

The Effect of Unresolved Complex Mixtures (UCM) on Isotopic Profile of Aromatic Hydrocarbons

Ivwurie W.

*Department of Chemistry, Federal University of Petroleum Resources,
P.M.B. 1221, Effurun, Delta State, Nigeria
Corresponding Author E-mail: wivwurie@yahoo.co.uk*

Abstract

Heavily biodegraded crude oil (Nigeria crude oil) was separated by open column chromatography into aliphatic, aromatic and polar fractions using appropriate organic solvents. Aromatic fraction containing UCM was spiked with standard PAHs to determine the effect of the UCM on isotopic data.

The deviations/fractionation of the PAHs isotopic values after doping ranges from -0.1 to -1.4 ‰ for all PAHs, the highest value recorded for fluoranthene and pyrene with deviation of -1.2 and -1.4 ‰, and this can be found at the highest point of the UCM.

Keywords: Polycyclic aromatic hydrocarbon, isotopic fractionation, biodegradation

Introduction

The stable carbon isotope ratios of organic compounds depend on their origin and fate in the environment and have been used to elucidate the origins of hydrocarbons in ancient depositional environments (1, 2). One of the factors that bring about unresolved complex mixtures is biodegradation of hydrocarbons, and this can bring about change in isotopic profiles of hydrocarbons (3).

The degradation of n-alkanes, cyclic and branched alkanes was reported by Bailey and Connan (4, 5). The shorter chained n-alkanes (C₆-C₁₅) are degraded prior to n-C₁₅⁺ compounds (5), with a decrease in the rate of biodegradation with increasing carbon chain length (6). Gough and Rowland (1990), Killops and Al-Juboori (1990) have shown that following the removal of the n-alkanes, the gas chromatogram of the saturated hydrocarbon fraction isolated from a crude oil is

dominated by an unresolved complex mixture (UCM) or hump composed of the more bacterially resistant compounds including various branched and cyclic alkanes(7,8).

The level of biodegradation of oil composition has been most elaborately studied for the saturated petroleum hydrocarbon fraction. Many reports have been published to classify the degree of biodegradation of given oil (5, 9). However, one of the most recent one is that given by Peters and Moldowan (10). It gives the order in which the compound classes of the oil are removed.

Huang *et al* (1996) (11) investigated the post-glacial variations in ^{14}C and ^{13}C profiles of individual aliphatic hydrocarbons and bulk organic matter for three stratified organic upland soils (peaty, podzol, and acid brown earth). They concluded that the rapid decreases of ^{14}C and ^{13}C profiles down the soil were mainly caused by degradation (microbial, chemical degradation and water washing) during early diagenesis. Keeling *et al* (1984) (12) also reported that fossil fuel burning has led to the depletion of atmospheric $\delta^{13}\text{C}$ by about 1 ‰, which explains the minute changes in the isotopic values of the organic matter over the last few hundred years.

O'Malley *et al.* (1994) (13) also observed that for samples with varying UCM contents, the maximum deviations from the mean values ranged from 0.1 to 0.4 ‰ for well-separated species and from 0.3 to 1.1 ‰ for high molecular mass isomers.

This research paper studies the effect of unresolved complex mixtures (UCM) on the isotopic composition of polycyclic aromatic hydrocarbons.

Method

20 mg of biodegraded Nigeria crude oil was dissolved in 2mls of DCM, which was followed by the introduction of 1 g of silica gel (activated at 180-200°C for 8-12 hrs) into the solution, followed by solvent removal in a rotary evaporator at a temperature $\leq 30^\circ\text{C}$. Thereafter, 20 g of the activated silica gel was packed into an open column (about 0.5 cm i.d.) with a glass-wool plug at the bottom. The crude oil-coated silica gel was then carefully transferred onto the top of the column and compacted. Elution of each fraction was performed using 40mls of n-hexane to elute the aliphatic fraction, 40mls of 25% hexane/DCM for the aromatics, and 40mls (1-1v/v) DCM/methanol mixture for the polar fraction respectively (14). All solutions obtained were then evaporated to dryness using a stream of nitrogen at temperatures below 30°C to give the different fractions.

Standard PAHs and aromatic fraction of biodegraded Nigerian crude oil with Unresolved complex mixtures (UCM) were analyzed separately using compound specific isotope ratio spectrometry, followed by the doping of the standard PAHs with severely biodegraded Nigeria crude oil (having UCM).

Results and Discussion

The isotopic distributions are presented in Figures 1 to 3 and Table 1

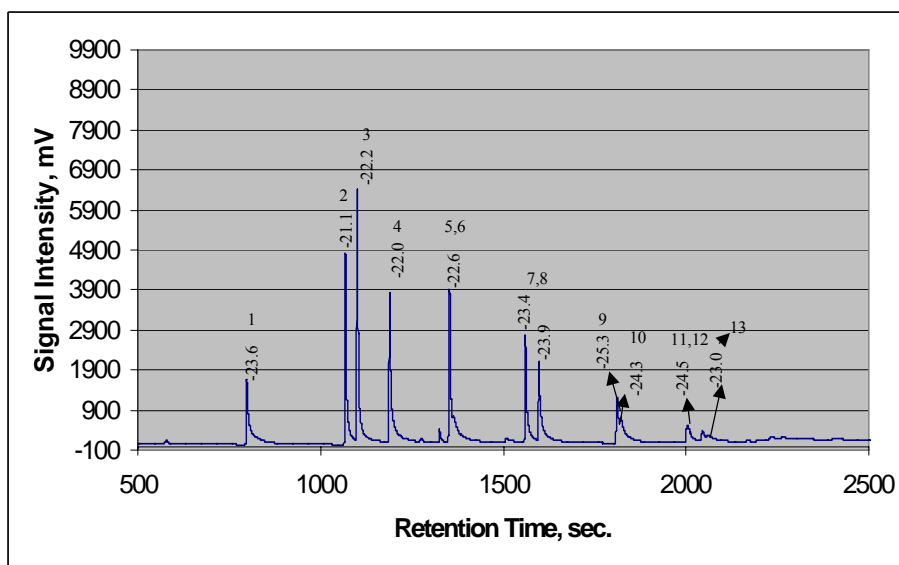


Figure 1 GC-IRMS m/z 44 chromatogram for standard PAHs giving their carbon stable isotope ratios

Key: 1. Naphthalene; 2. Acenaphthylene; 3. Acenaphthene; 4. Fluorene; 5. Phenanthrene; 6. Anthracene; 7. Fluoranthene; 8. Pyrene; 9. Benzo(a)anthracene; 10. Chrysene; 11. Benzo(b)fluoranthene; 12. Benzo(k)fluoranthene; 13. Benzo(a)pyrene

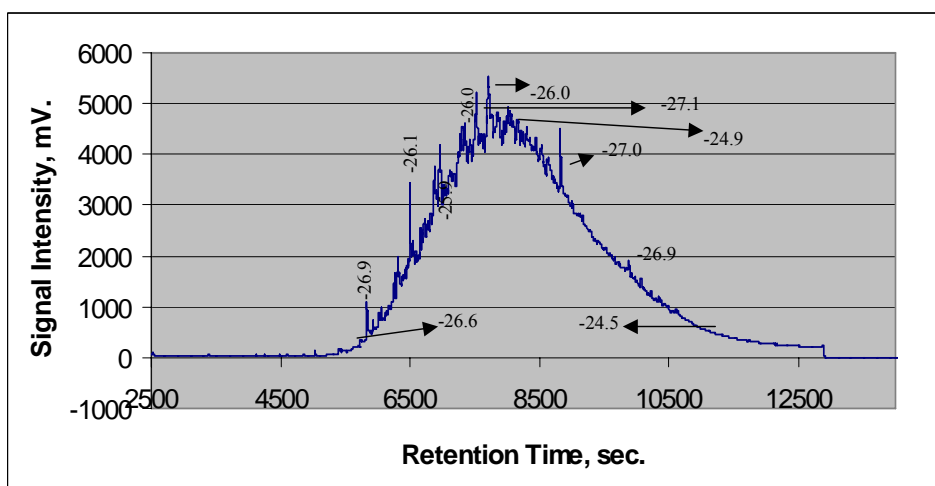


Figure 2 : GC-IRMS m/z 44 chromatogram for biodegraded Nigeria crude oil aromatics giving some of the carbon stable isotope ratios

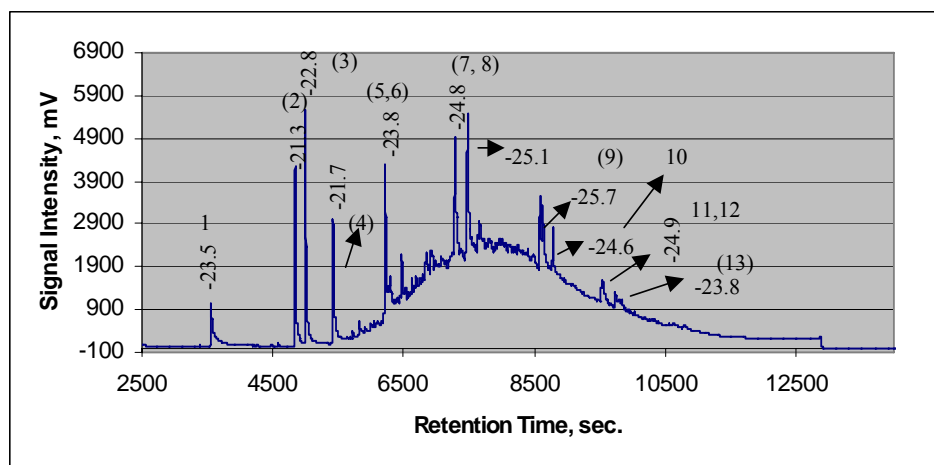


Figure 3 : GC-IRMS m/z 44 chromatogram for standard PAHs and biodegraded Nigeria crude oil aromatics giving some of the carbon stable isotope ratios

Key: 1. Naphthalene; 2. Acenaphthylene; 3. Acenaphthene; 4. Fluorene; 5. Phenanthrene; 6. Anthracene; 7. Fluoranthene; 8. Pyrene; 9. Benzo(a)anthracene; 10. Chrysene; 11. Benzo(b)fluoranthene; 12. Benzo(k)fluoranthene; 13. Benzo(a)pyrene

Table 1 : Isotopic data for standard PAHs and standard PAHs eluting on a UCM

Name and No of PAHs	$\delta^{13}\text{C}$ of standard PAHs	$\delta^{13}\text{C}$ of standard PAHs with UCM (of BNG sample)	Difference between the mean values
1. Naphthalene	-23.6	-23.5	-0.1
2. Acenaphthylene	-21.1	-21.3	-0.2
3. Acenaphthene	-22.2	-22.8	-0.6
4. Fluorene	-22.0	-21.7	-0.3
5. Phenanthrene	-22.6	-23.8	-1.2
6. Anthracene	-22.6	-23.8	-1.2
7. Fluoranthene	-23.4	-24.8	-1.4
8. Pyrene	-23.9	-25.1	-1.2
9. Benzo(a)anthracene	-25.3	-25.7	-0.4
10. Chrysene	-24.3	-24.6	-0.3
11. Benzo(b)fluoranthene	-24.5	-24.9	-0.4
12. Benzo(k)fluoranthene	-24.5	-24.9	-0.4
13. Benzo(a)pyrene	-23.0	-23.8	-0.8

Note: isotopic ratios listed represent the mean of 3 replicate measurements, BNG means biodegraded Nigeria crude oil aromatics

To test the effect of UCM on the isotopic distribution of aromatics in samples investigated, standard PAHs and a Nigerian crude oil aromatics with UCM were analysed separately using compound specific isotope ratio spectrometry, followed by the doping of the standard PAHs with the Nigerian crude oil aromatics, having the UCM. The isotopic distributions are presented in Figures 1 to 3 and Table 1. The deviations of the PAHs isotopic values after doping ranges from -0.1 to -1.4 ‰ for all PAHs, the highest value recorded for fluoranthene and pyrene with deviation of -1.2 and -1.4 ‰, and this can be found at the highest point of the UCM (See Figures 1 to 3). This significant deviation can affect the credibility of data needed for credible source apportionment studies. The implication of this is that isotopic ratio fractionation occurred in the standard PAHs profiles due to the UCM in the Nigerian crude oil aromatics, by a range of ± 0.1 to 1.4 ‰. Lancet *et al.*, (1993) (15) reported that a minimal difference of 2 ‰ is required and a difference of 4‰ is desired for acceptable precision and accuracy in co-processing of materials. Similarly, 'O'Malley *et al.* (1994) (14) also observed that for samples with varying UCM contents, the maximum deviations from the mean values ranged from 0.1 to 0.4 ‰ for well-separated species and from 0.3 to 1.1 ‰ for high molecular mass isomers. The isotopic fractionation which occurred in the standard PAHs profiles due to the UCM in the Nigerian crude oil aromatics, by a range of ± 0.1 to 1.4 ‰ is therefore consistent with literature reports.

Conclusion

Unresolved complex mixtures can lead to change in isotopic composition of hydrocarbons. The extent of alteration in isotopic signatures depends on the complexity of the unresolved complex mixture of the sample. If this alteration is significant, the credibility of isotopic data for analytical studies can become questionable.

References

- [1] Freeman, K.H., Hayes, J.M., Trendel, J.M. and Albrecht, P. (1990) Evidence from carbon isotope measurement for diverse origins of sedimentary hydrocarbons. *Nature*. 343, 254-256.
- [2] Mazeas, L., Budzinski, H. and Raymond, N. (2002). Absence of stable carbon isotope fractionation of saturated and polycyclic aromatic hydrocarbons during aerobic bacterial biodegradation. *Organic Geochemistry*. 33, 1259-1272.
- [3] Ivwurie, W. (2005) Source Apportionment and Use of Hydropyrolysis to elucidate sources of heavily biodegraded hydrocarbons. Unpublished PhD thesis. University of Nottingham.
- [4] Bailey, N.J.L., Jobson, A.M. and Rogers, M.A. (1973) Bacterial degradation of crude oil. Comparison of field and experimental data. *Chemical Geology*. 11, 203-211.

- [5] Connan, J. (1984) Biodegradation of crude oils in reservoirs. *In*: Brooks, J. and Welte, D. (eds.) *Advances in Petroleum Geochemistry*. Academic Press, London, U.K. pp 299-335.
- [6] Douglas, G.S., Bence, A.E., Prince, R.C., McMillen, S.J. and Butler, E.L. (1996) Environmental Stability of selected petroleum hydrocarbon source and weathering ratios. *Environmental Science and Technology*. 30, 2332-2339.
- [7] Gough, M.A. and Rowland, S.J. (1990) Characterisation of resolved complex mixtures of hydrocarbons in petroleum. *Nature*. 344, 648-650.
- [8] Killops, S.D. and Al-Juboori, M.A.H.A. (1990) Characterisation of the unresolved complex mixture (UCM) in the gas chromatogram of biodegraded petroleum. *Organic Geochemistry*. 15, 147-160.
- [9] Volkman, J.K., Alexander, R., Kagi, R.I. and Sheppard, P.N. (1984) Biodegradation of aromatic hydrocarbons in crude oil from the Barrow Sub-basin of Western Australia. *Organic Geochemistry*. 6, 619-632.
- [10] Peters, K.E. and Moldowan, J.M. (1993) *The Biomarker Guide*. Prentice-Hall, London, U.K., p 363.
- [11] Huang, Y., Bol, R., Harkness, D.D., Ineson, P. and Eglinton, G. (1996) Post-glacial variations in distributions, ¹³C and ¹⁴C contents of aliphatic hydrocarbons and bulk organic matter in three types of British acid upland soils. *Organic Geochemistry*. 24, 273-287.
- [12] Keeling, C.D., Carter, A.F. and Mook, W.G. (1984) Seasonal, latitudinal and secular variations in the abundance and isotopic ratios of atmospheric CO₂. 2. Results from oceanographic cruises in the tropical Pacific Ocean. *Journal of Geophysical Research*. 89, 4615-4628.
- [13] O' Malley, V.P., Abrajano, T.A. Jr. and Hellou, J. (1994) Determination of the ¹³C/¹²C ratios of individual PAH from environmental samples: can PAH sources be apportioned? *Organic Geochemistry*. 21, 809- 822.
- [14] Sun, Cheng-gong. (2001) Sourcing PAH in the environment. Unpublished PhD thesis. University of Strathclyde.
- [15] Lancet, M.S., Winschet, R.A., and Burke, F.P. (1993) Stable carbon isotope analysis of coprocessing materials. *Fuel*. 72, 1209-1217.