. The concept that with maturation aliphatic sulphur forms are lost and thiophenes represent the organic sulphur in higher rank coals is well documented in the literature. This is confirmed by a

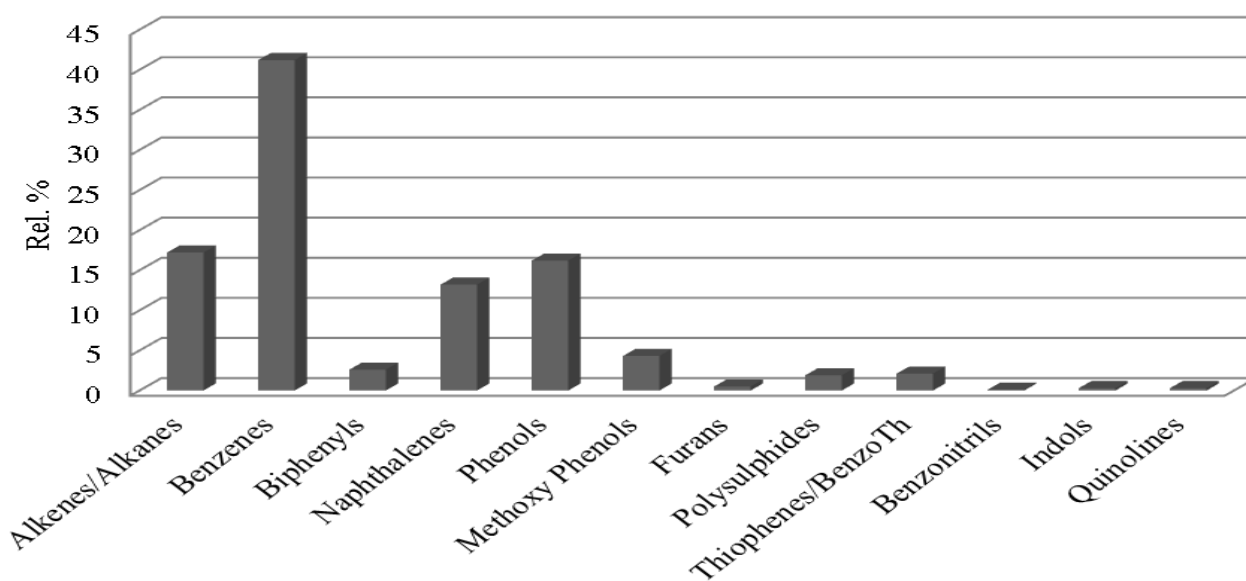


Fig. 1. Distribution of compound classes, in rel. %.

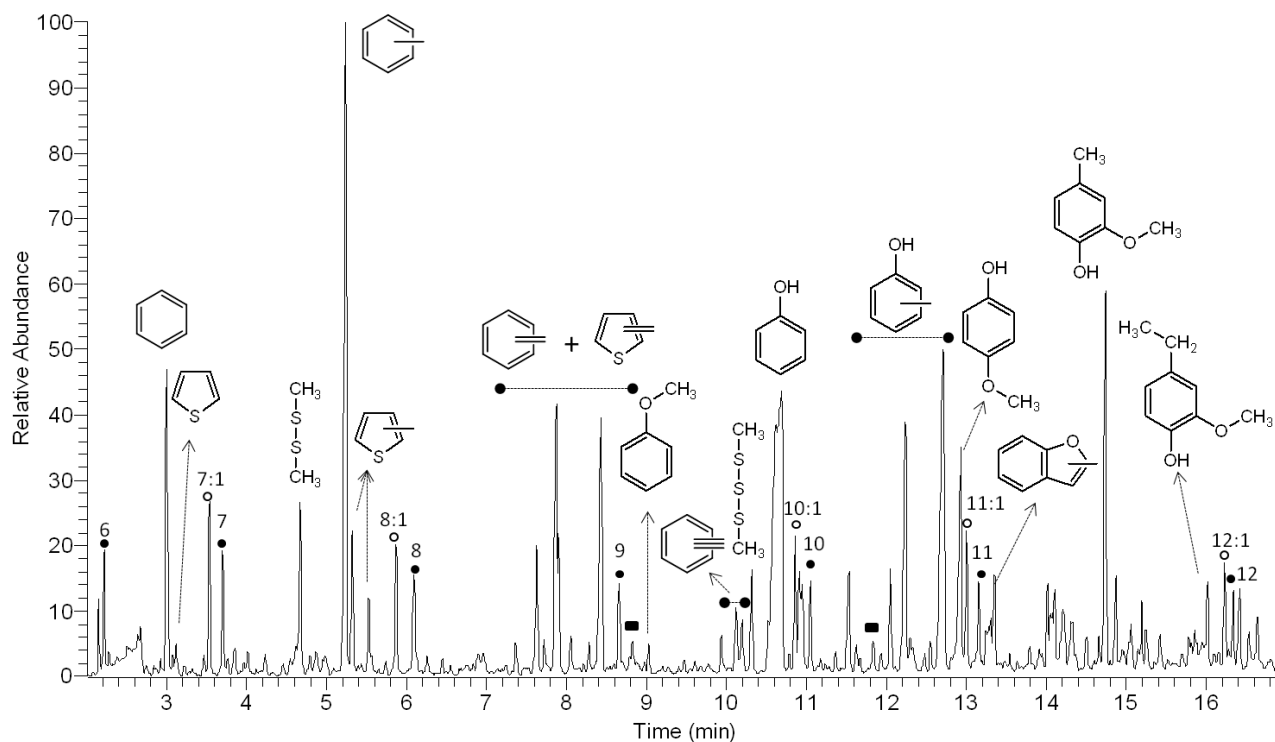


Fig. 2. TD-GC/MS of 250°C-550°C pyrolysis region.

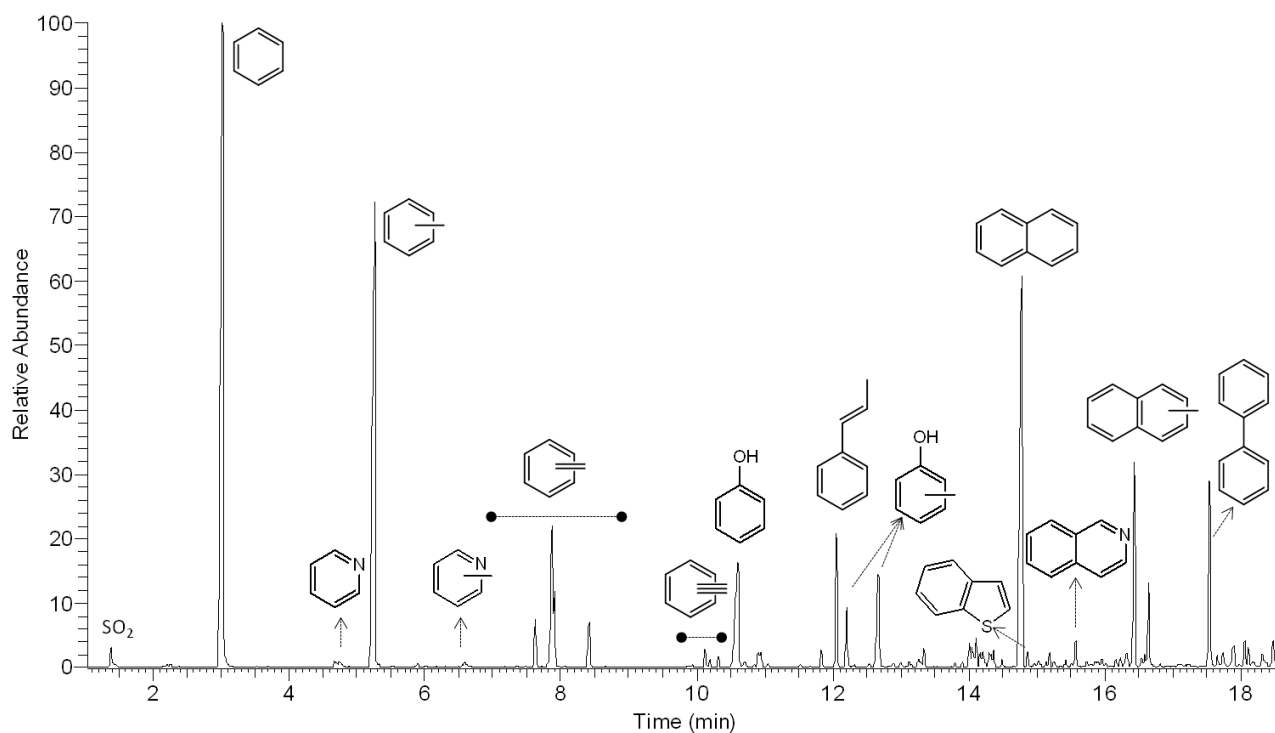


Fig. 3. TD-GC/MS of 550°C-950°C pyrolysis region

variety of instrumental techniques, i.e. non-destructive XPS, XANES and destructive ones, as wet chemical determination, and pyrolytic methods, all reviewed by Olivella et al. [13]. Simultaneously, AP-TPR measurements on different rank coals have

demonstrated that with maturation the amounts of both aliphatic and aromatic sulphides decrease, while the amount of thiophene sulphur increases [14]. Our results show that sulphur in sulphidic and thiophenic structures for leonardite HA is in

comparable amount. However, it should be stressed that pyrolytic experiments are conducted in a reducing atmosphere (hydrogen flow). It is already proved that in such circumstances most of the above mentioned sulphur containing compounds are reduced to H<sub>2</sub>S [15]. Therefore a general conclusion on organic sulphur distribution in leonardite HA should be regarded with precaution.

N-containing species are also registered and listed in Table 1. Some of N-compounds could have microbial origin, but others can be both of microbial and plant input [16-17]. Some amounts of N-compounds accompanied by carbohydrate pyrolysis products other than levosugars imply the presence of microbial organic matter. This point needs a special concern in the future.

Cyclopentenones, C<sub>n</sub>H<sub>2n-4</sub>O, with n=6 and 7 (Fig. 2), are largely associated with pyrolysis of plant-derived organic matter, especially when they are accompanied with rests of lignin and small contributions of N-compounds. The negligible contents of 2-methyl-2-cyclopenten-1-one (C<sub>6</sub>H<sub>8</sub>O, M<sup>+</sup> 96) and its dimethyl derivative (M<sup>+</sup> 110) in the pyrogram (Fig.2) could be attributed to products of carbohydrates pyrolysis [18].

## CONCLUSION

Structural study of leonardite humic acids from Kaz Daglari (Turkey) revealed some characteristics. From chemical point of view, according to the reductive pyrolysis data, their structural units are mainly composed by 1-2 aromatic cycles, condensed or coupled. Experimental data confirm sample low maturity as lignin residues and products of carbohydrate pyrolysis are still capable for identification. Results of pyrolysis give ground to assume that conifers are the predominant vegetation in the palaeomire. Heteroatoms are also admitted.

Leonardite humic acids from Kaz Daglari (Turkey) are characterized by high oxygen content. Therefore they are promising for an economically sustainable exploration as raw materials for agriculture, horticulture, cosmetics, drilling, filter systems products etc. However, attention should be

paid to the relative high content of the other heteroatoms, i.e. nitrogen 1.16% and sulphur 4.12%, and to consider their eventual harmful impact.

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## РЕДУКЦИОНЕН ПИРОЛИЗ НА ХУМИНОВИ КИСЕЛИНИ ОТ ЛЕОНАРДИТ

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(Резюме)

Хуминови киселини от леонардит от находище Каз Деглари (Турция) са изследвани чрез редукционен пиролиз. Пробата е пиролизирана в ток на водород в температурен интервал 250°C ÷ 950°C. Летливите вещества са задържани в две охладени с ледена баня тубички, запълнени с адсорбент Терах. За доказване на органичните съединения апаратурата за температурно програмирана редукция при атмосферно налягане (AP-TPR) е свързана в режим на "off-line" с апаратура за термично десорбционна газова хроматография - масспектрометрия (TD-GC-MS). По време на термичното разграждане на пробата е получена широка гама органични съединения. Алифатни съединения, в т.ч. *n*-алкени/*n*-алкани,  $nC_6 \div nC_{14}$ ; ароматни съединения в т.ч. бензоли, нафталини, бифенили; кислород съдържащи съединения, в т.ч. феноли, метокси феноли, фурани; сяросъдържащи съединения, в т.ч. ди- и три- полисулфиди, тиофени; и азотни съединения, в т.ч. бензонитрили, индоли и хинолини. Данните са интерпретирани количествено. Органичната маса на леонардита е богата на кислород, като фенолните структури са най-разпространени. Според данните от пиролиза „средните“ структурни единици на хуминови киселини от леонардита най-вероятно са изградени от 1-2 ароматни пръстени и/или ароматни системи от две ароматни ядра при директно свързване на ароматните цикли. Възможно е и участие на хетероатомни съединения на азота и сярата. Експерименталните данни от редукционния пиролиз доказват ниската зрялост на изследваната проба, указание за което са присъствието на остатъци от лигнин (метокси феноли) и разпадни продукти на въглеhidрати (2-циклопентен-1-он, 2-метил).