CHAPTER VIII

IDENTIFICATION OF NITROGENOUS COMPOUNDS IN TIRE-DERIVED OIL USING POWERFUL GCxGC/TOF-MS FOR BETTER ANALYSIS

8.1 Abstract

Nitrogen compounds can be formed in tire-derive oil (TDO) since N-containing curing agents are added during tire production. In refinery, they can be harmful to catalysts, and induce coke deposition; so, they need to be removed from oils. In this work, the two-dimensional gas chromatography coupled with a time-of-flight mass spectrometry (GCxGC/TOF-MS) was employed to identify and classify N-containing species based on hydrocarbon groups (aliphatic, alicyclic, and aromatic hydrocarbons) and carbon numbers for better understanding in further treatment. This work focused on the analysis of polar aromatics that are compounds with a nitrogenous atom substituted into a benzene ring. The results were reported in 3D (surface) and 2D (contour) plots of total ion chromatogram (TIC).The petroleum cuts and the amount of N compounds in TDOs were also analyzed using SIMDIST GC and CHNS analyzer. The results indicated that the identification of N-containing species in TDOs was successfully accomplished by using the effective GCxGC/TOF-MS. Approximately, 87 N-containing species in polar aromatics were detected, and classified into 10 groups according to their structures and carbon numbers. Most of N-containing species are distributed in the carbon number range of 6-18 (99.0 %), and are mostly in the azo compounds and amine groups. Diazabicycloheptenes such as 7,7-dimethyl-5-phenyl-, (1à,4à,5á)-2,3-diazabicyclo[2.2.1]hept-2-ene (m/z = 200.1313), and 1,4-diphenyl-2,3-diazabicyclo[2.2.1]hept-2-ene (m/z = 248.1313) was the new group found in TDOs. Moreover, it was found that N-containing compounds are highly distributed in kerosene and gas oil fractions.

8.2 Introduction

The disposal of waste tires has globally become a major environmental concern, attributed to the increase in automobile usage. The nuisance caused by the waste tires is that they are not bio-degradable and take several decades for degradation. One of the most powerful methods for tire elimination is pyrolysis since the process can transform waste tires into valuable products including gas, liquid, and solid. The liquid product or tire-derived oil (TDO) is likely to gain more the interest in nowadays since it can be used as fuel oil. However, there are some drawbacks from the degradation of waste tires because the obtained oil still contains hetero-atoms such as nitrogen atom. Thus, the N-containing compounds in TDO is elaborated in this work. The presence of these compounds results from the degradation of accelerators, activators, retarders, and anti-degradants in tires. They are considered as undesirable products since they affect the environment problems, causing the formation of NOx. Moreover, they posed the effects in refining procedure in particular fouling, catalyst poisoning, equipment corrosion, and gum formation. However, the obtained oil can be upgraded, aiming to remove the hetero-atoms, by using hydrated iron (III) chloride-clay adsorbent, hydrodenitrogenation (Wei *et al.*, 2015), ultrasound-assisted oxidative desulfurization process (Nunes *et al.*, 2014), and ionic liquid methods (Laredo *et al.*, 2015). Generally, the literatures reported the nitrogenous compounds in diesel (Cheng *et al.*, 2004; Laredo *et al.*, 2015; Matzke *et al.*, 2015), crude (Flego and Zannoni, 2011; Oldenburge *et al.*, 2014; Sim *et al.*, 2015), coker gas (Wei *et al.*, 2015), and shale oils (Tong *et al.*, 2013; Dijkmans *et al.*, 2015). The derivatives of indole, carbazole, aniline, quinoline, pyridine, and benzothiophene were the major of nitrogenous compounds in the oils.

Moreover, Mirmiran *et al.* (1992) characterized the nitrogenous compounds from the naphtha fraction of the used tire vacuum pyrolysis oil. This research divided naphtha fraction into three main groups; that are, hydrocarbon (mainly aromatics), oxygenate compounds, and nitrogenous compounds. The analytical separation technique relied on liquid-solid chromatography using dual packed silica gel and alumina column. The nitrogenous compounds were eluted with methanol. Thirty-one compounds were found by using gas chromatography/mass spectrometry (GC/MS) and confirmed by using gas chromatography/ atomic emission detection (GC/AED). The detected species were reported without grouping. The main nitrogenous compound in the naphtha fraction was pyridine. Furthermore, the fourier transform ion cyclotron resonance mass spectrometry (FTICP-MS) can be used to identify the elemental composition, bond equivalent, and carbon number based on ultra-high-resolution (Tong *et al.*, 2013; Oldenburg *et al.*, 2014; Sim *et al.*, 2015). However, FTICP-MS is not the quantitative analysis, and its maintenance cost causes the limitation on widespread availability. From the observations, the GC/MS might be the proper instrument for the classification of N-containing compounds in TDOs. Although the normal GC/MS can provide the detail on compositional information, the disadvantage is that it cannot interpret and resolve the overlap peaks of the complex hydrocarbon chromatogram. This is due to the several order of magnitudes of hydrocarbon matrix, their fragmentations can interfere with those of other hetero-compounds. Therefore, the comprehensive two-dimensional gas chromatography (GCxGC) is a lot more powerful for characterizing nitrogenous compounds (Flego and Zannoni, 2011). Even though the GCxGC is more powerful than other instruments, the hetero-atoms can still overlap with the complex hydrocarbons. To solve this interference, Dijkmans *et al.* 2015 suggested to precipitate asphaltene out of the oil prior to analysis. Previously, Pithakratanayothin and Jitkarnka (2014) attempted to identify sulfur compounds and classify them by using the comprehensive two-dimensional Gas Chromatography with Time of Flight Mass Spectrometer (GC×GC/TOF-MS). The result showed that this method was able to overcome the limitation of chromatogram interpretation, which is better for detection each group of hetero-atom structures.

Hence, the GCxGC/TOF-MS technique was expected as an alternative method for classification of the N-containing compounds in TDOs in this work for better understanding in further treatment. The same conditions stated in Pithakratanayothin and Jitkarnka (2014) were applied for the simultaneous identification of nitrogen species in TDOs. The amount of petroleum fractions and nitrogenous compounds in TDOs were also analysed using SIMDIST GC and CHNS analyser, respectively. Three samplings the TDOs from thermal pyrolysis for all analysis were taken in this study. The detected nitrogenous compounds in polar group were classified based on nitrogenous structures and their carbon numbers.

8.3 Experimental

8.3.1 Pyrolysis of Waste Tire

The pyrolysis process was conducted in the same conditions as Pithakratanayothin and Jitkarnka (2014). The schematic of this procedure was redrawn and illustrated in Figure 8.1. A waste passenger tire (Bridgestone TURANZA GR-80) was scraped and then sieved (20-40 mesh). Thirty grams of the scrap tire were heated from room temperature to 500 °C with heating rate of 10 °C/min. At the final temperature, the reaction was held for 120 min. The evolved gas was purged using a 25 mL/min of nitrogen though two condensers, aiming separate liquid product from incondensable gas. Finally, the obtained liquid was dissolved in n-pentane with the oil to n-pentane mass ratio of 1:40 for asphaltene separation. The obtained oil is called maltene.

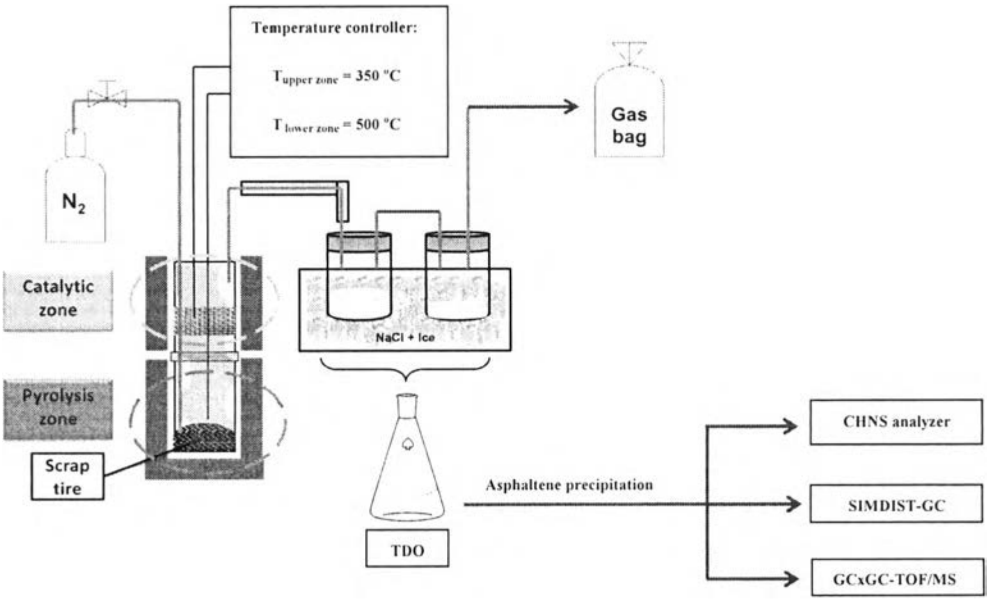


Figure 8.1 Schematic of the pyrolysis experiment.

8.3.2 Analysis of Nitrogen Compounds in Tire-derived Oil

Three samples of TDO from thermal pyrolysis were sampled in this study. All analysis were carried out by using 3 instruments, including CHNS analyzer, SIMDIST-GC, and GCxGC/TOF-MS.

Table 8.1 Analysis conditions of GCxGC-TOF/MS

Instruments	Conditions
Oven program	main GC oven: 50 °C, hold 2 min ramp 5 °C/min to 310 °C, hold 10 min secondary oven: 60 °C, hold 2 min ramp 5 °C/min to 320 °C, hold 10 min
Modulator	
- Time	4s for cycle time, 0.5s for holding time in repeat position
- Cryogen coolant	nitrogen (UHP, 99.999%) (set at least -80 °C of modulation trap temperature)
Detector voltage	1600 V
Injector	
- Temperature	250 °C
- Splitless	1 µL
Carrier gas	helium 99.99 % (flow rate 1 mL/min)
Mass range collection	30-500 m/z (transfer 100 spectra/s)
Data processing	S/N = 10
Similarity	700 up
Percentage area calculation	Dt

The elemental compositions of tire samples and the liquid products were firstly determined using a LECO® Elemental Analyzer (TruSpec® CHNS). Then, a maltene (30 µL), diluted in carbondisulfide (CS_2) (2 mL), was analyzed using a Varian GC-3800 simulated distillation gas chromatography (SIMDIST-GC) conformed to the ASTM-D2887 method for the petroleum fractions. The true boiling point curves were cut into petroleum fractions according to their boiling points; naphtha ($\leq$ 200 °C), kerosene (200-250 °C), light gas oil (251-300 °C), heavy gas oil (301-370 °C), and long residue ($\geq$ 371 °C). Furthermore, the diluted maltene was analyzed to identify the species of nitrogen using a two-dimensional Gas Chromatography with Time of Flight Mass Spectrometer (GC×GC/TOF-MS). The conditions are shown in Table 8.1. The Agilent gas chromatograph 7890 (Agilent Technologies, Palo Alto, CA, USA) was composed of a Pegasus® 4D TOF/MS (LECO, St. Joseph, MI, USA) and a thermal modulator. The instrument was operated by the cooperation of two GC columns. The 1st column was a non-polar Rtx®-5Sil MS with 30 m length × 0.25 mm ID × 0.25 μm film thickness installed in the main oven. The 2nd column was a polar Rxi®-17 MS with 1.79 m length × 0.15 mm ID × 0.10 μm film thickness installed in the second oven. The LECO ChromaTOF® software co-operating with NIST library was used to spectral match the nitrogen species detected from GCxGC/TOF-MS are displayed in surface plots (3D), contour (2D) plots and total ion chromatograms. Then, they were categorized according to their structures. Their distribution in each of petroleum fractions according to their boiling point, referred from Royal society of chemistry (2015) was also studied.

8.4 Results and Discussion

8.4.1 Compositions of Tire Samples and Pyrolytic Oils

The element compositions of tire and pyrolytic oil samples are mainly composed of carbon and hydrogen, followed by sulfur and nitrogen as reported in Table 8.2. Moreover, naphtha and kerosene are the main fractions in tire-derived oil, followed by light gas oil, heavy gas oil, and long residue as reported in Table 8.3.

Table 8.2 Elemental compositions (wt%) of tire samples and pyrolytic oils

Sample	C	H	N	S
Tire	77.10±0.00	6.57±0.01	0.48±0.01	2.05±0.00
Oil	69.10±0.42	9.62±0.15	0.40±0.04	1.27±0.00

Table 8.3 Petroleum fractions of tire-derived oil

Properties	Amount
Initial and final boiling points (^{o}C)	
Initial boiling point (IBP)	101-102
Final boiling point (FBP)	497-500
Petroleum Fractions (wt%)	
Naphtha	30.53±8.02
Kerosene	24.34±1.71
Light gas oil	17.73±2.15
Heavy gas oil	14.30±4.38
Long Residue	13.10±2.89

8.4.2 Identification of Nitrogenous Compounds in Tire-derived Oil

It is clearly seen that the hydrocarbons in maltene samples can be explicitly detected using GCxGC-TOF/MS as depicted in Figure 8.2a. In this work, nitrogenous species in maltene samples can be divided into 3 main groups; that are, (1) aliphatic hydrocarbons or saturated hydrocarbons (SATs) and olefins (OLEs), (2) alicyclic hydrocarbons that include naphthenes (NAPs) and terpenes (TERs), and (3) aromatic hydrocarbon, mostly polar-aromatics (PPAHs) as located in Figure 8.2b. According to IUPAC (1979), the PPAHs group is aromatic compounds with substituted hetero-atom into structure. Most of nitrogenous compounds in TDO are distributed in aromatic group (87.2 %) and aliphatic and alicyclic groups (12.8 %) as reported in Table 8.4. Thus, nitrogenous compounds in PPAHs group are consequently in-depth discussed.

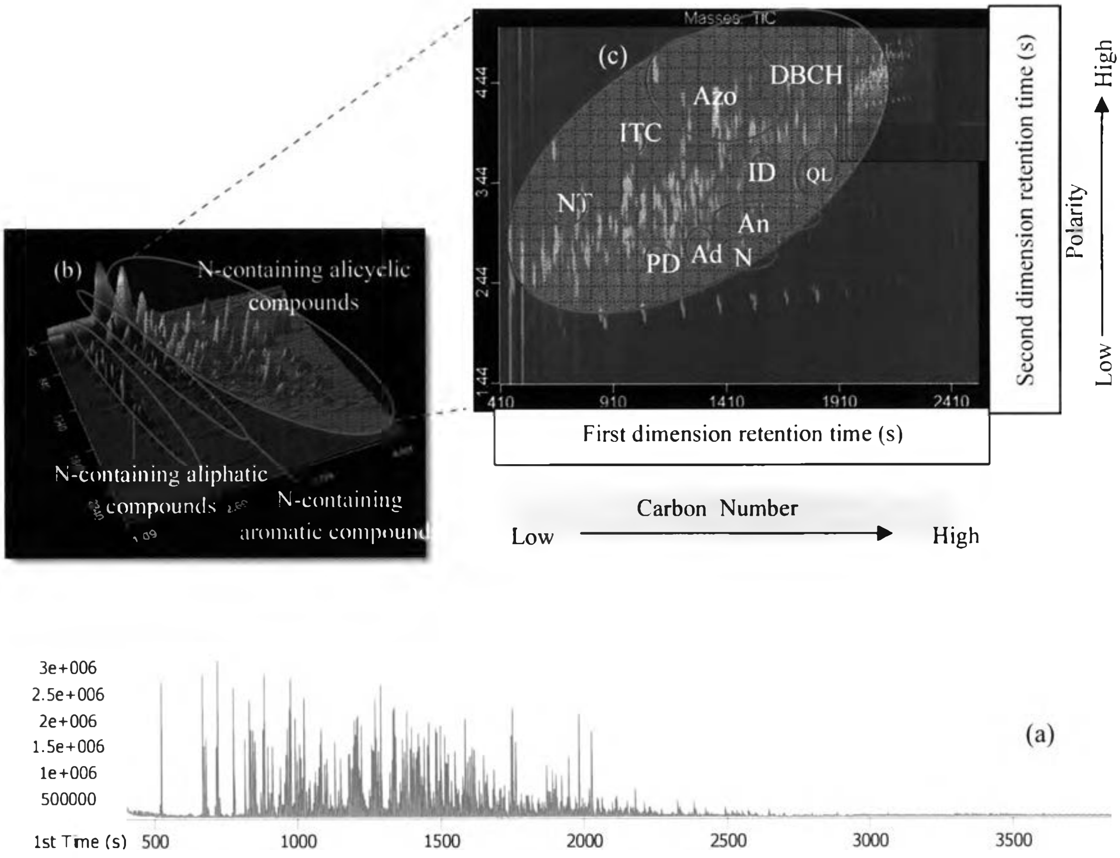


Figure 8.2 Overview of total ion chromatograms of maltene solution: (a) GCxGC-TOF/MS chromatogram, (b) surface plot (3D) of N-containing hydrocarbon compounds, and (c) contour plot (2D) showing the distribution of all groups of N-containing compounds of all compounds in tire-derived oil.

Table 8.4 Classification of N-containing species based on hydrocarbon groups

Groups of N-containing Compounds	Concentration in Maltene (% Area)	Total Number of Detected Species
Hydrocarbon groups		
Aliphatics (SATs and OLEs)	1.55±0.84	8±4
Alicyclics (NAPs and TERs)	11.21±1.04	19±3
Aromatics (PPAHs)	87.24±0.87	87±9
Total detected species		113±11

The nitrogenous compounds in PPAHs group, approximately 87.4 % of overall nitrogenous compounds in TDOs, were classified into 10 different groups according to their structures; that are, amines (An), amides (Ad), azo compounds (Az), diazabicycloheptenes (DBCH), indoles (ID), isothiocyanates (ITC), nitro compounds (N), nitriles (NT), pyridines (PD), and quinolines (QL) as located in Figure 8.2c and Figure 8.3. The overall distributions of nitrogen compounds are reported based on carbon numbers and structures in Table 8.5. The distribution of carbon number is mainly in the range of C6-C18 (99.0 %). The major part of N-containing compounds in PPAHs group is attributed from the presence of azo compounds and amines of 42.9 % and 11.6 %, respectively.

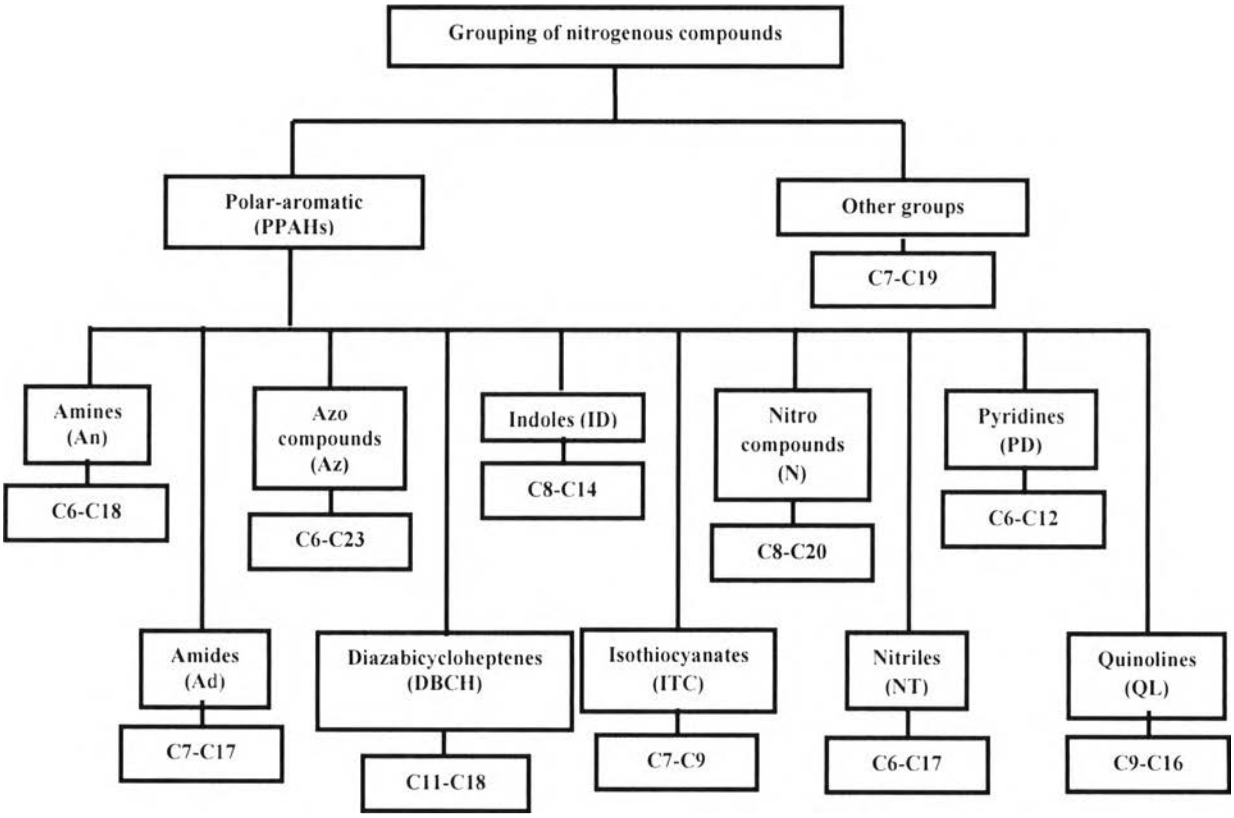


Figure 8.3 Classification of nitrogenous compounds in TDO.

Table 8.5 Average normalized nitrogenous composition (%) in tire-derived oil by groups and carbon numbers (An = amines, Ad = amides, Az = azo compounds, DBCH = diazabicycloheptenes, ID = indoles, ITC = isothiocyanates, N = nitro compounds, NT = nitriles, PD = pyridines, and QL = quinolines)

#C	An	Ad	Az	DBCH	ID	ITC	N	NT	PD	QL	Others	Total
5	-	-	-	-	-	-	-	-	-	-	0.26	0.26
6	6.08	-	0.01	-	-	-	-	0.01	0.04	-	0.48	6.61
7	0.09	0.17	32.26	-	-	8.02	-	1.09	0.06	-	0.58	42.27
8	0.59	0.07	8.05	-	0.05	0.48	0.41	0.06	0.13	-	1.32	11.16
9	0.36	-	0.76	-	0.18	0.14	1.03	0.10	0.02	0.13	0.56	3.27
10	0.14	-	0.01	-	0.04	-	-	0.08	0.09	0.27	1.84	2.46
11	-	-	1.28	0.98	0.05	-	0.12	-	-	3.38	1.77	7.59
12	0.64	0.15	0.04	-	0.14	-	0.17	0.28	0.02	0.40	2.26	4.12
13	0.14	1.16	0.10	5.97	-	-	0.02	1.60	-	0.06	0.41	9.44
14	1.97	-	0.07	-	0.01	-	-	1.24	-	-	1.82	5.10
15	1.60	-	-	-	-	-	-	-	-	-	-	1.60
16	0.02	-	0.13	-	-	-	0.43	0.17	-	0.04	0.43	1.21
17	-	0.11	0.03	1.97	-	-	-	0.91	-	-	-	3.02
18	0.01	-	-	0.65	-	-	-	-	-	-	0.46	1.12
19	-	-	-	-	-	-	-	-	-	-	0.17	0.17
20	-	-	-	-	-	-	0.24	-	-	-	-	0.24
21	-	-	-	-	-	-	-	-	-	-	-	0.00
22	-	-	0.08	-	-	-	-	-	-	-	0.14	0.22
23	-	-	0.05	-	-	-	-	-	-	-	0.01	0.05
24	-	-	-	-	-	-	-	-	-	-	0.07	0.07
Total	11.64	1.66	42.86	9.57	0.47	8.64	2.42	5.53	0.36	4.27	12.57	100.00

8.4.2.1 Amines (An)

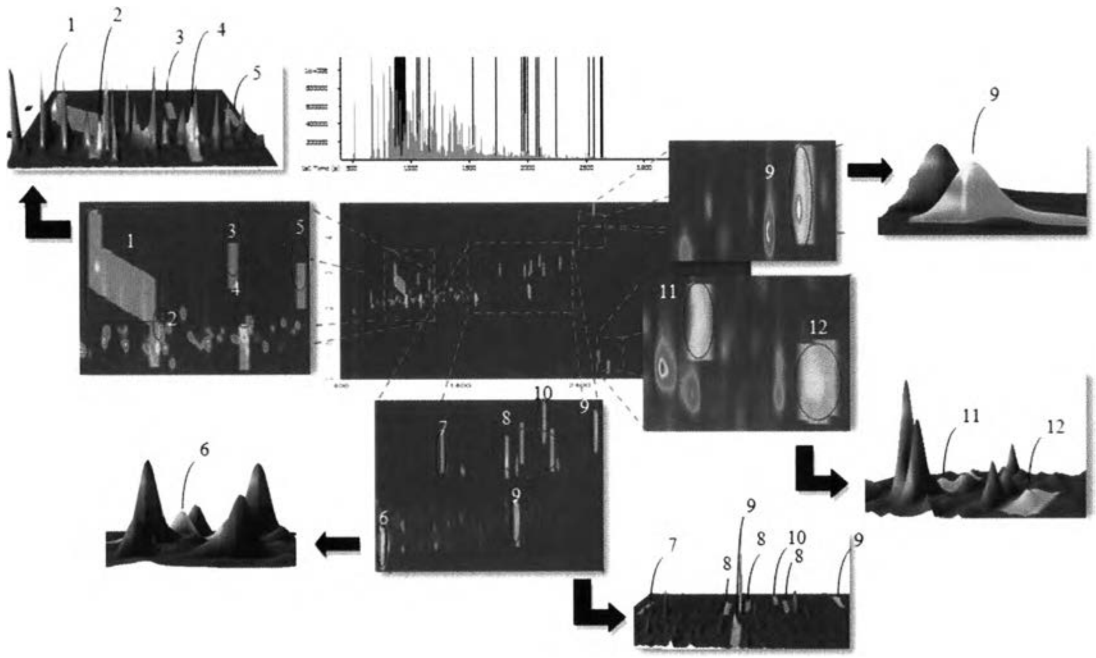


Figure 8.4 Total ion chromatogram of amines in PPAHs with selected ions (U): 30, 91, 93, 105, 106, 117, 148, 150 and 165.

Amines are the derivatives of ammonia containing a basic nitrogen atom. One or more of their hydrogen atoms have been replaced by alkyl or aryl group. The prefix "amino-" or the suffix "-amine" is typically the names of amine derivatives. Amines can be divided into three sub-categories; that are, primary (R-NH_2), secondary (R_2-NH), and tertiary (R_3-N) amines. Aniline as well as amino compounds are one of the primary amine groups. The main carbon number distribution of amines in TDO is in the range of C6-C18. The most dominant amines are aniline (m/z = 93.0578), (+-)-N-Benzyl-alpha-methyl-N-nitrosobenzylamine (m/z = 240.1263) and methyl-benzeneethanamine (m/z = 135.1040).

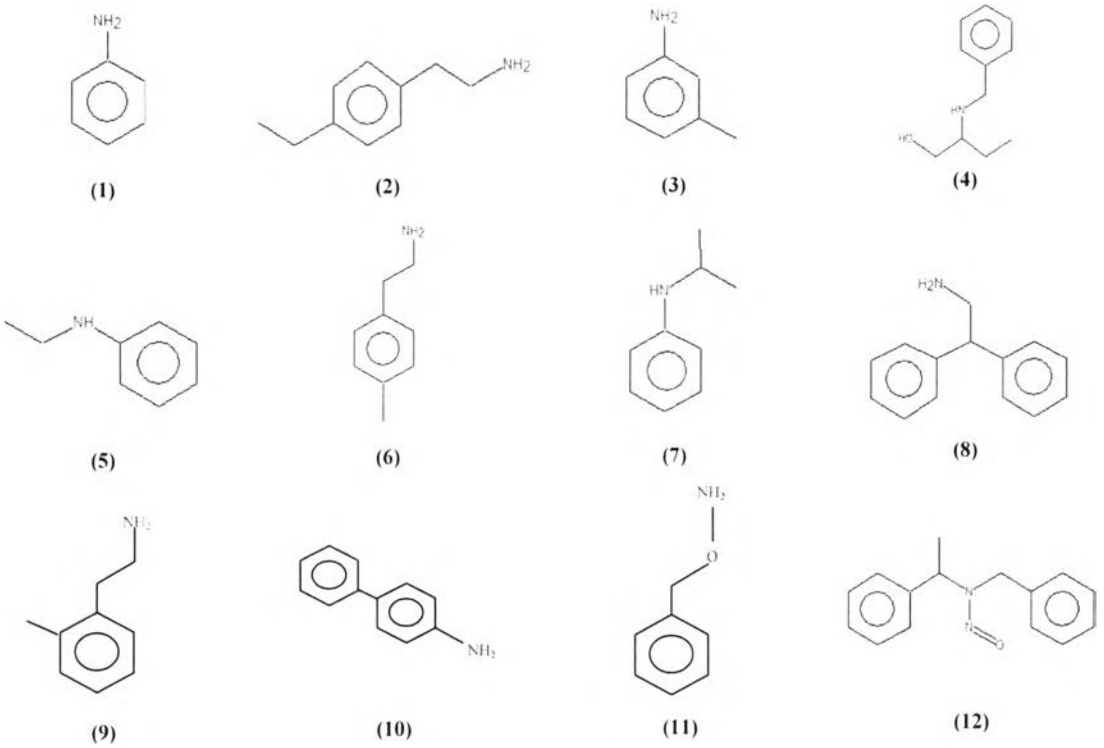


Figure 8.5 Structures of dominant N-containing compounds in amine group (for name, see peak no. in Table 8.6).

Table 8.6 Dominant N-containing compounds in amine group

Carbon No.	Peak No.	Name[a]	Exact Mass (m/z)	Unique Mass (U)
6	1	Aniline	93.0578	93
7	3	3-methyl-Benzenamine	107.0735	106
	11	O-(phenylmethyl)-Hydroxylamine	123.0684	91
8	5	N-ethyl-Benzenamine	121.0891	106
9	6	2-(p-Tolyl)ethylamine	135.1048	106
	7	N-(1-methylethyl)-Benzenamine	135.1048	120
	9	methyl-Benzeneethanamine	135.1040	91, 105, 150
10	2	4-Ethylphenethylamine	149.1204	117
11	4	(R)-(-)-2-Benzylamino-1-butanol	179.1310	148
13	10	4-Cyclohepta-2,4,6-trienylphenylamine	240.1268	105
14	8	2,2-Diphenylethylamine	197.1204	30, 165
15	12	(+-)-N-Benzyl-alpha-methyl-N-aminnitrosobenzylamine	240.1263	105

[a]Assigned compounds that are matched, based on the NIST library.

8.4.2.2 Amides (Ad)

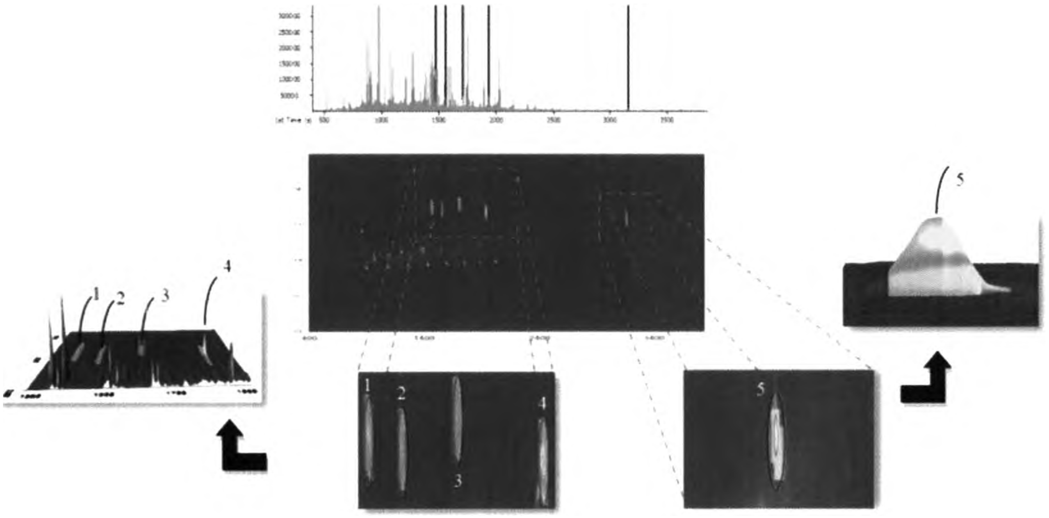
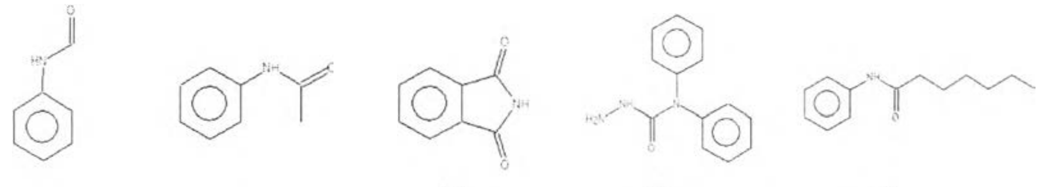


Figure 8.6 Total ion chromatogram of amides in PPAHs with selected ions (U): 66, 93, 147, and 169.

Amides are one of the derivatives of ammonia, which are normally derived from primary and secondary amines forming $R_1C(O)NHR_2$ and $RC(O)NR_1R_2$ formula, respectively. The prefix "carboxamido-" or "carbamoyl-" and the suffix "-amide" are typically the names of amide derivatives. The main carbon number distribution of amides in TDO is in the range of C7-C17. The most dominant amides are N,N-diphenyl-hydrazinecarboxamide (m/z = 227.1069), N-phenyl-heptanamide (m/z = 205.1467), and N-phenyl-formamide (m/z = 121.0538).



(1) (2) (3) (4) (5)

Figure 8.7 Structures of dominant N-containing compounds in amide group (for name, see peak no. in Table 8.7).

Table 8.7 Dominant N-containing compounds in amide group

Carbon No.	Peak No.	Name[a]	Exact Mass (m/z)	Unique Mass (U)
7	1	N-phenyl-Formamide	121.0538	66
8	2	N-phenyl-Acetamide	135.0684	93
	3	Phthalimide	147.0320	147
13	4	N,N-diphenyl-Hydrazinecarboxamide	227.1069	169
	5	N-phenyl-Heptanamide	205.1467	93

[a] Assigned compounds that are matched, based on the NIST library.

8.4.2.3 Azo Compounds (Az)

Azo compounds comprise the double bound of nitrogen atoms (R_1-N=N-R_2), which alkyl or aryl can be substituted R_1 and R_2 for more stable formation of derivatives. Alkyl azo compounds are aliphatic azo derivative compounds such as diazenes and diimides whereas aryl azo compounds such as benzothiazole and diphenyldiazene are normally more stable than alkyl azo compounds. From IUPAC system, the prefix and the suffix of azo compounds are "azo-" and "-diazene", respectively. The main carbon number of azo compounds in TDO is in the range of C6-C23. The most dominant azo compounds are benzothiazole (m/z = 135.0143), 2-methyl-benzothiazole (m/z = 133.0528) and 2-butyl-benzothiazole (m/z = 191.0769).

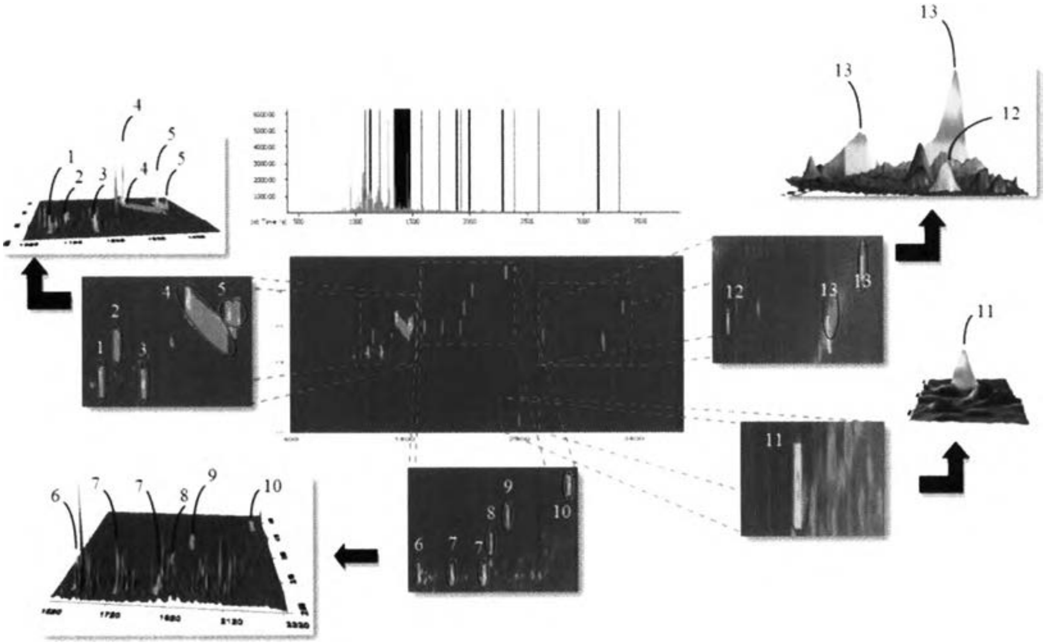


Figure 8.8 Total ion chromatogram of azo compounds in PPAHs with selected ions (U): 96, 108, 119, 132,133, 135, 148, 150, 163, 164, 210, and 211.

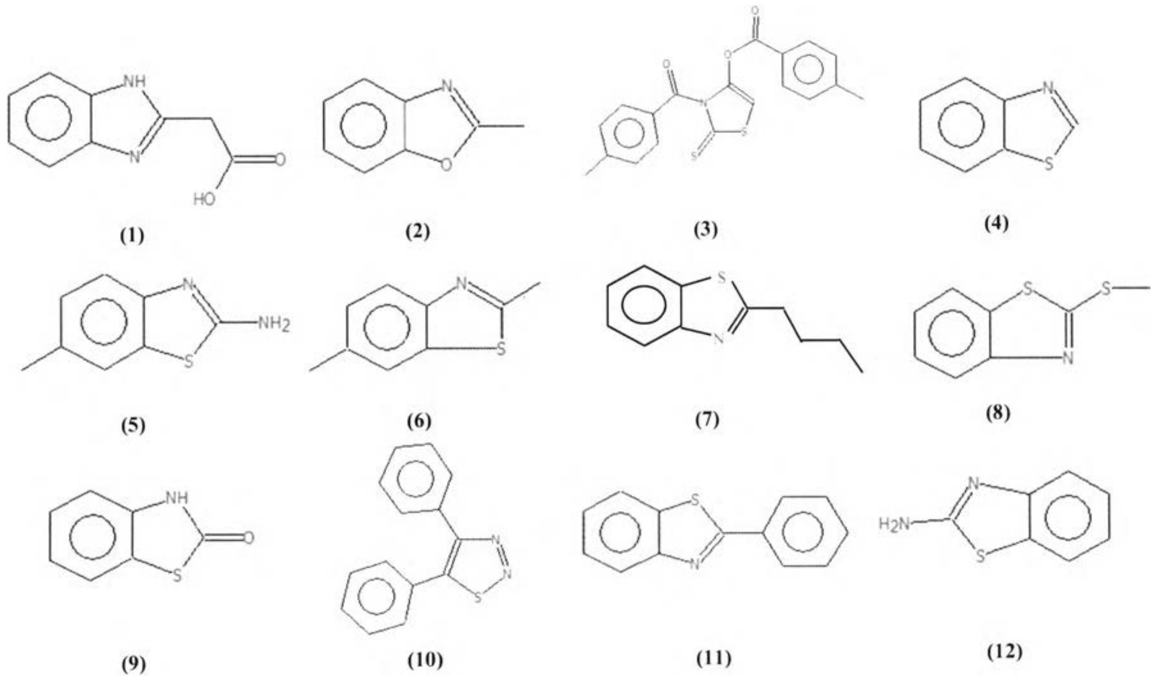


Figure 8.9 Structures of dominant N-containing compounds in azo compound group (for name, see peak no. in Table 8.8).

Table 8.8 Dominant N-containing compounds in azo compound group

Carbon No.	Peak No.	Name[a]	Exact Mass (m/z)	Unique Mass (U)
7	4	Benzothiazole	135.0143	108, 135
	9	2(3H)-Benzothiazolone	151.0092	96
	12	2-Benzothiazolamine	150.0252	150
8	2	2-methyl-Benzoxazole	133.0528	133
	5	2-methyl-Benzothiazole	149.0299	164
	8	2-(methylthio)-Benzothiazole	181.0020	148
9	1	2-benzimidazol-2-yl-Acetic acid	176.0586	132
	6	2,6-dimethyl-Benzothiazole	163.0456	163
11	7	2-butyl-Benzothiazole	191.0769	149
13	11	2-phenyl-Benzothiazole	211.0456	211
14	10	4,5-diphenyl-1,2,3-Thiadiazole	238.0565	210
19	3	3-(4-Methylbenzoyl)-2-thioxo-4-thiazolyl 4-methylbenzoate	369.0493	119

[a] Assigned compounds that are matched, based on the NIST library.

8.4.2.4 Diazabicycloheptenes (DBCH)

This is the first time that diazabicycloheptenes are reported found in tire derived oil, which are firstly detected using GCxGC/TOF-MS. This group is composed of a double bond in a ring between nitrogen atoms. Their structures are usual bicyclic compounds. The main carbon number distribution of diazabicycloheptenes in TDO is in the range of C11-C18. The most dominant diazabicycloheptenes are 7,7-dimethyl-5-phenyl-, (1à,4à,5á)-2,3-diazabicyclo[2.2.1] hept-2-ene (m/z = 200.1313), and 1,4-diphenyl-2,3-diazabicyclo[2.2.1]hept-2-ene (m/z = 248.1313).

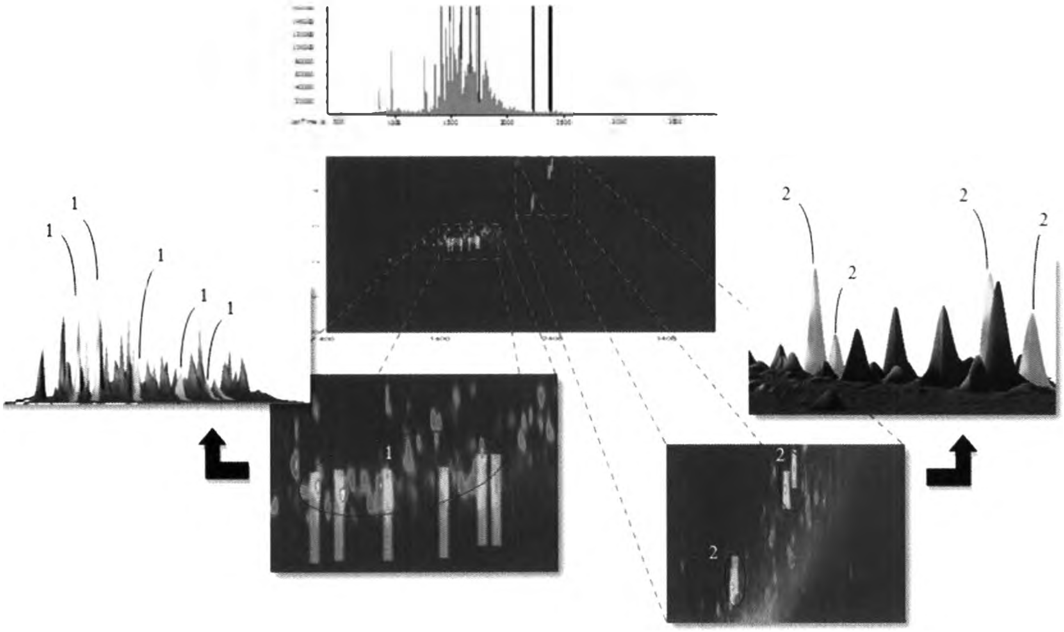
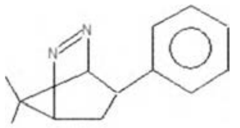


Figure 8.10 Total ion chromatogram of diazabicycloheptenes in PPAHs with selected ions (U): 94, 142, 155, 157, 172, and 220.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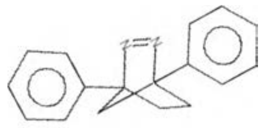

(2)

Figure 8.11 Structures of dominant N-containing compounds in diazabicycloheptene group (for name, see peak no. in Table 8.9).

Table 8.9 Dominant N-containing compounds in diazabicycloheptene group

Carbon No.	Peak No.	Name[a]	Exact Mass (m/z)	Unique Mass (U)
13	1	7,7-dimethyl-5-phenyl-, (1à,4à,5á)-2,3-Diazabicyclo[2.2.1]hept-2-ene	200.1313	94, 155, 157, 172
17	2	1,4-diphenyl-2,3-Diazabicyclo[2.2.1]hept-2-ene	248.1313	142, 220

[a]Assigned compounds that are matched, based on the NIST library.

8.4.2.5 Indoles (ID)

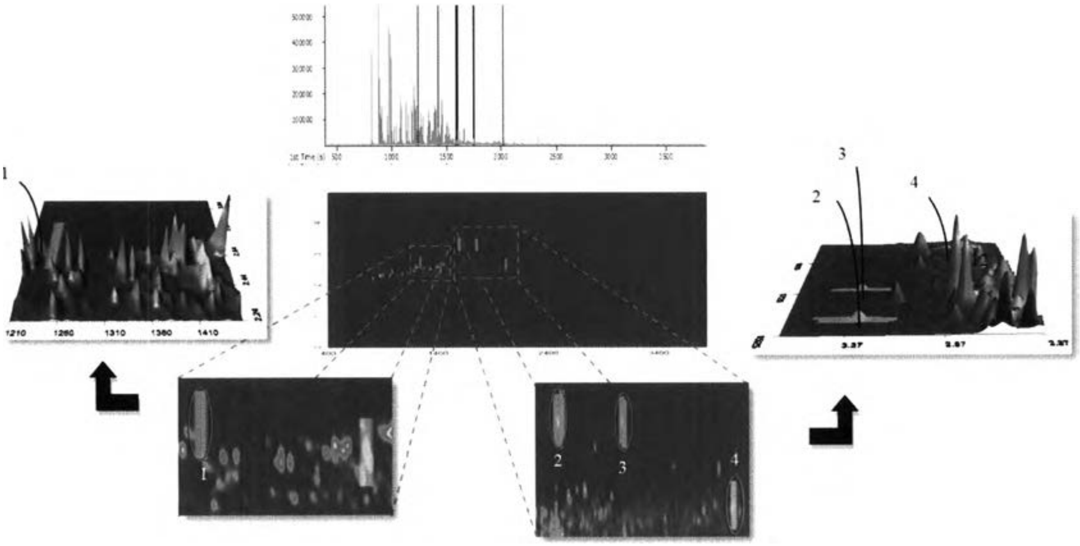
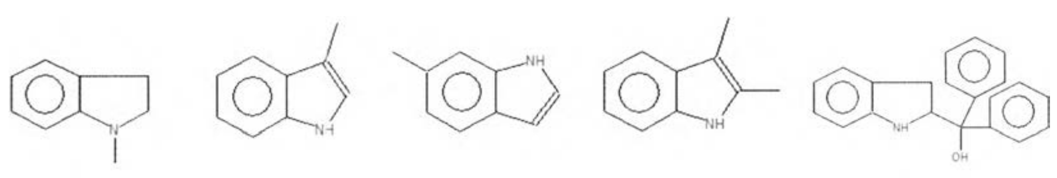


Figure 8.12 Total ion chromatogram of indoles in PPAHs with selected ions (U): 118, 130, 132, and 144.

Indole group is composed of the compounds with the association of nitrogen atom in a pyrrole ring connected to benzene ring. The $C_nH_{n-1}N$ is the indole formula. The suffix of its formula is called "-indole". Normally, indole compounds present in TDO possess the carbon numbers of 8 to 14 atoms. The most dominant indoles are 3-methyl-1H-indole (m/z = 131.0735), 2,3-dimethyl-1H-indole (m/z = 133.0891), and 2-(hydroxydiphenylmethyl)-indoline (m/z = 301.1467).



(1) (2) (3) (4) (5)

Figure 8.13 Structures of dominant N-containing compounds in indole group (for name, see peak no. in Table 8.10).

Table 8.10 Dominant N-containing compounds in indole group

Carbon No.	Peak No.	Name[a]	Exact Mass (m/z)	Unique Mass (U)
9	1	2,3-dihydro-1-methyl-1H-Indole	133.0891	132
	2	3-methyl-1H-Indole	131.0735	130
	3	6-methyl-1H-Indole	131.0735	130
10	4	2,3-dimethyl-1H-Indole	145.0891	144
21	5	2-(hydroxydiphenylmethyl)-Indoline	301.1467	118

[a] Assigned compounds that are matched, based on the NIST library.

8.4.2.6 Isothiocyanates (ITC)

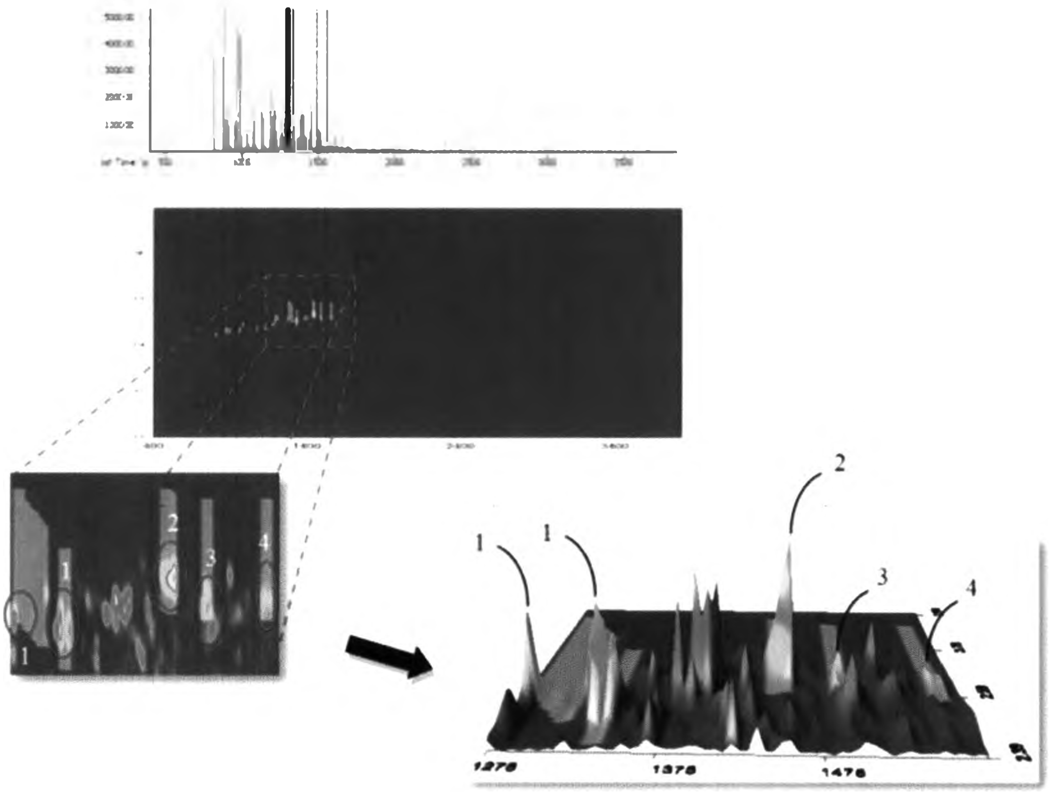
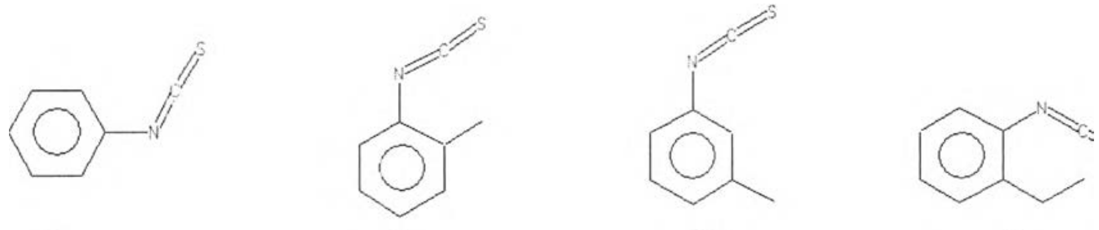


Figure 8.14 Total ion chromatogram of isothiocyanates in PPAHs with selected ions (U): 77, 135, 148, and 149.

Isothiocyanates are in the chemical group (R–N=C=S), formed by substituting the oxygen in the isocyanate group with a sulfur atom. Isothiocyanates present in TDO possess carbon numbers of 7 to 9 atoms. The most dominant isothiocyanates are isothiocyanato-benzene (m/z = 135.0143), 1-isothiocyanato-2-methyl-benzene (m/z = 149.0299), and 2-ethylphenyl-isothiocyanate (m/z = 163.0456).



(1) (2) (3) (4)

Figure 8.15 Structures of dominant N-containing compounds in isothiocyanate group (for name, see peak no. in Table 8.11).

Table 8.11 Dominant N-containing compounds in isothiocyanate group

Carbon No.	Peak No.	Name[a]	Exact Mass (m/z)	Unique Mass (U)
7	1	isothiocyanato-benzene	135.0143	77, 135
8	2	1-isothiocyanato-2-methyl-benzene	149.0299	149
	3	m-tolyl-isothiocyanate	149.0299	149
	4	2-ethylphenyl-isothiocyanate	163.0456	148

[a]Assigned compounds that are matched, based on the NIST library.

8.4.2.7 Nitro Compounds (N)

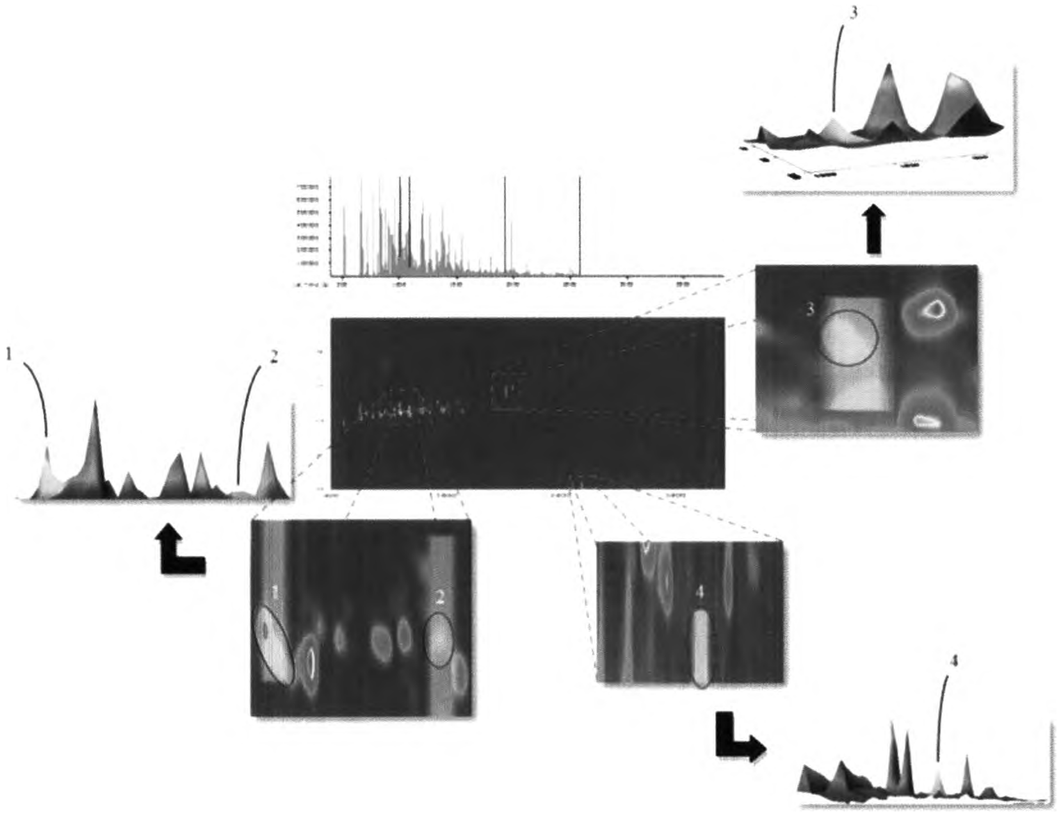
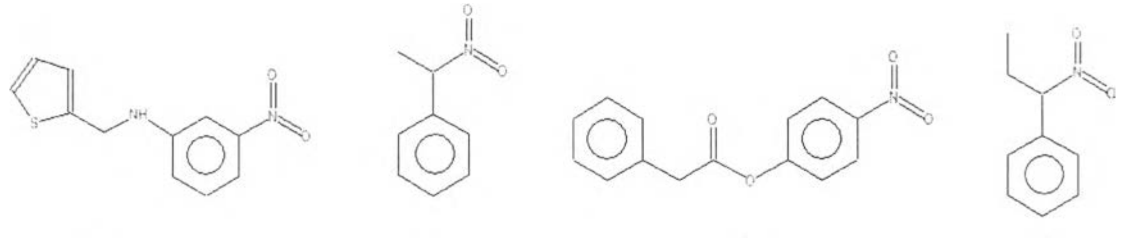


Figure 8.16 Total ion chromatogram of nitro compound in PPAHs with selected ions (U): 91, 97, 105, and 119.

Nitro compounds are organic compounds that contain one or more nitro functional groups (R–NO_2). The main carbon number distribution of nitro compounds in TDO is in the range of C8-C10. The most dominant nitro compounds are (1-nitroethyl)-benzene (m/z = 151.0633), (1-nitropropyl)-benzene (m/z = 165.0790), and 4-nitrophenyl ester phenylacetic acid (m/z = 257.0688).



(1) (2) (3) (4)

Figure 8.17 Structures of dominant N-containing compounds in nitro compound group (for name, see peak no. in Table 8.12).

Table 8.12 Dominant N-containing compounds in nitro compound group

Carbon No.	Peak No.	Name[a]	Exact Mass (m/z)	Unique Mass (U)
8	2	(1-nitroethyl)-Benzene	151.0633	105
9	4	(1-nitropropyl)-Benzene	165.0790	91
11	1	3-nitro-N-(2-thienylmethyl)-Benzenamine	234.0463	97
14	3	4-nitrophenyl ester Phenylacetic acid	257.0688	119

[a]Assigned compounds that are matched, based on the NIST library.

8.4.2.8 Nitriles (NT)

Nitriles are any organic compound that has a R−C≡N functional group. The prefix cyano- is used interchangeably with the term "nitrile" in industrial literature. Nitriles are found in many useful materials such as nitrile rubber. It is widely used as automotive and other seals since it is resistant to fuels and oils. The main carbon number distribution of nitriles is in the range of C7-C17. The most dominant nitriles are benzonitrile (m/z = 103.0422), (2,3-dihydro-1-methyl-1H-inden-1-yl)-propanedinitrile (m/z = 196.1000), and benzenepropanenitrile (m/z = 131.0735).

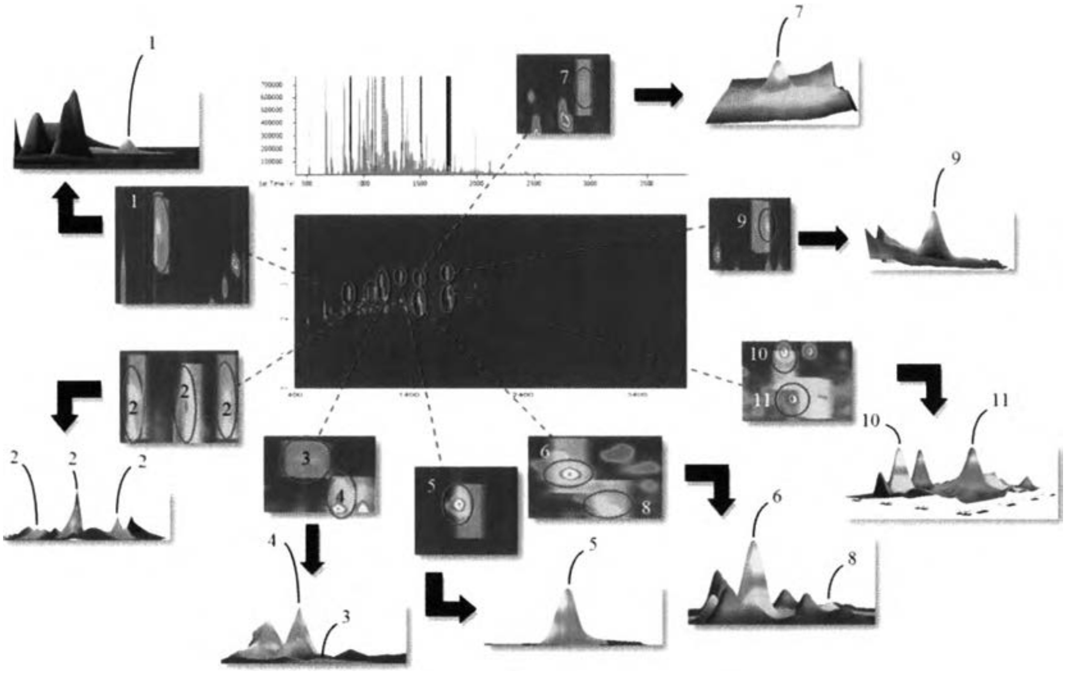


Figure 8.18 Total ion chromatogram of nitriles in PPAHs with selected ions (U): 90, 91, 103, 116, 119, 130, 131, and 159.

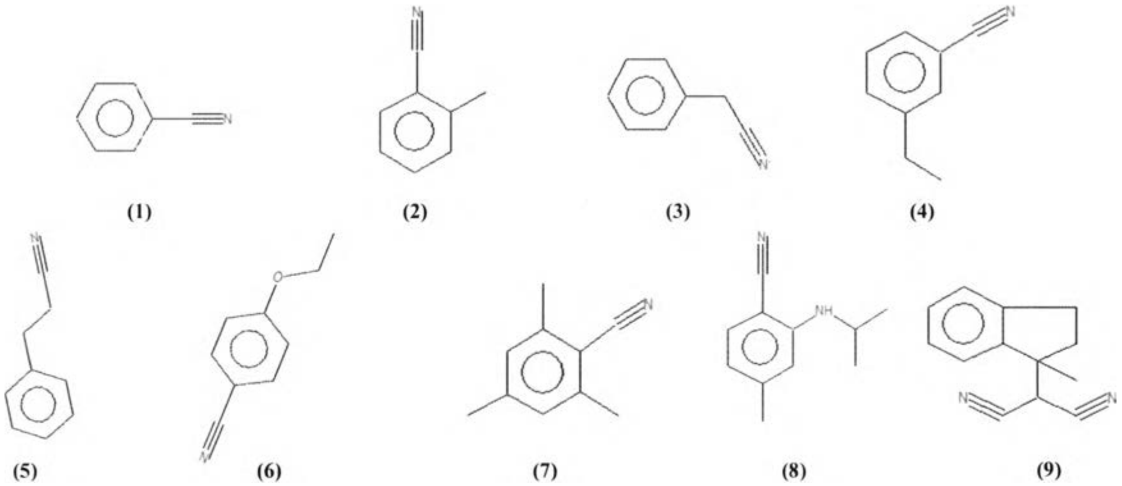


Figure 8.19 Structures of dominant N-containing compounds in nitrile group (for name, see peak no. in Table 8.13).

Table 8.13 Dominant N-containing compounds in nitrile group

Carbon No.	Peak No.	Name[a]	Exact Mass (m/z)	Unique Mass (U)
7	1	Benzonitrile	103.0422	103
8	2	2-methyl-Benzonitrile	117.0578	90
	3	Benzyl nitrile	117.0578	90
4	4	m-Ethylbenzonitrile	131.0735	116
	5	Benzenepropanenitrile	131.0735	91
	6	4-ethoxy-Benzonitrile	147.0684	119
10	7	2,4,6-trimethyl-Benzonitrile	145.0891	130
11	8	2-Isopropylamino-4-methyl-benzonitrile	174.1157	159
13	9	(2,3-dihydro-1-methyl-1H-inden-1-yl)-Propanedinitrile	196.1000	131

[a]Assigned compounds that are matched, based on the NIST library.

8.4.2.9 Pyridines (PD)

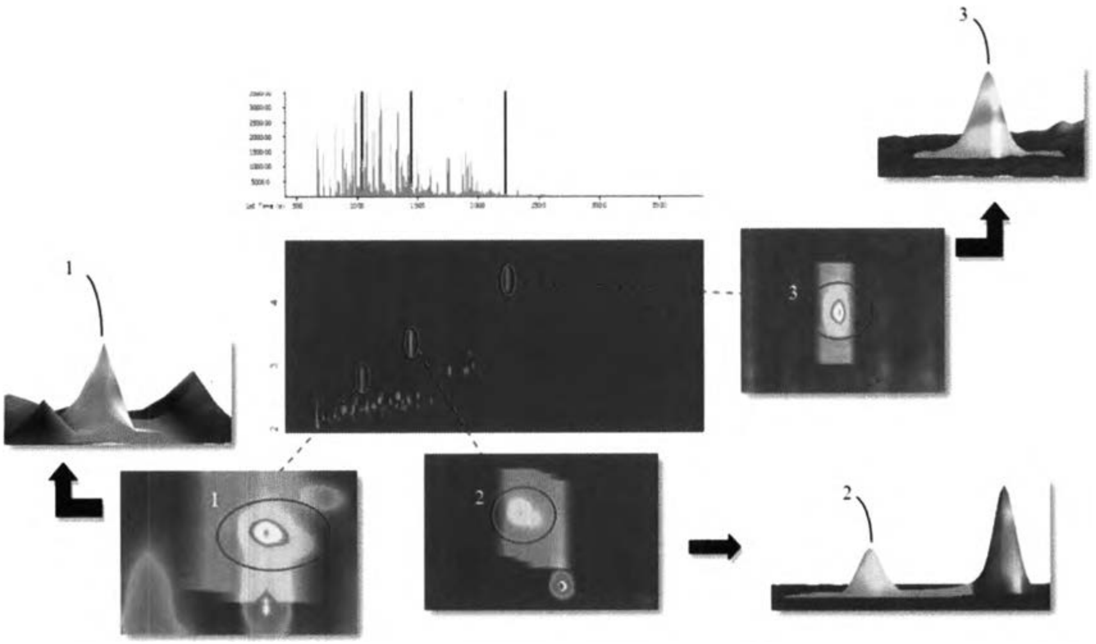
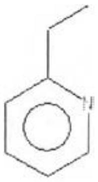
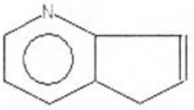


Figure 8.20 Total ion chromatogram of pyridines in PPAHs with selected ions (U): 106, 117, and 167.

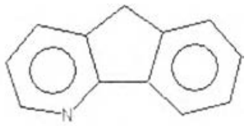
Pyridines are basic heterocyclic organic compounds with the chemical formula C_nH_nN. They are structurally related to benzene, with one methane group (=CH-) replaced by a nitrogen atom. The main carbon number distribution of pyridines in TDO is in the range of C6-C12. The most dominant pyridines are 5H-1-pyrindine (m/z = 117.0578), 2-ethyl-pyridine (m/z = 107.0735), and 5H-Indeno[1,2-b]pyridine (m/z = 167.0735).



(1)



(2)



(3)

Figure 8.21 Structures of dominant N-containing compounds in pyridine group (for name, see peak no. in Table 8.14).

Table 8.14 Dominant N-containing compounds in pyridine group

Carbon No.	Peak No.	Name[a]	Exact Mass (m/z)	Unique Mass (U)
7	1	2-ethyl-Pyridine	107.0735	106
8	2	5H-1-Pyrindine	117.0578	117
12	3	5H-Indeno[1,2-b]pyridine	167.0735	167

[a] Assigned compounds that are matched, based on the NIST library.

8.4.2.10 Quinolines (QL)

Quinolines are heterocyclic aromatic organic compounds with the chemical formula $C_nH_{n-2}N$. The main carbon number distribution of quinolines in TDO is in the range of C9-C16. The most dominant quinolines are 2,4-dimethyl-quinoline (m/z = 157.0891), 1-methyl-isoquinoline (m/z = 157.0891), and isoquinoline (m/z = 129.0578).

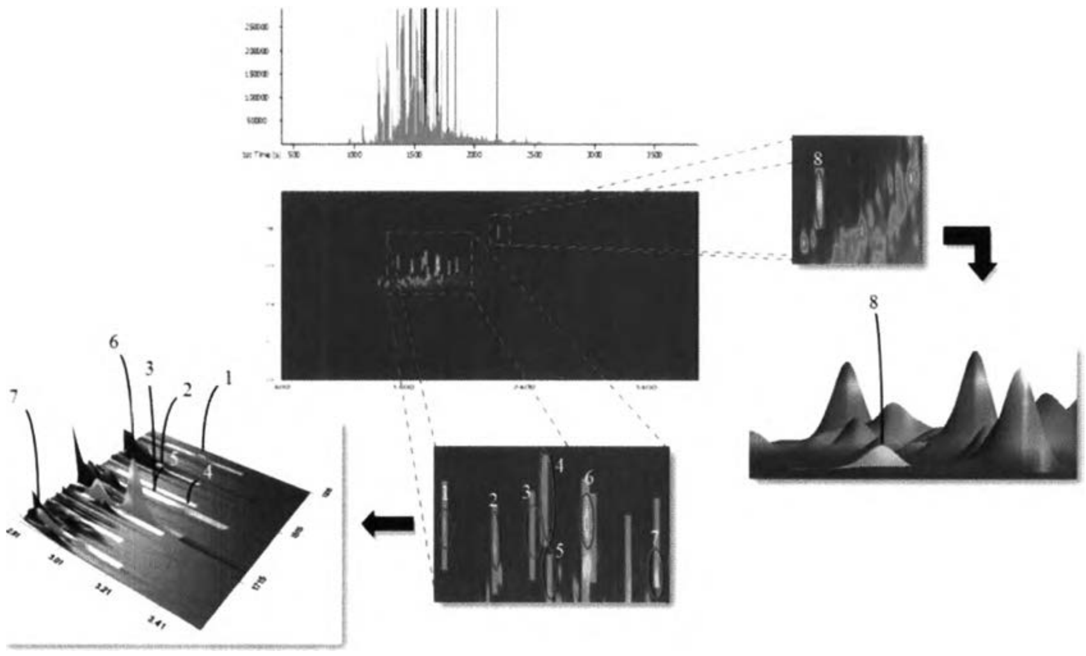


Figure 8.22 Total ion chromatogram of pyridines in PPAHs with selected ions (U): 129, 143, 157, 171, and 179.

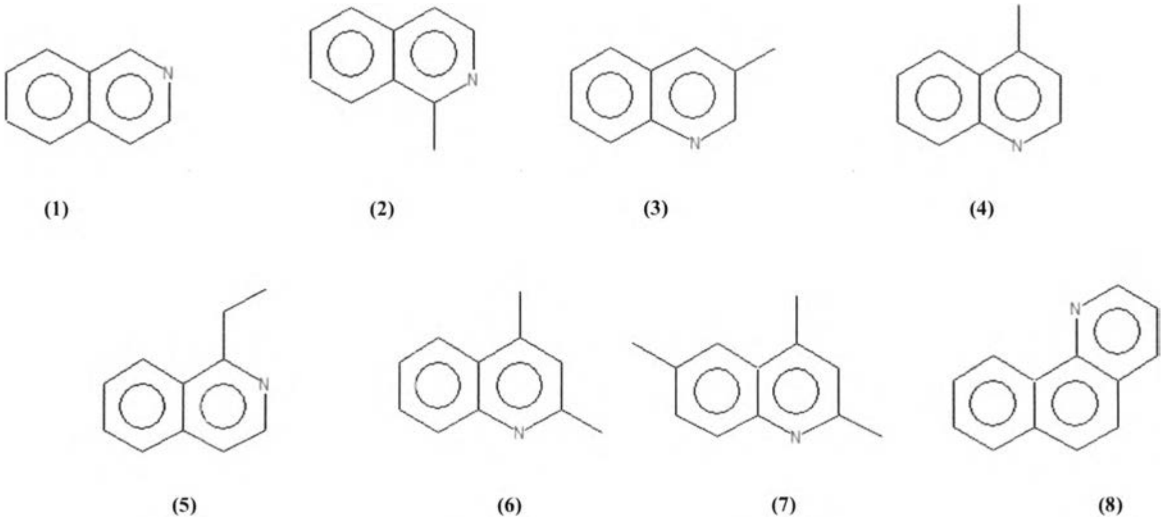


Figure 8.23 Structures of dominant N-containing compounds in quinoline group (for name, see peak no. in Table 8.15).

Table 8.15 Dominant N-containing compounds in quinoline group

Carbon No.	Peak No.	Name[a]	Exact Mass (m/z)	Unique Mass (U)
9	1	Isoquinoline	129.0578	129
10	2	1-methyl-Isoquinoline	143.0735	143
	3	3-methyl-Quinoline	143.0735	143
	4	4-methyl-Quinoline	143.0735	143
11	5	1-ethyl-Isoquinoline	157.0891	157
	6	2,4-dimethyl-Quinoline	157.0891	157
12	7	2,4,6-trimethyl-Quinoline	171.1048	171
13	8	Benzo[h]quinoline	179.0735	179

[a]Assigned compounds that are matched, based on the NIST library.

8.4.3 Nitrogenous Compounds in each Petroleum Fraction

Figure 8.24 illustrates the average distribution of N-containing compounds in each of petroleum fractions, based on the boiling points of nitrogen compounds (Royal Society of Chemistry, 2015).

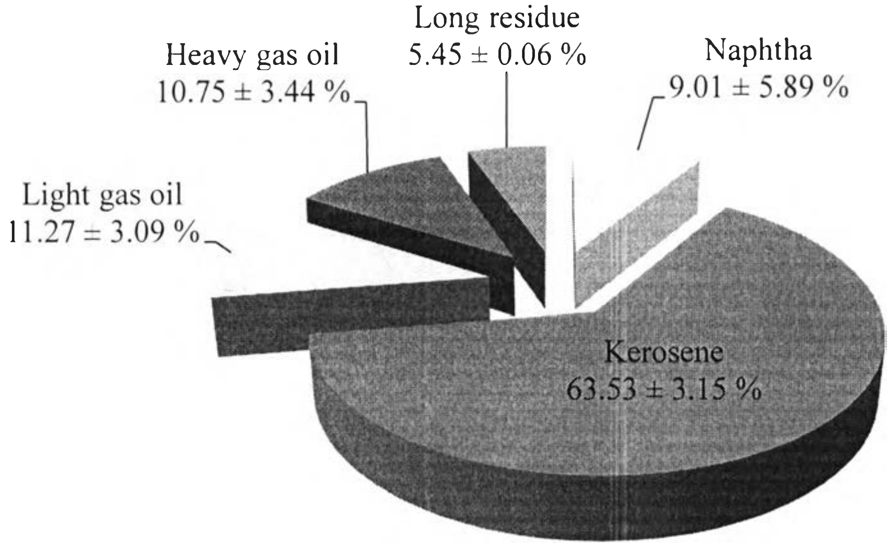


Figure 8.24 Average distribution of N-containing compounds in petroleum fractions.

The result shows that the distribution of nitrogenous compositions is mainly in kerosene (63.5 %), followed by gas oil (22.0 %), naphtha (9.0 %), and long residue (5.5 %).

In this study, the results show the different observations from Mirmiran *et al.* (1992) due to the different analysis method. The derivatives of pyridine, nitrile, nitro compound, amine, amide, azo compound, and quinoline have been found in tire-derived oil as similarly as Mirmiran *et al.* (1992). It is reasonable to state that the comprehensive GCxGC/TOF-MS gives the better identification of nitrogenous compounds because more nitrogenous compounds in tire-derived oil are detected, and all peaks of chromatograms are totally separated. Moreover, the derivatives of diazabicycloheptene can be firstly detected by using GCxGC/TOF-MS. 7,7-dimethyl-5-phenyl-, (1à,4à,5á)-2,3-diazabicyclo[2.2.1]hept-2-ene (m/z = 200.1313), and 1,4-diphenyl-2,3-diazabicyclo[2.2.1]hept-2-ene (m/z = 248.1313) are the dominant species in diazabicycloheptene group.

8.5 Conclusions

The two-dimensional gas chromatography coupled with a time-of-flight mass spectrometry (GCxGC/TOF-MS) was employed to identify and classify N-containing species in polar aromatic group based on carbon numbers and their structures. The identification of N-containing species in TDOs was successfully accomplished using the effective GCxGC-TOF/MS for better understanding in further treatment. The good separation indicated that N compounds can be divided into aromatic group (87.2 %) and aliphatic and alicyclic groups (12.8 %). Approximately, 87 nitrogenous species in PPAHs group were detected, and classified into 10 groups according to their structures and carbon numbers; that are, amines (An), amides (Ad), azo compounds (Az), indoles (ID), isothiocyanates (ITC), nitro compounds (N), nitriles (NT), pyridines (PD), quinolines (QL), and especially diazabicycloheptenes (DBCH) that was firstly detected in tire-derived oil. Most of N-containing species are distributed in the carbon numbers of 6-18 (99.0 %), and are mostly in the Azo group (42.9 %). Moreover, based on nitrogenous boiling points, N compounds are mostly distributed in kerosene (63.5 %).

8.6 Acknowledgements

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