



ABSTRACT

There is current interest in the fate and effects of crude oil spillages in land and water and the remediation of crude oil contaminated soil. Herein we present a detailed chromatographic and spectroscopic analysis of crude oil residue in the Niger Delta region of Nigeria. Our study explores the use of sorption, linear solvation energy relationship (LSER), multivariate analysis and spectroscopic studies using ultra violet visible, infrared spectroscopy, high resolution ¹H nuclear magnetic resonance (¹H NMR), and two-dimensional heteronuclear single quantum correlation (HSQC) spectroscopy for the characterization of structural differences between samples in relation to the age of oil residue in the Niger Delta. Multivariate analysis (PCA and ANOVA) was then applied to obtain variations in samples by assigning different proton environment to obtain structural differences in the samples with different history of spillages. The spectroscopic data obtained showed the variation in the classes of hydrocarbon present in the younger and older oil residue were a function of age of spillage. ANOVA calculations for SARA composition of the oil residue show that there are differences in the amount of saturates and aromatic, suggesting transformational changes with an increase in the resin and polar fraction content as age of oil spill increases. The PCA applied to the ¹H NMR and the HSQC results explained nearly 84 % and 94 % respectively, the total variance of the complex mixture. Our results suggest that the combined sorption and spectroscopic data indicate that time evolution of the crude oil sample may follow a predictable pattern and may be useful when the age of a spill is known. However, explicit extrapolation of the present results to other environments may not be possible because these changes depend strongly on the original chemical composition of the crude oil and the variable exposure conditions along the time. In addition we report also the solubility of crude oil residue in contaminated soil (log S_s) from six locations in the Niger Delta region of Nigeria in different solvents determined by batch desorption technique . The correlated parameters allow an explanation of the main factors to consider when implementing the best technical option for crude oil-contaminated soil remediation by soil washing.

CONTACT: Menkiti Nnamdi David
Address: Ahmadu Bello University, Zaria, Kaduna State, Nigeria.
Email: ndmenkiti@abu.edu.ng
Phone: 08062947191

Sorption, Chromatographic, Spectroscopic, and Chemometric Analysis of Oil Residues in Contaminated Soils in the Niger Delta Region of Nigeria.

Menkiti, Nnamdi David,^{a,b*} Isanbor, Chukwuemeka^a, Ayejuyo Olusegun^a, Doamekpor Louis. Korbla^c , and Osei-Twum, Emmanuel Yaw^c

^aUniversity of Lagos Akoka, Nigeria, ^bAhmadu Bello University, Zaria, ^cUniversity of Ghana, Legon, Ghana.

INTRODUCTION

Crude oil exploration and subsequent oil spill on the terrestrial environmental are continually posing a threat to the ecosystem. Once entering the environment, oil spilled is subjected to a variety of weathering processes, such as evaporation, dissolution, dispersion, flushing due to wave energy, emulsification, photochemical oxidation, microbial biodegradation, and adsorption to suspended matter and deposition onto surfaces. This spills have been a major environmental hazard to the oil producing areas of the Niger Delta region in Nigeria. Therefore, treatment of crude oil contaminated site requires a fundamental understanding of the composition and physical properties of the oil residue. Our study explore the use of sorption, linear solvation energy relationship (LSER), multivariate analysis and spectroscopic studies using ultra violet visible, infrared spectroscopy, high resolution ¹H nuclear magnetic resonance (¹H NMR), and two-dimensional heteronuclear single quantum correlation (HSQC) spectroscopy and GC weathering indices for the characterization of structural differences between samples in relation to the age of oil residue in the Niger Delta.

MATERIALS AND METHODOLOGY

- The whole crude extract and fractions were analyzed using ultra-violet visible, infrared spectroscopic, 1D and 2D NMR.
- Organic cosolvent was used to determine the solubility and solute-solvent interaction of the oil residue in the soil.
- A forward stepwise multiple linear regression techniques were used to obtain the relationship between solubility (log S_s) of oil residue in the selected solvent and polarity indexes (comprising of molecular descriptors) of solvents.
- Results from spectroscopy analysis were used to carry out a principal component analysis (PCA) to obtain the most important trend between the oil residue and the time of the spill.

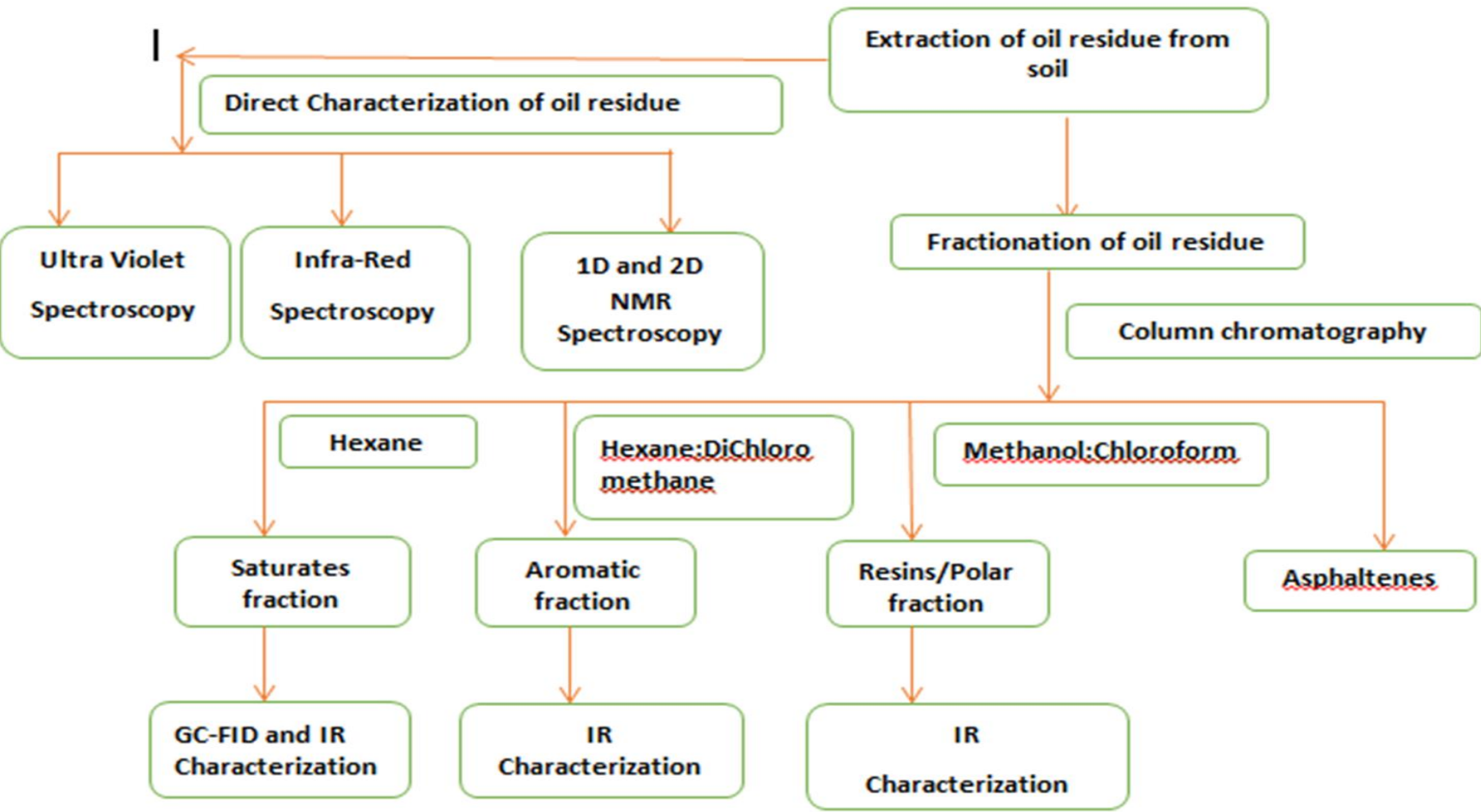


Figure 1: Characterization scheme of oil residue

RESULTS

Table 1: Sample code and time of spill									
Sample	S1	S2	S3	S4	S5	S6	B1	B2	
Time of spill (years)	10	8	8	5	2	1	1	1	
Designation	Older residue			Younger residue					

Table 2: ANOVA of SARA composition of oil residue				
	Saturates	Aromatics	Resins	Asphaltene
p-value ^b	0.0069	0.037	1.134	1.23
R ²	0.870	0.895	0.290	0.213
Tukey post hoc test ^c	1	1	0	0

Table 3: Summary of Model					
R	R ²	Standard deviation	Scales	Model equation	
0.778	0.605	0.163	SP, E _{CT(A)}	log S _w = -0.009E _{CT(A)} - 1.245SP + 2.482	
0.859	0.737	0.167	SP, V _m	log S _w = 0.005V _m + 0.454SP + 0.701	

Table 4: Euclidean distance between FC and oil residue samples									
Sample	S1	S2	S3	S4	S5	S6	B1	B2	
Distance	1.2	1.7	1.5	1.5	0.7	0.9	2.8	2.8	

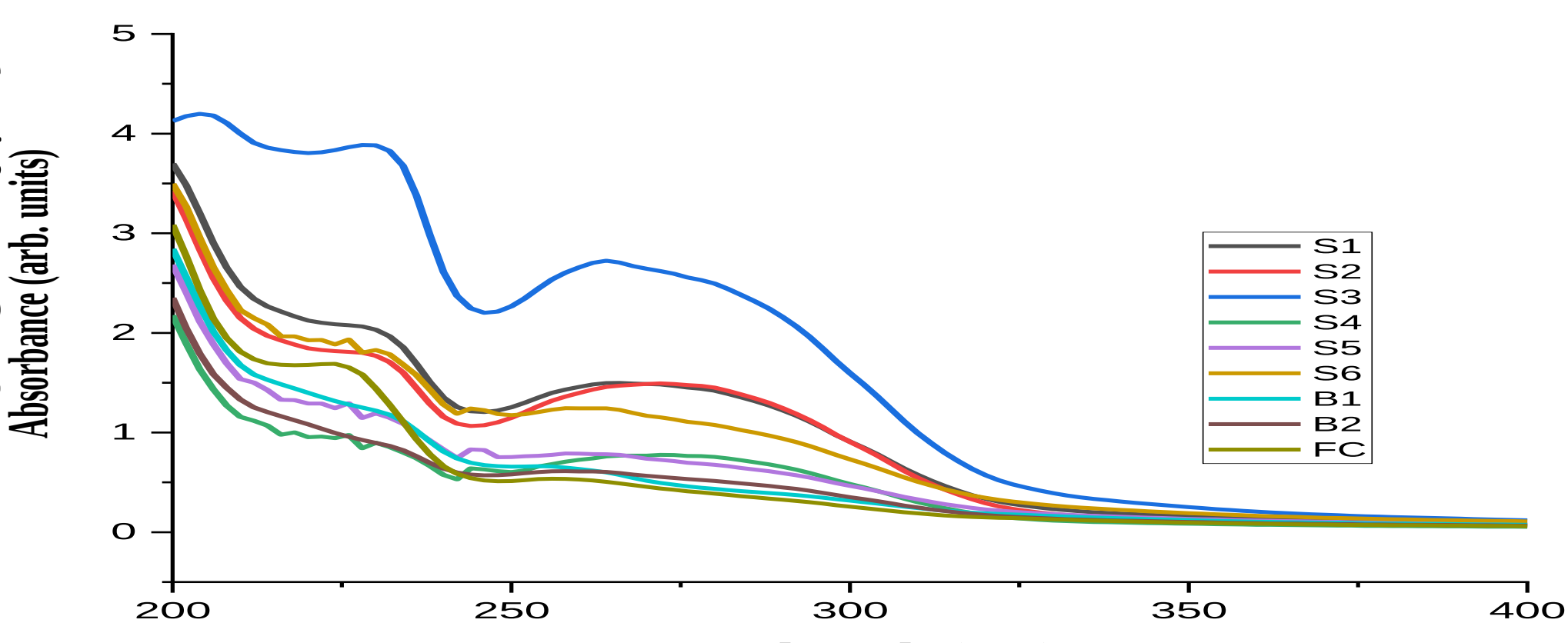


Figure 2: UV-Visible spectrum of oil residues.

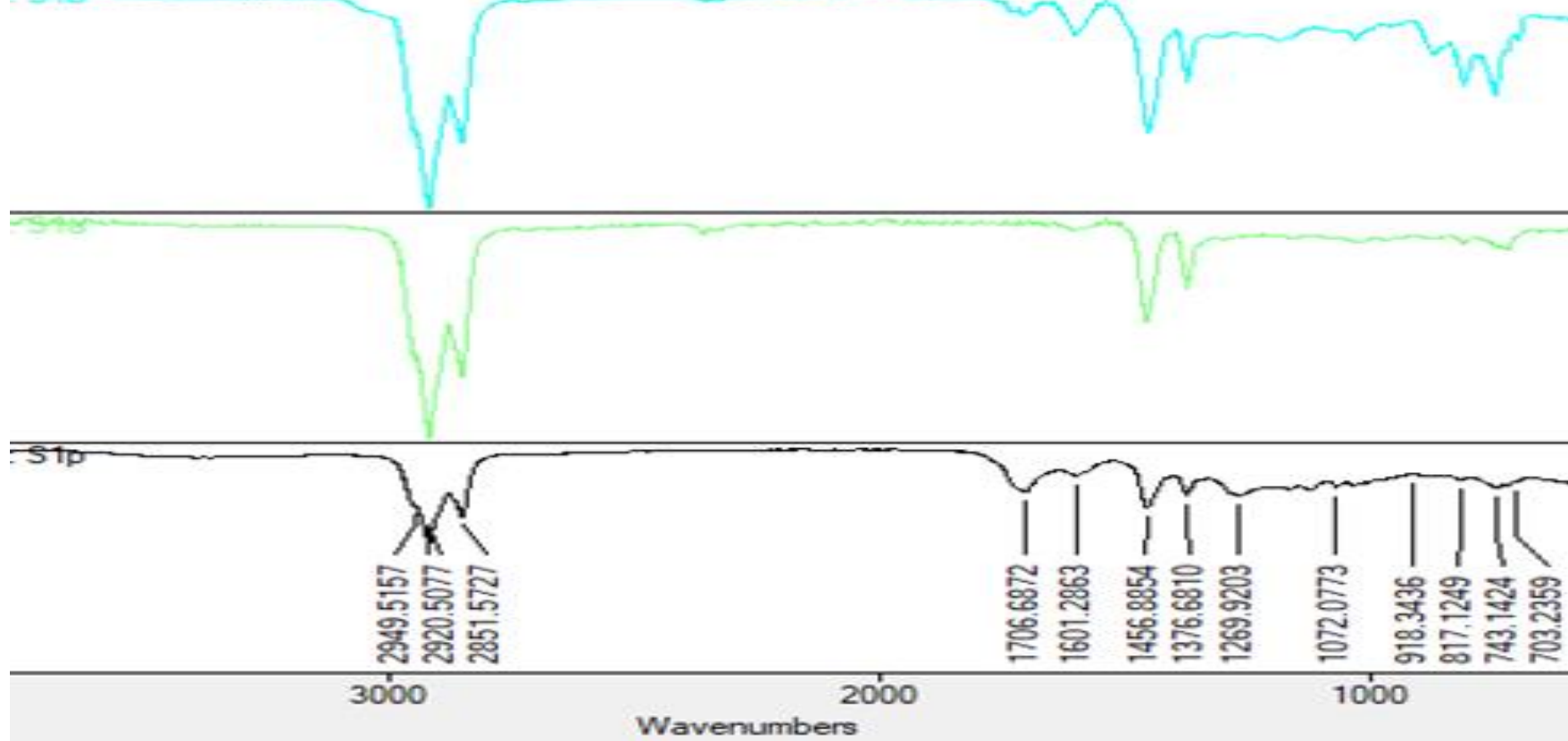


Figure 3: Spectra data of Saturate (S1a), Aromatic (S1b) and Polar (S1p) fractions of sample S1.

DISCUSSIONS

- At 0.1 significance level, saturates and aromatic composition are significantly different in the old and younger residues (Table 2).
- Polarizability of solvent is responsible for the dissolution of oil residue in solvents (Table 3).
- The absorption ratio A225/256 and A248/278 from UV are good estimators for petroleum of different weathering profiles. (Figure 2)
- Sulfoxide, aromatic and carbonyl index obtained from IR are more valuable in evaluating changes in oil residue over time. (Figure 3)
- For both the UV and IR spectroscopic measurements, two PCs were captured that explained 87 % and 71 % of the total variance respectively.
- Samples S2, S3, S4, S5, B1, and B2 gave a fairly acceptable and positive regression value (R²) of 0.8463 and 0.9117 for the classes of hydrocarbon present in the oil residue at the selected wavelength.
- Older residues (S1, S2 S3) were characterized by HA, H4, and HCOOH. The presence of these compounds has been suggested to be due to the transformation of aromatic compounds as well as the increase in PAHs.
- Sulfoxide, aromatic and carbonyl index obtained from IR are more valuable in evaluating changes in oil residue over time (Figure 6).
- -CH₃-CH₂, aliphatic and aromatic content of the oil residue are controlling index from HSQC measurement (Figure 7).

CONCLUSION

- The main factor responsible for grouping is aliphatic and aromatic composition.
- If the time of spill is known, UV, IR , GC and NMR spectroscopy would be a useful tool in evaluating the structural and compositional transformation of oil residue in the environment.

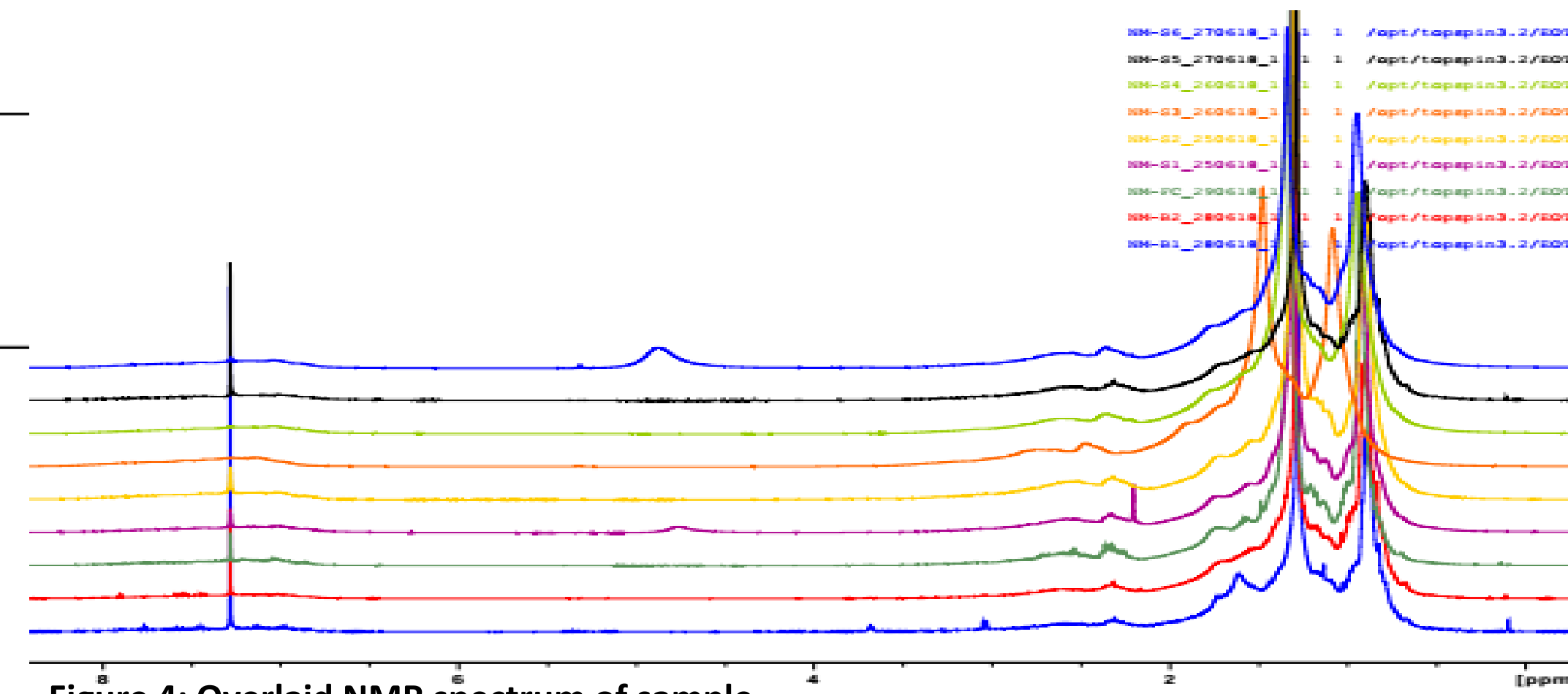


Figure 4: Overlaid NMR spectrum of sample.

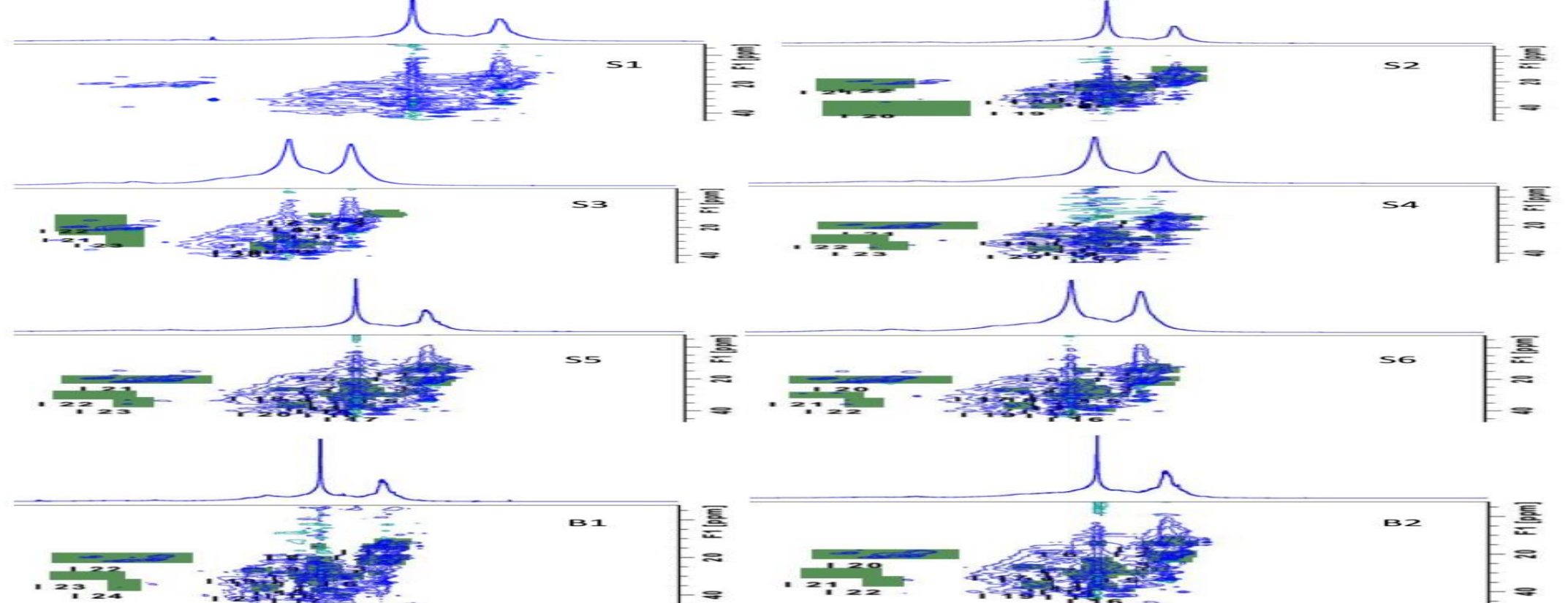


Figure 5: Fingerprint of the expanded HSQC -NMR SPECTRA Figure 4: Overlaid NMR spectrum of sample (δC/δH 10-45/0.3-3 ppm).

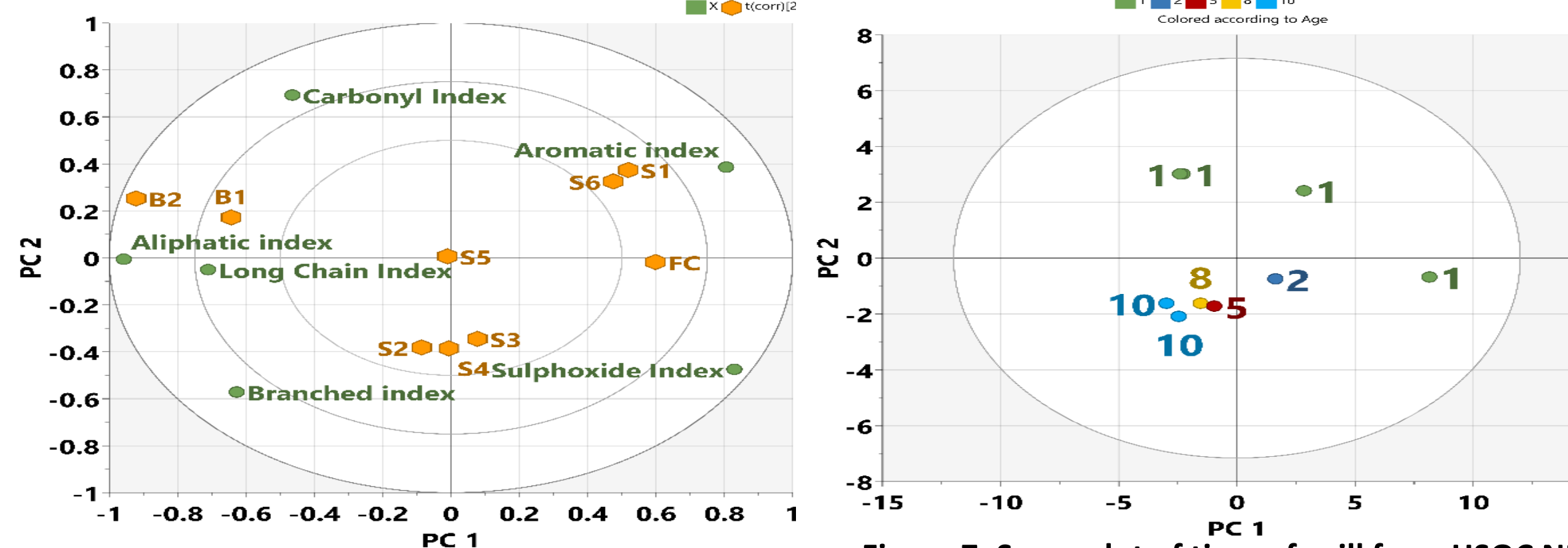


Figure 6: Component plot loading showing sample and spectrometric index.

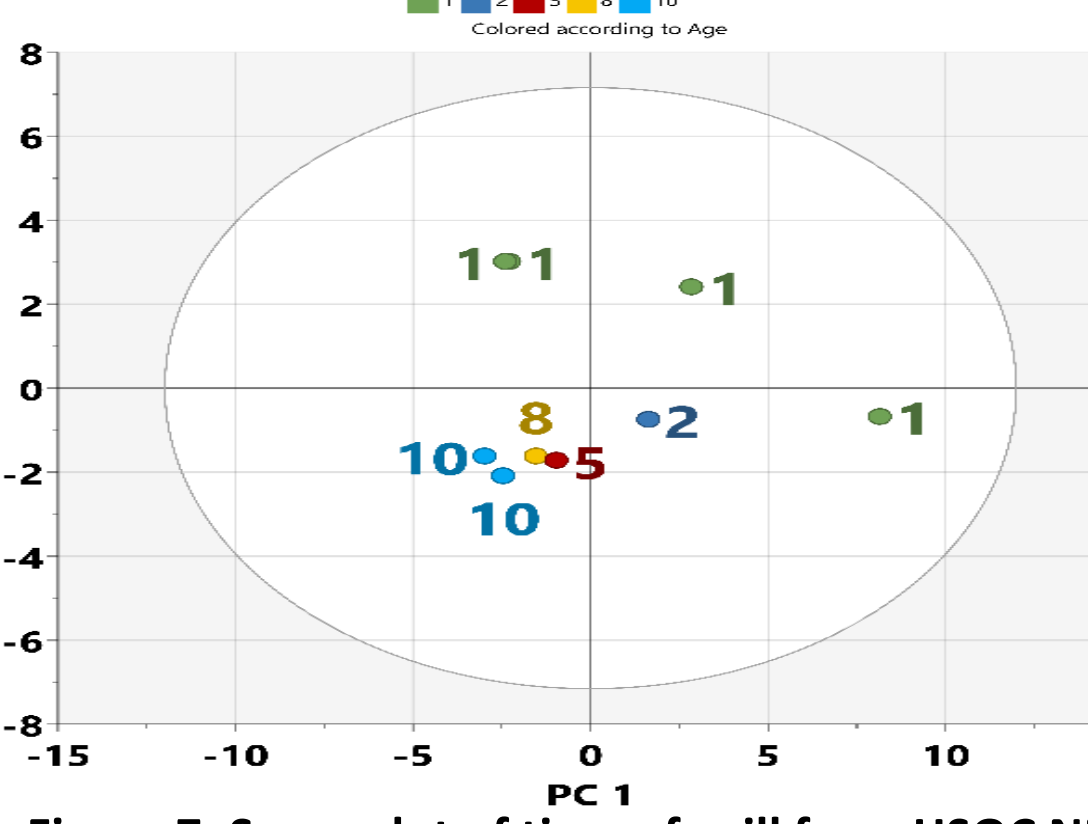


Figure 7: Score plot of time of spill from HSQC NMR Parameters.