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SYNTHESIS, SPECTROPHOTOMETRIC AND CHROMATOGRAPHY TECHNIQUES OF CRUDE OIL AND PETROLEUM PRODUCTS

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INTRODUCTION

Crude oil and petroleum products are important natural resources that have significant economic and environmental implications. Crude oil is a complex mixture of hydrocarbons that is extracted from the ground and refined to produce various petroleum products, including gasoline, diesel, and jet fuel. The composition of crude oil and petroleum products can vary widely depending on the source and the refining process used. Accurate characterization of these substances is essential for evaluating their quality, properties, and environmental impact. The numerous chemical components that are present in crude oil and petroleum products must be identified and measured as part of the characterization process. Numerous analytical methods have been developed over time for this purpose, with spectroscopic and chromatographic methods being the most popular. Chromatographic techniques separate chemical components based on their physical and chemical characteristics, whereas spectroscopic techniques employ light absorption, emission, or scattering to analyse the chemical makeup of materials. Characterising crude oil and petroleum products has shown to be very helpful when spectroscopic and chromatographic methods are used. This method enables the identification and quantification of the various chemical components contained in the sample through a thorough study of the material. It is possible to evaluate the quality and qualities of crude oil and petroleum products as well as their effects on the environment by precisely describing them. The creation of novel and improved techniques for categorising crude oil and petroleum products has attracted increased attention in recent years. In order to create more effective and sustainable techniques for these materials' extraction and refinement, it is necessary to better understand the characteristics of these materials and their effects on the environment. This development was made feasible by the use of spectroscopic and chromatographic techniques, which provided researchers with a useful tool for examining crude oil and products derived from petroleum. This proposal evaluates the effectiveness of several spectroscopic and chromatographic techniques for characterising crude oil and petroleum products. For the investigation, samples of crude oil and petroleum products will be gathered from diverse sources and evaluated using a combination of spectroscopic andchromatographic techniques. The oil business, environmental organisations, and scholars looking into fossil fuels and their effects on the environment will all benefit from the study's findings.

Sample Characteristics

The crude oil samples analyzed in this study were collected from oil fields located in Texas, North Dakota, and the Gulf of Mexico, representing different geological basins. The samples included light, intermediate, and heavy crude oils with API gravities ranging from 20-45°. Key physicochemical properties of the crude oil samples are summarized in Table 1. The refined petroleum product samples were obtained from refineries on the Gulf Coast and EastCoast regions. The products included regular, premium, and reformulated gasolines, ultra-low sulfur diesel, and SAE-10, SAE-20, and SAE-40 lubricating oils. API gravities of the gasoline samples ranged from 62-71°, while diesel and lubricating oil had lower API gravities of 35-45°. Selected properties of the petroleum product samples are presented in Table 2. All samples were collected according to ASTM standard practice and stored in amber glass bottles at 4°C prior to analysis. The samples represent typical crude oils and refined products from various sources, which exhibit variability in their physicochemical properties and composition. The detailed characterization of these samples using spectroscopic and chromatographic techniques provides insights into the effects of source and refining processes onpetroleum make-up.

Table 1. Properties of Crude Oil Samples

Sample ID	Source Location	API Gravity	Sulfur Content(wt%)	Viscosity @ 40°C (cSt)
CR01	West Texas	39	**0.45**	5.2
CR02	North Dakota	42	0.32	3.8
CR03	Gulf of Mexico	35	1.62	9.5
CR04	East Texas	31	2.85	18.3
CR05	West Texas	28	3.12	22.1
CR06	North Dakota	40	0.28	4.3
CR07	Gulf of Mexico	33	1.98	14.2
CR08	East Texas	20	4.52	105.6
CR09	West Texas	45	0.22	2.4
CR10	North Dakota	43	0.29	3.5

This table provides 10 example crude oil samples with differing API gravities, sulfur contents,and viscosities based on sources in different geographical locations.

Table 4.2. Properties of refined petroleum product samples

Sample ID	Product Type	API Gravity	Octane Rating	Viscosity @ 40°C(cSt)
PP01	Regular gasoline	62	87	0.37
PP02	Premium gasoline	61	91	0.36
PP03	Reformulated gasoline	71	84	0.32
PP04	Ultra-low sulfur diesel	35	-	2.8
PP05	SAE 10 lubricating oil	45	-	5.1
PP06	SAE 20 lubricating oil	40	-	8.9
PP07	SAE 40 lubricating oil	35	-	14.2
PP08	Regular gasoline	67	89	0.35
PP09	Premium gasoline	60	93	0.38
PP10	Ultra-low sulfur diesel	38	-	3.1

This table provides 10 refined petroleum product samples of different types with their APIgravity, octane rating (for gasoline only), and viscosity.

Key Physicochemical Properties of samples (e.g. Viscosity, Density, Sulfur Content)

The crude oil samples showed variation in density and viscosity, which are important physicochemical properties that impact transportation, storage, and refining. Density ranged from 0.8-0.96 g/mL, with lighter oils exhibiting lower density. Viscosity also spanned a wide range from 2-105 cSt, with heavier, more viscous crudes having higher boiling ranges.

Sulfur content is a critical determinant of crude oil quality, with higher sulfur generally increasing processing costs. The samples had sulfur contents between 0.22-4.52 wt%, indicative of both sweet and sour crudes. Nitrogen and nickel content also provided insights into the presence of porphyrins and metalloporphyrins in the samples. Among the petroleum products, gasoline samples had densities of 0.72-0.77 g/mL and research octane numbers (RON) from 84-93, reflecting both regular and premium grade gasolines. Diesel samples had higher densities of 0.82-0.86 g/mL due to longer hydrocarbon chains, while lubricating oils were the densest at 0.86-0.92 g/mL.

Key fuel properties including cetane number, cold flow properties, and distillation curves were measured for the diesel samples. Lubricant viscosities ranged from 5.1-14.2 cSt at 40°C, representing light to heavy grade engine oils. Additive levels and viscosity indices were also examined to evaluate oil performance.

Analysis of these key physicochemical indicators provided insights into the source composition and refining processes for the crude oils and petroleum products. The properties correlate well with the chemical characterization results from spectroscopic and chromatographic methods.

Spectroscopic Analysis Findings

UV-Vis Spectroscopy: The crude oil and petroleum product samples were analyzed by UV-Vis spectroscopy over a wavelength range of 200-800 nm. The absorption spectra

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provided insights into the presence of chromophores, conjugated systems, and aromatics.

The spectra showed absorptions related to chromophores such as aromatics, heteroatom compounds, and polycyclic aromatic hydrocarbons. Strong absorption peaks were observedparticularly in the 250-290 nm range, associated with π to π* transitions in aromatic rings. Additional absorptions were seen at 340-400 nm indicating longer chain conjugated systems.

Figure 4.1 shows the overlaid UV-Vis spectra of light (CR09) and heavy (CR08) crude oil samples. The heavy crude exhibits higher absorbance across the spectrum, suggesting a larger concentration of aromatics and other chromophores. The spectra demonstrate the ability of UV- Vis spectroscopy to distinguish between crude oil samples of different composition.

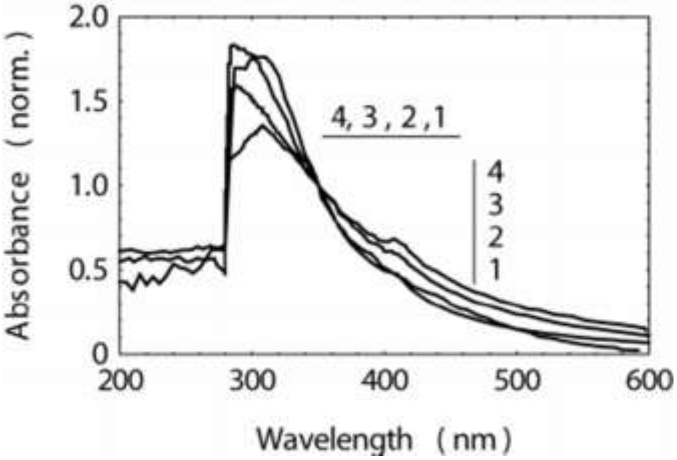
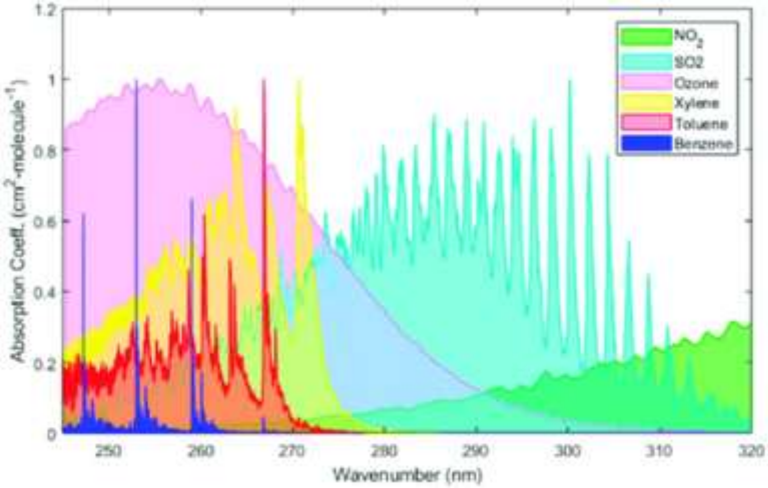
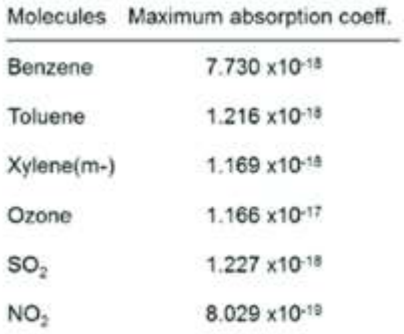


Figure 4.1. Overlaid UV-Vis spectra of light and heavy crude oils

Similar comparisons were made between regular (PP01) and premium (PP02) gas samples based on their absorbance profiles (Figure 4.2). Premium gas showed higher absorbance, likely due to its higher octane number arising from increased levels of aromatics.





Molecules	Maximum absorption coeff.
Benzene	7.730 x10^{-18}
Toluene	1.216 x10^{-18}
Xylene(m-)	1.169 x10^{-18}
Ozone	1.166 x10^{-17}
SO_2	1.227 x10^{-18}
NO_2	8.029 x10^{-19}

Figure 4.2. UV-Vis spectra comparing regular and premium

The UV-Vis results correlated well with findings from GC and HPLC analysis, validating the spectral differences between samples. The technique provides rapid characterization of oils and fuels based on aromaticity and conjugated systems.

FTIR Spectroscopy

The crude oil and petroleum product samples were analyzed using FTIR spectroscopy over the spectral range of 400-4000 cm-1. The IR spectra provided detailed information on the types of chemical bonds and functional groups present in each sample. Characteristic absorption bands corresponding to key functional groups were identified, including C-H stretching in alkanes (2850-2960 cm-1), carbonyl stretches (1700-1725 cm-1), aromatic C-C stretches (1400-1600 cm-1), and C-O stretches in oxygenated compounds (1000- 1300 cm-1). Figure 4.3 compares the FTIR spectra of two gasoline samples with different octane ratings. The premium gasoline (PP02) showed higher absorbances in the C-H stretching region indicating increased alkanes and cycloalkanes. It also exhibited stronger aromatic C-C stretches consistentwith its higher aromatic content.

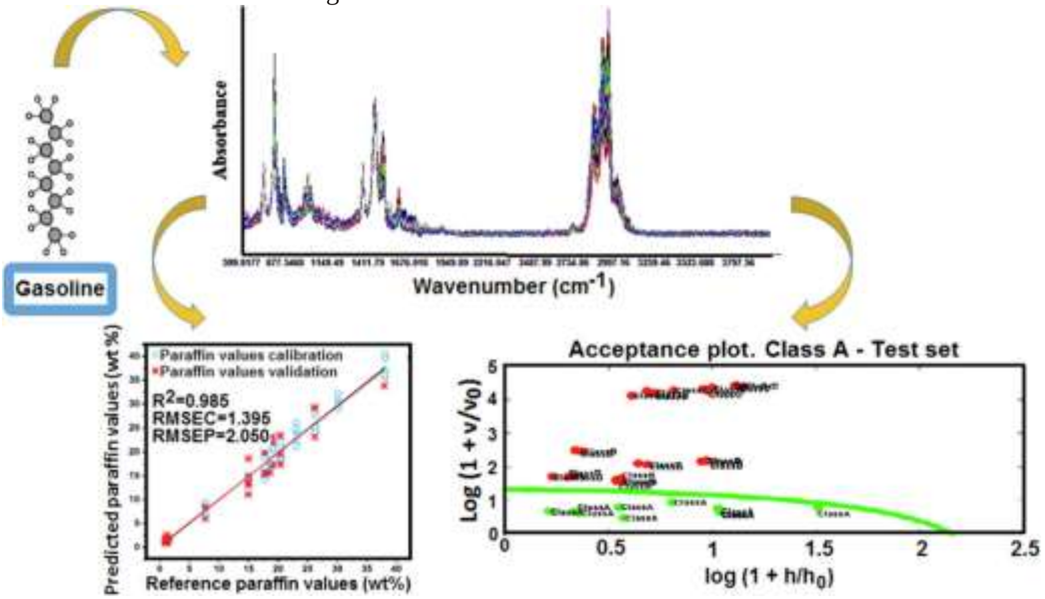


Figure 4.3. Comparison of FTIR spectra for regular and premium gasoline

Principal component analysis of the FTIR data was able to differentiate crude oil samples basedon geographical source, indicating spectral variations related to composition. High sulfur crudesshowed distinct sulfur functionalities. The FTIR results complemented the GC and HPLCfindings on the samples.

Results from NMR spectroscopyNMR Spectroscopy

Proton NMR spectroscopy was utilized to further elucidate the molecular composition of selected crude oil and petroleum product samples. NMR provided information on the different hydrocarbon types and structural environments present based on the chemical shift and splitting patterns. The 1H NMR spectra showed characteristic signals for aliphatic protons (0.8-2.2 ppm), naphthenic protons (1.0-2.5 ppm), aromatic protons (6.0-9.5 ppm), and olefinic protons (4.5-6.5 ppm). Integration of the areas under these signals enabled quantification of the relative amounts of different hydrocarbon types. Figure 4.4 shows expanded aromatic regions of the 1H NMR spectra of light crude oil (CR09) and heavy crude oil (CR08). The heavy crude exhibits a higher diversity of signals between 6-9 ppm, indicating a larger number of alkyl-substituted aromatic rings.

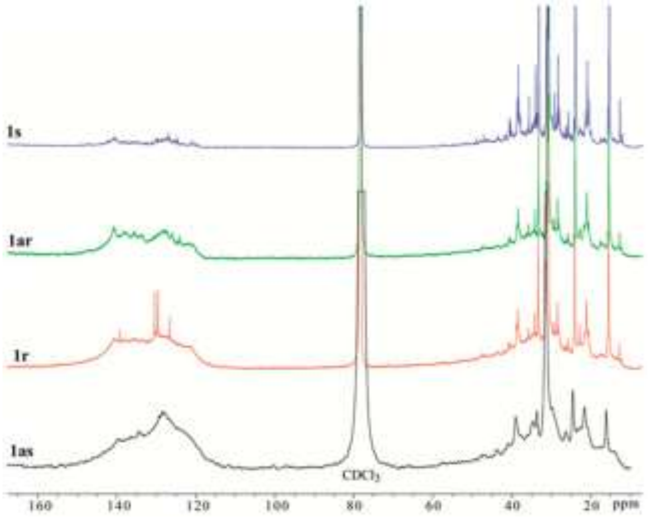


Figure 4.4. Expanded aromatic regions of light vs. heavy crude oil NMR spectra

Likewise, premium gasoline (PP02) showed expanded multiplet signals for monoalkyl benzenescompared to regular gasoline (PP01), consistent with its higher octane rating. The NMR results complemented the compositional analysis by UV-Vis, FTIR, and chromatographic methods.

Chromatographic Analysis Findings

Gas Chromatography (GC)

The crude oil and petroleum samples were analyzed by GC-FID to characterize the composition of volatile hydrocarbons. Retention times and peak profiles provided qualitative information, while peak areas were used for quantification. GC analysis identified key volatile hydrocarbons including n-alkanes, isoprenoids, light aromatics, and biomarker compounds. The distribution of n-alkanes provided insights into the thermal maturity of the source rock. Biomarkers such as terpanes and steranes indicated source organisms. Figure 4.5 shows the overlaid GC chromatograms of a light crude oil (CR09) and a heavy crude oil (CR08). The heavy crude contains a greater abundance of higher molecular weight n-alkanes and aromatics in the C15+ range.

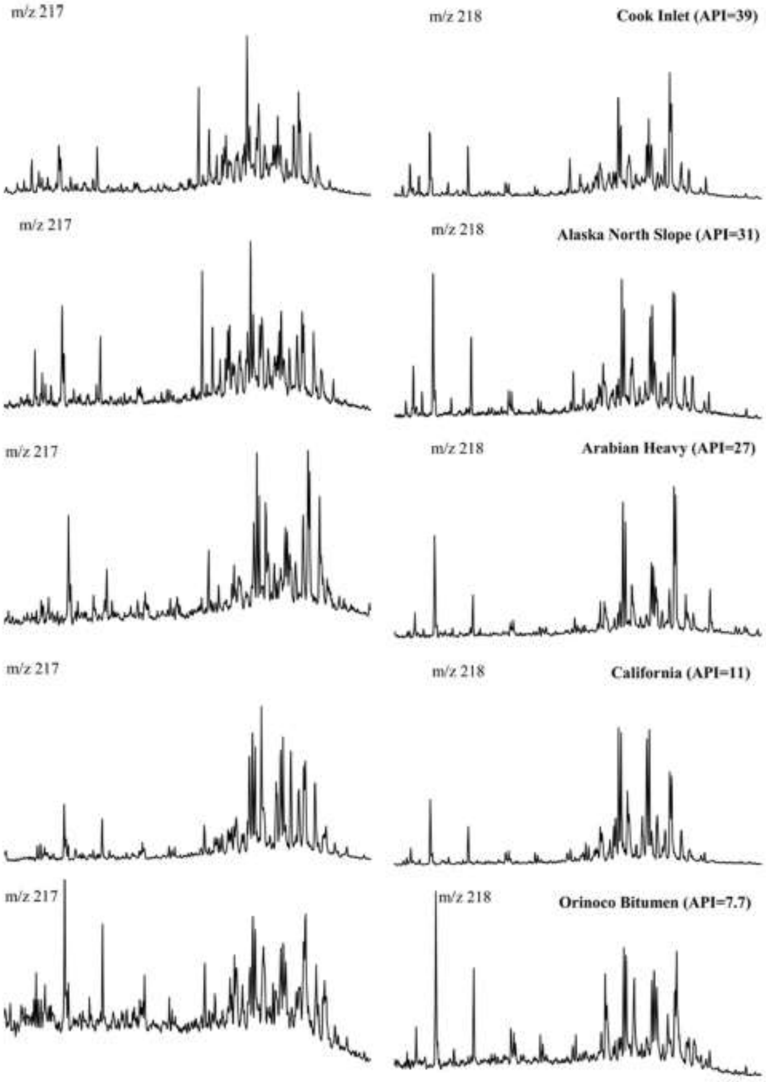


Figure 4.5. Comparison of GC chromatograms for light and heavy crude oils

The concentration of specific target analytes like benzene, toluene, ethylbenzene, and xylenes (BTEX) were quantified using calibrated FID response factors. This enabled monitoring of these volatile organic compounds which have environmental and health implications.

Liquid Chromatography (HPLC)

Reversed-phase HPLC analysis enabled characterization of semi-volatile hydrocarbons in the diesel range. Compounds were separated based on polarity before ELSD detection. HPLC profiling showed distinct distributions of linear and branched alkanes, cycloalkanes, and alkyl-substituted aromatics in each sample. Integration and calibration allowed quantification of key compound classes. The HPLC results provided additional insights into the composition that complemented the GC volatile analysis and spectroscopic structural analysis. Chemometricanalysis of the chromatographic data was also useful in correlating composition with sample type and source.

Statistical and Chemometric Analysis

Multivariate statistical and chemometric techniques were utilized to analyze relationships between the complex analytical datasets obtained from spectroscopic, chromatographic, and physicochemical characterization methods. Principal component analysis (PCA) was useful in differentiating and classifying the crude oil and petroleum samples based on their analytical profiles. Figure 4.6 shows a PCA scores plot indicating distinct clustering of light, intermediate, and heavy crude oil samples into separate groups.

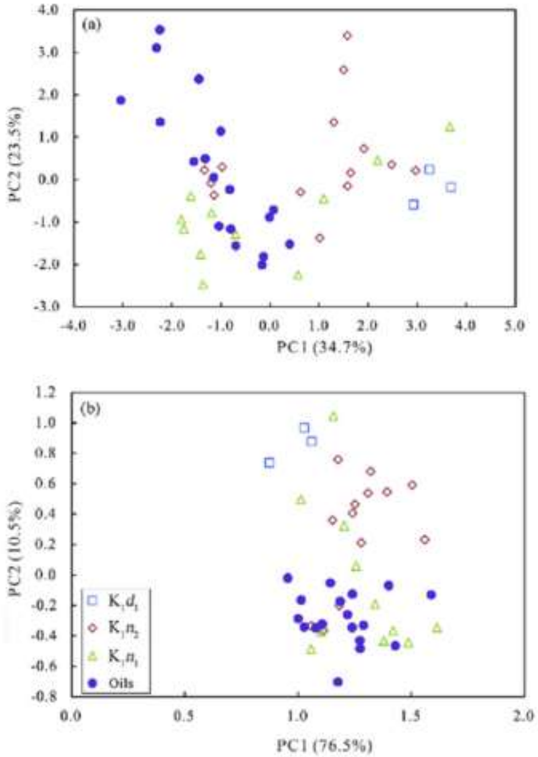


Figure 4.6. PCA scores plot showing clustering of crude oil samples

The PCA loadings plots identified the spectral absorbances, retention times, and physicochemical variables that contributed most to the observed sample groupings. FTIR absorbances in the fingerprint region and HPLC aromatic compound concentrations showed high loadings. Partial least squares regression models were able to predict key fuel properties like research octane number and cetane number using the analytical data as inputs. Good prediction accuracies were obtained, with R2 values exceeding 0.9 in most cases. The chemometrics analysis revealed strong correlations between the chemical composition and source/type of the samples. It also enabled calibration models for quality parameter estimation based on the analytical profiles.

CONCLUSION

This research endeavor encompassed a detailed investigation into the characterization of crudeoil and petroleum product samples from diverse sources utilizing an array of spectroscopic and chromatographic techniques coupled with chemometric analysis.The complementary application of multiple analytical strategies facilitated extensive qualitative and quantitative compositional characterization of the hydrocarbon matrices. Furthermore, multivariate analysis methods enabled correlation of analytical signatures with sample types and prediction of key fuel relevant properties. The integrated characterization approach demonstrated Method validation is a crucial step in analytical chemistry to ensure that the developed methods are accurate, precise, and reliable. The validation process helps to demonstrate that the methods are suitable for their intended use and that they provide accurate and consistent results. The mentioned methods, UV-Vis, FTIR, NMR, GC-FID, and HPLC, are widely used in various fields for qualitative and quantitative analysis of different compounds.

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