FULL LENGTH ARTICLE

Chemometric representation of molecular marker data of some Niger Delta crude oils

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Chemometric; Molecular maker; Star diagram; Depositional environments; Organic matter

Abstract Chemometric representation of data is the most preferred and adopted method of research reporting in contemporary times. Data are easily discerned and interpreted. Molecular maker parameters of some crude oils from the Nigerian's Delta region are chemometrically expressed after data treatment using multivariate statistical analyses, other graphical representations were the star diagram and triangular (ternary) plot. The results indicated discrimination of samples into two genetic families corresponding to their primary oil fields. These groupings were more obvious for results obtained via principal component analysis. Genetic groupings are principally due to compositional differences which are commonly attributed to unique source rock depositional environments and/or sourcing organic matter. The two families of oils identified have both terrestrial inputs, but differ comparatively by relative marine inputs.

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1. Introduction

The advent of chromatographic techniques in exploratory petroleum analysis has resulted in exploring techniques of handling the characteristically inherent large data sets. Chemometrics, the application of multivariate statistical techniques for large data sets provides for recognition of patterns and extraction of useful information from measured data. Its applications include understanding the affinities among samples or variables and making accurate predictions about unknown samples.

In exploratory petroleum analysis, chemometric data analysis is mainly employed which comprise the PCA (principal component analysis) and HCA (hierarchical cluster analysis). In the HCA, distances between samples are compared by means of dendrogram which presents a simple view of sample groups in the data set, the cluster distance is the measure of similarity between samples. The PCA reduces numerous variables into a few set of variables within which the most relevant information is concentrated and best explains the variations in the data set.

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Odden and Kvalheim [1], Cheng et al. [2], Xiong et al. [3] demonstrated the use of chemometrics for classifying oils and source rocks belonging to different genetic families. This study employs the use of chemometrics which significantly discriminates the suite of samples used from the Niger Delta into two genetic families. Prior to, these oils are inferred to have been sourced from similar formation within the same petroleum system.

2. Geology of the study area

The study area lies within the Niger-Delta; its geology is therefore typical of the Niger Delta Basin. The area forms a part of a geological sequence of the Quaternary and Tertiary formations of the Niger Delta, consisting mainly of three main geologic formations, which are: the Benin Formation, the Agbada Formation, and the Akata Formation. The tertiary Niger Delta has accumulated sediments that are over 10 kilometers thick. The primary source rock is the Upper Akata formation, which comprise the marine shale facies of the Delta, with possible contributions from intercalated marine shale of the Lower Agbada formation [4].

Sundararaman et al. [5] indentified three geological units as individual petroleum systems, thus the lower cretaceous (lacustrine), upper cretaceous-lower Paleocene (marine), and tertiary (deltaic). However, Michele et al. [6] earlier stated the Akata–Agbada petroleum system as active in the Niger Delta region. The sandstone facies within the Agbada formation are potential reservoirs, however turbidite sands in the Upper Akata formation are a potential target in deep water offshore.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>U2T</th>
<th>U7L</th>
<th>U4L</th>
<th>U45</th>
<th>KD01</th>
<th>KD02</th>
<th>KD03</th>
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<tr>
<td>Pr/Ph</td>
<td>4.05</td>
<td>2.31</td>
<td>2.31</td>
<td>1.88</td>
<td>3.36</td>
<td>3.44</td>
<td>3.40</td>
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<td>Pr/n-C17</td>
<td>0.56</td>
<td>1.30</td>
<td>1.35</td>
<td>0.77</td>
<td>0.48</td>
<td>0.45</td>
<td>0.44</td>
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<tr>
<td>Ph/n-C18</td>
<td>0.16</td>
<td>0.16</td>
<td>0.65</td>
<td>0.42</td>
<td>0.16</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>nC25/nC18</td>
<td>0.53</td>
<td>0.49</td>
<td>0.67</td>
<td>0.64</td>
<td>0.40</td>
<td>0.38</td>
<td>0.37</td>
</tr>
<tr>
<td>CPI</td>
<td>1.01</td>
<td>0.72</td>
<td>1.08</td>
<td>1.02</td>
<td>1.09</td>
<td>1.02</td>
<td>1.04</td>
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<tr>
<td>(Pr + C13)/ (Ph + C13a)</td>
<td>1.52</td>
<td>1.52</td>
<td>1.58</td>
<td>1.26</td>
<td>1.40</td>
<td>1.53</td>
<td>1.50</td>
</tr>
<tr>
<td>Ts/Tm</td>
<td>1.19</td>
<td>0.82</td>
<td>0.79</td>
<td>0.86</td>
<td>1.25</td>
<td>1.15</td>
<td>1.47</td>
</tr>
<tr>
<td>Ts/(Ts + Tm)</td>
<td>0.54</td>
<td>0.45</td>
<td>0.44</td>
<td>0.46</td>
<td>0.56</td>
<td>0.53</td>
<td>0.59</td>
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<tr>
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<td>0.65</td>
<td>0.69</td>
<td>0.67</td>
<td>0.64</td>
<td>0.65</td>
<td>0.60</td>
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<tr>
<td>Pr/C19hop</td>
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<td>0.72</td>
<td>0.72</td>
<td>1.03</td>
<td>0.32</td>
<td>0.31</td>
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<tr>
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<td>0.72</td>
<td>1.03</td>
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<td>0.04</td>
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<td>0.01</td>
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<td>0.06</td>
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<td>0.56</td>
<td>0.52</td>
<td>0.56</td>
<td>0.55</td>
<td>0.55</td>
<td>0.58</td>
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<tr>
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<td>6.57</td>
<td>8.35</td>
<td>6.86</td>
<td>7.39</td>
<td>7.03</td>
<td>7.20</td>
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<tr>
<td>20S(20S + 20R)</td>
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<td>0.51</td>
<td>0.50</td>
<td>0.63</td>
<td>0.55</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Figure 1 PCA score plot of crude oil samples.

Figure 2 PCA loading plot.
3. Materials and methods

3.1. Sampling and Sample preparation

Seven crude oil samples collected from reservoirs at different stratigraphic depths ranging from 9800 ft to 10,400 ft from producing fields onshore Niger Delta were used for this research. The crude oils were collected in glass vials with Teflon caps and stored in the refrigerator at a temperature of less than 4°C.

3.2. Fractionation of the oils

The crude oils were fractionated into saturates, aromatics and polar fractions using column chromatography. The column was plugged with extracted cotton wool to serve as a pad on which stationary phase silica gel (SiO$_2$) rested, while petroleum ether was the mobile phase. About 2 g of Alumina was added to keep the surface stable. The oil samples were introduced, then 70 ml of petroleum ether was added to elute the aliphatic fraction followed by 70 ml of dichloromethane (DCM) to elute the aromatic fractions, and 70 ml of methanol to elute the polars (resins). The aliphatic fractions were reduced with nitrogen stream to near 1ml and diluted with dichloromethane for the GC–MS analysis.

3.3. Gas chromatography–mass spectroscopy analysis (GC–MS)

The GC-MS analyses for the aliphatic hydrocarbons of the oils were performed using a Hewlett-Packard 5890II GC with a split/splitless injector (280°C) linked to a Hewlett-Packard 5972 MSD with an electron voltage of 70 eV, filament current of 220 µA, source temperature of 160°C, a multiplier voltage 1600 V and interface temperature 300°C. The acquisition was controlled by an HP Vectra PC chemstation computer in both full scan and selected ion modes. The sample (1 µl) in DCM was injected by an HP7673 auto-sampler and the split opened after 1 min. Separation was performed on a fused silica capillary column (30 m × 0.25 mm i.d.) coated with 0–25 µm, 5% phenylmethylsilicone (HP-5). The GC was temperature programed for 40–300°C at 4°C per minute and held at a final temperature for 20 mins. The carrier gas was helium (flow 1 ml/min., pressure of 50 KPa, slit at 30 ml/min.). The acquired data were on DAT tape for later processing. The data were processed using Chem Station G1701BA (version B.01.001989-1998) software and peak integration was done with the RTE integrator.

3.4. Chemometric statistical procedure

Chemometric data analysis comprises both the PCA (principal component analysis) and the HCA (hierarchical cluster analysis). The PCA was carried out as factor analysis using 19 parameters/variables (Table 1) obtained from the crude oil samples, the first two (2) factors were extracted and the extraction method adopted is PCA (principal component analysis), varimax rotation was applied for maximum variations. The first two factors explained 54.1% and 26.5% of the variations respectively. Graphs derived were the score and loading plots. The HCA was also carried out using the same variables. Complete linkage method was adopted and distance measured is Squared Euclidean, two (2) clusters were extracted and a dendrogram was derived using Minitab version 15 for the chemometric analysis.

4. Results and discussion

4.1. Chemometric analysis

The PCA loadings and score plots were obtained from the PC analysis of the chromatographic data of the oil samples (Table 1) and are illustrated in Figs. 1 and 2. The score plot (Fig. 1) indicates significant discrimination of the oils into two (2) groups. These groupings fit into the respective oil fields. The distribution of the samples on the score plot shows that samples 5, 6 and 7 are grouped together and samples 1, 2, 3, and 4 are also grouped together but directed opposite each other diagonally far from the center. This indicates a significant positive correlation within the groups but significant dissimilarity between the groups. Decoding the samples using the input data, samples 1, 2, 3 and 4 correspond to U2T, U7L, U4L, U45 from Umutu oil field in the South–West Niger Delta, while samples 5, 6, and 7 correspond to KD01, KD02 and KD03 from the Bomu oil field in the South–South Niger Delta.
The distribution resulting in the placement of the two oil fields on the opposite sides of the center of the score plots indicates a significant negative correlation of the oils.

The loading plot (Fig. 2) represents the distribution for the first six variables C1–C6, which are Pr/Ph, Pr/n-C17, Ph/n-C18, nC25/nC18, CPI, and (Pr + C17)/(Ph + C18) respectively. The plot shows that C2, C3 and C4 which correspond to Pr/n-C17, Ph/n-C18, nC25/nC18 control the relationship within the Umutu oils, while C1 and C5 which correspond to Pr/Ph and CPI control the relationships within the Bomu oil field for these suite of variables.

The dendrogram (Fig. 3) was obtained from the HC analysis of the molecular marker data of the crude oil samples. The observations are grouped into two families. The first comprises samples 1, 5, 6 and 7, while the second group comprises samples 2, 3 and 4. The first group has about 80% similarity while the second group has about 60% similarity. The first group corresponds to the Bomu oil field samples except sample 1 which is of Umutu oil field, while the second group comprises the Umutu oil field samples. The placement of sample 1 in group 1 could imply that it bears similar values for some parameter with the group. However, there is discrimination of the samples into the respective oil fields. The higher percentage in similarity of the Bomu oil field samples is also portrayed by the polar plot.

4.2. Polar plot (star plot)

Polar plots have been extensively employed for reservoir studies [7,8]. This concept rests on the fact that similar samples bear similar profiles. The polar plot in this study (Fig. 4) indicates a fair grouping of the samples. The crude oil samples KD01, KD02 and KD03 (indicated with bold lines) were fairly grouped, while the crude oil samples U2T, U7L, U4L and U45 (indicated with broken lines) did not show any regular/significant grouping, this could imply slight variations among the samples which could be due to reservoir heterogeneities as a result of the peculiar dynamics of the reservoir infilling processes [9].

4.3. Ternary plot

The ternary plot has been employed to distinguish oils from different source rocks or facies within a source rock [10–12]. A cluster on the plot indicates high similarity of the clustering samples implying a single source of the oils. The % C27, % C28 and % C29 steranes of various samples were used for the plot (Fig. 5), it shows a fair grouping of the samples, which essentially implies that the samples have noticeable but no significant difference in terms the relative amounts of C27, C28, C29 steranes which vary with principal sourcing organic matter of the oils [13–15]. The samples except U2T, U7L show principally terrestrial inputs with fair tendency for minor marine inputs.

5. Conclusion

Analytical data of some Niger Delta oils were chemometrically represented, this involved a principal component and hierarchical cluster analysis. The result from the PCA indicates significant discrimination of the oils into their respective groupings reflecting their oil fields. The result implied strong positive correlations within the groups but strong negative correlations between the groups. The result from the HCA also indicates fair groupings, the Bomu oils show very high similarity to each other compared to the Umutu oils. The star plot and the triangular plots were also employed. There were no significant groupings in the star and triangular plots.

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