

Identification of organic matters in Slovak brown coal

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Identifikácia organických látok v slovenskom hnedom uhľí

Vzorky slovenského hnedého uhlia z lokality Cigeľ a Handlová boli podrobené nadkritickej fluidnej extrakcii (SFE) oxidom uhličítym, modifikovaným 5 % metanolom. Extrakty, získané metódou SFE, boli podrobené plynovej chromatografii s hmotnostno-spektrometrickou identifikáciou (GC - MS). Porovnaním s literárnymi údajmi hmotnostnej spektroskopie, prístroja boli k jednotlivým pikom priradené najpravdepodobnejšie vzorce a zlúčeniny. Identifikácia potvrdila organické komponenty, ako kaurány a deriváty kyseliny kauránovej, s významnou biologickou aktivitou.

Key words: hnedé uhlie, organické látky, plynová chromatografia, hmotnostná spektroskopia.

Introduction

The mass spectroscopy (MS) represents one of the most important tools of identifying various compounds. The hyphenation of gas chromatography (GC) with MS is used very often. The mentioned technique enables the identification of separated compounds as well as reaction mechanisms of diterpene degradation. By this method the dehydrogenation products of the reactions of α - phyllocladane with selene, sulphur and copper (II) sulphide (Alexander et al., 1988) were investigated. The composition of the extract, minorite and coelute components was also investigated. The identification of the separate compounds was done by the comparison with the spectra of a standard (using the library), MS spectra published in previous articles or the identification requires a MS spectrum solution. In many cases the GC - MS analyses indicate differences in the composition of molecular biomarkers present in German or Canadian coal (Heppenheimer et al., 1992). The GC - MS analysis of distillates from lignite confirmed the presence of hydrocarbons with the sesqui- and diterpene skeleton (Stacioli et al., 1993). The articles dealing with the SFE extraction followed by the GC - MS identification of phyllocladanes obtained from the plants (Singh et al., 1994, Agrawal et al., 1995) or from their water solutions (Singh et al., 1994) are well known. The method GC - MS gives an opportunity to identify the enantiomeres composition of cyclodextrine column (Lewinshon et al., 1993). The detailed chemical (GC - MS), morphological and anatomical study of the plant fossil leads to the important knowledge of the in relationship between the biodegradation, morphological structure, and the content of extractive organic matters of coal (Disnar et al., 1994).

The aim of this work was to identify the composition of extractive organic matter of biological interest in the selected samples of Slovakian coals using a comparative method.

Material and methods

Two coal samples were extracted: from the mine Cigeľ (sample 1) and mine Handlova (sample 2). Both coal samples were milled below 0,061 mm. The chemicals used in the SFE were of analytical grade of purity purchased from Merck (Darmstadt, Germany). The SFE analysis was performed with the device Hewlett Packard SFE (USA). The polarity of the extraction eluate (CO₂) was modified by the temperature and pressure regulatin and with the addition of methanol. The GC - MS analyses were performed with the SATURN II device, Varian (USA). The conditions of the analysis were as follows: the column : DB - 5,30 m x 0,25 mm i.d. (J & W, USA), carrying gas: helium; the temperature programme: 100 - 300 °C, 4 °C/min, 65 - 135 °C, 25 °C/min, 135 - 300 °C, 4 °C/min; the conditions for the MS detector: ionisation energy 70 eV, scan 40 - 540 m/z, 1 scan/sec; the source temperature:

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250 °C. The selected temperature and chromatographic column showed a satisfactory separation ability of the system.

MS data procedure

On the basis of the fragmentograms obtained from the on-line GC-MS analyses and chromatographic data it was possible to ascribe the separate peaks (characterised with the retention time) to the corresponding molecular weights of the compounds and to identify them. To compare it with the library data, to each peak the most probable formulas have been attached. The results are documented as a group of peaks of the basic chromatogram.

Results and discussion

In the extracts of the sample 1 was the highest percentage content determined for 6 – tridecenoic acid. The compounds of terpenoid behaviour, asulene derivatives, derivatives of podocarpic acid (substituted acid, alcohol, esters of podocarpa - 15 - oic acid, ketones) were also identified. The presence of the matters having character of kauranoic acid its derivatives was not confirmed (Table 1).

Table 1. The collection of retention parameters, computed identification MS parameters and chemical formulas of the organic matters separated from the coal extract of the mine Cigel.

Nr. of peak	Retention time (sec)	Molecular ion M+	Formula	Name of the compound
1	947	206	C ₁₅ H ₂₆	1H-cycloasulene
2	973	UE		Asulene derivatives
3	1 266	183; 198	C ₁₅ H ₁₈	1,4-dimethyl-7-(1-methylasulene)
4	1 744	246; 260	C ₁₆ H ₁₉ O ₂ ; C ₂₂ H ₃₂ O ₃	Crinan; Podocarpa-8,11,13-triene 17-oic acid
5	1 768	246; 260	C ₁₄ H ₂₂ N ₄ ; C ₁₅ H ₁₆ O ₄	4,6-Bispiperidimepyrimidine; 2H-1-benzpyra-2-one
6	1 785	278	C ₁₉ H ₃₄ O	8β-podocarpa-7α-ol
7	1 870	262; 274	C ₁₈ H ₃₀ O; C ₂₀ H ₃₄	Unidentified derivates of anthracene
8	2 006	290	C ₂₀ H ₃₄ O	Kaurane-13-ol
9	2 106	320	C ₂₁ H ₃₆ O ₂	13-isopropyl, methylester podocarpic-15-acid
10	2 143	UE	C ₁₉ H ₃₂ O ₂	6-tridecene acid ester
11	2 218	UE	C ₂₀ H ₃₀	Fenanthrene and phenole derivatives
12	3 025	286	C ₂₀ H ₃₀ O	Podocarpa-8,11,13-triene - 17 - oic acid; podocarpa-7-ene-3-on

*UE - Not determined value due to the mixture of similar derivatives

The higher content of 13 - kauranol at the retention time of 2 006 s and m/z = 290 was found. The representative sample extract contained mainly derivatives of podocarpic acid (podocarpa - 8, 11, 13 - triene - 17 - oic acid, 8 b - podocarpene - 7 a - ol, isopropyl, methylester of podocarpa - 15 - oic acid). The highest percentage content of important extractable matters in the extract of the coal sample 2 was found for methylester of kauranoic acid at the retention time 2 148 s (Table 2). The extract contained a different range of the compounds in comparison it with the sample 1. The dominant categories of the matters are podocarpene derivatives (podocarpa - 7 - en - 3- one, podocarpa - 8, 11, 13 - triene, and 17 - oic acid). Kauranoic acid methylester has been found at the retention time 2 148 s, m/z = 292, C₂₁H₃₄O₂. The kauranoic acid derivatives and kaurene compounds were tested as the potential active components with a proposal biological activity. The ent - kauranes isolated from varieta Isidou geseuroides (Sun et al., 1995) have a pronounced cytotoxic activity. The derivatives of kaurenic acid play an important role for Trypanosoma cruzi (Alves et al., 1995). Instead both coal samples are too rich in naphthalene and the phenanthrene derivatives. In the comparative method of the identification of compounds the use of retention characteristics, in the first step the retention time, plays an important role. The drift observed when comparing the same compound identified in both samples represents a possibility of the presence of another additional compound in the peak of the separated solute and in this case it must be identified by comparing it with the standard. The unusual types of compounds have been identified whose origin is not in the biological compounds matter from which the coal was transformed.

Table 2. The collection of retention parameters, computed identification MS parameters and chemical formulas of the organic matters separated from the coal extract of the mine Handlova.

Nr. of peak	Retention time (sec)	Molecular ion M+	Formula	Name of the compound
1	973	206	UE	1H-3 α -7-metanoasulene
2	986	192; 206	UE	Antracene, phenanthrene, naftalene, cyclohexane and its derivatives
3	1 008	191; 206	UE	Cyclohexane and its derivatives
4	1 016	308		Linoleic acid ethylester
5	1 112	222	C ₁₆ H ₃₀	Decahydro-9-ethyl-4,4,8,10-tetramethylnaphtalene
6	1 171	220	C ₁₅ H ₂₄ O	Santalol
7	1 250	220; 238	C ₁₅ H ₂₆ O ₂	Kulamrine
8	1 290	229; 244; 286	UE	4-piperidino-1-oxo-1,2-dihydroptalazine; 3-phenatrole; podocarpa-7-ene-3one, 13 β methyl-13-vinyl
9	1 707	272; 384; 414; 370	C ₂₀ H ₃₂ ; C ₂₈ H ₄₈ ; C ₂₇ H ₄₂ O ₃ ; C ₂₇ H ₄₆	Naphtalene and phenthrene derivatives
10	1 808	260	C ₁₉ H ₃₂ ; C ₁₆ H ₂₄ N ₂₀	Androstane derivatives
11	1 871	234; 370	C ₁₅ H ₂₂ O ₂ ; C ₂₇ H ₄₆ ; C ₂₁ H ₃₆ O	Cholestanes, pregnanoles mixture
12	2 148	318; 292	C ₂₁ H ₃₄ O ₂	Kauranoic acid methylester
13	2 220	270; 284; 272; 302	C ₂₀ H ₃₀ O ₂	Phenanthrene, antracene and naphtalene derivatives: podocarpa-8,11,13-triene-7 β -13-diole
14	2 802	428	C ₃₀ H ₅₂ O	Lanostane-3-one
15	2 568	282; 442; 288; 604	C ₁₈ H ₃₄ O ₂ ; C ₃₀ H ₅₀ O ₂	2(3H) furanone; olean-12-ene
16	3 048	314; 328	C ₂₁ H ₃₀ O ₂	Dronobinole; 3 -phenanthrole and its derivatives
17	3 075	204; 292; 410; 440	C ₁₅ H ₂₄ ; C ₂₈ H ₄₀ O ₇	unidentified matters
18	3 109	300; 346; 388; 342	C ₂₀ H ₂₈ O ₂ ; C ₂₀ H ₂₆ O ₅	Podocarpa-8,11,13-triene-3-one, 13-hydroxy-14-isopropylacatate
19	3 094	248; 302; 202	C ₁₆ H ₂₄ O ₂ ; C ₂₀ H ₃₀ O ₂ ; C ₁₅ H ₂₂	Nonanoic acid methysylester; Kaur-16-ene-18-oic acid
20	2 966	302; 344	UE	Podocarpa-8,11,13-triene;
21	2 980	328; 344; 286; 330	C ₂₂ H ₃₂ O ₂ ; C ₂₂ H ₃₂ O ₃ ; C ₂₀ H ₃₆ O; C ₂₀ H ₂₆ O ₄	3-phenantrenole; podocarpa-8,11,13-triene-17-oic acid; podocarpa-7-ene-3pme;
22	3 004		UE	Pregnene derivates
23	3 015	286; 328; 344	C ₁₉ H ₂₆ O ₂	Podocarpa-8,11,13-triene,17-oic acid, 12-hydroxy-13-isopropylethylester
24	3 025	286; 328; 330	C ₂₀ H ₃₀ O; C ₂₂ H ₃₂ O ₂ ; C ₂₀ H ₂₆ O ₄	2-phenthreol derivatives; isocarnasole
25	3 025	314; 344	C ₂₁ H ₃₀ O ₂ ; C ₂₂ H ₃₂ O ₃	Phenthrene derivatives

*UE - Not determined value due to the mixture of similar derivatives

Conclusions

The GC - MS analysis of the SFE extracts from two samples of Slovakian coal has been performed. The separated compounds were identified with the MS detector. Comparing the retention characteristics and mass values with those given in the MS library the most probable molecular weight and chemical formula have been assigned to each separated peak. A difference between the extract composition from the two samples has been found. The Cigel mine sample contained predominantly podocarpane derivatives while the Handlová mine sample showed a wide variety of kauranes derivatives. The semipreparative extraction and following MS identification is the task of this research for the future experiments.

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