Journal of Chromatography, 368 (1986) 291–298
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 890

IDENTIFICATION OF SOME POLYCYCLIC NITROGEN-CONTAINING COMPOUNDS IN COAL-DERIVED OIL

S. MORIMOTO, F. MORISHITA and T. KOJIMA*
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo, Kyoto (Japan)
(First received February 27th, 1986; revised manuscript received June 16th, 1986)

SUMMARY

A systematic method for the identification of aza-arenes in coal-derived oil was developed. The basic nitrogen-containing substances were extracted with 6 *M* hydrochloric acid and fractionated sequentially by using gel chromatography and thin-layer chromatography (TLC) on an alumina plate. The aza-arenes in these fractions were separated by using glass capillary gas chromatography. Individual compounds in the column effluent were trapped in a system consisting of a valve for flow switching and a trapping tube made from a glass capillary. The fluorescence spectra of nanogram to subnanogram amounts of trapped compounds were measured. Some attempts were made to identify components based on their TLC R_F values and their fluorescence spectra, in addition to their mass spectra.

INTRODUCTION

In recent years, synthetic fuels from coal have attracted of increasing interest because of their potential as alternative energy sources. It is now well established that a large number of polycyclic aromatic compounds are present in coal-derived products. Nitrogen-containing polycyclic aromatic compounds have been found to exhibit pronounced carcinogenic and mutagenic effects in biological systems. As a result, the development of methods for the identification and determination of such compounds is important. Various types of nitrogen-containing compounds are present in coal liquefaction products and this complexitity has led to the development of a wide variety of analytical methods aimed at achieving improved separations for the chemical characterization of synthetic fuels[1–11].

In our laboratory, multi-stage analytical methodology for the separation and identification of nitrogen-containing compounds in coal-derived oils has been developed. This integrated multi-stage chromatographic method employs aqueous acid extraction for the isolation of basic nitrogen compounds from coal oil, followed by gel permeation chromatography (GPC) with subsequent thin-layer chromatography (TLC) on an alumina plate. The combination of these separation techniques produces fractions that are chemically much less complex than the starting crude materials.

0021-9673/86/$03.50

This method facilitates the subsequent gas chromatographic (GC) characterization of coal-derived oil. The applicability of the method to the characterization of diaromatic aza-arenes has been extensively examined and reported in a previous paper[12]. In this paper some experimental results on the characterization of three-ring aza-arenes by the multi-stage analytical approach are reported.

EXPERIMENTAL

The coal-derived oil investigated was obtained from the slurry phase hydrogenation of Taiheiyo coal at the Nippon Kokan facility, Kanagawa, Japan. Samples were collected from refinery products with the plant operating in the recycle mode. A heavy distillate was used in this investigation without further hydrotreatment. Fig. 1 is the schematic diagram of the multi-stage separation method. The nitrogen-containing bases were extracted with 6 *M* hydrochloric acid. After re-extraction in their free form into methylene chloride at pH 12 or above, followed by removal of the solvent, the basic substances were fractionated by GPC and subsequently by TLC.

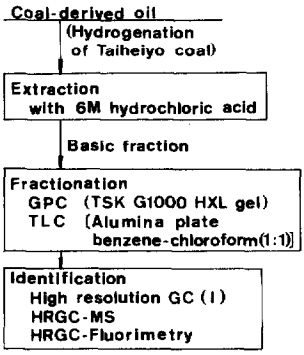

Fig. 1. Schematic diagram of systematic analysis of basic nitrogen-containing polycyclic aromatic compounds in coal-derived oil.

GPC was performed on a column (60 cm × 7.8 mm I.D.) packed with TSK G1000 HXL gel. Tetrahydrofuran was used as the developing solvent and a flow-rate of 1 ml/min was maintained in all GPC experiments. TLC separations were performed on an alumina plate (20 cm × 20 cm, 0.25 mm thick, Alumina 150 F254; Merck, Darmstadt, F.R.G.). After activation at 120°C for 1 h, the plates were developed by ascending elution in benzene–chloroform (1:1). The development time for a 10 cm run was about 45 min. The spots were observed under a UV lamp. The R_F values of the cut-off points for the fractions were 0.18, 0.31, 0.50, 0.66 and 0.77, and thus six fractions were scraped off the plate and extracted with methylene chloride.

After this two-stage fractionation, each TLC fraction was examined by GC on a fused-silica column. Mass and fluorescence spectra were utilized for the aquisition of structural information on aza-arenes eluted from the GC column. Mass spectrometric measurements were performed on a Hitachi RM-50 gas chromatography–mass spectrometry (GC–MS) instrument. The GC–MS conditions were as follows:

column, coated with OV-101 (25 m × 0.32 mm I.D.); carrier gas, helium; flow-rate, 0.8 ml/min; injection mode, on-column; column temperature, 250°C; ionization source temperature, 200°C; ionizing energy, 70 eV.

Prior to fluorimetric analysis, the effluent from the GC column was trapped. The GC separation for this purpose was carried out on a Shimadzu 2D gas chromatograph under the following conditions: column, coated OV-101 (25 m × 0.32 mm I.D.); carrier gas, nitrogen; flow-rate 1.8 ml/min; injection mode, split (splitting ratio, 1:50); column temperature, column 250°C; injector and flame ionization detector temperature, 300°C.

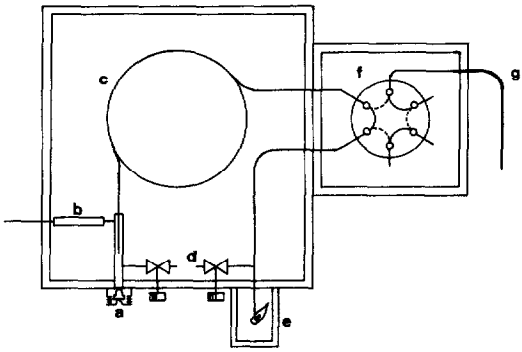

Fig. 2. Trapping system for effluents from capillary column for subsequent measurement of fluorescence spectra. a = Injector; b = splitter; c = fused-silica column; d = make-up gas; e = flame ionization detector; f = six-port valve; g = trapping tube (40 cm × 0.25 mm I.D.).

The trapping system shown in Fig. 2 consists of a six-port valve for flow switching and a trapping tube constructed from a fused-silica glass tube (40 cm × 0.25 mm I.D.). Once the desired GC peak had been trapped, the capilijlary tube was removed and the trapped material was eluted from the capillary tube by injecting methanol. A spectrofluorimeter (Shimadzu RF540) was used with the following settings: slit arrangement, excitation 10 nm, emmission 10 nm; volume of microcell, 0.35 ml (path length 10 mm).

RESULTS AND DISCUSSION

Fig. 3 shows the results of the GPC separation of the aza-arene fraction. The arrows show the elution positiosns of standard compounds. Three subfractions were selected, as shown in Fig. 3, so that the aza compounds would be generally grouped in separate subfractions according to the number of fused aromatic rings. The TLC separation of GPC fraction No. 3 is shown in Fig. 4. The standard compounds were satisfactorily separated and the order of decreasing R_F values is as follows; benzo-[*h*]quinoline, 8-methylquinoline (compounds having one *peri* CH or CH_3 group) > acridine (compound having two *peri* hydrogens) > quinoline, phenanthridine, benzo[*f*]quinoline (compounds having one *peri* hydrogen) > isoquinoline (compound having a non-sterically hindered aza-nitrogen). The chromatographic system used

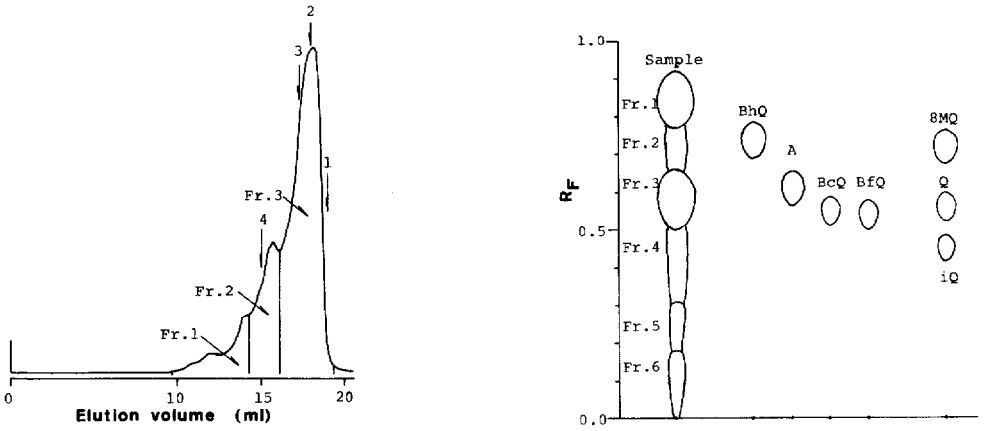

Fig. 3. GPC separation of basic fraction in coal-derived oil. Column: 60 cm × 7.8 mm I.D. TSK G1000 HXL gel; mobile phase, tetrahydrofuran; detector, refractive index. Standards: 1, pyridine (mol.wt. 79); 2, quinoline (mol.wt. 129); 3, acridine (mol.wt. 179); 4, dibenzacridine (mol.wt. 279).

Fig. 4. Thin-layer chromatographic behaviour of GPC fraction 3 in Fig. 3 on an alumina plate. Developing solvent: benzene–chloroform (1:1). BhQ = benzo[*h*]quinoline; A = acridine; BcQ = phenanthridine; BfQ = benzo[*f*]quinoline; 8MQ = 8-methylquinoline; Q = quinoline; iQ = isoquinoline.

gave interesting results in that compounds with a non-sterically hindered aza-nitrogen are strongly attracted to the adsorbent. Of all the standard compounds isoquinoline has the lowest R_F value. The hydrogen atom and CH or CH_3 group in the *peri* position in acridine or quinoline have a sufficient steric effect to decrease the strong attraction of the aza-nitrogen to the alumina. It is noteworthy that TLC is an effective method not only as a means of pre-fractionation, but also as a qualitative means for obtaining information about the structural environment around the aza-nitrogen atom[13,14].

Fig. 5 shows the results obtained from GC separation after the TLC fractionation of GPC fraction No. 3. Fig. 5b, c and d show the gas chromatograms of three TLC fractions and Fig. 5a shows the gas chromatogram of GPC fraction No. 3 before TLC fractionation. Comparison of the former three chromatograms with the latter indicates that the complexity of the GPC cut is indeed greatly reduced. The reduction in the complexity of the chromatogram makes identification easier.

GC–MS was used for the identification of specific components in the chromatograms in Fig. 5b–d. Assignments of the major components are given in Table I. As even mass spectra do not permit the determination of the position of the aza-nitrogen atom in individual aza compounds, a number of compound types are given for a given atomic composition. Only typical compound types are given in Table I. It is known that the mass spectra of aza compounds give little relevant structural information for identifying specific isomers and the use of complementary information can greatly facilitate the identification problem and simplify structural elucidation. Mass spectra and retention index data are complementary to each other. In a previous paper[12], we gave a method for predicting retention indices from the molec-

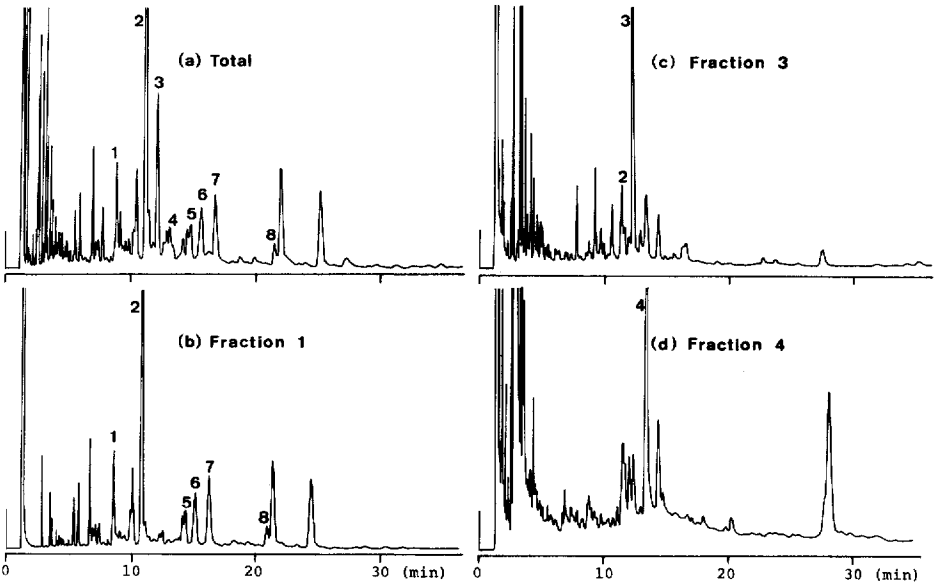

Fig. 5. Gas chromatograms of TLC fractions from GPC fraction 3. Column: OV-101, fused silica (25 m × 0.32 mm I.D.), 250°C. (a) = Gas chromatogram of GPC fraction 3; (b) gas chromatogram of TLC fraction 1 (R_F 0.77–1.00); (c) gas chromatogram of TLC fraction 3 (R_F 0.50–0.66), (d) gas chromatogram of TLC fraction 4 (R_F 0.31–0.50). Assignment of peaks 1–8 is given in Table I.

ular structures of diaromatic aza compounds and proposed an identification method based on comparison of the observed retention indices with the calculated values.

In this paper we show that fluorescence spectrometry can be used for the identification of aza-heterocyclic ring systems. Despite the great advances in spectroscopic methods, the only spectral technique generally applicable to nanogram or subnanogram amounts of compounds such as those separated on glass capillary columns is fluorescence spectrometry. The fluorescence spectra of alkylated aza compounds show a red shift of a few nanometres from those of the parent aza compounds.

TABLE I

ASSIGNMENT OF COMPOUND TYPES IN SOME GAS CHROMATOGRAPHIC PEAKS FROM MASS SPECTRA

No.	*Mol.wt.*	*Possible formula*	*Typical compound type*
1, 2, 3, 4	179	$C_{13}H_9N$	Tricyclic aza-arene
5, 6	193	$C_{14}H_{11}N$	C_1-alkyltricyclic aza-arene
7, 8	207	$C_{15}H_{13}N$	C_2-alkyltricyclic aza-arene

However, as alkyl substituents have only a slight effect on the spectra of the aza compounds, fluorescence spectrometry allows compounds with the same aromatic fused ring system to be identified as a single parent structure[15,16]. Fig. 6 shows the fluorescence emission spectra of some tricyclic aza-arenes. The fluorescence spectra of phenanthridine, benzo[*f*]quinoline and benzo[*h*]quinoline have an emission maximum at about 370 nm: this similarity of the spectra indicates that the position of the aza-nitrogen atom in the ring system does not have a significant effect on the fluorescence spectra. Therefore, compounds having a fused ring system classified as a phenanthrene type can be grouped under the same structure by fluorescence spectrometry. On the other hand, comparison of the spectra of aza compounds of the phenanthrene type with that of acridine indicates that fluorescence spectrometry allows the identification of two kinds of fused ring systems, namely the phenanthrene and anthracene types.

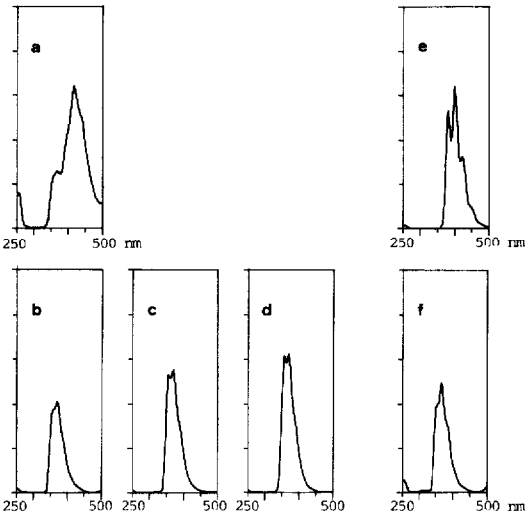

Fig. 6. Fluorescence emission spectra of some standard tricyclic aromatic compounds. Excitation: 250 nm. (a) Acridine; (b) phenanthridine; (c) benzo[*f*]quinoline; (d) benzo[*h*]quinoline; (e) anthracene; (f) phenanthrene.

It is expected that fluorescence emission spectrometry coupled with glass capillary gas chromatography will provides a convenient method for the determination of aza-heterocyclic ring systems in coal-derived oil. The identification of isomers can easily be achieved by mass spectrometry when combined with the qualitative information supplied by fluorescence spectrometry. By using the trapping system shown in Fig. 2, nanogram amounts of aza compounds were trapped with about 60% efficiency.

Molecular structures were predicted on the basis of the combination of information from the mass and fluorescence spectra and the TLC fractionation. Table II shows the results from the identification of GC peaks. Peak 4 represents a molecular weight of 179. Its fluorescence spectrum has a maximum at about 365 nm, which

TABLE II

ASSIGNMENT OF SOME GAS CHROMATOGRAPHIC PEAKS BY USING INFORMATION FROM MASS SPECTRA, RETENTION INDEXES (*I*), FLUORESCENCE EMISSION SPECTRA AND TLC FRACTIONATION

No.	*I*	*Mol.wt.*	*TLC fraction No.*	*Emission maximum (nm)*	*Possible compound*
1	1760.9	179	1	320	Unknown
2	1853.9	179	1 and 2	370	Benzo[*h*]quinoline
3	1884.9	179	3	370	Benzo[*f*]quinoline or phenanthridine
4	1914.6	179	4	365	Benz[*f*]- or -[*h*] isoquinoline
5	1959.9	193	1	320	Unknown
6	1981.4	193	1	370	C_1-benzoquinoline (phenanthrene type)
7	2008.0	207	1	320	Unknown
8	2104.3	207	1	365	C_2-benzoquinoline (phenanthrene type)

suggests that it is of the phenanthrene type. After TLC fractionation this unknown substance is found mainly in fraction 4, which suggests that the nitrogen atom should not be hindered sterically, similarly to isoquinoline. These results lead to only two possibilities: benz[*f*]isoquinoline and benz[*h*]isoquinoline.

In a similar manner, peaks 6 and 8 can be considered to be of the phenanthrene type with a highly hindered nitrogen atom. Peaks 2 and 3 are concluded to be benzo[*h*]quinoline and benzo[*f*]quinoline and/or phenanthridine, respectively, because of the excellent agreement between the retention indices of the unknown and authentic standards; benzo[*f*]quinoline and phenasnthridine could not be separated from each other on an OV-101 column. This conclusion is consistent with the results from the TLC separation and the fluorescence spectra. Peaks 1, 5 and 7 could not be identified. However, they belong to the same TLC fraction. All their fluorescence spectra show an emission maximum at the same wavelength. Each of their retention indices is considerably lower than those of corresponding isomers. Therefore, it is thought that these unknowns have the same common fused ring.

ACKNOWLEDGEMENTS

This work was partially supported by a Grand-in-Aid for Environmental Science from the Ministry of Education of Japan. We thank Mr. N. Sakai and Mr. F. Yoshida for preparing the coal-derived oil.

REFERENCES

1 P. Burchill, A. A. Herod, J. P. Mahon and E. Pritchard, *J. Chromatogr.*, 265 (1983) 223.
2 B. A. Tomkins and C.-H. Ho, *Anal. Chem.*, 54 (1982) 91.
3 J. M. Schmitter, I. Ignatiadis, P. Arpino and G. Guiochon, *Anal. Chem.*, 55 (1983) 1685.

4 D. M. Jewell, J. H. Weber and H. P. Lancher, *Anal. Chem.*, 44 (1972) 1391.
5 D. W. Later, M. L. Lee, K. D. Bartle, R. C. Kong and D. L. Vassilaros, *Anal. Chem.*, 53 (1981) 1612.
6 D. A. Haugen, M. J. Peal, K. M. Suhrbler and V. L. Stamoudes, *Anal. Chem.*, 54 (1982) 32.
7 M. Novotny, R. Kump, F. Merli and L. J. Todd, *Anal. Chem.*, 52 (1980) 401.
8 I. Ignatiadis, J. H. Schmitter and G. Guiochon, *J. Chromatogr.*, 246 (1982) 23.
9 J. M. Schmitter, I. Ignatiadis and G. Guiochon, *J. Chromatogr.*, 248 (1982) 203.
10 D. W. Later, T. G. Andros and M. L. Lee, *Anal. Chem.*, 55 (1983) 2126.
11 D. W. Later and B. W. Wright, *J. Chromatogr.*, 289 (1984) 183.
12 S. Imamichi, T. Kodama, F. Morishita and T. Kojima, *Bunseki Kagaku*, 34 (1985) 1430.
13 E. Sawicki, W. C. Elbert and T. W. Stanley, *J. Chromatogr.*, 17 (1965) 120.
14 C. R. Engel and E. Sawicki, *J. Chromatogr.*, 31 (1967) 109.
15 J. R. Kershaw, *Fuel*, 62 (1983) 1430.
16 T. Vo-Dinh, G. H. Moller, D. W. Abbott, R. L. Moody, C. Y. Ma and C. H. Ho, *Anal. Chim. Acta*, 175 (1985) 181.