

**EVALUATION OF SATURATED AND AROMATIC HYDROCARBONS OIL-OIL
MATURITY CORRELATION PARAMETERS BY FACTOR AND
CLUSTER ANALYSES (SE PANNONIAN BASIN, SERBIA)**

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Twenty three crude oils from the Serbian part of the Pannonian Basin (14 from the Vojvodina Province Banat depression and 9 from the Drmno depression) were investigated aimed at evaluation of oil-oil maturity correlation parameters based on distribution and abundance of saturated biomarkers and alkylarene constituents. It is well known that in addition to maturity, they all depend on some other organic geochemical factors, such as origin, sedimentation environment, catalytic effect of minerals, migration and biodegradation. Therefore, factor and cluster analyses were used as a tool for interpreting the mentioned parameters. Saturated biomarkers, alkylnaphthalenes and alkylphenanthrenes were analysed by GC and GC-MS. Based on distribution and abundance of these compounds, numerous maturity parameters were calculated (Peters *et al.*, 2004; Stojanović *et al.*, 2006).

Factor analyses using varimax rotation were first run separately, of maturity parameters based on abundance of *n*-alkanes and isoprenoids, steranes and triterpanes, alkylnaphthalenes, and finally alkylphenanthrenes. These factor analyses yielded 9 important “maturity” factors (corresponding formulae with loadings of parameters and percents of variance are given in Appendix). Subsequently, all “maturity” factors obtained in individual factor analyses, showing higher than 30% of variance, were involved in a new factor analysis, as well as in cluster analysis using Ward method (Table 1). In that way all maturity parameters based on saturated biomarkers and alkylarenes were evaluated, considering the fact that the observed factors represented their linear combinations. The results showed that in correlation of oils from the Banat depression, the most important were maturity parameters based on isomerization reactions of thermodynamically less stable α -methylnaphthalenes, dimethylnaphthalenes and methylphenanthrenes into more stable isomers with methyl groups in β -position in aromatic rings ($F_{1\text{alkylnaphthalenes}}$ and $F_{1\text{alkylphenanthrenes}}$ with extremely high loadings in factor 1; Table 1a). Factors $F_{1\text{steranes+terpanes}}$, based on isomerisation reactions in aliphatic chains of saturated biomarkers, transformations of steranes into diasteranes and C_{29} -hopane into C_{29} Ts, as well as $F_{2\text{alkylnaphthalenes}}$, based on isomerisations $\alpha \rightarrow \beta$ in rings of trimethylnaphthalenes, having high

loadings values, determined factor 2. In the last significant, factor 3, high loadings were observed with $F_{1\text{alkanes+isoprenoids}}$ and $F_{2\text{steranes+terpanes}}$ which included parameters based on transformations in rings of saturated biomarkers and $T_m \rightarrow T_s$ (Table 1a). Hierarchy and agreement between factors/parameters were additionally checked and approved by cluster analyses using Ward method (Table 1b). Finally, using all factors in factor and cluster analyses, according to maturity, the investigated crude oils were precisely classified into five groups. The differences in maturity between the Vojvodina and Drmno depression crude oils were observed, as well as between some oils originating from the Vojvodina locality.

| a) Varimax rotated component matrix | | | | b) Hierarchical cluster analysis using Ward method | |
|-------------------------------------|--------|-------|-------|--|--|
| Variables | Factor | | | Group | Factors |
| | 1 | 2 | 3 | | |
| $F_{1\text{alkanes+isoprenoids}}$ | -0.32 | -0.10 | 0.83 | I | $F_{1\text{alkylnaphtalenes}}$, $F_{1\text{alkylphenanthrenes}}$ |
| $F_{2\text{alkanes+isoprenoids}}$ | -0.65 | -0.31 | -0.37 | II | $F_{1\text{steranes+terpanes}}$, $F_{2\text{alkylnaphtalenes}}$, $F_{2\text{alkylphenanthrenes}}$ |
| $F_{1\text{steranes+terpanes}}$ | 0.10 | 0.90 | -0.06 | | |
| $F_{2\text{steranes+terpanes}}$ | 0.29 | 0.03 | 0.89 | III | $F_{2\text{steranes+terpanes}}$, $F_{1\text{alkanes+isoprenoids}}$ |
| $F_{1\text{alkylnaphtalenes}}$ | 0.92 | -0.02 | 0.03 | IV | $F_{2\text{alkanes+isoprenoids}}$ |
| $F_{2\text{alkylnaphtalenes}}$ | 0.03 | 0.88 | -0.20 | | |
| $F_{1\text{alkylphenanthrenes}}$ | 0.92 | 0.08 | -0.14 | | |
| $F_{2\text{alkylphenanthrenes}}$ | 0.09 | 0.67 | 0.36 | | |

Table 1. Results of factor (a) and cluster (b) analyses of “maturity factors” based on saturated biomarkers’ and alkylarenes’ maturity parameters.

APPENDIX

$F_{1\text{alkanes+isoprenoids}} = 0.95 \times \text{CPI} + 0.90 \times \text{CPI}_1 + 0.76 \times \text{Phyt}/n\text{-C}_{18} + 0.37 \times \text{Pr}/n\text{-C}_{17} - 0.09 \times \text{Pr}/\text{Phyt} - 0.02 \times \Sigma \text{odd}(n\text{-C}_{21}\text{-}n\text{-C}_{33})/\Sigma \text{even}(n\text{-C}_{12}\text{-}n\text{-C}_{20})$ (40.50 %); $F_{2\text{alkanes+isoprenoids}} = 0.92 \times \Sigma \text{odd}(n\text{-C}_{21}\text{-}n\text{-C}_{33})/\Sigma \text{even}(n\text{-C}_{12}\text{-}n\text{-C}_{20}) + 0.89 \times \text{Pr}/n\text{-C}_{17} + 0.57 \times \text{Phyt}/n\text{-C}_{18} - 0.55 \times \text{Pr}/\text{Phyt} + 0.19 \times \text{CPI}_1 - 0.03 \times \text{CPI}$ (38.56 %);

$F_{1\text{steranes+terpanes}} = 0.92 \times \text{C}_{29}\text{Ts}/\text{C}_{29}\text{-hopane} + 0.77 \times \text{C}_{31}(\text{S})/(\text{S})+(\text{R})\text{-hopanes} + 0.73 \times \text{C}_{27}\beta(\text{S})\text{-diasterane}/\text{C}_{27}\beta(\text{S})\text{-diasterane} + \text{C}_{27}\alpha(\text{R})\text{-sterane} + 0.69 \times \alpha(\text{S})/\alpha(\text{S})+\alpha(\text{R})\text{-steranes} - 0.51 \times \text{C}_{29}\text{-moretane}/\text{C}_{29}\text{-hopane} + 0.39 \times \text{C}_{29}\beta(\text{R})/\beta(\text{R})+\alpha(\text{R})\text{-steranes} + 0.38 \times \text{Ts}/\text{Ts}+\text{Tm} + 0.30 \times \text{C}_{30}\text{-moretane}/\text{C}_{30}\text{-hopane}$ (38.54 %);

$F_{2\text{steranes+terpanes}} = -0.86 \times \text{C}_{30}\text{-moretane}/\text{C}_{30}\text{-hopane} + 0.78 \times \text{C}_{29}\beta(\text{R})/\beta(\text{R})+\alpha(\text{R})\text{-steranes} + 0.72 \times \text{Ts}/\text{Ts}+\text{Tm} + 0.61 \times \alpha(\text{S})/\alpha(\text{S})+\alpha(\text{R})\text{-steranes} + 0.53 \times \text{C}_{27}\beta(\text{S})\text{-diasterane}/\text{C}_{27}\beta(\text{S})\text{-diasterane} + \text{C}_{27}\alpha(\text{R})\text{-sterane} - 0.20 \times \text{C}_{29}\text{-moretane}/\text{C}_{29}\text{-hopane} + 0.14 \times \text{C}_{29}\text{Ts}/\text{C}_{29}\text{-hopane} - 0.08 \times \text{C}_{31}(\text{S})/(\text{S})+(\text{R})\text{-hopanes}$ (32.38 %);

$F_{1\text{alkylnaphtalenes}} = 0.86 \times \text{ENR} + 0.84 \times \text{MNR} + 0.83 \times \text{TNR}_3 + 0.83 \times \text{TNY} + 0.83 \times \text{DNx} - 0.64 \times \alpha/\text{BDN}_1 + 0.63 \times \text{DNR}_1 + 0.29 \times \text{TNR}_1 + 0.07 \times \text{TNR}_2$ (49.12 %); $F_{2\text{alkylnaphtalenes}} = 0.94 \times \text{TNR}_2 + 0.84 \times \text{TNR}_1 + 0.56 \times \text{DNR}_1 - 0.52 \times \alpha/\text{BDN}_1 + 0.44 \times \text{DNx} + 0.42 \times \text{MNR} + 0.38 \times \text{TNY} + 0.16 \times \text{ENR} - 0.04 \times \text{TNR}_3$ (30.28 %);

$F_{1\text{alkylphenanthrenes}} = 0.96 \times \text{DMPI}_1 + 0.95 \times \text{MPR}_1 + 0.92 \times \text{MPI}_3 + 0.47 \times \text{MTR} + 0.20 \times \text{MDR} + 0.15 \times \text{DMPI}_1 + 0.06 \times \text{DMPI}_2 + 0.05 \times \text{PAI}_1$ (37.22 %); $F_{2\text{alkylphenanthrenes}} = -0.90 \times \text{PAI}_1 + 0.88 \times \text{MDR} + 0.75 \times \text{MTR} - 0.48 \times \text{DMPI}_1 + 0.35 \times \text{MPI}_3 + 0.24 \times \text{MPR}_1 - 0.20 \times \text{MPI}_1 + 0.11 \times \text{DMPI}_2$ (32.38 %); $F_{3\text{alkylphenanthrenes}} = 0.93 \times \text{DMPI}_2 + 0.73 \times \text{DMPI}_1 - 0.23 \times \text{MTR} + 0.14 \times \text{MPI}_1 - 0.08 \times \text{MDR} + 0.07 \times \text{MPI}_3 + 0.07 \times \text{MPR}_1 - 0.05 \times \text{PAI}_1$ (18.62 %).

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