CHROMATOGRAPHIC FINGERPRINTING OF SUB-BITUMINOUS COAL EXTRACTS

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ABSTRACT

Four sub-bituminous coals were investigated by solvent extraction (benzene/methanol, 3:1 (v/v)), silica gel adsorption chromatography, and the aliphatic hydrocarbon fractions, by gas chromatography. The chromatograms of the n-hexane eluates showed very strong similarities with a distribution around C_{12} -C_{16}. One of the extracts also displayed a prominent peak at C_{18}. The similarities can serve as "fingerprints" for other coals. The retention data for the n-hexane adducts of the aliphatic fractions are also presented and discussed.

INTRODUCTION

The dwindling recoverable resources and the politics of demand and supply of petroleum has stimulated research into the use of coal and its derivatives as sources of synthetic crudes and chemicals[1]. Knowledge of the chemical composition of coal is an essential aid in the determination of process variables such as temperature and pressure which govern the choice of solvents for extraction and the method of isolating the hydrocarbon fractions. Separation and procedures for characterizing petroleum are less extensively used, but equally applicable to coal liquids[2]. Of major importance in coal research are the paraffinic hydrocarbons. These can be divided into the main classes: n-alkanes, singly branched alkanes, acyclic isoprenoids and cyclic diterpanes, triterpanes and steranes[2]. The first two of these are the most plentiful in coal. Most of these hydrocarbons have been identified in Hungarian coal samples of different ranks[3]. One of the ways of isolating straight chain alkanes from coal is by urea adduction. The process of adduction results from one compound (the host) enclosing another (the guest) owing to its properties such as polarity and steric factors.

Adduction is not an ordinary chemical process where bonds are formed or broken; rather, it depends on spatial arrangement and interactions where van der Waals forces and oriented dipoles play an important role[4]. Pure urea crystallizes in a tetragonal arrangement but during the formation of complexes with n-alkanes, the urea molecules build up a hexagonal framework in a helical way in whose channels are located the guest molecules.

Chromatography, especially gas chromatography, is responsible for most of the identifications of the individual alkanes. The detailed patterns of abundance can act as fingerprints and can aid correlation studies of the origins of coal.

This paper reports an investigation carried out on four Nigerian sub-bituminous coals (Onyeama, Okpara, Okaba and Owukpa) using simple solvents. The urea-adducts obtained from the extracted and fractionated materials were analysed by gas chromatography.

EXPERIMENTAL

Materials

The coal samples (Onyeama, Okpara, Okaba and Owukpa) were obtained from the Nigerian Coal Corporation, Enugu. Benzene, n-hexane, methanol, urea and silica gel were purchased from either BDH or M & B and were of Analar grade. Chromatographic grade silica gel was activated in an oven at 160°C for 24 hours; the urea was activated using 4% methanol while the coal samples were ground to pass a 200 mesh (75μm) sieve.

Solvent extraction

The coal samples were extracted in a Soxhlet apparatus using a mixture of benzene and methanol in the ratio of 3:1 (v/v). Each sample was extracted batch-wise for 98 hr. at low heat. The extracts were reduced to one-third their volumes using a rotary evaporator. Further concentration was carried out on a hot plate under a stream of nitrogen gas for one hour.

Silica gel adsorption chromatography

This technique is used in coal research especialy to separate coal liquids into different hydrocarbon groups such as the aliphatics, aromatics and the polar fractions using suitable solvents.

The silica gel was made into a slurry with n-hexane. The slurry was packed into a glass column

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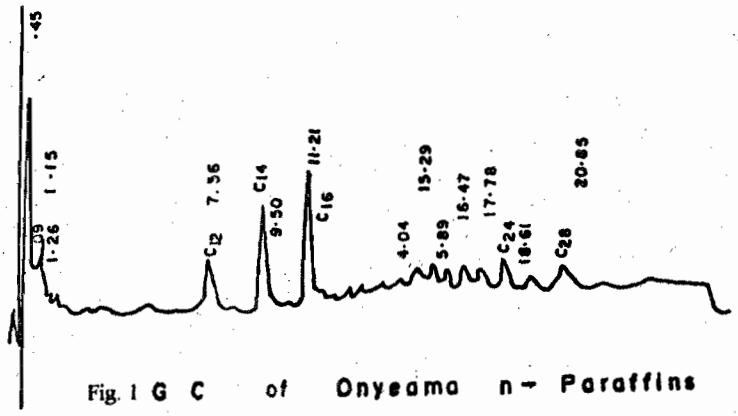

Fig. 1 G C of Onyeama n- Paraffins

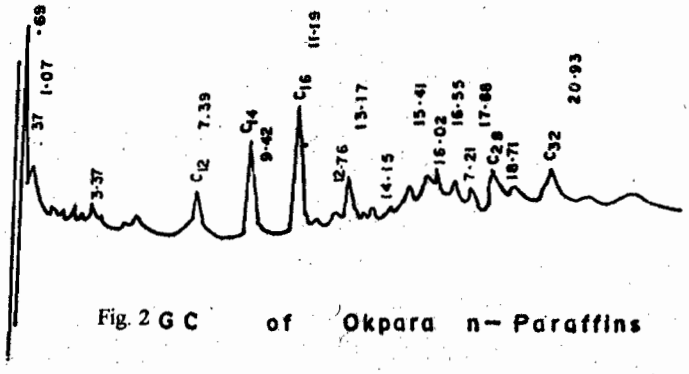

Fig. 2 G C of Okpara n- Paraffins

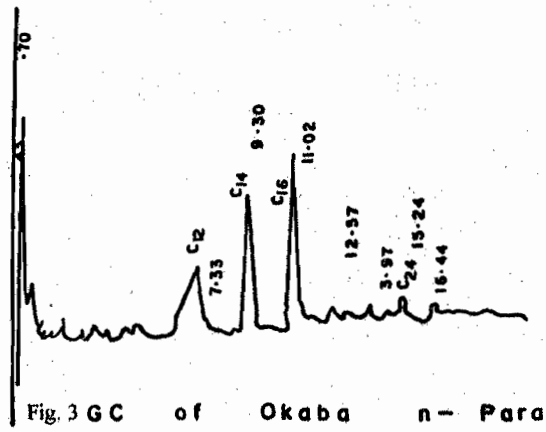

Fig. 3 G C of Okaba n- Paraffins

Table 1: Retention data of the prominent peaks

Sample	Peak No.	Retention Time (min)	Area %
Onyeama	3	7.56	5866
	4	9.50	12087
	5	11.21	16453
Okpara	3	7.39	4467
	4	9.42	12081
	5	11.19	17023
	6	13.17	5800
Okaba	3	7.33	11375
	4	9.30	19040
	5	11.02	22919
Owukpa	3	7.59	4310
	4	9.52	11718
	5	11.65	15803

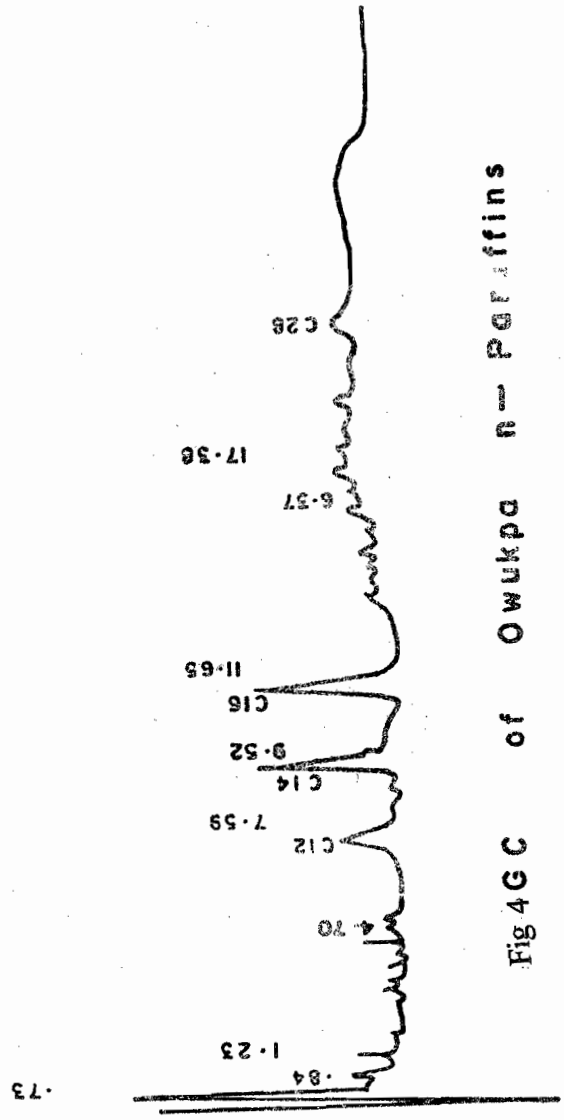

Fig 4 G C of Owukpa n — Paraffins

(80cm x 1.25cm). 2g of the extract was dissolved in 5cm³ of benzene and poured into the column. 100cm³ of each of n-hexane, benzene and methanol was used to elute the bed. Benzene and methanol eluates were concentrated as described above and reserved for size-exclusion chromatographic and infra-red spectral studies already reported elsewhere[5], while the n-hexane eluate was kept for urea-adduction which is reported hereunder.

Urea-adduction

The urea was mixed with the n-hexane eluate in the ratio of 2:1 (w/w). The mixture was stirred for 10 minutes at 1600 rpm at room temperature. The adducts were filtered under suction, washed with ice-cold benzene and air-dried. Decomposition of the adducts was carried out in hot water at 80°C. The solubility of urea in water is almost 100%. Thus, in hot water, the adducts readily dissolved to release the traped n-alkanes which were separated with a separating funnel and analysed on GC.

Gas chromatographic analysis

The analyses were carried out on a Varian instrument Model 3700 equipped with flame ionization detector. The column was stainless steel (2m x 0.124") coated with 10% SP 2100. The separated n-alkanes were first dissolved in carbon disulphide before injection into the column. Operating parameters were as follows:

Support material:	WHP (100-120mesh)
Carrier gas:	Nitrogen
Flow-rate:	10ml/min.
Detector temperature:	320°C
Injector temperature:	300°C
Initial oven temperature:	60°C, programmed at 15°C/min.

RESULTS AND DISCUSSION

The chromatograms for Onyeama, Okpara, Okaba and Owukpa samples are presented in Figures 1-4, respectively. Chromatograms show peaks between

C_{12} and C_{32}. However, the maximum concentrations are found at C_{12} -C_{16} for three of the samples (Onyeama, Okaba and Owukpa) while Okpara sample displays a maximum at C_{12} -C_{18}. Peaks with maxima in this region have been observed before. For instance, Spence and Vahrman[6], working with low temperature tar, observed a maximum at C_{17} - C_{21}. Again, Johnston and Jones[7], used urea adduction to isolate n-alkanes from tobacco leaves with a gass chromatographic maximum at C_{18} -C_{21}.

Another important feature in this investigation is the small peaks evolving between the regularly spaced n-alkanes peaks at higher carbon atom numbers. These are mono-methyl branched alkanes that adducted with the normals. Marquart et al.[8] also made this observation. The appearance of these peaks is not surprising since branched-chain alkanes can still form inclusion-complexes with urea depending on the position of the methyl side-chain.

The present analysis shows very striking similarities both in the distribution pattern and concentration around C_{12} -C_{18}. The similarities are rather remarkable because the geographical distance between the coal mines are large. This can serve as fingerprints for characterizing other coals. Information about n-alkane distribution in coals can provide crucial evidence about the origion of this most abundant fossil and can serve as "biological markers". The retention times of prominent peaks for all the samples are listed in Table 1. Considering their retention times, there is a rather striking regularity in the time it took the prominent n-alkanes to elute. All the prominent peaks were eluted in 7-12 min. in all the samples.

CONCLUSION

The result of the gas chromatographic analysis can be used as fingerprints to characterize other ocals due to similar distribution pattern and concentration for all the samples. The retention times showed striking regularity in terms of the time it took to elute the prominent n-alkanes for all the coals.

REFERENCES

1. Coleman, H.J., Dooley, J.E., Hirsch, D.E. and Thomson C.J., Anal. Chem., 1973, 45, 1724.
2. Bartle, K.D., Jones, D.W and Pakdel, H., in Karr, C. Jnr., ed., Analytical Methods for Coal and Coal Products, vol. 11, pp. 209-218, Academic Press, New York, 1978.
3. Alexander, G. and Hażai, I., J. Chromatogr., 1981, 217, 19.
4. Smolkova-Keulemansova, E. and Krysl, S., J. Chromatogr., 1980, 184, 347.
5. Akpabio, I.O., Sambo, A.S., Khan, M and Muazu, M., Jour. Ren. Energy, 4,2.
6. Spence, J.A. and Vahrman, M., J. Appl. Chem., 1967, 17, 143.
7. Johnston, R.L. and Jones, L.A., Anal. Chem., 1968, 40, 1728.
8. Marquart, J.R., Dellows, G.B. and Freitas, E.R., Anal. Chem., 1968, 40, 1633.

accepted *31/1/97*

received *22/10/96*