

APPLICABILITY OF INFRARED ALIPHATIC STRETCHING REGION FOR CHARACTERISATION OF OILS OF THE SAME GENETIC TYPE

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The work focuses on the applicability of infrared (IR) aliphatic stretching region for characterisation of oils of the same genetic type underlining IR spectroscopy's obvious advantage as a robust and inexpensive analytical technique capable of simultaneously collecting information on all organic matter (OM) components, irrespective of their chemical nature, molecular weight or physical state. Paraffinic crude oils (56 samples) from the Turija-Sever oil field (southeastern part of the Pannonian Basin, Serbia) were studied. Our previous investigations based on detailed interpretation of biomarkers and aromatic hydrocarbons showed that the oils are similar, originate from mixed aquatic/terrestrial sources and were generated from Tertiary source rocks in an early stage of oil window (vitrinite reflectance ~ 0.65 %). However, certain slight differences among the oils were observed. They are reflected in a higher contribution of algal OM to the group I oils which were formed in reducing environment (western part of the field), compared to the oils from eastern part of the field (group II) with lower contribution of algal OM, formed under dysoxic conditions (Stevanović et al., 2019).

IR spectra of Turija-Sever oils are dominated by stretching, bending and rocking vibrations of aliphatic methyl and methylene groups. Stretching region 2800–3000 cm^{-1} was decomposed into five Lorentzian bands and CH_2/CH_3 branching factor calculated from the ratio of deconvoluted asymmetric stretching peaks (Painter et al., 1981). Definitive 3–4 cm^{-1} red shift between crudes with the least and most methyls per methylene group was found for both symmetric and asymmetric CH_2 stretching modes, whereas CH_3 asymmetric stretching mode only fluctuates by $\pm 1 \text{ cm}^{-1}$. By analogy with chain-melting phase transitions in phospholipid membranes it was suggested that the observed peak behaviour is characteristic of the onset of *gauche* rotamer formation in mostly *trans* polymethylene fragments with increasing degree of methyl substitution (Mantsch, McElhaney, 1991). Interestingly, a cross-plot of the CH_2/CH_3 ratios calculated from the corresponding symmetric and asymmetric peak absorbances after deconvolution exhibited an absence of correlation. Perusal of deconvoluted absorbances reveals that while both peaks of methylene are closely proportional in magnitude in all spectra, the methyl peaks are in disarray. To our knowledge, this fact has hitherto received little attention in the literature. Although in the original spectra of Turija-Sever oils CH_3 symmetric stretching is poorly resolved from the adjacent CH_2 feature, it is still possible to read the intensity of the former from the inflection at 2868–2870 cm^{-1} . When symmetric vs. asymmetric CH_2/CH_3 peak absorbances ratios from the original spectra were plotted, correlation becomes apparent. Test runs of the fitting program on synthetic spectra obtained from the sum of five ideal Lorentzians using different initial approximations for the fit parameters confirmed high algorithm sensitivity to the intensity and width of the symmetric methylene peak notwithstanding the fact that its contribution to the aliphatic stretching region is the lowest among all vibrational modes and in this study amounts to only 6–7 % in terms of the area. The findings allude to the necessity of introducing additional vibrational modes in order to accommodate for the diversity of steric and chemical environment of CH_n groups in oil as noted earlier for coal.

Cross-plot between the normal to isoprenoid alkanes sum ratio, $\Sigma(n\text{-C}_{10} - n\text{-C}_{40})/\Sigma(i\text{-C}_{13} - i\text{-C}_{20})$, derived from whole oil gas chromatography (GC-FID) and the IR CH_2/CH_3 branching factor segregates Turija-Sever oils into two identical groups (I and II) previously established based on biomarkers and aromatic hydrocarbons. The group I oils showed values of the $\Sigma(n\text{-C}_{10} - n\text{-C}_{40})/\Sigma(i\text{-C}_{13} - i\text{-C}_{20})$ ratio varying between 4.58 and 6.28, whereas CH_2/CH_3 branching factor, ranged from 2.61 to 3.15. Group II is characterized by greater values of both parameters. The $\Sigma(n\text{-C}_{10} - n\text{-C}_{40})/\Sigma(i\text{-C}_{13} - i\text{-C}_{20})$ ratio increases from 7.70 to 11.65, associated with CH_2/CH_3 in range 3.06 – 3.88 (Fig. 1). Although higher branching factor is usually associated with lower OM maturity (Lis et al., 2005), enhanced CH_2/CH_3 ratio for group II oils indicate that in the case of uniform OM maturity greater average length of polymethylene fragments results from a higher content of long chain *n*-alkanes signifying an increased impact of terrigenous OM (land plant waxes). Furthermore, generally high CH_2/CH_3 ratios (>1.63) for both groups of oils are consistent with low maturity. More detailed inspection of the cross-plot reveals a markedly more pronounced correlation between the IR and GC-FID parameters for the second ($R^2 = 0.69$) compared to the first group of oils ($R^2 = 0.02$). This result is in agreement with a higher contribution of aquatic OM to group I oils enriched in methyl- and dimethylalkanes, originating mainly from cyanobacteria and *Botryococcus braunii* race A. Since the $\Sigma(n\text{-C}_{10} - n\text{-C}_{40})/\Sigma(i\text{-C}_{13} - i\text{-C}_{20})$ ratio derived from GC-FID did not include methylated alkanes with the exception of regular isoprenoids, whereas IR spectra are sensitive to all methyl moieties, variation of the CH_2/CH_3 branching factor for the group I oils supersedes the *n*-alkanes/isoprenoids/ ratio. For the group II oils, enriched in terrigenous OM, isoprenoids are the main source of aliphatic CH_3 groups, thus improving the correlation.

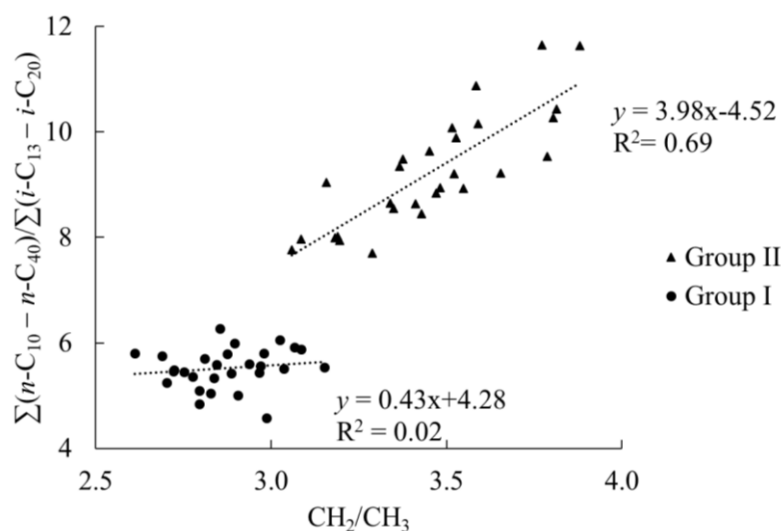


Figure 1. Ratio of normal to isoprenoid alkane sums from vs. CH_2/CH_3 branching factor. Dotted lines represent linear fits.

References

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