

# THE STRUCTURAL CHARACTERISATION OF FOSSIL RESINS BASED ON MASS SPECTRA OBTAINED IN GC/MS MODE ON PYROLISED SAMPLE

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## Introduction

The purpose of the present papers is the application of the pyrolysis gas chromatography in combination with mass spectrometry (Py-GC-MS) to characterisation of the fossilised resins. Fossilised resins of conifers are known as amber. The most significant deposit of amber in Europe occurs along the southern shores of the Baltic Sea<sup>1</sup>. Amber from these deposits is known as Baltic amber. Other sources of amber lie in Romania (known as Romanit), North America, Canada and China. While Baltic amber has been extensively investigated from many years only few works have been published on Romanit<sup>2</sup>.

Pyrolysis gas chromatography in combination with mass spectrometry has shown to be powerful techniques for analysing a wide variety of polymeric samples<sup>3</sup>. The utility of these methods varies from obtaining simple fingerprinting information to the identification of characteristic pyrolysis product. The results obtained on a particular sample depend of the pyrolytic methods and several other experimental conditions such as pyrolysis temperature, sample size, type of column, flow rate and temperature variations<sup>4</sup>.

In order to achieve reproducible results, it is necessary to attain pyrolysis at a controlled temperature followed by efficient trapping of pyrolysis products onto column. Curie-point pyrolysis is characterised by a rapid inductive heating ( $5000 \text{ K s}^{-1}$ ) of a ferromagnetic wire containing a small amount of sample material ( $10 \mu\text{g}$ ).

To increase the sensitivity of method controlled temperature program was used for a quantity of sample of few mg. The decomposition products were identified using mass spectra data base or mass spectra information about molecular mass or unsaturation degree. The sample is characterised by molecular distribution vs. unsaturated degree ( $z=0$ ;  $z=-12$ ).

## Experimental

### *Sample preparation*

A quantity of 1-3mg Romanian amber was ground to a powder and then heated for 1 min at  $575^\circ\text{C}$ . The decomposition products were washed with 3ml of  $\text{CH}_2\text{Cl}_2$ . After concentration at 0.5 ml the sample was injected in GC. The sample of fossil resin (Romanite) was collected from an East-Carpathian place of Romania.

### *Instrumentation*

Py-CG-MS analyses were performed using a Perkin Elmer Gas Chromatograph (model 990) coupled to a double focusing mass spectrometer MAT 311.

*GC condition.* A homemade GC column was used. The column characteristic was the following: 2m length, internal diameter 4mm, stationary phase OV-17 (polymer of methyl silicone). The column was heated from  $60^\circ\text{C}$  to  $300^\circ\text{C}$  with  $8^\circ\text{C}/\text{min}$  and maintained 10 min at the final temperature.

The ion source of the mass spectrometer was operated to electron energy of 70eV, current emission of 100  $\mu$ A and to a temperature of 180°C.

### Results and discussions

The GC/MS chromatogram (total ion current) obtained in the conditions as in experimental is shown in the Fig. 1 and the identification of the compounds is shown in the Table 1.

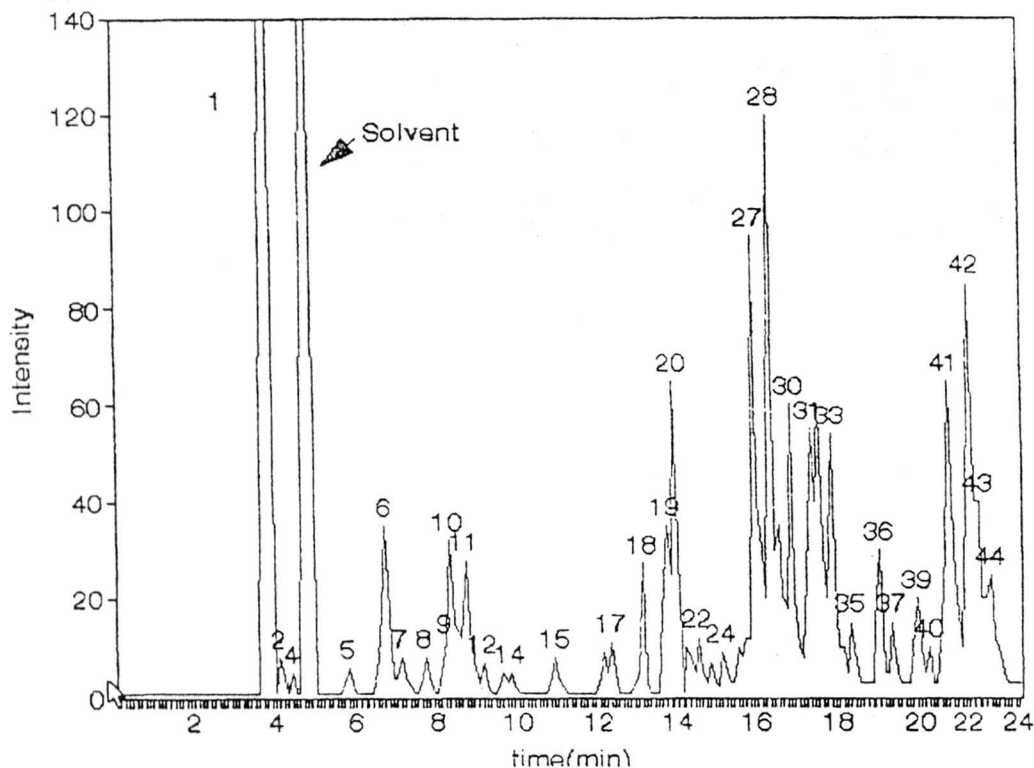


Fig. 1. The TIC chromatogram of the compounds obtained by pyrolysis of resin sample

The most prominent components are a variety of diterpenoid acids. Among them are the octahydrotrimethyl and octahydrotetramethyl-naphthalenes and their carboxylate derivatives. More numerous are completely or partially aromatized compounds, including alkyl-benzene, cymene and naphthalene. Our results are in good correlation with early reported composition of fossil resins/2/. For every compound the unsaturation degree ( $z$ ) were estimated. The distribution of the compounds vs.  $z$  is shown in the Table 2.

The main contribution of the detected compounds are situated between  $z = -4$  and  $z = -10$  with the maximum on  $z = -6$ . The obtained distribution is shown in the Fig.2

Table 1.

The identification of compounds resulting from pyrolysis of the fossilised resin (Romanite).  
The number corresponds to the peak number from Fig 1

1. M=70: C <sub>5</sub> H <sub>10</sub> ( $z=0$ ), 1,2 dimethyl trans-cyclopropene
2.-5?
6. M=92: C <sub>7</sub> H <sub>8</sub> ( $z=-6$ ), Toluene+M=110:C <sub>8</sub> H <sub>14</sub> ( $z=-1$ ), 4,5 dimethyl 1,3 hexadiene
7. M=124: C <sub>9</sub> H <sub>16</sub> ( $z=-1$ ), 2,4 Heptadiene
8. M=108: C <sub>8</sub> H <sub>12</sub> ( $z=-4$ ), 2,4,6 octatriene, all trans
9. M=136: C <sub>10</sub> H <sub>16</sub> ( $z=-4$ ), 3,7 dimethyl-1,3,6 trioctene (beta-cymene).
10. M=106: C <sub>8</sub> H <sub>10</sub> ( $z=-6$ ), (m+p)-xylene
11. M=124: C <sub>9</sub> H <sub>16</sub> ( $z=-2$ ), 3,3,5 trimethylcyclohexene+M=136: C <sub>10</sub> H <sub>16</sub> ( $z=-4$ ) Camphene (2:3)
12. M=122: C <sub>9</sub> H <sub>14</sub> ( $z=-4$ )

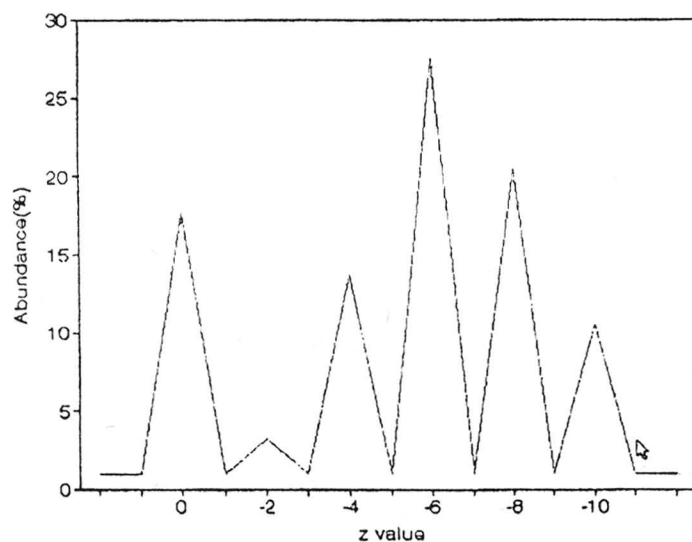
13. M=120: C<sub>9</sub>H<sub>12</sub> (z=-6), isopropylbenzene (Cumene)
14. M=138: C<sub>10</sub>H<sub>18</sub> (z=-2), trepan
15. M=134: C<sub>10</sub>H<sub>14</sub> (z=-6), (m+p) methylisopropylbenzene (cymene)+M=120(z=-6), 1methyl, 3ethylbenzene
- 16.?
17. M=134: C<sub>10</sub>H<sub>14</sub> (z=-6), o-cymene
18. M=162: C<sub>12</sub>H<sub>18</sub> (z=-6), C6-Benzene
19. M=176: C<sub>13</sub>H<sub>20</sub> (z=-6), C7-Benzene
20. M=178: C<sub>13</sub>H<sub>22</sub> (z=-4), 1,2,3,4,4a,5,8,8a-octahydro-1,4a,6-trimethylnaphtalene
- 21.-26?
27. M=192: C<sub>14</sub>H<sub>24</sub> (z=-4): 1,2,3,4,4a,7,8,8a octahydro-1,4a,5,6-tetramethylnaphtalene
28. M=190: C<sub>14</sub>H<sub>22</sub> (z=-6), C4-hexahydronaphtalene
29. M=202: C<sub>15</sub>H<sub>22</sub> (z=-8), Sesquiterpena+M=190: C<sub>14</sub>H<sub>22</sub> (z=-6)
30. M=204: C<sub>15</sub>H<sub>24</sub> (z=-6), C5-hexahydronaphtalene+M=202: C<sub>15</sub>H<sub>22</sub> (z=-8), C5-tetrahydronaphtalene.
31. M=204: C<sub>15</sub>H<sub>24</sub> (z=-6) C5-hexahydronaphtalene +M=202: C<sub>15</sub>H<sub>22</sub> (z=-8) C5-tetrahydronaphtalene. (1:1)
32. M=202: C<sub>15</sub>H<sub>22</sub> (z=-8), 1,2,3,4 tetrahydro-1, 6-dimethyl-4-(1-methylethyl) naphthalene
33. M=204: C<sub>15</sub>H<sub>24</sub> (z=-6) C5-hexahydronaphtalene+M=202: C<sub>15</sub>H<sub>22</sub> (z=-8) C5-tetrahydronaphtalene (3:2)
- 34.?
35. M=202: C<sub>15</sub>H<sub>22</sub> (z=-8)
36. M=186: C<sub>4</sub>-Dihydronaphtalene (z= -10)
37. M=202: C<sub>5</sub>-Tetrahydronaphtalene (z= -8)
- 38.?
39. M=244: C<sub>18</sub>H<sub>28</sub> (z=-8), C8-Tetraline
- 40.?
41. M=258: C<sub>19</sub>H<sub>30</sub> (z=-8), C9-Tetraline
42. M=242: C<sub>18</sub>H<sub>26</sub> (z=-10), C8-Dihydronaphtalene
43. M=256: C<sub>19</sub>H<sub>28</sub> (z=-10), C9-Dihydronaphtalene
44. M=256: C<sub>17</sub>H<sub>36</sub>O, Hydroxy-C8-Tetraline

Table 2

The compound distribution as a unsaturated degree (z=0, z=-12)

Nr. peak	A	%	z=0	z=-2	z=-4	z=-6	z=-8	z=-10	z=-12	z=x
1	220,00	17,68	17,68	0	0	0	0	0		0
2	20,00	1,61								1,61
3	8,00	0,64								0,64
4	12,00	0,96								0,96
5	7,00	0,56								0,56
6	32,00	2,57		1,54		1,03				
7	8,00	0,64		0,64						
8	6,00	0,48			0,48					
9	6,00	0,48			0,48					
10	31,00	2,49				2,49				
11	26,00	2,09		0,84	1,25					
12	7,00	0,56			0,56					
13	2,00	0,16				0,16				
14	2,00	0,16		0,16						
15	6,50	0,52				0,52				
16	8,00	0,64								0,64
17	9,00	0,72				0,72				
18	22,00	1,77				1,77				
19	32,00	2,57				2,57				

Nr. peak	A	%	z=0	z=-2	z=-4	z=-6	z=-8	z=-10	z=-12	z=x
20	59,00	4,74			4,74					
21	2,00	0,16								0,16
22	3,00	0,24								0,24
23	1,00	0,08								0,08
24	6,00	0,48								0,48
25	6,00	0,48								0,48
26	3,00	0,24								0,24
27	77,00	6,19			6,19					
28	106,0	8,52				8,52				
29	36,00	2,89				1,44	1,44			
30	56,00	4,50				3	1,5			
31	51,00	4,10				2,05	2,05			
32	53,00	4,26					4,26			
33	49,00	3,94				1,58	2,36			
34	3,00	0,24								0,24
35	13,00	1,04					1,04			
36	29,00	2,33						2,33		
37	16,00	1,29					1,29			
38	3,00	0,24								0,24
39	19,00	1,53					1,53			
40	4,00	0,32								0,32
41	62,00	4,98					4,98			
42	82,00	6,59						6,59		
43	20,00	1,61						1,61		
44	21,00	1,69				1,69				
Total	1244,5	100	17,7	3,18	13,71	27,54	20,45	10,53	0	6,90

Fig. 2. The distribution of compounds vs. unsaturated degree ( $z$ )

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