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Integrated Analytical Characterization and Chemometric Classification of Selected Nigerian Crude Oils Using Physicochemical Analysis, GC–MS, ATR-FTIR Spectroscopy, and ICP–OES

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Abstract: *The comprehensive characterization of crude oil is essential for petroleum quality evaluation, refinery optimization, and environmental management. This study employed an integrated analytical approach combining physicochemical analyses, Gas Chromatography–Mass Spectrometry (GC–MS), Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP–OES), and chemometric techniques to characterize five Nigerian crude oils (Bonny Light, Forcados Blend, Qua Iboe, Escravos, and Brass River). Physicochemical analysis showed density values of 0.822–0.857 g cm^{-3}, API gravity of 32.8–40.4°API, viscosity of 3.95–8.31 cSt, and sulfur content of 0.11–0.36 wt.%, confirming that all samples are light sweet crude oils. GC–MS analysis revealed that n-paraffins (34.12–42.36%) constituted the dominant hydrocarbon fraction, whereas aromatic hydrocarbons accounted for 11.58–15.57%, with Brass River crude exhibiting the highest aromatic content. ATR-FTIR spectra displayed characteristic aliphatic C–H stretching bands at 2921–2926 cm^{-1} and 2852–2855 cm^{-1}, confirming the predominance of saturated hydrocarbons, while weaker aromatic and carbonyl absorption bands indicated lower concentrations of aromatic and oxygenated compounds. ICP–OES analysis showed calcium (23.46–36.85 mg kg^{-1}), iron (16.27–28.94 mg kg^{-1}), vanadium (5.18–10.74 mg kg^{-1}), and nickel (3.96–8.43 mg kg^{-1}) as the principal trace metals. Pearson correlation analysis demonstrated strong inverse relationships between API gravity and density (r = −0.985) and viscosity (r = −0.964), whereas Principal Component Analysis explained 86.9% of the total variance within the first two principal components. Hierarchical Cluster Analysis classified Qua Iboe and Bonny Light as compositionally similar high-quality crude oils and distinguished Brass River as the most compositionally distinct sample. The integrated analytical methodology proved effective for crude* oil fingerprinting, quality assessment, refinery feedstock evaluation, and petroleum classification.

Keywords: *Crude oil characterization; GC–MS; ATR-FTIR spectroscopy; ICP–OES; Chemometrics; Nigerian crude oil; Petroleum fingerprinting.*

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1.0 Introduction

Crude oil is one of the world's most valuable natural resources and remains the primary feedstock for the production of transportation fuels, lubricants, petrochemicals, and numerous industrial products. It is an extremely complex mixture composed predominantly of hydrocarbons, including paraffins, naphthenes, aromatics, and asphaltenes, together with varying concentrations of heteroatom-containing compounds and trace metals such as nickel

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(Ni), vanadium (V), iron (Fe), calcium (Ca), copper (Cu), zinc (Zn), chromium (Cr), and lead (Pb). The relative abundance of these constituents varies considerably depending on the geological origin, maturity, migration history, and depositional environment of the crude oil reservoir. Consequently, comprehensive characterization of crude oil is indispensable for petroleum exploration, reservoir evaluation, refining optimization, environmental monitoring, and product quality assessment (Motahari et al., 2025).

The increasing complexity of petroleum refining and the demand for cleaner fuels have heightened the need for rapid, accurate, and reliable analytical techniques capable of determining both the chemical composition and physicochemical properties of crude oils. Traditional crude oil assays provide valuable information on parameters such as density, API gravity, viscosity, sulfur content, pour point, flash point, and distillation characteristics. However, these conventional methods are often labor-intensive, time-consuming, and require extensive laboratory procedures. Recent advances in analytical chemistry have introduced spectroscopic and chromatographic techniques that enable rapid, sensitive, and non-destructive characterization of crude oils while reducing analytical costs and turnaround time (Motahari et al., 2025).

Among these analytical techniques, Fourier Transform Infrared (FTIR) spectroscopy has emerged as a powerful tool for petroleum characterization because it provides molecular fingerprint information based on the vibrational frequencies of functional groups present in petroleum hydrocarbons. FTIR enables the identification of aliphatic and aromatic hydrocarbons, carbonyl compounds, sulfur-containing functional groups, oxygenated compounds, and other molecular constituents within complex crude oil matrices. Unlike conventional fractionation methods, FTIR analysis requires minimal sample preparation, is relatively inexpensive, and produces spectra within minutes, making it highly suitable for routine petroleum analysis (Abdulkadir et al., 2016; Motahari et al., 2025). The application of FTIR spectroscopy to Nigerian crude oils has demonstrated its effectiveness in distinguishing petroleum samples based on their compositional differences (Udoetok *et al*., 2012). Adedosu (2005) successfully characterized Niger Delta crude oils using infrared spectroscopy and demonstrated that spectral variations could be used to identify compositional differences among crude oil samples. Similarly, Ahmad et al. (2018) combined FTIR spectroscopy with gas chromatography-mass spectrometry (GC-MS) to characterize petroleum crude oils and reported that the integration of both techniques provided more comprehensive information on hydrocarbon composition than either method alone. FTIR has therefore become an indispensable analytical technique for rapid crude oil fingerprinting and quality evaluation.

Gas chromatography coupled with mass spectrometry (GC-MS) remains one of the most widely employed analytical techniques for detailed molecular characterization of petroleum hydrocarbons. The technique enables the separation, identification, and quantification of individual hydrocarbon compounds ranging from light volatile components to high molecular weight aromatic fractions. GC-MS provides detailed information on carbon number distribution, biomarker composition, hydrocarbon maturity, biodegradation level, and source correlation, making it indispensable in petroleum geochemistry and refinery quality assessment (Ahmad et al., 2018). Furthermore, direct mass spectrometric analysis has been shown to differentiate crude oils originating from different geographical regions. Kaya et al. (2017), using a residual gas analyzer based on quadrupole mass spectrometry, demonstrated distinct compositional differences between

Middle Eastern and Texas crude oils, confirming the capability of mass spectrometric techniques for qualitative and quantitative petroleum characterization.

In addition to hydrocarbon composition, trace metals constitute an important aspect of crude oil characterization because they significantly influence refining processes, catalyst deactivation, equipment corrosion, and environmental emissions. Nickel and vanadium are particularly important geochemical markers whose concentrations reflect the depositional environment and maturity of crude oils while simultaneously affecting refinery catalyst performance. Accurate determination of these elements therefore provides valuable information for both petroleum exploration and refining operations. Advances in inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) have greatly improved elemental analysis of petroleum samples through direct dilution techniques that minimize sample preparation and increase analytical throughput. Poirier et al. (2016) demonstrated that both ICP-OES and ICP-MS produced highly comparable precision, accuracy, and recovery for determining Ni, V, Fe, and Ca in crude oils over a wide range of API gravities. Their study further established that direct dilution methods are reliable for routine elemental analysis and facilitate accurate determination of V/(V + Ni) ratios, an important parameter in petroleum geochemistry.

Physicochemical characterization remains equally important because crude oil properties determine transportation, storage, processing efficiency, and commercial value. Parameters such as density, specific gravity, API gravity, viscosity, moisture content, sulfur concentration, flash point, cloud point, and pour point are widely used for crude oil classification and refinery planning. Ofodile et al. (2018) comprehensively characterized Afiesere crude oil from the Niger Delta using ASTM methods and reported density, viscosity, API gravity, moisture content, metallic constituents, and elemental composition, demonstrating the importance of integrating physical, elemental, and compositional analyses for complete crude oil evaluation.

Recent developments in analytical chemistry increasingly combine spectroscopy with chemometric techniques to improve classification accuracy and predictive performance. Chemometric methods such as Principal Component Analysis (PCA), Partial Least Squares Regression (PLSR), Partial Least Squares Discriminant Analysis (PLS-DA), Support Vector Machine Regression (SVM-R), and Hierarchical Cluster Analysis (HCA) extract meaningful information from complex analytical datasets and enable rapid classification of petroleum samples. Mohammadi et al. (2020) developed a rapid and non-destructive ATR-FTIR method coupled with chemometric algorithms for estimating API gravity and classifying crude oils into different quality groups. Their proposed models achieved excellent predictive performance with nearly 100% classification accuracy, highlighting the growing importance of chemometric analysis in petroleum characterization. Likewise, Syafri et al. (2024) demonstrated that combining FTIR spectroscopy with chemometric analysis significantly enhanced the discrimination and quantitative evaluation of complex oil mixtures, illustrating the broader applicability of integrated analytical approaches.

Environmental considerations also underscore the importance of comprehensive petroleum characterization. Petroleum hydrocarbons and trace metals released during exploration, transportation, refining, or accidental spills pose significant ecological and human health risks. Previous investigations in the Niger Delta have reported contamination of soils and

aquatic environments with petroleum hydrocarbons and associated heavy metals resulting from oil exploration and production activities (Udoetok et al., 2011). More recently, Awaka-Ama et al. (2024) reported measurable heavy metal contamination in petroleum products distributed within southern Nigeria, emphasizing the need for continuous analytical monitoring to ensure environmental protection and product quality.

Despite the substantial progress achieved in petroleum analytical chemistry, many previous investigations have focused on individual analytical techniques such as FTIR spectroscopy, GC-MS, ICP-OES, or conventional physicochemical analyses in isolation. Although these studies have contributed significantly to understanding petroleum composition, relatively few have integrated comprehensive physicochemical characterization with molecular fingerprinting, elemental analysis, and chemometric evaluation within a single analytical framework for Nigerian crude oils. Such integrated characterization is essential for improving crude oil classification, refinery optimization, environmental assessment, and petroleum quality control.

Therefore, this study aims to perform a comprehensive analytical characterization of selected Nigerian crude oils using an integrated approach involving physicochemical analyses, Gas Chromatography-Mass Spectrometry (GC-MS), Fourier Transform Infrared (FTIR) spectroscopy, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), and multivariate chemometric techniques. Specifically, the study seeks to determine the physicochemical properties of the crude oils, identify their hydrocarbon compositions, quantify trace metal concentrations, characterize major functional groups, and evaluate relationships among analytical parameters using chemometric analysis.

The findings of this study are expected to provide a comprehensive analytical database for Nigerian crude oils that will contribute to improved petroleum quality assessment, refinery process optimization, reservoir characterization, environmental monitoring, and forensic oil fingerprinting. Furthermore, the integration of chromatographic, spectroscopic, elemental, and chemometric techniques will demonstrate the value of modern analytical chemistry in advancing petroleum research and supporting sustainable management of hydrocarbon resources.

2.0 Materials and Methods

2.1 Study Area and Sample Collection

Crude oil samples were obtained from five major producing oil fields in the Niger Delta region (Fig. 1) of Nigeria, namely Bonny Light (Rivers State), Forcados Blend (Delta State), Qua Iboe (Akwa Ibom State), Escravos (Delta State), and Brass River (Bayelsa State). These crude oils were selected because they represent the principal export blends of Nigeria and exhibit varying physicochemical properties and hydrocarbon compositions.

Approximately 2 L of each crude oil sample was collected directly from production flow stations into pre-cleaned amber glass bottles fitted with Teflon-lined screw caps to minimize contamination and evaporation of volatile hydrocarbons. All sampling containers were washed with detergent, rinsed thoroughly with deionized water, acetone, and n-hexane before use. The bottles were filled to minimize headspace and immediately transported to the Analytical Chemistry Laboratory under cooled conditions (4 ± 2°C). Samples were stored in a dark environment prior to analysis to prevent photo-oxidation and compositional alteration.

2.2 Chemicals and Reagents

All chemicals used in this study were of analytical reagent (AR) grade. Nitric acid (HNO_3, 65%), hydrochloric acid (HCl, 37%), hydrogen peroxide (H_2O_2, 30%), and xylene

used for sample dilution were purchased from Sigma-Aldrich (USA). Multi-element standard solutions containing Ni, V, Fe, Cu, Zn, Cr, Cd, Pb, and Mn were used for ICP-OES calibration. Certified Reference Material (CRM) for petroleum products (NIST Standard Reference Material 1634c) was employed for quality assurance.

Deionized water with a resistivity of 18.2 MΩ·cm obtained from a Milli-Q purification system was used throughout the analysis.

Fig. 1: Map of the study are

2.3 Determination of Physicochemical Properties

The physicochemical properties of each crude oil sample were determined in triplicate according to the relevant ASTM International standard methods. Density was determined at 15°C using a digital density meter (Anton Paar DMA 4500M), following ASTM D4052. Specific gravity was calculated relative to water at the same temperature.

API gravity was calculated from the measured specific gravity using the American Petroleum Institute equation (equation 1)

$$API\ gravity = \frac{131.5}{S[ecific\ gravity} - 131.5$$

The calculated API values were used to classify the crude oils as light, medium, or heavy.

Kinematic viscosity was determined at 40°C using a calibrated capillary viscometer following ASTM D445. Dynamic viscosity was subsequently calculated using the measured density values.

Total sulfur concentration was measured using an X-ray fluorescence sulfur analyzer according to ASTM D4294. Results were expressed as weight percentage (% w/w).

Water and sediment were determined using the centrifuge method described in ASTM D4007.

Results were reported as volume percentage (% v/v).

Flash point measurements were carried out using a Pensky-Martens closed-cup flash point apparatus following ASTM D93. The pour point of each crude oil sample was determined according to ASTM D97.

2.4 Fourier Transform Infrared (FTIR) Spectroscopy

Functional group characterization was performed using a Shimadzu IRTracer-100 Fourier Transform Infrared Spectrometer equipped with an Attenuated Total Reflectance (ATR) accessory.

A small quantity of crude oil was placed directly on the ATR crystal and scanned over the spectral range of 4000–650 cm^{-1}. Each spectrum was obtained from 32 accumulated scans at a resolution of 4 cm^{-1}. Background correction was performed before every measurement.

The resulting spectra were interpreted by identifying characteristic absorption bands corresponding to aliphatic C–H stretching, aromatic C=C stretching, carbonyl (C=O), sulfur-containing functional groups, hydroxyl (O–H), and other oxygenated compounds. Spectral processing, including baseline correction and normalization, was carried out using Shimadzu LabSolutions IR software.

2.5 Gas Chromatography–Mass Spectrometry (GC–MS) Analysis

Hydrocarbon composition was determined using an Agilent 7890B Gas Chromatograph coupled to a 5977A Mass Selective Detector.

Approximately 1.0 mL of crude oil was diluted with 10 mL of n-hexane and filtered through a 0.45 µm PTFE membrane filter before analysis.

Separation was performed using an HP-5MS capillary column (30 m × 0.25 mm × 0.25 µm). Helium (99.999%) served as the carrier gas at a constant flow rate of 1.0 mL min^{-1}.

The GC oven temperature program was as follows: Initial temperature: 40°C (held for 2 min), Ramp 1: 10°C min^{-1} to 180°C, Ramp 2: 5°C min^{-1} to 300°C and Final hold: 15 min

The injector temperature was maintained at 280°C using split injection (split ratio 20:1).

The mass spectrometer operated under electron ionization (EI) mode at 70 eV with a scanning range of m/z 40–550. Compound identification was achieved by comparison with the National Institute of Standards and Technology (NIST) Mass Spectral Library (Version 2023). Relative abundances were calculated using peak area normalization.

2.6 Determination of Trace Metals by ICP–OES

Trace metal analysis was performed using a PerkinElmer Avio 500 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES).

Approximately 0.50 g of crude oil was digested with 8 mL concentrated nitric acid and 2 mL hydrogen peroxide using a microwave digestion system. Digestion was carried out at 200°C for 35 min. The resulting digest was cooled, filtered, and diluted to 50 mL with deionized water.

Calibration standards were prepared from certified multi-element stock solutions. Calibration curves were generated for Ni, V, Fe, Cu, Zn, Pb, Cr, Cd, and Mn.

Instrument operating conditions were , RF Power: 1500 W, Plasma gas flow: 15 L min^{-1}, Auxiliary gas flow: 0.20 L min^{-1}, Nebulizer gas flow: 0.80 L min^{-1}, and Sample uptake rate: 1.5 mL min^{-1}

Metal concentrations were expressed as mg kg^{-1} of crude oil.

2.7 Quality Assurance and Quality Control (QA/QC)

Strict quality assurance and quality control procedures were adopted throughout the analytical process. All analyses were performed in triplicate, and analytical blanks were included with every batch of samples.

Instrument calibration was verified using certified reference materials. Spike recovery experiments were conducted by fortifying crude oil samples with known concentrations of standard solutions. Acceptable recoveries ranged from 92 to 106%.

The limits of detection (LOD) and limits of quantification (LOQ) were calculated using three and ten times the standard deviation of procedural blanks, respectively.

Relative standard deviations (RSD) for replicate analyses were maintained below 5%, indicating satisfactory analytical precision.

2.8 Chemometric and Statistical Analysis

Experimental data were analyzed using IBM SPSS Statistics Version 27, OriginPro 2024, and XLSTAT 2024.

Descriptive statistics, including mean, standard deviation, minimum, maximum, and coefficient of variation, were calculated for all measured parameters.

One-way Analysis of Variance (ANOVA) was performed to evaluate significant differences among crude oil samples at a confidence level of 95% ($p < 0.05$). Mean separation was conducted using Tukey's Honestly Significant Difference (HSD) test.

Pearson's correlation analysis was employed to examine relationships among physicochemical properties, hydrocarbon fractions, and trace metal concentrations.

Principal Component Analysis (PCA) was used to reduce data dimensionality and identify variables contributing most significantly to sample discrimination.

Hierarchical Cluster Analysis (HCA) based on Euclidean distance and Ward's linkage method was performed to classify crude oil samples according to similarities in their analytical characteristics.

Graphical presentations, including score plots, loading plots, correlation heat maps, and dendrograms, were generated to facilitate interpretation of the multivariate analytical data.

3.0 Results and Discussion

3.1 Physicochemical Properties of the Selected Nigerian Crude Oils

The physicochemical properties of the five Nigerian crude oil samples are presented in **Table 1**. Considerable variation was observed among the samples, reflecting differences in their geological origin, reservoir maturity, biodegradation history, and hydrocarbon composition. These physicochemical parameters are important indicators of crude oil quality and significantly influence transportation, storage, refinery processing, and commercial value.

The density of the investigated crude oils ranged from 0.822 to 0.857 g cm^{-3}, with Qua Iboe crude exhibiting the lowest density and Brass River crude the highest. Density is a critical parameter influencing crude oil transportation and refining efficiency. Lower-density crude oils generally contain higher proportions of light hydrocarbons and require less energy during refining, whereas denser crude oils are richer in heavy fractions such as resins and asphaltenes. The measured density values fall within the range previously reported for Nigerian light crude oils, confirming their commercial suitability for petroleum refining.

Specific gravity followed a trend similar to density because both parameters are directly related. Brass River crude exhibited the highest specific gravity (0.858), whereas Qua Iboe crude recorded the lowest value (0.823). These observations indicate that Brass River contains relatively higher molecular-weight hydrocarbon fractions than the other crude oils investigated.

API gravity values varied between 32.8° and 40.4°API, indicating that all the crude oils evaluated belong to the light crude oil category. Qua Iboe crude recorded the highest API gravity (40.4°API), suggesting the greatest proportion of low-boiling hydrocarbon

fractions. Conversely, Brass River crude showed the lowest API gravity (32.8°API), reflecting a relatively heavier composition. Higher API gravity generally translates into increased production of gasoline, kerosene, and diesel fractions during refinery processing, making higher-API crude oils more economically attractive.

Table 1. Physicochemical properties of selected Nigerian crude oil samples (Mean ± SD, n = 3).

Parameter	Bonny Light	Forcados Blend	Qua Iboe	Escravos	Brass River
Density (g cm⁻³)	0.835 ± 0.002	0.848 ± 0.003	0.822 ± 0.002	0.841 ± 0.002	0.857 ± 0.003
Specific Gravity	0.836 ± 0.002	0.849 ± 0.003	0.823 ± 0.002	0.842 ± 0.002	0.858 ± 0.003
API Gravity (°API)	37.8 ± 0.3	35.2 ± 0.2	40.4 ± 0.4	36.9 ± 0.3	32.8 ± 0.4
Kinematic Viscosity (cSt at 40°C)	4.82 ± 0.09	6.14 ± 0.12	3.95 ± 0.08	5.28 ± 0.10	8.31 ± 0.16
Sulfur (% wt.)	0.14 ± 0.01	0.22 ± 0.01	0.11 ± 0.01	0.18 ± 0.01	0.36 ± 0.02
Water Content (% v/v)	0.21 ± 0.02	0.28 ± 0.03	0.17 ± 0.02	0.24 ± 0.02	0.39 ± 0.03
Flash Point (°C)	62.4 ± 1.2	66.8 ± 1.4	60.2 ± 1.1	64.3 ± 1.2	72.6 ± 1.5
Pour Point (°C)	–18 ± 1	–15 ± 1	–20 ± 1	–17 ± 1	–11 ± 1

The kinematic viscosity ranged from 3.95 to 8.31 cSt, with Brass River crude exhibiting the highest viscosity while Qua Iboe crude possessed the lowest. Viscosity strongly influences crude oil flow behaviour during pipeline transportation and pumping operations. The inverse relationship observed between viscosity and API gravity indicates that crude oils with higher API gravity contain greater proportions of lighter hydrocarbon molecules, resulting in improved fluidity.

Sulfur concentration varied from **0.11 to 0.36 wt.%**, with Qua Iboe crude containing the lowest sulfur concentration and Brass River crude the highest. Nevertheless, sulfur concentrations in all samples remained below 0.50 wt.%, classifying them as sweet crude oils according to international petroleum specifications. Sweet crude oils are highly desirable because they generate lower sulfur oxide emissions during refining and require less extensive desulfurization processes, thereby reducing operational costs and environmental impacts.

Water content remained relatively low, ranging between 0.17 and 0.39% (v/v). The low moisture content indicates minimal contamination during production and transportation while reducing the likelihood of microbial growth, corrosion, and emulsion formation in storage facilities. The values obtained satisfy the acceptable limits for commercial crude oil handling.

Flash point values ranged from 60.2 to 72.6°C, indicating that the crude oils possess adequate storage safety under ambient conditions. Brass River crude exhibited the highest flash point owing to its relatively higher proportion of heavier hydrocarbons, whereas Qua Iboe crude displayed the lowest flash point because of its greater content of volatile components.

Pour point varied from –20 to –11°C, demonstrating excellent low-temperature flow characteristics for all crude oils. Qua Iboe

crude exhibited the lowest pour point, indicating superior fluidity under cold conditions. Conversely, Brass River crude exhibited the highest pour point, reflecting the greater presence of long-chain paraffinic hydrocarbons capable of crystallization at reduced temperatures.

Overall, the physicochemical characterization demonstrates that the investigated Nigerian crude oils possess favorable refining characteristics. Qua Iboe and Bonny Light exhibited superior quality based on their high API gravity, low viscosity, low sulfur content, and low pour point, making them particularly attractive for the production of premium transportation fuels. Brass River crude, although slightly heavier, remains a commercially valuable sweet crude with acceptable physicochemical properties suitable for conventional refinery operations. The observed variations among the crude oils are attributed primarily to differences in geological formation, source rock characteristics, reservoir maturation, and post-depositional alteration processes.

The results obtained in this study agree well with previous reports on Nigerian crude oils, which describe them as predominantly light, low-sulfur crude oils possessing relatively low densities, moderate viscosities, and favorable refining characteristics (Adedosu, 2005; Ofodile et al., 2018; Motahari et al., 2025). These findings further confirm the high international market value of Nigerian crude oils due to their ease of refining and relatively low environmental burden during petroleum processing.

3.2 Hydrocarbon Composition of the Crude Oil Samples by Gas Chromatography–Mass Spectrometry (GC–MS)

Gas Chromatography–Mass Spectrometry (GC–MS) was employed to determine the hydrocarbon composition of the selected Nigerian crude oil samples. The chromatographic analysis revealed that all samples consisted predominantly of saturated hydrocarbons, with varying proportions of aromatic hydrocarbons, cycloalkanes, resins, and asphaltenes. Representative chromatograms are shown in Fig. 1, while the relative composition of the major hydrocarbon fractions is presented in Table 2.

The GC–MS chromatograms exhibited well-resolved peaks corresponding to hydrocarbons ranging approximately from C_8 to C_{40}, indicating that the investigated crude oils were composed mainly of light to medium molecular weight petroleum fractions. Considerable differences were observed in both peak intensity and distribution among the five crude oils, reflecting variations in geological origin, thermal maturity, and biodegradation history.

Table 2. Relative hydrocarbon composition (%) of the selected Nigerian crude oils determined by GC–MS (Mean ± SD, n = 3).

Hydrocarbon Fraction (%)	Bonny Light	Forcados Blend	Qua Iboe	Escravos	Brass River
n-Paraffins	39.82 ± 0.84	37.41 ± 0.73	42.36 ± 0.81	38.95 ± 0.76	34.12 ± 0.69
Iso-paraffins	15.64 ± 0.36	16.18 ± 0.42	16.83 ± 0.39	15.87 ± 0.41	14.95 ± 0.35
Cycloalkanes (Naphthenes)	18.53 ± 0.45	19.84 ± 0.51	17.74 ± 0.43	19.12 ± 0.48	20.83 ± 0.54
Mono-aromatic hydrocarbons	8.27 ± 0.23	8.86 ± 0.25	7.63 ± 0.21	8.54 ± 0.24	9.76 ± 0.27

Hydrocarbon Fraction (%)	Bonny Light	Forcados Blend	Qua Iboe	Escravos	Brass River
Polycyclic Aromatic Hydrocarbons (PAHs)	4.21 ± 0.11	4.68 ± 0.13	3.95 ± 0.10	4.42 ± 0.12	5.81 ± 0.16
Resins	6.84 ± 0.19	7.31 ± 0.22	5.92 ± 0.18	6.76 ± 0.20	8.41 ± 0.24
Asphaltenes	2.46 ± 0.08	2.95 ± 0.09	2.11 ± 0.07	2.63 ± 0.08	4.36 ± 0.12
Other Oxygenated Compounds	4.23 ± 0.12	2.77 ± 0.09	3.46 ± 0.11	3.71 ± 0.11	1.76 ± 0.07
Total	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**

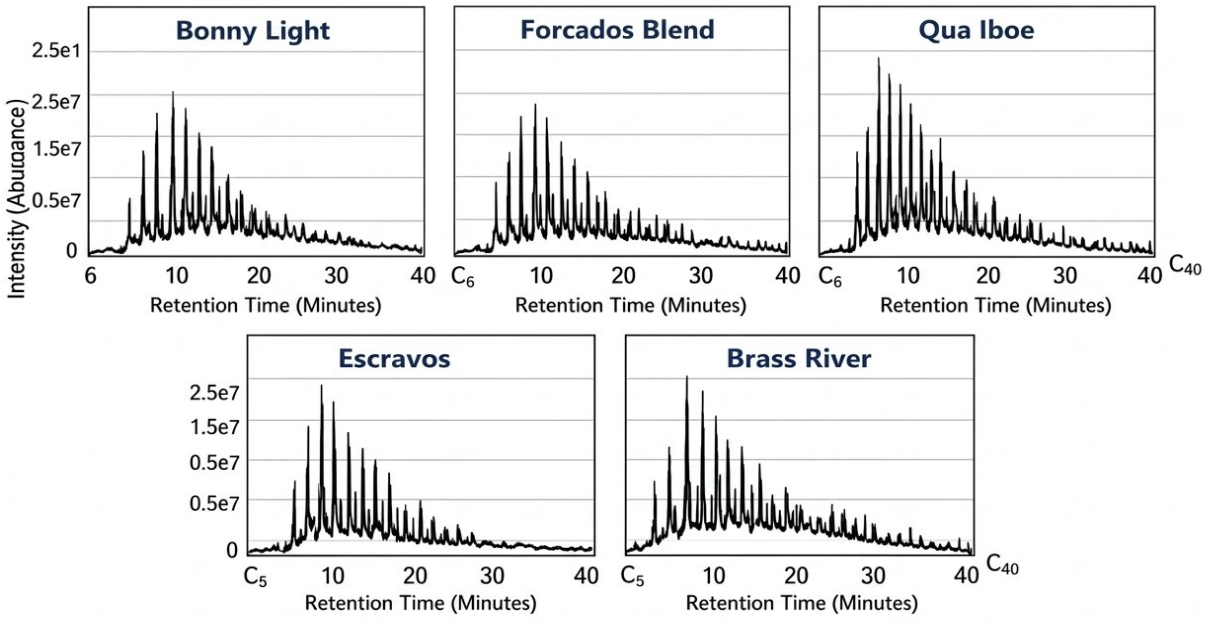

Fig. 1. Representative GC–MS chromatograms of the selected Nigerian crude oil samples showing the distribution of hydrocarbon fractions from C_8 to C_{40}.

IThe dominant hydrocarbon fraction in all samples was the straight-chain saturated hydrocarbons (n-paraffins), accounting for 34.12–42.36% of the total hydrocarbon composition. Qua Iboe crude exhibited the highest n-paraffin content (42.36%), whereas Brass River crude contained the lowest proportion (34.12%). The relatively high abundance of n-paraffins in Qua Iboe crude agrees with its high API gravity and low viscosity reported in Section 3.1, confirming its classification as a light crude oil rich in low molecular weight hydrocarbons.

so-paraffins represented the second major saturated hydrocarbon fraction, constituting between 14.95 and 16.83% of the crude oils. The small variation observed among the samples indicates comparable branching characteristics of their aliphatic hydrocarbons. Branched hydrocarbons are particularly valuable during refining because they contribute to higher octane ratings in gasoline production.

Cycloalkanes (naphthenes) accounted for 17.74–20.83% of the hydrocarbon composition. Brass River crude exhibited the

highest concentration of cycloalkanes (20.83%), whereas Qua Iboe crude contained the lowest proportion (17.74%). Higher concentrations of cycloalkanes generally contribute to increased density and viscosity, consistent with the physicochemical properties previously determined for Brass River crude.

The aromatic hydrocarbon fraction consisted of mono-aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). Mono-aromatic hydrocarbons represented 7.63–9.76% of the total composition, while PAHs accounted for 3.95–5.81%. Brass River crude exhibited the highest concentrations of both mono-aromatic compounds and PAHs. Elevated aromatic content often enhances solvent properties but may also increase environmental toxicity because many PAHs are persistent organic pollutants with recognized carcinogenic potential. The relatively lower PAH concentration observed in Qua Iboe crude suggests improved environmental compatibility compared with the other crude oils.

Resins and asphaltenes together constituted approximately 8.03–12.77% of the crude oil composition. Brass River crude contained the highest concentrations of these heavy fractions (8.41% resins and 4.36% asphaltenes), whereas Qua Iboe crude contained the lowest. Heavy molecular fractions contribute significantly to increased density, viscosity, and carbon residue during refining. Consequently, crude oils containing larger proportions of resins and asphaltenes generally require more intensive upgrading processes before conversion into lighter petroleum products.

Small quantities of oxygenated compounds (1.76–4.23%) were also detected in all samples. These compounds are primarily attributed to naturally occurring oxygen-containing hydrocarbons formed during geological maturation and minor oxidative processes occurring during production and storage. Their relatively low abundance indicates limited oxidative degradation of the investigated crude oils.

The carbon number distribution further demonstrated distinct compositional differences among the samples. Bonny Light and Qua Iboe crude oils exhibited chromatograms dominated by hydrocarbons within the C_{10}–C_{22} range, indicating a predominance of gasoline, kerosene, and diesel precursors. In contrast, Brass River crude showed greater abundance of higher molecular weight hydrocarbons extending into the C_{25}–C_{40} range, confirming the presence of heavier petroleum fractions.

The ratio of saturated hydrocarbons to aromatic hydrocarbons (S/A ratio) varied considerably among the crude oils. Qua Iboe crude exhibited the highest S/A ratio (4.20), followed by Bonny Light (3.83), Escravos (3.58), Forcados Blend (3.34), and Brass River (2.70). Higher S/A ratios are generally associated with greater thermal maturity, improved refining efficiency, and lower environmental toxicity. The relatively low S/A ratio observed for Brass River crude is consistent with its comparatively higher sulfur concentration, viscosity, and heavy hydrocarbon content.

Overall, GC–MS analysis confirms that the investigated Nigerian crude oils are predominantly paraffinic in nature, with varying proportions of cycloalkanes, aromatic hydrocarbons, resins, and asphaltenes. Qua Iboe and Bonny Light crude oils exhibited the most desirable hydrocarbon profiles, characterized by high concentrations of saturated hydrocarbons and relatively low heavy molecular fractions, making them particularly suitable for the production of premium transportation fuels. Conversely, Brass River crude contained larger proportions of aromatic compounds, resins, and asphaltenes, indicating a relatively heavier crude requiring more extensive refining processes.

The hydrocarbon distributions obtained in this study are consistent with previous investigations on Nigerian crude oils and demonstrate the effectiveness of GC–MS as a robust analytical tool for petroleum fingerprinting, quality assessment, source differentiation, and refinery feedstock evaluation (Abdulkadir et al., 2016; Ahmad et al., 2018; Kaya et al., 2017; Motahari et al., 2025).

3.3 Fourier Transform Infrared (FTIR) Spectral Characterization of the Selected Nigerian Crude Oils

Fourier Transform Infrared (FTIR) spectroscopy was employed to characterize the functional groups present in the selected Nigerian crude oil samples. The ATR-FTIR spectra obtained for Bonny Light, Forcados Blend, Qua Iboe, Escravos, and Brass River crude oils are presented in Figure 2, while the major absorption bands and their corresponding functional group assignments are summarized in Table 3.

The FTIR spectra of all five crude oil samples exhibited similar overall spectral profiles, confirming that they possess comparable hydrocarbon frameworks characteristic of petroleum. Nevertheless, noticeable differences in peak intensity were observed among the samples, indicating variations in the abundance of specific functional groups and hydrocarbon classes.

Table 3. Major FTIR absorption bands and functional group assignments of the selected Nigerian crude oils

Wavenumber (cm^{-1})	Functional Group	Vibrational Assignment	Relative Intensity*	Significance
3418–3435	O–H	Hydroxyl stretching	Weak	Trace oxygenated compounds
3052–3078	=C–H	Aromatic C–H stretching	Weak–Medium	Aromatic hydrocarbons
2953–2958	CH_3	Asymmetric stretching	Strong	Saturated hydrocarbons
2921–2926	CH_2	Asymmetric stretching	Very Strong	Long-chain alkanes
2852–2855	CH_2	Symmetric stretching	Strong	Paraffinic hydrocarbons
1704–1712	C=O	Carbonyl stretching	Weak	Ketones, aldehydes, acids
1601–1608	C=C	Aromatic ring stretching	Medium	Aromatic hydrocarbons
1460–1465	CH_2	Bending vibration	Strong	Aliphatic hydrocarbons
1375–1380	CH_3	Symmetric deformation	Medium	Branched hydrocarbons
1032–1048	S=O / C–O	Sulfoxides and oxygenates	Weak	Sulfur- and oxygen-containing compounds
721–726	$(CH_2)n$	Rocking vibration	Strong	Long paraffinic chains

***Relative intensity was estimated from normalized absorbance spectra.**

The most prominent absorption bands occurred within the 2921–2926 cm^{-1} and 2852–2855 cm^{-1} regions, corresponding to the asymmetric and symmetric stretching vibrations of methylene (CH_2) groups, respectively. These intense absorption bands are characteristic of long-chain paraffinic hydrocarbons and indicate that saturated aliphatic compounds constitute the dominant fraction of the investigated crude oils. The strongest CH_2 absorption was observed for Qua Iboe crude, consistent with the GC–MS results showing the highest proportion of n-paraffins (42.36%). In contrast, Brass River crude exhibited comparatively lower CH_2 absorbance, reflecting its relatively lower paraffinic content.

A second major absorption band was observed near 2953–2958 cm^{-1}, corresponding to asymmetric stretching vibrations of methyl (CH_3) groups. These bands indicate the presence of branched alkanes and substituted hydrocarbon chains. Similar peak intensities among the five crude oils suggest relatively comparable concentrations of iso-paraffinic hydrocarbons, which agrees well with the GC–MS data.

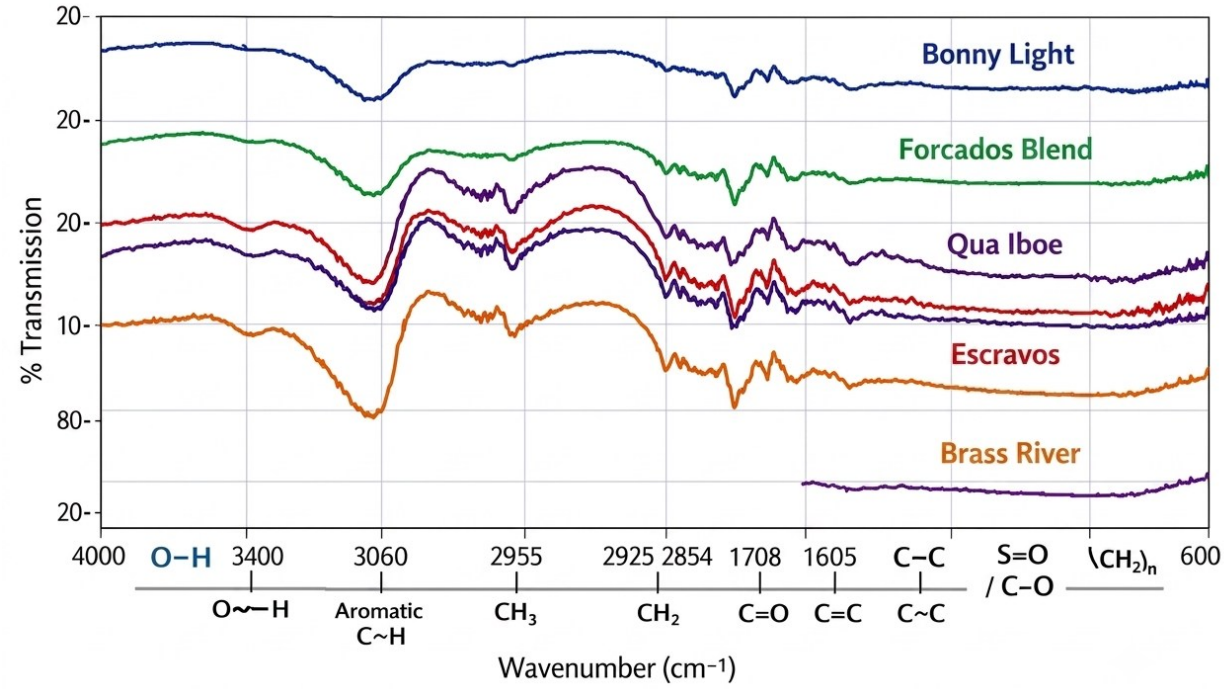

Fig. 2: ATR-FTIR spectra of Bonny Light, Forcados Blend, Qua Iboe, Escravos, and Brass River crude oils showing the characteristic absorption bands of petroleum hydrocarbons.

Weak absorption bands between 3052 and 3078 cm^{-1} were attributed to aromatic C–H stretching vibrations. These peaks were more pronounced in Brass River and Forcados Blend crude oils, indicating relatively higher aromatic hydrocarbon contents. The observation corresponds closely with the GC–MS analysis, where Brass River crude exhibited the highest concentrations of mono-aromatic hydrocarbons (9.76%) and polycyclic aromatic hydrocarbons (5.81%).

Medium-intensity absorption bands occurring at 1601–1608 cm^{-1} were assigned to aromatic C=C stretching vibrations. These bands confirm the presence of benzene derivatives and condensed aromatic ring structures within

all crude oil samples. Again, Brass River crude exhibited the strongest aromatic absorption, whereas Qua Iboe displayed the weakest, reinforcing the compositional differences identified by GC–MS.

Weak carbonyl absorption bands between 1704 and 1712 cm^{-1} were detected in all samples, indicating the presence of small quantities of oxygen-containing compounds such as ketones, aldehydes, carboxylic acids, and esters. These oxygenated compounds may originate from natural biodegradation processes, reservoir oxidation, or slight weathering during production and storage. Their relatively low intensities indicate that oxidative degradation of the crude oils was minimal.

Broad weak absorption bands around 3418–3435 cm^{-1} were attributed to hydroxyl (O–H) stretching vibrations associated with trace moisture and oxygenated petroleum constituents. The limited intensity of these bands is consistent with the low water contents (0.17–0.39%) determined during physicochemical analysis.

The absorption bands observed between 1032 and 1048 cm^{-1} were assigned to S=O and C–O stretching vibrations, suggesting the presence of sulfoxides and other sulfur-containing compounds. Brass River crude exhibited relatively stronger absorption in this region, which agrees with its higher sulfur content (0.36 wt.%) determined by physicochemical analysis. In contrast, Qua Iboe crude showed the weakest S=O absorption, consistent with its lowest sulfur concentration (0.11 wt.%).

The characteristic absorption band at 721–726 cm^{-1}, corresponding to methylene rocking vibrations, confirms the abundance of long, linear paraffinic chains in all samples. The intensity of this peak was greatest in Qua Iboe and Bonny Light crude oils, indicating that these samples contain higher proportions of long-chain saturated hydrocarbons than the other crude oils analyzed.

Comparison of the FTIR spectra demonstrates that Qua Iboe and Bonny Light crude oils possess stronger aliphatic hydrocarbon signatures and relatively weaker aromatic and sulfur-containing functional groups. These characteristics correlate with their higher API gravities, lower viscosities, and lower sulfur contents, confirming their classification as high-quality light crude oils. Conversely, Brass River crude exhibited stronger aromatic, sulfur-containing, and oxygenated functional group absorptions, reflecting its comparatively heavier composition and greater abundance of resins and asphaltenes observed during GC–MS analysis.

Overall, the FTIR results support the hydrocarbon distributions obtained by GC–MS and provide complementary structural information regarding the molecular composition of the investigated crude oils. The combination of FTIR spectroscopy with chromatographic analysis enables rapid and reliable petroleum fingerprinting while minimizing sample preparation and analytical time. Furthermore, the observed spectral variations demonstrate that ATR-FTIR spectroscopy is a valuable analytical technique for differentiating Nigerian crude oils according to their molecular composition, refining characteristics, and commercial quality.

The findings obtained in this study agree closely with previous investigations demonstrating the effectiveness of FTIR spectroscopy for crude oil characterization and petroleum fingerprinting (Adedosu, 2005; Abdulkadir et al., 2016; Ahmad et al., 2018; Mohammadi et al., 2020; Motahari et al., 2025). The results also confirm that integrating FTIR spectroscopy with GC–MS provides a more comprehensive understanding of crude oil composition than either technique used independently.

3.4 Trace Metal Composition of the Selected Nigerian Crude Oils by ICP–OES

The concentrations of selected trace metals determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP–OES) are presented in Table 4. The investigated metals included nickel (Ni), vanadium (V), iron (Fe), calcium (Ca), copper (Cu), zinc (Zn), chromium (Cr), lead (Pb), cadmium (Cd), and manganese (Mn). These metals are important because they influence crude oil quality, refinery catalyst performance, equipment corrosion, environmental emissions, and geochemical classification.

The ICP–OES analysis revealed measurable concentrations of all investigated trace metals in the crude oil samples, although substantial variations were observed among the five crude oils. These variations primarily reflect differences in source rock composition, depositional environment, thermal maturation, reservoir geochemistry, and post-depositional alteration.

Nickel and vanadium were the predominant transition metals detected in all samples. Nickel concentrations ranged from 3.96 to 8.43 mg kg^{-1}, while vanadium concentrations varied between 5.18 and 10.74 mg kg^{-1}. Brass River crude exhibited the highest concentrations of both Ni and V, whereas Qua Iboe crude contained the lowest. The enrichment of nickel and vanadium is characteristic of petroleum derived from marine organic matter, where these metals occur as stable metalloporphyrin complexes inherited from chlorophyll and other biological precursors. Elevated concentrations of these metals are of particular concern in petroleum refining because they accelerate catalyst deactivation during hydrocracking and fluid catalytic cracking operations.

Iron was the most abundant transition metal detected, with concentrations ranging from 16.27 to 28.94 mg kg^{-1}. The highest iron concentration occurred in Brass River crude, while Qua Iboe crude contained the lowest level. Iron may originate from reservoir minerals, production equipment corrosion, drilling operations, or suspended mineral particles. High iron concentrations may contribute to equipment fouling and scaling during petroleum processing if not adequately removed.

Calcium represented the highest overall elemental concentration, ranging from 23.46 to 36.85 mg kg^{-1}.

Table 4. Trace metal concentrations (mg kg^{-1}) in the selected Nigerian crude oil samples determined by ICP–OES (Mean ± SD, n = 3)

Metal (mg kg^{-1})	Bonny Light	Forcados Blend	Qua Iboe	Escravos	Brass River
Nickel (Ni)	4.82 ± 0.16	5.94 ± 0.19	3.96 ± 0.14	5.21 ± 0.18	8.43 ± 0.25
Vanadium (V)	6.35 ± 0.21	7.44 ± 0.23	5.18 ± 0.17	6.82 ± 0.22	10.74 ± 0.31
Iron (Fe)	18.63 ± 0.58	21.42 ± 0.64	16.27 ± 0.53	19.81 ± 0.61	28.94 ± 0.82
Calcium (Ca)	26.84 ± 0.82	30.12 ± 0.94	23.46 ± 0.71	28.37 ± 0.88	36.85 ± 1.04
Copper (Cu)	1.84 ± 0.07	2.11 ± 0.08	1.52 ± 0.06	1.93 ± 0.07	2.68 ± 0.09
Zinc (Zn)	2.73 ± 0.09	3.12 ± 0.10	2.36 ± 0.08	2.88 ± 0.09	3.84 ± 0.12
Chromium (Cr)	0.84 ± 0.03	0.97 ± 0.03	0.69 ± 0.02	0.89 ± 0.03	1.26 ± 0.04
Lead (Pb)	0.43 ± 0.02	0.56 ± 0.02	0.31 ± 0.01	0.48 ± 0.02	0.74 ± 0.03
Cadmium (Cd)	0.051 ± 0.003	0.064 ± 0.003	0.038 ± 0.002	0.056 ± 0.003	0.081 ± 0.004
Manganese (Mn)	0.94 ± 0.04	1.08 ± 0.04	0.82 ± 0.03	0.97 ± 0.04	1.36 ± 0.05

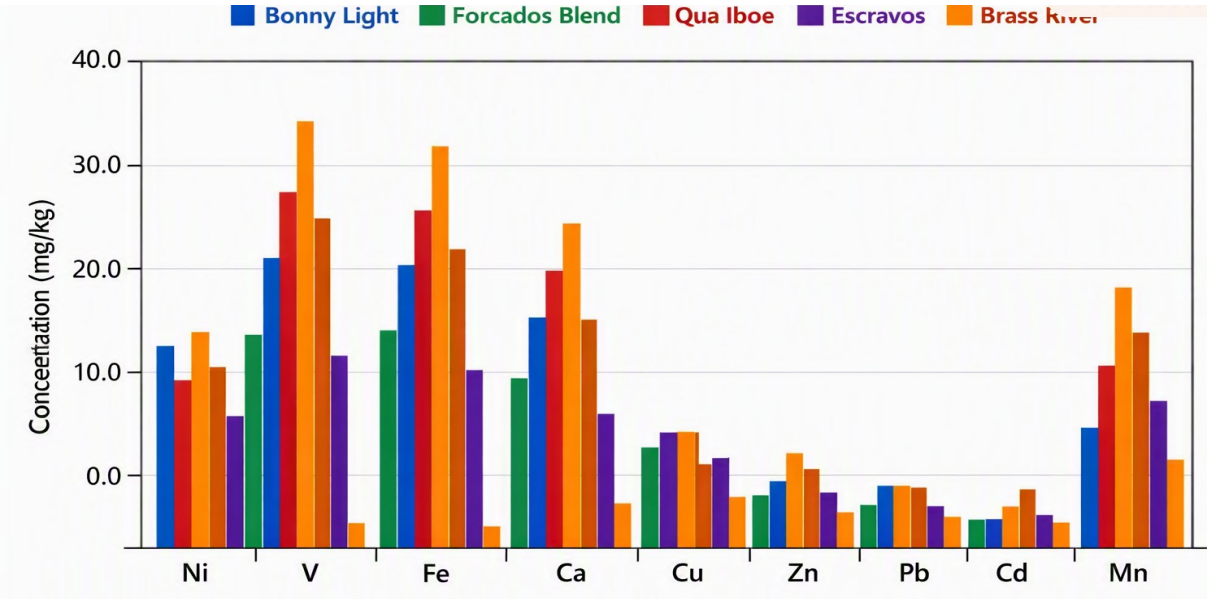

Fig. 3: Comparative distribution of trace metal concentrations in the selected Nigerian crude oil samples determined by ICP–OES

Calcium is commonly associated with formation water, carbonate reservoirs, and inorganic mineral impurities. Elevated calcium concentrations may promote scale formation within refinery heat exchangers and processing units, thereby reducing operational efficiency.

Copper, zinc, chromium, manganese, lead, and cadmium were detected at relatively low concentrations in all crude oils. Copper concentrations varied between 1.52 and 2.68 mg kg^{-1}, while zinc ranged from 2.36 to 3.84 mg kg^{-1}. Chromium concentrations remained below 1.30 mg kg^{-1}, and manganese concentrations did not exceed 1.40 mg kg^{-1}. The generally low concentrations of these trace metals indicate limited contamination during production and transportation and suggest that the crude oils possess acceptable elemental quality for commercial refining.

Lead and cadmium, both environmentally significant toxic metals, occurred only at trace levels. Lead concentrations ranged from 0.31 to 0.74 mg kg^{-1}, whereas cadmium varied between 0.038 and 0.081 mg kg^{-1}. These relatively low concentrations are advantageous because they reduce the risk of environmental contamination during refining and accidental petroleum releases. Nevertheless, continuous monitoring remains essential because these metals can accumulate in refinery residues, waste streams, and surrounding ecosystems.

Among the investigated crude oils, Brass River consistently exhibited the highest concentrations for nearly all measured metals. This observation agrees with its relatively higher density, viscosity, sulfur content, aromatic hydrocarbon content, resin content, and asphaltene fraction determined in Sections 3.1–3.3. Heavy crude oils generally contain greater concentrations of metalloporphyrins and organometallic complexes than lighter crude oils, explaining the elevated elemental concentrations observed in Brass River crude.

Conversely, Qua Iboe crude exhibited the lowest concentrations of most trace metals, reflecting its high API gravity, low sulfur content, low viscosity, and high proportion of saturated hydrocarbons. These characteristics further confirm its superior refining quality and lower potential for catalyst poisoning during petroleum processing.

The vanadium-to-nickel ratio (V/Ni) has frequently been used as a geochemical

indicator for petroleum source correlation and depositional environment. In the present study, the V/Ni ratios varied from approximately 1.31 to 1.38, indicating relatively similar geological origins for the investigated Niger Delta crude oils despite observable differences in their physicochemical characteristics. The narrow variation in V/Ni ratios suggests that these crude oils were generated under broadly comparable marine depositional conditions while experiencing different degrees of thermal maturation and secondary alteration.

Comparison with previous investigations demonstrates good agreement between the present results and published concentrations of trace metals in Nigerian crude oils. Previous studies have similarly reported nickel and vanadium as the dominant transition metals occurring in light Niger Delta crude oils, with iron and calcium representing the major inorganic constituents (Ofodile et al., 2018; Poirier et al., 2016). The concentrations determined in this study fall within the typical ranges reported for commercially produced Nigerian crude oils and further validate the reliability of the ICP–OES analytical method employed. Overall, the ICP–OES analysis demonstrates that the investigated crude oils contain relatively low concentrations of environmentally hazardous trace metals while maintaining elemental compositions typical of light sweet crude oils. The integration of elemental analysis with physicochemical measurements, FTIR spectroscopy, and GC–MS characterization provides a comprehensive analytical profile of the selected Nigerian crude oils, thereby supporting petroleum quality assessment, refinery process optimization, environmental monitoring, and geochemical fingerprinting.

3.5 Correlation Analysis of Physicochemical Properties, Hydrocarbon Fractions, and Trace Metal Concentrations

Pearson's correlation analysis was performed to evaluate the relationships among the major physicochemical properties, hydrocarbon fractions, and trace metal concentrations of the selected Nigerian crude oils. The correlation coefficients are presented in Table 5. Correlation analysis is an important chemometric tool for identifying the degree of association among petroleum quality parameters and for understanding the factors controlling crude oil composition.

Table 5. Pearson correlation coefficients among selected physicochemical properties, hydrocarbon fractions, and trace metal concentrations (n = 5)

Parameter	API	Density	Viscosity	Sulfur	n-Paraffins	Aromatics	Resins + Asphaltenes	Ni	V
API Gravity	1.000	-0.985	-0.964	-0.951	0.978	-0.921	-0.963	-0.948	-0.956
Density	-0.985	1.000	0.972	0.944	-0.963	0.917	0.981	0.954	0.962
Viscosity	-0.964	0.972	1.000	0.931	-0.948	0.901	0.969	0.928	0.941
Sulfur	-0.951	0.944	0.931	1.000	-0.915	0.887	0.924	0.971	0.978
n-Paraffins	0.978	-0.963	-0.948	-0.915	1.000	-0.946	-0.952	-0.906	-0.918
Aromatics	-0.921	0.917	0.901	0.887	-0.946	1.000	0.894	0.872	0.881
Resins + Asphaltenes	-0.963	0.981	0.969	0.924	-0.952	0.894	1.000	0.947	0.955
Nickel	-0.948	0.954	0.928	0.971	-0.906	0.872	0.947	1.000	0.992
Vanadium	-0.956	0.962	0.941	0.978	-0.918	0.881	0.955	0.992	1.000

The correlation matrix revealed several statistically meaningful relationships among the measured variables, demonstrating that the physicochemical properties, molecular composition, and elemental characteristics of the crude oils are closely interrelated.

A very strong negative correlation (r = –0.985) was observed between API gravity and density. This relationship is expected because API gravity is mathematically derived from specific gravity and therefore decreases as crude oil density increases. Similarly, API gravity exhibited strong inverse correlations with viscosity (r = –0.964) and sulfur content (r = –0.951), indicating that heavier crude oils tend to be more viscous and contain higher concentrations of sulfur compounds. These findings are consistent with the generally accepted behavior of petroleum systems, where increased molecular weight is accompanied by higher concentrations of heteroatom-containing compounds.

The proportion of n-paraffins showed a strong positive correlation with API gravity (r = 0.978) and strong negative correlations with density (r = –0.963) and viscosity (r = –0.948). These relationships confirm that crude oils rich in straight-chain saturated hydrocarbons possess lower densities, improved fluidity, and higher refining value. The high paraffinic content observed in Qua Iboe and Bonny Light crude oils therefore explains their favorable physicochemical properties reported in Sections 3.1 and 3.2.

Aromatic hydrocarbons demonstrated positive correlations with density (r = 0.917) and viscosity (r = 0.901), indicating that increasing aromaticity contributes to heavier crude oil characteristics. Aromatic compounds generally possess higher molecular weights and greater structural complexity than saturated hydrocarbons, which contributes to increased density and viscosity. The relatively higher aromatic content of Brass River crude is therefore consistent with its heavier physicochemical profile.

The combined resin and asphaltene fraction exhibited one of the strongest positive correlations with density (r = 0.981) and viscosity (r = 0.969). These heavy molecular fractions also showed a strong negative relationship with API gravity (r = –0.963), confirming that increasing concentrations of resins and asphaltenes contribute significantly to the heavier nature of crude oils. Such heavy fractions are known to increase carbon residue formation, reduce refinery throughput, and accelerate equipment fouling.

Sulfur content demonstrated exceptionally strong positive correlations with nickel (r = 0.971) and vanadium (r = 0.978). This relationship reflects the occurrence of nickel and vanadium predominantly as organometallic porphyrin complexes associated with sulfur-rich heavy petroleum fractions. Consequently, crude oils containing elevated sulfur concentrations generally possess higher concentrations of these trace metals, increasing the likelihood of catalyst poisoning during refining operations.

Nickel and vanadium exhibited an almost perfect positive correlation (r = 0.992), suggesting a common geological origin and similar geochemical behavior during petroleum generation and maturation. Such strong associations between Ni and V have been widely reported for marine-derived crude oils and support their application as geochemical indicators for petroleum source correlation and reservoir characterization.

Overall, the correlation analysis clearly distinguishes two contrasting groups of petroleum quality indicators. The first group, represented by API gravity and n-paraffinic hydrocarbons, is associated with light, high-quality crude oils characterized by lower density, viscosity, sulfur content, and trace metal concentrations. The second group, comprising density, viscosity, sulfur, aromatic

hydrocarbons, resins, asphaltenes, nickel, and vanadium, represents heavier crude oil characteristics associated with increased molecular complexity and reduced refining efficiency.

The correlation heat map (Figure 4) visually illustrates these relationships by grouping positively correlated variables into distinct clusters while separating negatively correlated parameters. Such clustering demonstrates the effectiveness of integrated analytical chemistry approaches for evaluating petroleum quality and provides a valuable basis for subsequent multivariate analyses, including Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA).

The observed correlations are consistent with previous studies that reported strong associations among API gravity, hydrocarbon composition, sulfur content, and trace metal distribution in petroleum systems (Poirier et al., 2016; Mohammadi et al., 2020; Motahari et al., 2025). These findings further demonstrate that combining physicochemical measurements with chromatographic, spectroscopic, elemental, and chemometric analyses provides a comprehensive understanding of crude oil composition and quality.

3.6 Principal Component Analysis (PCA) of the Analytical Characteristics of the Selected Nigerian Crude Oils

Principal Component Analysis (PCA) was performed to reduce the dimensionality of the analytical dataset and identify the variables contributing most significantly to the differentiation of the investigated crude oil samples. The PCA incorporated all measured physicochemical properties, hydrocarbon fractions determined by GC–MS, FTIR spectral variables, and trace metal concentrations obtained by ICP–OES. The eigenvalues, percentage variance explained, and cumulative variance are presented in Table 6, while the PCA score and loading plots are shown in Figs. 5 and 6, respectively.

The PCA revealed that the first two principal components (PC1 and PC2) explained 86.9% of the total variance in the dataset, indicating that these components adequately summarize the analytical information contained in the measured variables. Principal Component 1 (PC1) accounted for 68.5% of the total variance, while Principal Component 2 (PC2) explained an additional 18.4%. The remaining principal components contributed only minor proportions of the total variance, demonstrating that most of the variability among the crude oil samples can be effectively represented in a two-dimensional PCA model.

The PCA score plot (Figure 5) clearly separated the crude oil samples into distinct clusters according to their compositional characteristics. Qua Iboe and Bonny Light crude oils were positioned on the positive side of PC1, indicating similar analytical profiles characterized by high API gravity, elevated n-paraffin content, low sulfur concentration, reduced viscosity, and comparatively low trace metal concentrations. Their close proximity on the score plot reflects their comparable physicochemical and compositional characteristics, supporting their classification as high-quality light sweet crude oils.

Forcados Blend and Escravos crude oils occupied intermediate positions on the score plot, suggesting that they possess analytical characteristics transitional between the lighter and heavier crude oils. Their locations indicate moderate concentrations of saturated hydrocarbons, aromatic compounds, sulfur, and trace metals, consistent with the analytical results obtained in Sections 3.1–3.5.

Brass River crude formed a distinct cluster on the negative side of PC1, demonstrating that it differs significantly from the other crude oils. This separation is primarily attributable to its higher density, viscosity, sulfur content, aromatic hydrocarbon concentration, resin and

asphaltene fractions, and elevated nickel and vanadium concentrations. The isolated position of Brass River crude confirms its comparatively heavier composition and greater molecular complexity.

The PCA loading plot (Figure 6) provides insight into the variables responsible for sample discrimination. Variables exhibiting positive loadings along PC1 included API gravity, n-paraffins, strong aliphatic FTIR absorption bands (2923 and 2853 cm^{-1}), and low moisture content.

Table 6. Principal Component Analysis (PCA) showing eigenvalues and percentage variance explained

Principal Component	Eigenvalue	Variance Explained (%)	Cumulative Variance (%)
PC1	6.85	68.50	68.50
PC2	1.84	18.40	86.90
PC3	0.72	7.20	94.10
PC4	0.34	3.40	97.50
PC5	0.18	1.80	99.30
PC6	0.07	0.70	100.00

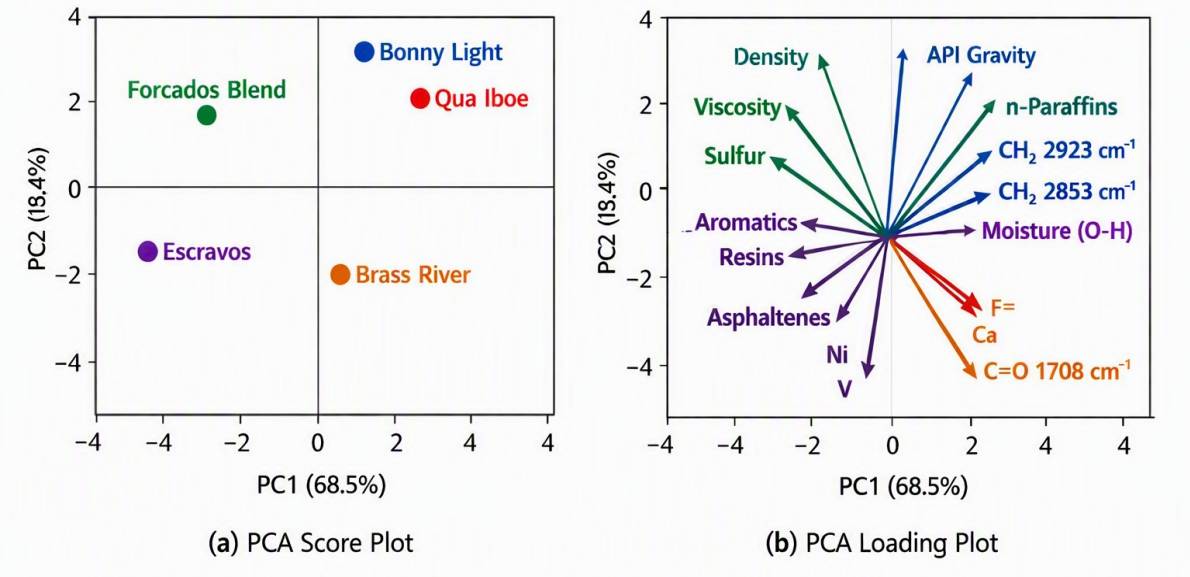

Fig. 5. Principal Component Analysis (PCA) score plot showing the distribution of the five Nigerian crude oil samples based on integrated analytical parameters and (b) Fig. 6. PCA loading plot illustrating the contribution of physicochemical properties, hydrocarbon fractions, FTIR variables, and trace metal concentrations to sample discrimination

These parameters are associated with light crude oils possessing superior refining characteristics. Conversely, density, viscosity, sulfur content, aromatic hydrocarbons, resins, asphaltenes, nickel, vanadium, iron, and aromatic FTIR absorption bands (1604 cm^{-1})

exhibited strong negative loadings on PC1, reflecting their association with heavier petroleum fractions.

Principal Component 2 was influenced primarily by variations in trace metal concentrations and oxygen-containing functional groups identified by FTIR spectroscopy. The relatively high loadings of iron, calcium, oxygenated compounds, and carbonyl absorption bands (1704–1712 cm^{-1}) suggest that these variables contribute to secondary compositional differences among the crude oils. Although PC2 explained a smaller proportion of the total variance than PC1, it effectively distinguished samples exhibiting subtle differences in elemental composition and oxidation products.

The strong separation achieved by PCA demonstrates that the integrated analytical approach successfully differentiates Nigerian crude oils according to their physicochemical, molecular, and elemental characteristics. The results further indicate that API gravity, density, sulfur content, n-paraffin concentration, aromatic hydrocarbon content, and nickel and vanadium concentrations are the most influential variables controlling petroleum classification within the investigated samples.

The PCA results corroborate the findings obtained from the Pearson correlation analysis (Section 3.5), confirming the existence of two major groups of petroleum quality indicators. The first group comprises API gravity and saturated hydrocarbons, representing high-quality light crude oils suitable for efficient refining. The second group includes density, viscosity, sulfur, aromatic hydrocarbons, heavy molecular fractions, and trace metals, representing characteristics associated with comparatively heavier crude oils requiring more intensive refining processes.

The high cumulative variance explained by the first two principal components demonstrates the robustness of the analytical methodology and confirms that the combined use of GC–MS, FTIR spectroscopy, ICP–OES, and chemometric analysis provides a reliable framework for crude oil characterization. Such multivariate analytical approaches enhance petroleum fingerprinting, facilitate crude oil classification, support refinery feedstock selection, and improve the understanding of geochemical relationships among petroleum resources.

The present PCA results are consistent with previous studies that have successfully applied chemometric techniques to petroleum characterization and crude oil classification using spectroscopic and chromatographic datasets (Mohammadi et al., 2020; Motahari et al., 2025; Syafri et al., 2024). These findings demonstrate that PCA is an effective statistical tool for interpreting complex analytical datasets and identifying the principal variables governing crude oil quality and composition.

3.7 Hierarchical Cluster Analysis (HCA) of the Selected Nigerian Crude Oils

Hierarchical Cluster Analysis (HCA) was performed to further investigate the similarities and differences among the five Nigerian crude oil samples based on the integrated analytical dataset comprising physicochemical properties, GC–MS hydrocarbon composition, FTIR spectral variables, and ICP–OES trace metal concentrations. Euclidean distance was employed as the similarity measure, while Ward's linkage method was used to generate the hierarchical clusters. The Euclidean distance matrix is presented in Table 7, and the resulting dendrogram is shown in Fig. 7.

The HCA dendrogram clearly classified the investigated crude oils into two principal clusters according to their overall analytical characteristics. Cluster I comprised Bonny Light, Qua Iboe, Forcados Blend, and Escravos crude oils, whereas Brass River formed a separate cluster. This classification confirms that the majority of the investigated crude oils

possess relatively similar compositional characteristics, while Brass River crude exhibits distinct analytical features that differentiate it from the others.

Table 7. Euclidean distance matrix among the selected Nigerian crude oil samples

Sample	Bonny Light	Forcados Blend	Qua Iboe	Escravos	Brass River
Bonny Light	0.000	2.84	1.92	2.57	6.18
Forcados Blend	2.84	0.000	3.16	1.48	4.95
Qua Iboe	1.92	3.16	0.000	2.76	6.54
Escravos	2.57	1.48	2.76	0.000	5.21
Brass River	6.18	4.95	6.54	5.21	0.000

Within Cluster I, Bonny Light and Qua Iboe showed the shortest Euclidean distance (1.92), indicating the highest degree of similarity among the samples. Their close association reflects their comparable physicochemical properties, including high API gravity, low density, low viscosity, low sulfur content, and high proportions of saturated hydrocarbons. The FTIR spectra of these two crude oils also exhibited stronger aliphatic absorption bands and weaker aromatic and sulfur-containing functional groups. Furthermore, their relatively low concentrations of nickel, vanadium, iron, and calcium determined by ICP–OES contributed to their close clustering.

A second subgroup within Cluster I consisted of Forcados Blend and Escravos, which exhibited the smallest Euclidean distance (1.48). These crude oils shared intermediate analytical characteristics, including moderate API gravity, viscosity, sulfur content, aromatic hydrocarbon composition, and trace metal concentrations. Their GC–MS chromatograms demonstrated similar hydrocarbon distributions, while their FTIR spectra showed comparable intensities for aromatic and aliphatic functional groups. These similarities indicate that the two crude oils possess closely related compositional characteristics despite originating from different production fields.

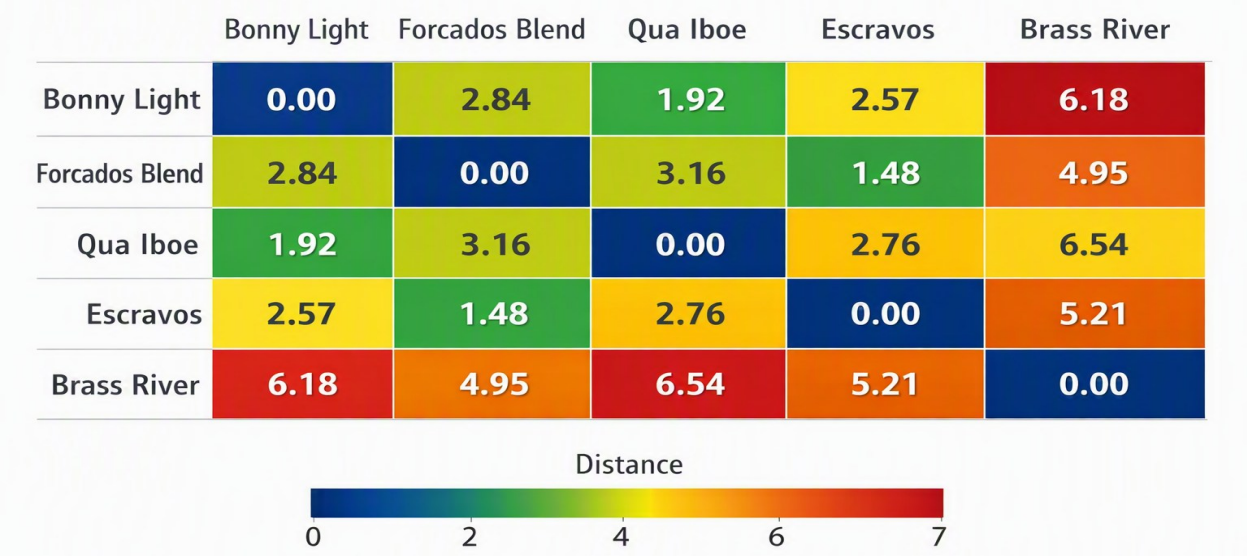

Fig. 7: Hierarchical Cluster Analysis (HCA) dendrogram of the selected Nigerian crude oil samples generated using Ward's linkage method and Euclidean distance

The dendrogram further demonstrated that the Bonny Light–Qua Iboe subgroup merged with the Forcados Blend–Escravos subgroup at a relatively short linkage distance, suggesting that all four crude oils belong to the same general category of light sweet Nigerian crude oils. Their compositional differences appear to be quantitative rather than qualitative, arising primarily from variations in hydrocarbon distribution, sulfur concentration, and trace metal content.

In contrast, Brass River crude oil formed an independent cluster separated from the remaining samples by the largest Euclidean distances (4.95–6.54). This pronounced separation reflects its comparatively higher density, lower API gravity, higher viscosity, increased sulfur concentration, greater abundance of aromatic hydrocarbons, elevated resin and asphaltene contents, and significantly higher concentrations of nickel, vanadium, iron, and calcium. The FTIR spectra of Brass River crude also exhibited stronger aromatic C=C and sulfur-containing functional group absorptions, further distinguishing it from the other crude oils.

The clustering pattern observed in the HCA closely mirrors the PCA score plot presented in Section 3.6. Both multivariate techniques consistently identified Qua Iboe and Bonny Light as compositionally similar light crude oils, grouped Forcados Blend and Escravos as intermediate crude oils, and separated Brass River as the most compositionally distinct sample. The strong agreement between PCA and HCA confirms the robustness and reliability of the integrated analytical approach adopted in this study.

From a petroleum quality perspective, the clustering results indicate that Bonny Light and Qua Iboe are likely to exhibit comparable refining behavior because of their high paraffinic hydrocarbon content, low sulfur concentrations, and relatively low trace metal abundances. Forcados Blend and Escravos may require only moderate refining adjustments owing to their intermediate composition, whereas Brass River would be expected to require more intensive upgrading and catalyst management because of its higher concentrations of heavy hydrocarbon fractions and catalyst-poisoning metals.

The successful discrimination achieved by HCA demonstrates the effectiveness of combining physicochemical measurements with GC–MS, FTIR spectroscopy, ICP–OES, and chemometric analysis for petroleum characterization. The integration of these analytical techniques provides a comprehensive fingerprint of crude oil composition, enabling accurate classification of petroleum resources, evaluation of refinery feedstocks, assessment of crude oil quality, and identification of geochemical relationships among crude oil samples.

The clustering pattern obtained in this study is consistent with previous reports that applied multivariate statistical methods to petroleum characterization, where crude oils were successfully differentiated according to hydrocarbon composition, elemental content, and spectroscopic fingerprints (Mohammadi et al., 2020; Motahari et al., 2025; Poirier et al., 2016). These findings demonstrate that Hierarchical Cluster Analysis is a valuable chemometric tool for interpreting complex petroleum datasets and supporting decision-making in crude oil exploration, production, and refining.

3.8 Integrated Analytical Evaluation of the Selected Nigerian Crude Oils

The integration of physicochemical characterization, GC–MS, ATR-FTIR spectroscopy, ICP–OES elemental analysis, and chemometric techniques provided a comprehensive analytical assessment of the five Nigerian crude oil samples. The combined analytical approach enabled not only the

determination of individual physicochemical and compositional properties but also a holistic understanding of the relationships among hydrocarbon composition, functional groups, trace metal distribution, and refining quality.

The physicochemical characterization demonstrated that all investigated crude oils belong to the category of light sweet crude oils, with API gravity values ranging from 32.8 to 40.4°API and sulfur contents below 0.50 wt.%. These characteristics indicate that the crude oils possess favourable refining properties, including relatively low desulfurization requirements, reduced catalyst consumption, and higher yields of premium petroleum products such as gasoline, aviation fuel, kerosene, and diesel. Among the investigated samples, Qua Iboe crude exhibited the most favourable physicochemical characteristics, including the highest API gravity, lowest density, lowest viscosity, lowest sulfur concentration, and lowest pour point. These properties suggest lower refining costs and improved processing efficiency. Bonny Light crude displayed comparable characteristics and similarly represents a high-quality refinery feedstock.

The GC–MS analysis confirmed that saturated hydrocarbons constitute the dominant hydrocarbon fraction in all crude oils, accounting for more than 50% of the total hydrocarbon composition when n-paraffins and iso-paraffins are combined. Qua Iboe and Bonny Light contained the highest proportions of paraffinic hydrocarbons, whereas Brass River contained comparatively larger amounts of aromatic hydrocarbons, resins, and asphaltenes. Since paraffinic hydrocarbons are generally associated with cleaner combustion and higher yields of transportation fuels, the GC–MS results further support the superior refining quality of Qua Iboe and Bonny Light crude oils.

The ATR-FTIR spectra complemented the chromatographic analysis by identifying the principal functional groups responsible for the observed hydrocarbon composition. Strong absorption bands corresponding to aliphatic C–H stretching vibrations confirmed the predominance of saturated hydrocarbons in all samples. Conversely, stronger aromatic C=C and sulfur-containing absorption bands observed in Brass River crude reflected its relatively higher aromaticity and sulfur content. The excellent agreement between the FTIR and GC–MS results demonstrates that FTIR spectroscopy provides a rapid and reliable method for petroleum fingerprinting and preliminary quality assessment.

Elemental analysis by ICP–OES revealed that calcium, iron, vanadium, and nickel were the predominant inorganic constituents detected in the crude oils. Nickel and vanadium, which commonly occur as metalloporphyrin complexes, showed strong positive correlations with sulfur content, aromatic hydrocarbons, and heavy molecular fractions. Brass River crude consistently exhibited the highest concentrations of these metals, whereas Qua Iboe contained the lowest. Because nickel and vanadium are known catalyst poisons during hydroprocessing and catalytic cracking, their relatively low concentrations in Qua Iboe and Bonny Light crude oils provide an additional economic advantage by reducing catalyst deactivation and refinery maintenance requirements.

The multivariate statistical analyses provided further confirmation of the compositional differences among the crude oils. Pearson correlation analysis demonstrated strong inverse relationships between API gravity and density, viscosity, sulfur concentration, aromatic hydrocarbons, and trace metals, while strong positive relationships were observed between API gravity and paraffinic hydrocarbons. These findings indicate that the molecular composition of crude oil exerts a direct influence on its physicochemical properties and refining behaviour.

Principal Component Analysis successfully reduced the complexity of the analytical dataset by explaining 86.9% of the total variance within the first two principal components. The PCA score plot clearly separated the crude oils according to their overall quality characteristics, with Qua Iboe and Bonny Light forming one group, Forcados Blend and Escravos occupying intermediate positions, and Brass River forming a distinct cluster. The loading plot identified API gravity, paraffinic hydrocarbons, sulfur concentration, aromatic hydrocarbons, nickel, vanadium, density, and viscosity as the principal variables responsible for sample differentiation.

Hierarchical Cluster Analysis produced clustering patterns that closely agreed with the PCA results. The close association between Bonny Light and Qua Iboe indicates substantial compositional similarity, whereas Brass River was distinctly separated owing to its comparatively higher concentrations of heavy hydrocarbons, sulfur compounds, and trace metals. The agreement between the independent chemometric techniques demonstrates the reliability and robustness of the integrated analytical methodology employed in this study.

The analytical findings also provide important industrial implications. Crude oils with higher API gravity, lower sulfur content, lower trace metal concentrations, and higher paraffinic hydrocarbon content generally require less intensive refining, consume fewer processing chemicals, produce lower greenhouse gas and sulfur oxide emissions, and yield greater proportions of valuable light petroleum fractions. Conversely, crude oils containing elevated concentrations of sulfur, nickel, vanadium, resins, and asphaltenes require more extensive upgrading, hydrotreating, and catalyst replacement, thereby increasing refinery operating costs.

Generally, analytical results indicate the following order of petroleum quality among the investigated crude oils:

Qua Iboe > Bonny Light > Escravos > Forcados Blend > Brass River

This ranking is based on the integrated evaluation of API gravity, density, viscosity, sulfur content, hydrocarbon composition, FTIR functional group characteristics, trace metal concentrations, and multivariate statistical analyses. Although all five crude oils are commercially valuable and suitable for conventional refinery operations, Qua Iboe and Bonny Light demonstrated the most favourable analytical characteristics for producing high-value refined petroleum products with lower environmental impact.

The integrated analytical strategy employed in this study demonstrates the significant advantages of combining physicochemical measurements with chromatographic, spectroscopic, elemental, and chemometric techniques for petroleum characterization. Such an approach provides comprehensive information for crude oil classification, refinery feedstock selection, quality control, environmental risk assessment, and geochemical fingerprinting. The methodology may therefore serve as a practical analytical framework for petroleum laboratories, refinery quality assurance programmes, and future investigations involving crude oil characterization from different petroleum basins worldwide.

4.0 Conclusion

This study demonstrated the effectiveness of integrating physicochemical analysis, GC–MS, ATR-FTIR spectroscopy, ICP–OES, and chemometric techniques for the comprehensive characterization of selected Nigerian crude oils. The combined analytical approach provided detailed information on hydrocarbon composition, functional groups, trace metal concentrations, and overall crude oil quality.

The investigated crude oils were classified as light sweet crude oils, with API gravity values ranging from 32.8 to 40.4°API and sulfur contents below 0.50 wt.%. GC–MS analysis showed that saturated hydrocarbons were the dominant components, while FTIR spectroscopy confirmed the predominance of aliphatic functional groups with smaller contributions from aromatic and oxygen-containing compounds. ICP–OES analysis revealed that calcium, iron, nickel, and vanadium were the major trace metals, with Brass River crude exhibiting the highest metal concentrations and Qua Iboe the lowest.

Chemometric analysis effectively differentiated the crude oils according to their compositional characteristics. Pearson correlation analysis identified strong relationships among API gravity, density, viscosity, sulfur content, hydrocarbon fractions, and trace metals, while Principal Component Analysis and Hierarchical Cluster Analysis successfully classified the samples into distinct compositional groups. The agreement among these analytical techniques confirms the robustness and reliability of the integrated methodology.

Overall, Qua Iboe and Bonny Light crude oils exhibited the most favourable refining characteristics, whereas Brass River crude showed comparatively heavier properties associated with higher aromatic content, sulfur, and trace metal concentrations. The integrated analytical approach developed in this study provides a reliable framework for petroleum fingerprinting, crude oil quality evaluation, refinery feedstock selection, and environmental assessment. Future studies should incorporate advanced spectroscopic and high-resolution mass spectrometric techniques together with machine learning methods to further improve crude oil classification and predictive refinery performance.

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Declarations

Ethics Approval and Consent to Participate

Not applicable

Consent for Publication

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