

Effect of Acid-Clay Treatment on Nitrogen Compound Distribution in Fuels from Shale Oil

Steven A. Holmes and William E. Blanton

Western Research Institute
P. O. Box 3395, University Station
Laramie, Wyoming 82071

INTRODUCTION

The properties of fuels have been studied extensively in relation to the effects of processing on them and their effect on thermal and/or storage instability. Studies indicate nitrogen species in hydrotreated fuels derived from shale oil have deleterious effects on fuel stability (1). The speciation of nitrogen compounds at ppm levels in fuel provides information regarding fuel stability and allows possible selection of antioxidant additives. However, little information is available regarding speciation of nitrogen compounds at trace levels in fuels.

Comparing physicochemical properties of an oil before and after processing has provided insight to processing effects. Nitrogen compound-type distributions in crude shale oil and in fuels produced by catalytic hydrotreatment have been studied (2,3). Catalyst selectivity toward hydrodenitrogenation of different nitrogen types has been determined. Other oil-upgrading schemes have incorporated acid treatment of shale oils (4). In 1979, Standard Oil of Ohio (Sohio) hydrotreated shale oil to remove 80 percent of its nitrogen; however, about 3350 ppm nitrogen remained in the hydrotreated products (5). These products were subsequently treated with acid and clay to remove residual fuel-bound nitrogen and color bodies, making the finished products storage stable. Finished jet fuel contained less than one ppm nitrogen, and finished diesel fuel contained 23 ppm nitrogen. Sohio reported that acid-clay treatment also removed non-nitrogen containing compounds.

With the development of high resolution gas chromatographic capillary columns and computer data base reduction systems, analytical techniques have allowed efficient speciation of nitrogen compounds in fuels (6). The following work presents the speciation of nitrogen compounds in hydrotreated and finished fuels derived from shale. A comparison of these compound types is used to discuss effects of acid-clay treatment of the fuels. An analysis of the nitrogen types in the finished fuel is discussed in terms of their reactivity toward fuel instability.

EXPERIMENTAL

Hydroprocessing of Shale Oil

Shale oil from the Paraho direct heat retort was hydroprocessed by Sohio under a contract with the U.S. Departments of Energy and Defense (5). Whole crude oil was catalytically hydrotreated over a nickel-molybdenum catalyst and then fractionated by distillation to maximize yields of military transportation fuels, jet fuels (JP-5 and JP-8) and diesel fuel marine (DFM). Each hydrotreated fuel was treated with acid and clay. About 10.8 kg of 93 weight percent sulfuric acid was used to contact each bbl of fuel; the acid-treated fuel was separated from the acid sludge and passed through clay filters, a clay contactor, and final filter to product storage. An antioxidant was added to the acid-clay treated fuel. The effect of acid-clay treatment on nitrogen compound-type distribution was investigated by analyzing the compositions of the hydrotreated DFM and the finished DFM.

Fractionation by Adsorption Chromatography

Preparative alumina adsorption chromatography was used to fractionate the hydrotreated DFM and finished DFM into hydrocarbon and nitrogen fractions. An accurately weighed amount of hydrotreated DFM (about 10 grams) was diluted with 100 ml of hexane and pumped onto basic alumina in a 0.9 cm i.d. x 50 cm glass column. An additional 100 ml of hexane eluted the hydrocarbon fraction from basic alumina. The nitrogen fraction was backflushed from the column with 40 volume percent ethanol in toluene. Because some nitrogen compounds remained in the hydrocarbon fraction, this fraction was chromatographed again on neutral alumina into hydrocarbon and pyridine fractions. An accurately weighed amount of the finished DFM (about 174 grams) was diluted with 1800 ml hexane and pumped onto neutral alumina. An additional 100 ml of hexane eluted the hydrocarbon fraction from the column and the nitrogen fraction was backflushed from the neutral alumina with 40 volume percent methanol in benzene. Rates for sample charging and fraction elution were 6 ml/min. Solvents were carefully removed from fractions under reduced pressure. Solvent-free fractions were weighed and stored under nitrogen in refrigerated amber glass containers until compound-type analyses.

Analytical Methods

Elemental nitrogen in the fuels and their fractions was determined by chemiluminescence detection. Standard solutions ranging from 3×10^{-2} M to 5×10^{-5} M 9-methylcarbazole in toluene were used as calibrants. Amounts of basic nitrogen were determined by potentiometric titration analysis using acetonitrile-toluene and acetic anhydride-toluene with perchloric acid in dioxane as titrant (3). These reported values are accurate within ± 3 relative percent. Infrared spectra were obtained with a Perkin-Elmer model 621 grating spectrophotometer. The nitrogen-containing fractions were diluted in methylene chloride, and spectra recorded in the absorbance mode using solvent compensation with a matched pair of potassium chloride infrared cells of path length 0.5 mm.

High resolution gas chromatographic analysis (HRGC) of the nitrogen-containing fractions was done with an HP model 5730A equipped with a capillary column inlet system. A 60-meter DB-1 fused silica capillary column was used with a glass effluent splitter (1:1) for simultaneous flame ionization (FID) and nitrogen-phosphorous detection (NPD). Helium was used as carrier gas. Column linear flow velocity was 20 cm/sec. Samples were diluted with methylene chloride, and splitless injections having a 45-second delay time were used with a 30°C initial oven temperature for the nitrogen-containing fractions from the hydrotreated DFM. A 140°C initial oven temperature was used for the nitrogen fraction from the finished DFM. Oven temperature was programmed to 300°C at 2°C/min.

Similar gas chromatographic conditions described above were employed for compound-type analysis by high resolution gas chromatography/mass spectrometry (HRGC/MS). An upgraded HP model 5985 was used with an interface temperature of 300°C. Source temperature was 200°C, and ionization voltage was 70V. A mass range from 45 to 500 amu was scanned.

RESULTS AND DISCUSSION

Concentration of Nitrogen Compounds by Chromatography

The nitrogen compounds in the fuels were concentrated to facilitate detailed compound-type characterization. Two nitrogen-containing fractions from the hydrotreated DFM and one nitrogen fraction from the finished DFM were generated by alumina adsorption chromatography. A pyridine fraction from the hydrotreated DFM was identified by its distinct infrared absorbances at 1598 cm^{-1} (C=C stretch) and 1557 cm^{-1} (C=N stretch), suggesting the presence of pyridinic compounds. The absence of these absorbances in the finished DFM confirmed the lack of a pyridine fraction

as well as pyridinic compounds. The nitrogen fractions from both fuels displayed N-H stretching at 3460 cm^{-1} , suggesting the presence of pyrrolic compounds.

Nitrogen compounds comprised 6 weight percent and 0.13 weight percent of the hydrotreated DFM and finished DFM (Table 1), respectively. The low nitrogen contents in the pyridine fraction (2.92 weight percent) and in the nitrogen fraction from the finished DFM (1.62 weight percent) suggest the presence of non-nitrogen containing compounds. However, excellent nitrogen recovery was obtained. About 99 percent and 91 percent of the nitrogen from the hydrotreated DFM and finished DFM, respectively, was concentrated in the pyridine and nitrogen fractions.

Amounts of basic nitrogen were determined in each of the nitrogen-containing fractions and are presented in Table 2. All the nitrogen in the pyridine fraction was weak base (pKa 7 to 9), suggesting the presence of pyridine derivatives. The potentiometric titration analysis of the nitrogen fraction from the hydrotreated DFM indicates not only pyridinic compounds but also the presence of arylamines and hydrogenated indoles and/or quinolines (pKa 2 to 7), and indoles and carbazoles (nonbasic nitrogen). The nitrogen fraction from the finished DFM contains predominantly nonbasic nitrogen which does not undergo extensive acetylation (27 percent) in acetic anhydride; this suggests the presence of nonactive hydrogens in indole- and/or carbazole-type compounds.

HRGC/FID/NPD and HRGC/MS Analysis

HRGC with simultaneous detection by FID and NPD was used to establish optimal gas chromatographic conditions for the HRGC/MS analysis presented below. Acceptable peak resolution without tailing was achieved on the apolar chromatographic column. In Figure 1, the one-to-one peak correspondence of each detector response to the components in the nitrogen fraction from the hydrotreated DFM suggests that this fraction contains compounds with at least one nitrogen atom. Phosphorous is not expected to be present in these fractions. However, in Figure 2 the FID/NPD responses of the species from the finished DFM indicate few nitrogen compounds which have long column retention times (initial oven temperature, 140°C). FID/NPD responses for species in the pyridine fraction indicate the presence of non-nitrogen-containing compounds. The nitrogen species in the pyridine fraction are distributed about intermediate column retention times compared with the longer times for species in the nitrogen fractions.

Nitrogen in the pyridine fraction is primarily found in the isomers of alkyl-substituted dihydropyridines, pyridines, quinolines, and tetrahydroquinolines shown in Table 3. It is noteworthy that many different isomers of alkyltetrahydroquinolines are indicated relative to fewer alkylquinolines. The buildup of tetrahydroquinolines is indicative of the rate determining step in the hydrogenation of quinoline. The large number of isomers of alkylpyridines has been observed previously (7). Not listed for the pyridine fraction are non-nitrogen-containing compounds which include alkyl-substituted benzenes, naphthenes, biphenyls, and 9-H fluorenes. Because compound-type sensitivity factors were not available at the time of analysis, quantitative data were not obtained.

Large numbers of isomers of alkyltetrahydroquinolines and alkylpyridines are indicated by HRGC/MS analysis of the nitrogen fraction from hydrotreated DFM. These results are listed in Table 3. Infrared absorbances at 3375 cm^{-1} (N-H stretch) and 1612 cm^{-1} and potentiometric titration analysis (pKa 2 to 7) suggest that arylamines are also in this fraction. Because chemical ionization was not done, analysis by electron impact ionization cannot differentiate arylamines from pyridines. Previous work (8) showed about 15 percent of the pyridines may be comprised of arylamines. In addition, alkyl-substituted pyrroles, indoles, and carbazoles are present.

The retention time of carbazole in the total ion current chromatogram (TICC) of the nitrogen fraction from the hydrotreated DFM is indicated in Figure 3. The ex-

tracted ion current profiles (EICP) of methylcarbazoles and dimethylcarbazoles are shown in Figure 4. These compound types have long column retention times, and they comprise minor amounts of nitrogen in the fuel as indicated by their ion intensities.

The HRGC/MS analysis of the nitrogen fraction from the finished DFM was facilitated by matching its FID/NPD chromatograms (Figure 2) with that of its TICC. Mass spectral fragmentation patterns of the few nitrogen-containing compounds in this fraction are tentatively identified as carbazole, methylcarbazoles, and dimethylcarbazoles. Except for the ion intensity of carbazole in the finished DFM, relative intensities of the alkylcarbazoles in the finished DFM agree very well with those in the hydrotreated DFM. No other nitrogen types were identified; however, this does not preclude minor amounts undetected at baseline levels. The non-nitrogen-containing compounds were alkyl-substituted naphthalenes and 9-H fluorenes.

Effect of Acid-Clay Treatment on Nitrogen Compound Distribution

A comparison of the nitrogen compound distributions in fuels before and after acid-clay treatment demonstrates which nitrogen types are susceptible to removal. Acid-clay effectively removed 99.3% of the nitrogen from the hydrotreated DFM. As expected, basic nitrogen compounds such as arylamines form salts in reaction with acid; pyridine derivatives adsorb into acidic medium and/or participate in electrophilic substitution reactions, and both compound types are removed as acid sludge. A pyridine fraction was present only in the hydrotreated fuel and was completely removed by the acid-clay treatment. Very weak base and nonbasic nitrogen compounds such as indoles, which experience adsorption and/or acid catalysis and polymerization reactions, are effectively removed by acid-clay treatment. Interestingly, some carbazole derivatives survive acid-clay treatment. Earlier work (8) showed carbazole derivatives constituted about 66 ppm nitrogen in the hydrotreated DFM. Therefore, acid-clay removed almost two-thirds of the carbazole derivatives from the hydrotreated DFM. Nonbasic carbazoles are soluble in mineral acids; their relative unreactivity allows some to remain in the finished fuel.

In the acid-clay treatment of jet fuel (JP-8), nitrogen was not detected in the finished fuel. High resolution mass spectrometric analysis of the hydrotreated JP-8, which contained 3000 ppm nitrogen, indicated similar nitrogen-type distribution to that in the hydrotreated DFM, except carbazole derivatives were not detected. Acid and clay effectively removed all nitrogen types from the JP-8 fuel. Carbazole derivatives in transportation fuels are the nitrogen compounds least affected by acid-clay treatment.

The importance of determining residual nitrogen types in finished fuels relates to fuel stability. Aromatic nitrogen compounds have measurable sediment under low temperature storage conditions. Work reported (9) on model compounds has indicated that symmetrical, highly condensed aromatic nitrogen compounds appear less reactive than the partially hydrogenated counterparts or highly alkylated heterocyclics. These model compound studies suggest carbazole derivatives do not participate as significantly in sediment formation as do pyrrole and indole derivatives. Synergistic effects also play an important role in sediment formation particularly as the hydrocarbon matrix becomes more complex: n-decane<jet fuel<diesel fuel. The nitrogen distributions in the finished DFM and JP-8 fuels indicate these fuels may be storage stable. However, non-nitrogen compound types in these fuels may very well affect fuel stability.

In summary, the analytical techniques presented have been applied successfully to the analysis of moderate and trace quantities of nitrogen in fuels. The determination of nitrogen compound distributions aid in understanding the effects of fuel processing and in discussing fuel stability.

ACKNOWLEDGMENTS

The authors are indebted to E. T. Robinson of Sohio for discussions of this work. The authors thank the following personnel at WRI for their technical contributions: L. F. Thompson, F. A. Barbour, S-L Chong, and M. Harnsberger. They also thank R.E. Robertson for reviewing the manuscript and M. E. Marron for editorial suggestions.

LITERATURE CITED

1. Frankenfeld, J. W., W. F. Taylor, and D. W. Brinkman. Exxon R and E Co., U.S. Department of Energy Contract Report No. DOE/BC/10045-12 (1981).
2. Bett, A., T. G. Harney, T. W. Matheson, and K. C. Pratt. Fuel, 62, 1445 (1983).
3. Holmes, S. A. and L. F. Thompson. Preprints, Div. of Petrol. Chem., ACS, 29 (1), 269 (1984).
4. Reif, H. E., J. P. Schwedock, and A. Schneider. "An Exploratory Research and Development Program Leading to Specifications for Aviation Turbine Fuel From Whole Crude Shale Oil, Part V," Final Report AFWAL-TR-81-2087, March 1982. Available from NTIS.
5. Evin, C. G. and E. T. Robinson. "The Commercial-Scale Refining of Paraho Crude Shale Oil Into Military Fuels," Office of Naval Research, Navy Contract N0014-79-C-0061, Sept. 1979.
6. Ellis, L. C., and P. T. Crisp. J. Chrom., 292, 355 (1984).
7. Cooney, J. V., E. J. Beal, and R. N. Hazlett. Preprints, Div. of Petrol. Chem., ACS, 29 (1), 247 (1984).
8. Holmes, S. A., and L. F. Thompson. Fuel, 62, 709 (1983).
9. Frankenfeld, J. W., W. F. Taylor, and D. W. Brinkman. Exxon R and E Co., U.S. Department of Energy Contract Report No. DOE/BC/10045-23 (1982).

DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement.

Table 1. Nitrogen Content in Fractions from Fuels Derived from Shale

Fractions	Weight Percent Sample	Weight Percent Nitrogen	Nitrogen (Weight Percent of Sample)
Hydrotreated DFM			
Pyridine Fraction	1.46	2.92	0.043
Nitrogen Fraction	4.58	6.31	0.289
Hydrocarbon Fraction	91.5	11 ppm	10 ppm
Recovery (%)	98	NA	99
Finished DFM			
Nitrogen Fraction	0.13	1.62	21 ppm
Hydrocarbon Fraction	94.2	2 ppm	2 ppm
Recovery (%)	94	NA	100

Table 2. Distribution of Basic Nitrogen Contents in Fractions from Fuels Derived from Shale

Fractions	Weight Percent of Nitrogen		
	Weak Base pKa 7 to 9	Very Weak Base pKa 2 to 7	Nonbasic Nitrogen
Hydrotreated DFM			
Pyridine Fraction	2.92	--	--
Nitrogen Fraction	4.78	0.76	0.77
Finished DFM			
Nitrogen Fraction	0.04	0.06	1.52

Table 3. Compound Classes in Fractions from Hydrotreated DFM

Compound Class ^a	No. of Isomers in Fraction		Compound Class	No. of Isomers in Fraction	
	Pyridine	Nitrogen		Pyridine	Nitrogen
Dihydropyridines			Quinolines		
C ₇	6	--	C ₀	--	1
C ₈	4	--	C ₁	--	1
C ₉	4	--	C ₂	1	2
Pyridines ^b			C ₃	4	6
C ₂	--	3	C ₄	7	4
C ₃	--	21	C ₅	4	2
C ₄	4	28	Indoles		
C ₅	10	44	C ₁	--	4
C ₆	15	42	C ₂	--	5
C ₇	29	33	C ₃	--	8
C ₈	24	21	C ₄	--	16
C ₉	30	26	C ₅	--	18
C ₁₀	19	39	C ₆	--	24
C ₁₁	21	33	C ₇	--	18
C ₁₂	17	11	C ₈	--	2
C ₁₃	9	2	Pyrrole		
C ₁₄	2	--	C ₁₀	--	1
Tetrahydroquinolines			Carbazoles		
C ₁	--	11	C ₀	--	1
C ₂	--	19	C ₁	--	3
C ₃	3	30	C ₂	--	1
C ₄	11	22	Acridines/ Phenanthridines/ Benzoquinolines		
C ₅	13	37		2	--
C ₆	9	28			
C ₇	2	13			
C ₈	1	--			

^a Listing of C_x refers to the number of carbons in substituents on the heteroaromatic compound.

^b Alkylarylamines are included with pyridines in the nitrogen fraction.

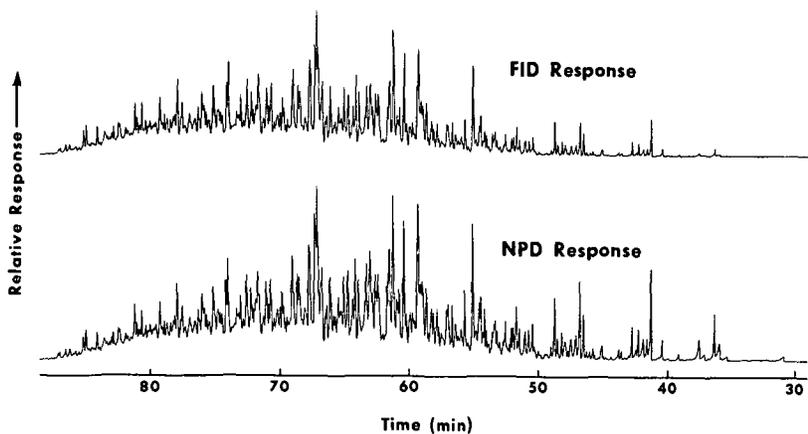


Figure 1. HRGC Chromatograms of Nitrogen Fraction from Hydrotreated DFM (Initial Oven Temperature, 30°C)

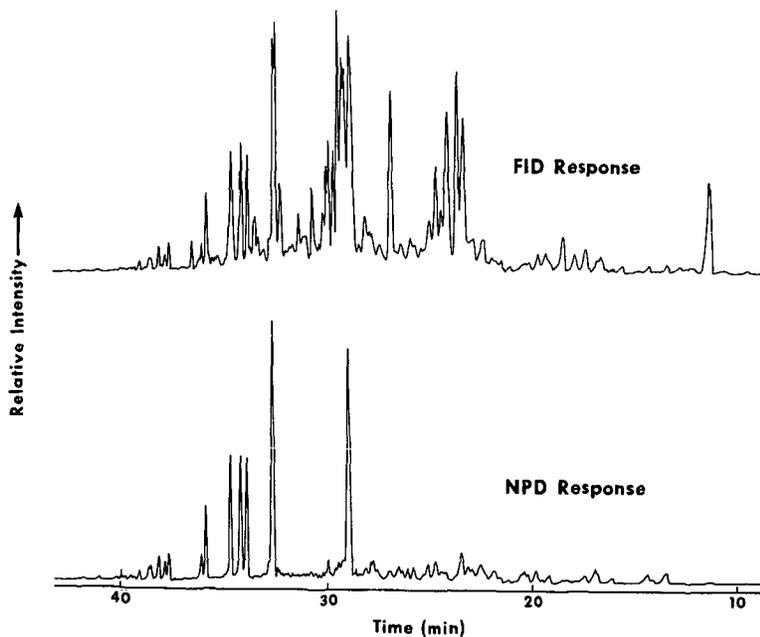


Figure 2. HRGC Chromatograms of Nitrogen Fraction from Finished DFM (Initial Oven Temperature, 140°C)

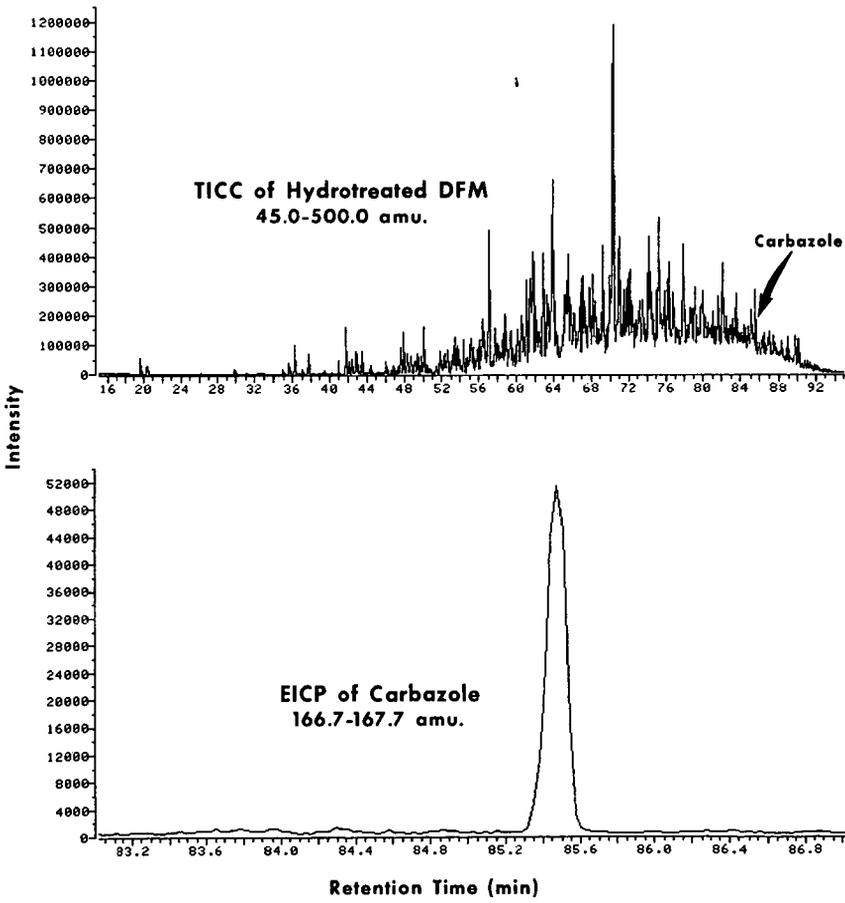


Figure 3. HRMS/GC Analysis of Hydrotreated DFM

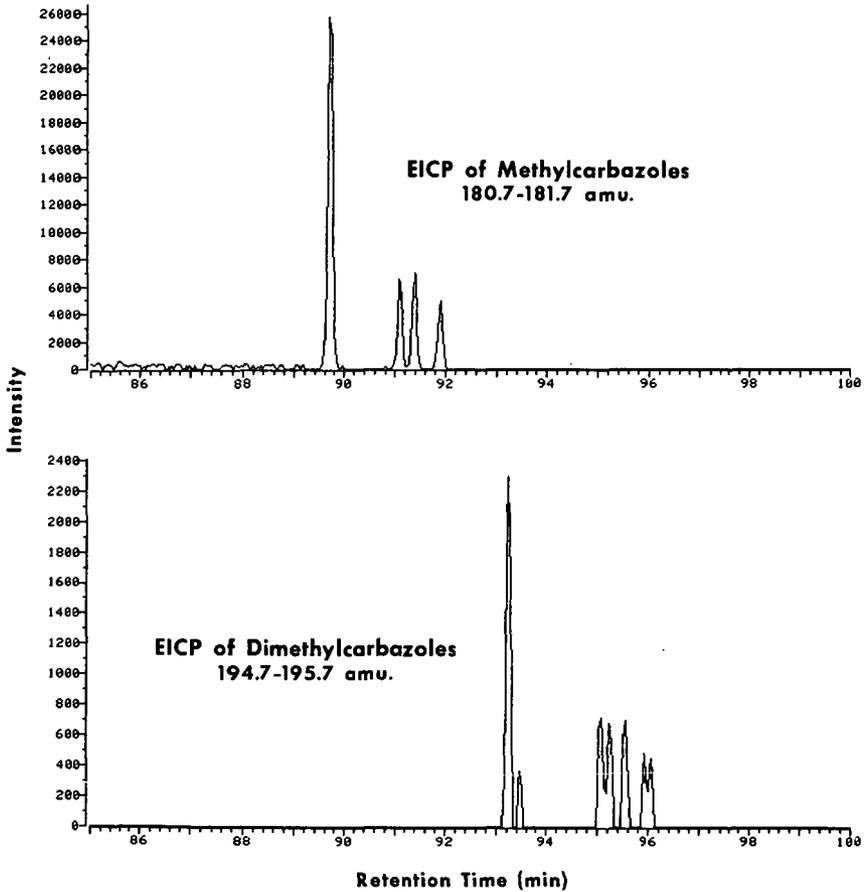


Figure 4. Extracted Ion Current Profile of Alkylcarbazoles