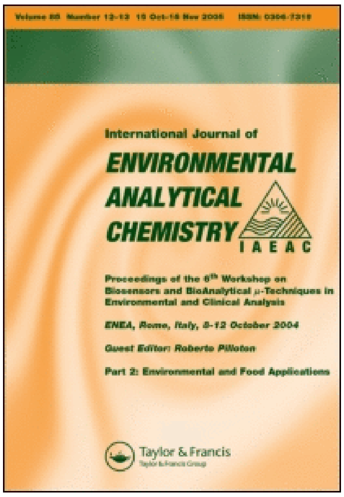

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Mass Spectrometric Analysis of Azaarenes in a Coal Tar*

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A coal tar sample taken from a well located on the site of a former coal tar distillation plant was dissolved in methylene chloride and fractionated into acids, bases, and neutrals by acid/base partitioning. Alumina chromatography was used to separate the base fraction intc five fractions, one of which contained the azaarenes. These fractions were subjected to gas chromatography/mass spectrometry. The fraction containing the azaarenes was also analyzed by ammonia chemical ionization and thermospray liquid chromatography/mass spectrometry. Sixteen different azaarenes ranging from MW 143 to MW 301 and seven isomers of azabenzopyrene were detected in the coal tar. The identification and the environmental significance of these compounds are discussed.

KEY WORDS: Azaarenes, gas chromatography/mass spectrometry, thermospray liquid chromatography/mass spectrometry, direct thermospray/mass spectrometry, coal tar.

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INTRODUCTION

Azaarenes are nitrogen analogs of the polycyclic aromatic hydrocarbons (PAH). They have been detected in urban air samples[1-5] at concentrations of 0.01 to 0.5 ng/m^3. Marine and freshwater sediments as well as street dust were found to contain azaarenes at 0.1 to 0.5 mg/kg.[6,7] Wakeham[7] concluded that most of the azaarenes detected in surface sediments have anthropogenic origins and that the atmospheric fallout and street dust may be a possible source. Several investigators[8-11] suggested that coal burning processes are a likely source of azaarenes and a free-radical mechanism to that proposed for PAHs has been suggested.[12] The source of nitrogen in azaarenes is not known, but natural and synthetic fuels were found to contain azaarenes.[13-18] Azaarenes have also been found in groundwater in the vicinity of an underground coal gasification facility,[19] coal burning effluents,[9,10] wood preservative wastewater,[20] and municipal wells in the Minneapolis–St. Paul, Minnesota area.[21]

Techniques for the quantitative determination of azaarenes have been summarized recently by Steinheimer and Ondrus.[22] In the case of complex environmental matrices no single analytical technique allows the unambiguous identification of azaarenes. This is complicated by the lack of standards but even more importantly by the fact that the azaarenes require prefractionation prior to instrumental analysis. Identification of azaarenes, in the presence of other nitrogen bases such as amino-PAHs, is difficult because the electron impact mass spectra of aromatic amines, either primary, secondary, or tertiary, and azaarenes are virtually identical.

In this paper, we report on the determination of azaarenes in a coal tar. These compounds were isolated from the methylene chloride soluble fraction of the tar by acid/base partitioning and alumina chromatography. Identification was performed by high resolution gas chromatography/low resolution mass spectrometry (GC/MS). Ammonia chemical ionization was used to confirm the molecular weights of the azaarenes isolated from the coal tar. Thermospray direct mass spectrometry (MS) and thermospray liquid chromatography mass spectrometry (LC/MS) was also used for confirmation purposes and to verify if any higher molecular weight azaarenes might be present in Fraction 3 of the coal tar. To our best knowledge, this is the first report on the determination of azaarenes by thermospray direct MS and thermospray LC/MS in a coal tar.

To assess the environmental impact of the azaarenes detected in the coal tar, we have taken groundwater samples from 10 wells located on the same site where the coal tar was obtained from. This site is in the city of St. Louis Park, Minnesota. A coal tar distillation and wood preserving facility operating at this site between 1918 and 1972 resulted in extensive groundwater contamination. In 1932, water taken from the first municipal well drilled within 1000 m from the plant had a coal-tar taste and subsequently the well was closed. Since 1978, seven other municipal wells have been closed because they were contaminated with polynuclear aromatic hydrocarbons (PAHs).

EXPERIMENTAL SECTION

Materials

Azaarenes of purity >97 percent were obtained from Aldrich Chemical Co. (Milwaukee, Wisconsin). Deuterated compounds: 9H-carbazole-$^2H_3$, quinoline-$^2H_7$, acridine-$^2H_9$, and 2-naphthylamine-$^2H_7$ were obtained from MSD Isotopes, Division of Merck Frosst Canada Inc. (Montreal, Canada). Stock solutions at concentration of 1 to 10 mg/ml were prepared in benzene:methylene chloride (1:9) and were stored at $-10\,°C$. Four internal standards: 1,4-dichlorobenzene-$^2H_4$ (IS-1), fluorene-$^2H_{10}$ (IS-2), phenanthrene-$^2H_{10}$ (IS-3), and terphenyl-$^2H_{14}$ (IS-4) (MSD Isotopes, Montreal, Canada) were spiked into each extract immediately prior to GC/MS analysis. Methylene chloride was distilled-in-glass from Burdick & Jackson (Muskegon, Michigan) and acetone, tetrahydrofuran, and methanol were from J. T. Baker Resi-analyzed (Phillipsburgh, New Jersey).

Sample collection

The coal tar was taken from well W-23 (city of St. Louis Park, Minnesota) by Eugene A. Hickok and Associates, Inc. in 1982.

Groundwater samples were taken in December 1984 from wells SLP-8, SLP-15, SLP-6, SLP-4, W-24, W-40, W-14, W-23, W-133, and W-48. Location of the wells in the city of St. Louis Park area is shown in Figure 1. Six of the wells (SLP-8, SLP-15, SLP-6, SLP-4, W-24, W-40 and W-14) were sampled in duplicate using resin cartridges. Grab samples were obtained for wells W-23, W-133 and

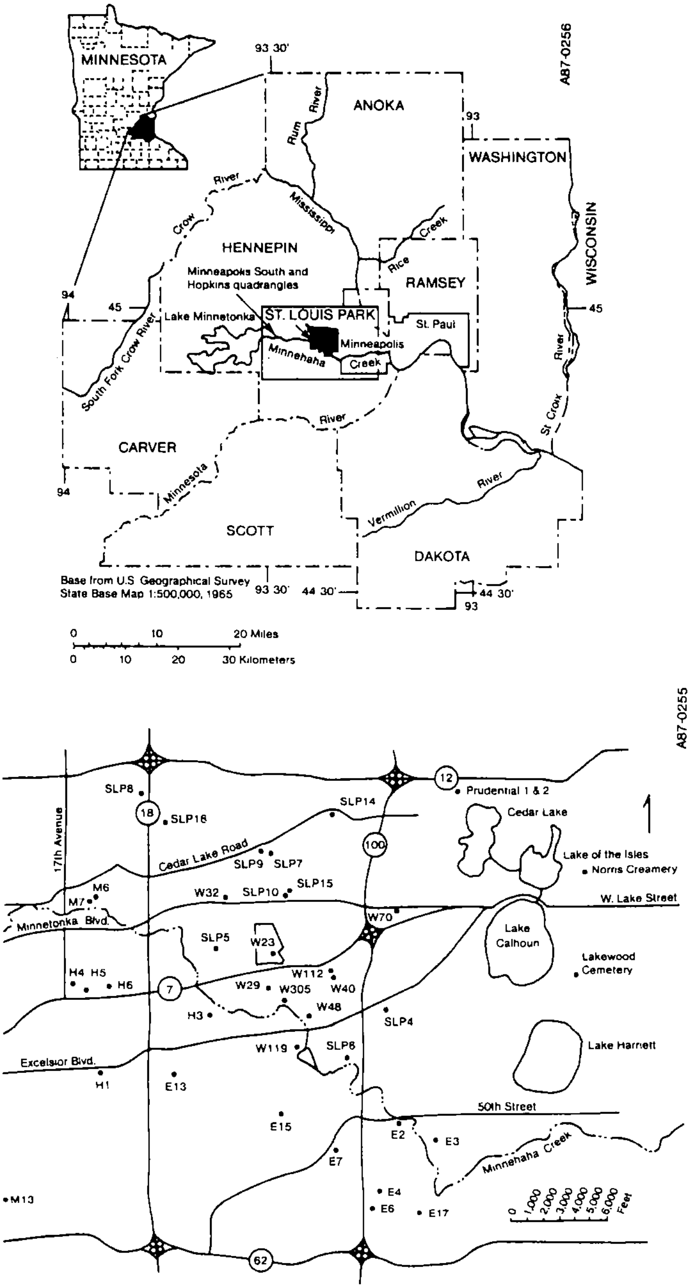


Figure 1 Locations of the city of St. Louis Park, the Minneapolis South and Hopkins Quadrangles, Lake Minnetonka, and Minnehaha Creek in the Minneapolis–St. Paul Metropolitan area (top). Location of wells W-23, SLP-8, SLP-15, SLP-6, SLP-4, W-40, W-48 in the St. Louis Park area (bottom).

W-48. Sampling was performed using a peristaltic pump and a sampling train made of Teflon™ having two parallel flow channels each fitted with a 20–30 μm Teflon filter followed by a 5–10 μm Teflon filter, a resin cartridge, a sample splitter, and a C_{18} Sep-pak™ cartridge. The C_{18} Sep-pak cartridge was used to verify whether any breakthrough of the organics through the resin cartridge occurred.

Glass cartridges (1.5 cm ID × 20 cm length) were obtained from Pierce Chemical Co. (Rockford, Illinois) and were modified so that the Teflon fittings could not be separated from the glass cartridge. Each cartridge was packed with 1.8 ml dry C_{18} reverse phase resin and a mixture of XAD-4™/XAD-8™ resins in the ratio of 3:2. The resins were precleaned prior to use with methanol, acetone, tetrahydrofuran, and methylene chloride (4 h each) in a Soxhlet extractor.

Procedures

The tar sample was processed as shown in Figure 2. An aliquot of 4.71 g of the tar was dissolved in 90 ml of methylene chloride. The solution was filtered through a preweighed 0.45 μm Millipore filter (Millipore Corp., Bedford, Massachusetts) to remove any material that did not dissolve in methylene chloride. The methylene chloride extract was further fractionated into: acids, neutrals, bases, and N-heterocyclic bases as described below. Bases were recovered by partitioning the methylene chloride extract with 50 ml of 10 percent H_2SO_4, three times. The aqueous layer which contained the bases was adjusted to pH >13 with KOH, and was extracted three times with methylene chloride (100 ml). The organic layer was partitioned three times with 50 ml of 10 percent KOH. After this partitioning, the organic layer contained the neutral compounds and the aqueous KOH solution contained the acids. The aqueous solution was then acidified to pH <1.6 with concentrated H_2SO_4 and extracted with methylene chloride, three times, to recover the acids.

The bases fraction was fractionated using alumina chromatography according to a procedure developed by Pereira *et al.*[21] The neutral alumina column (1 cm ID × 10 cm height; 5 g) was prewashed with two bed volumes of hexane prior to the addition of sample extract; five fractions were collected using the following eluents: 10 ml of hexane (Fraction 1), 10 ml of benzene (Fraction 2), 10 ml of methylene chloride (Fraction 3), 10 ml of 1:1 methylene

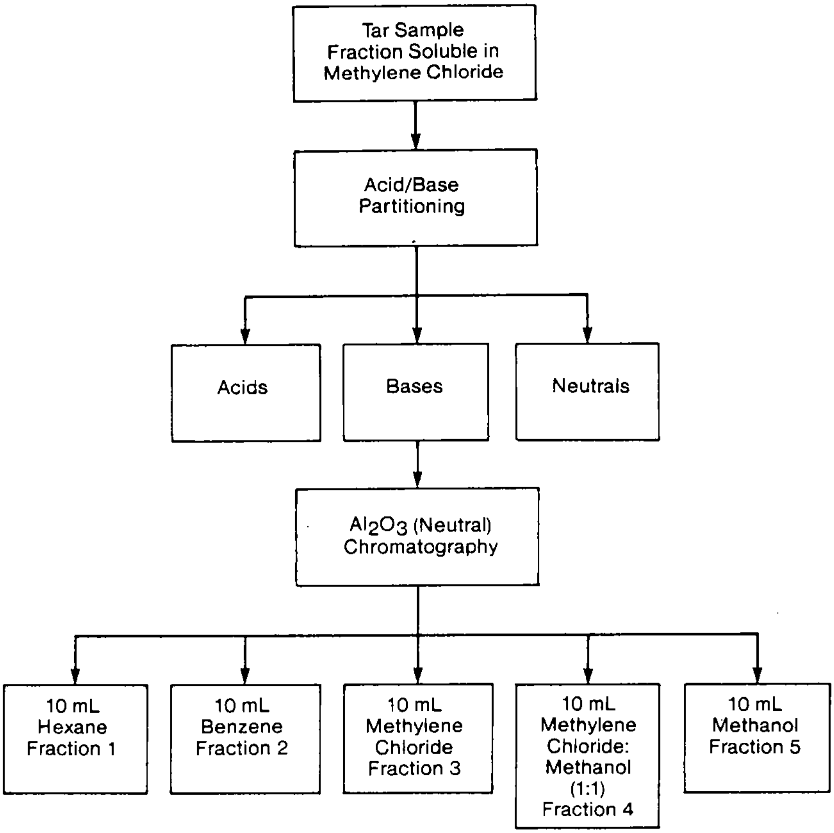


Figure 2 Fractionation scheme for the methylene chloride-soluble fraction of the coal tar to separate the azaarenes.

chloride:methanol (Fraction 4), and 10 ml of methanol (Fraction 5). Fraction 3 contained the N-heterocyclic bases and was concentrated to 1 ml.

Adsorbed organics were eluted from the resin cartridge with 350 ml of acetone–methylene chloride (20:80). The elution step was accomplished by installing the cartridge into a Perkin Elmer Series 4 high pressure liquid chromatograph and eluting it with solvent (350 ml) at 5 ml/min. The extract contained approximately 20 ml of water which was separated and extracted three times with 20 ml of methylene chloride. The organic layer and the methylene chloride extracts were combined, passed through a column of anhydrous sodium sulfate, and concentrated in a Kuderna Danish evaporator. No acid/base partitioning or alumina chromatography cleanup was performed on any of the well extracts, except for W-23 extract. Final volume of the well extracts was 2 ml.

Analysis

A Finnigan 4021 quadrupole mass spectrometer (Finnigen–MAT, San Jose, California) coupled to a Finnigan 9610 gas chromatograph and an Incos 2300 data system was used for the GC/MS analysis. Calibration standards and the tar fractions were injected manually using an on-column injector (J & W Scientific, Folsom, California). Compound separations were performed on a 30 m × 0.32 mm ID DB-5 fused silica capillary column (J & W Scientific, Folsom, California). The GC operating conditions were as follows: temperature program from 30 °C to 300 °C at 4 °C/min with a 4 min initial hold; transfer line 280 °C; helium at 10 psi. The MS operating conditions were as follows: electron energy 70 eV; emission current 300 μA; mass range 35–500 amu; scan rate 465 amu/sec; electron multiplier voltage 1800 V; ion source temperature 300 °C. Calibration of the mass spectrometer was checked daily, using decafluorotriphenylphosphine (DFTPP); resolution and focusing were adjusted to meet the DFTPP criteria.[24]

Chemical ionization spectra were obtained with ammonia (99.998 percent purity) as reagent gas. Ammonia was obtained from Matheson Gas Products (Newark, California). The ammonia reagent gas was used at an ion source pressure of 0.3 to 0.4 torr and ion source temperature of 250 °C and it was introduced into the ion source via the direct probe inlet. The GC/MS operating conditions for chemical ionization were identical to those given for the electron impact mode except that the mass range was 90–500 amu, the scan rate was 410 amu/sec, and the electron multiplier voltage was set at 1925 V.

Liquid chromatographic separations were performed on a 25 cm × 4 mm ID C_{18}-bonded reverse phase column and a DuPont model 8822 high-pressure liquid chromatograph equipped with a solvent gradient system model 8820 and a UV spectrophotometer. The solvent was acetonitrile/water programmed linearly from 60 percent acetonitrile to 100 percent acetonitrile in 30 min at 1.2 ml/min.

A Finnigan thermospray LC/MS interface installed on a Finnigan 4800 mass spectrometer was used for all the thermospray LC/MS analyses reported here. All thermospray MS studies were carried out with the filament on. The MS operating conditions were as follows: electron energy 70 eV, mass range 120–450 amu; scan rate 165 amu/sec; electron multiplier voltage 3000 V; emission current 500 μA; vaporizer temperature 90 °C; jet temperature 230 °C; ion source temperature 290 °C.

RESULTS AND DISCUSSION

GC/MS analysis

The specific compounds identified in the coal tar and their concentrations are given in Tables 1 and 2. Reconstructed ion chromatograms (RIC) for the coal tar fractions (neutral, acid, basic) are shown in Figure 3. Compounds listed in Table 1 as "PAHs" were positively identified and their concentrations were obtained by internal standard calibration.[24] The remainder of the compounds in Table 1, except for acridine and 9H-carbazole, were tentatively identified and exhibit concentration values which are semiquantitative only. The semiquantification was achieved by dividing the RIC areas of the respective compounds to the internal standard phenanthrene-d_{10} spiked in each fraction at known concentration.

The procedures used to identify each GC peak involved selection of a background substracted spectrum and the comparison of this spectrum against our EPA priority pollutant library or against the NBS library.[25] The computer search provided the match indexes (e.g. for Incos software FIT, PURITY and RFIT) that were used in identifying the compounds. Whenever an identification was made, mass chromatograms for the eight most intense ions in the mass spectrum were plotted. This allowed the identification of other isomers and assignment of coeluting peaks. We regarded the identifications as positive identifications only in those cases where we had authentic standards available for analysis, otherwise the identifications are only tentative. Because of the many possible isomers of alkylated benzenes and other PAHs, no attempt was made to distinguish among these isomers.

Table 1 Organic compounds detected in the coal tar by high resolution GC/MS

Compound name	*MW*	*Concentration* (*μg/g*)			
		Base	*Acid*	*Neutrals*	*Fraction 3*
PAHs					
Naphthalene	128	29	18	7 200	<5
Acenaphthylene	152	66	51	3 300	<5
Acenaphthene	154	36	24	6 200	<5
Fluorene	166	60	43	7 400	<5
Phenanthrene	178	270	240	18 000	<5
Anthracene	178	36	40	4 000	<5
Fluoranthene	202	200	190	14 000	<5
Pyrene	202	160	150	11 000	<5
Chrysene	228	4	56	1 100	<5
Benzo(a)anthracene	228	100	75	[a]	<5
Benzo(b)fluoranthene	252	120	110	6 800	<5
Benzo(k)fluoranthene	252	71	70	7 600	<5
Benzo(a)pyrene	252	74	67	7 000	<5
Indeno(1,2,3-c,d)pyrene	276	34	34	4 000	<5
Dibenzo(a,h)anthracene	276	13	12	1 300	<5
Benzo(g,h,i)perylene	278	60	43	7 400	<5
Other aromatic hydrocarbons[b]					
Indene	116	<5	<5	170	<5
Propenylbenzene	118	<5	<5	260	<5
C_3-Alkylbenzene (3 isomers)	134	<5	<5	370	<5
C_4-Alkylbenzene (6 isomers)	148	<5	<5	390	<5
Dihydromethylindene (2 isomers)	132	<5	<5	200	<5
1-Methylnaphthalene	142	<5	<5	5 500	<5
2-Methylnaphthalene	142	18	12	6 200	<5
Biphenyl	154	<5	<5	2 700	<5
C_2-Alkylnaphthalene (6 isomers)	156	9.6	10	15 000	<5
Methylbiphenyl (2 isomers)	168	<5	<5	1 100	<5
C_3-Alkylnaphthalene	170	<5	<5	5 200	<5
Dimethylbiphenyl	182	16	7.8	<50	<5
$C_{14}H_{12}$ (2 isomers)	180	<5	<5	6 600	<5
Methylphenanthrene or methylanthracene (4 isomers)	192	85	120	14 000	<5
Phenylnaphthalene	204	25	31	2 500	<5
C_2-Alkylphenanthrene or anthracene	206	<5	<5	150	<5
Methylfluoranthene or methylpyrene (3 isomers)	216	100	100	9 700	<5
Methylchrysene or methylbenzoanthracene (3 isomers)	242	<5	<5	1 100	<5
Methyl benzopyrene	266	<5	<5	2 400	<5

Table 1 Continued

Compound name	*MW*	*Concentration (μg/g)*			
		Base	*Acid*	*Neutrals*	*Fraction 3*
Sulfur, oxygen, nitrogen, heterocyclics[b, c]					
Benzothiophene	134	<5	<5	240	<5
Dibenzothiophene	184	<5	9.7	3 100	<5
Dibenzofuran	168	31	<5	6 600	<5
Methyldibenzofuran	172	25	<5	5 600	<5
Methylquinoline	143	26	<5	<50	[c]
Acridine	179	74	<5	<50	55
$C_{14}H_{11}N$	193	40	<5	<50	[c]
$C_{15}H_9N$	203	100	<5	<50	[c]
$C_{18}H_{13}N$	243	26	<5	<50	[c]
$C_{19}H_{11}N$ + unknown	253	94	<5	<50	[c]
$C_{20}H_{13}N$	267	25	<5	<50	[c]
9H-Carbazole	167	<5	<5	50	<5

[a] Not able to quantitate because compound was poorly resolved from chrysene.
[b] Values given for concentration are semiquantitative only.
[c] Values given for concentration are semiquantitative only.
[e] See Table 2 for specific identifications of azaarenes.
MW—Molecular weight.

Phenanthrene, fluoranthene, pyrene, C_2-alkylnaphthalenes, and methylphenanthrene or methylanthracene were found in the tar sample at concentrations ranging from 11 000 to 18 000 μg/g. Most of the other PAHs and their alkyl-substituted homologs were in the range of 1000 to 10 000 μg/g. Sulfur heterocyclics (benzothiophene and dibenzothiophene) and oxygen heterocyclics (benzofuran and dibenzofuran) were also detected at relatively high concentrations. These concentrations apply to the neutral fraction as the other fractions were significantly lower.

The base and acid fractions contained a small quantity (1 to 5 percent) of the PAHs detected in the neutral fraction. Nonetheless, this was expected when dealing with such a matrix in which a few compounds were at concentrations above 10 000 μg/g. Our evaluation studies using standards of azaarenes (acridine, 9H-carbazole), 2-naphthylamine, 4-amino-biphenyl, acids (phenol, methyl-phenols, chlorinated phenols), and PAHs (naphthalene, acenaphthene, anthracene, phenathrene, fluoranthene, pyrene, chrysene, benzo(a)pyrene)

Table 2 Compounds identified in Fraction 3 of the coal tar extract

Peak no.	*Scan no.*	*Compound identification*	*MW*	*Electron impact mass spectrum m/z (relative intensity)*	*Approximate concentration (μg/g)*
1	1297	Methylquinoline	143	143(100) 115(14) 128(14) 142(12) 143(12)	6.7
2	1515	Dimethylquinoline	157	157(100) 156(37) 158(13) 115(13) 142(10)	4.8
2	1556	Dimethylquinoline	157	157(100) 156(22) 115(17) 158(13) 142(12)	5.5
3	1909	Azafluorene	167	167(100) 166(30) 139(21) 140(20)	5.5
4	2171	Acridine	179	179(100) 178(21) 180(15) 89(13) 90(12) 151(10)	55
4	2171	Acridine-$^2H_9$	188	188(100) 187(18) 186(18) 189(15) 93(16)	
5	2321	$C_{14}H_{11}N$ (methylacridine)	193	193(100) 192(16) 194(16) 165(15) 83(15) 97(12) 96(0)	2.6
5	2337	$C_{14}H_{11}N$ (methylacridine)	193	193(100) 194(19) 192(14) 165(14) 83(23) 97(19) 96(14)	5.7
5	2359	$C_{14}H_{11}N$ (methylacridine)	193	193(100) 192(35) 194(18) 165(14) 83(23) 97(11) 96(10)	7.0
5	2384	9-Methyl acridine	193	193(100) 192(35) 191(17) 194(16) 96(14) 97(12) 83(10)	3.9
6	2581	$C_{15}H_9N$ (azapyrene)	203	203(100) 204(17) 88(13) 101(9.2) 102(8.7) 176(8.3)	18
6	2609	$C_{15}H_9N$ (azapyrene)	203	203(100) 204(17) 88(21) 176(13) 101(12) 202(9.3)	28
6	2686	$C_{15}H_9N$ (azapyrene)	203	203(100) 88(18) 202(14) 175(8.8) 102(8.4) 176(7.7)	30
6	2727	$C_{15}H_9N$ (azapyrene)	203	203(100) 88(19) 204(15) 202(14) 87(12) 175(8)	10
7	2680	$C_{16}H_{11}N$ (methylazapyrene)	217	Coeluting with $C_{15}H_9N$	3.0
7	2709	$C_{16}H_{11}N$ (methylazapyrene)	217	217(100) 216(27) 109(21) 189(17) 218(17) 190(3)	4.1
7	2804	$C_{16}H_{11}N$ (methylazapyrene)	217	217(100) 216(29) 108(24) 218(17) 214(6.8) 215(6.8)	19
7	2855	$C_{16}H_{11}N$ (methylazapyrene)	217	217(100) 216(29) 108(19) 214(16) 218(15) 188(12)	2.0
16	2960	$C_{17}H_{13}N$ (dimethylazapyrene)	231	231(100) 232(27) 231(27) 216(22)	4.5
8	3066	$C_{17}H_{11}N$ (azachrysene)	229	229(100) 230(19) 228(16) 115(13) 227(12) 101(9.5)	68
8	3121	$C_{17}H_{11}N$ (azachrysene)	229	229(100) 230(22) 100(13) 227(12) 88(12) 114(11)	5.8
8	3172	$C_{17}H_{11}N$ (azachrysene)	229	229(100) 100(29) 228(25) 230(19) 200(17) 201(16)	1.5

Table 2 Continued

Peak no.	Scan no.	Compound identification	MW	Electron impact mass spectrum m/z (relative intensity)	Approximate concentration (μg/g)
9	3214	$C_{18}H_{13}N$ (methylazachrysene)	243	243(100) 242(31) 121(24) 241(22) 244(18) 240(11)	17
9	3223	$C_{18}H_{13}N$ (methylazachrysene)	243	243(100) 121(27) 242(26) 244(20) 241(17) 108(9.0)	15
9	3253	$C_{18}H_{13}N$ (methylazachrysene)	243	243(100) 241(46) 121(41) 242(34) 244(31) 108(27)	3.0
10	3418	$C_{19}H_{11}N$ (azabenzopyrene)	253	253(100) 254(22) 127(16) 251(14) 252(13) 126(12)	12
10	3462	$C_{19}H_{11}N$ (azabenzopyrene)	253	253(100) 254(22) 127(19) 251(13) 252(12) 112(12)	4.9
10	3505	$C_{19}H_{11}N$ (azabenzopyrene)	253	253(100) 127(30) 252(13) 254(12) 251(12)	4.0
10	3515	$C_{19}H_{11}N$ (azabenzopyrene)	253	253(100) 254(22) 127(18) 252(12) 126(13) 251(12)	20
10	3538	$C_{19}H_{11}N$ (azabenzopyrene)	253	253(100) 254(21) 112(10) 252(13) 251(13) 111(12)	6.7
10	3549	$C_{19}H_{11}N$ (azabenzopyrene)	253	253(100) 254(21) 112(17) 252(16) 113(16) 251(14)	27
10	3564	$C_{19}H_{11}N$ (azabenzopyrene)	253	253(100) 254(21) 112(17) 126(15) 251(14) 252(12)	6.0
11	3606	$C_{20}H_{13}N$ (methylazabenzopyrene)	267	267(100) 268(22) 266(13) 133(9.3)	2.0
11	3655	$C_{20}H_{13}N$ (methylazabenzopyrene)	267	267(100) 132(45) 266(30) 239(24) 106(23) 268(23)	1.0
11	3679	$C_{20}H_{13}N$ (methylazabenzopyrene)	267	267(100) 265(68) 134(45) 264(39) 266(38) 132(25)	1.0
17	3927	$C_{21}H_{11}N$[a]	277	277(100) 278(25) 132(12) 137(12) 276(12) 139(12)	4.0
12	3799	$C_{21}H_{13}N$ (dibenzoacridine)	279	279(100) 280(59) 277(50) 140(44) 278(20) 275(14)	3.4
12	3809	$C_{21}H_{13}N$ (dibenzoacridine)	279	279(100) 140(24) 280(18) 278(12) 277(10) 125(9.1)	3.4
12	3858	$C_{21}H_{13}N$ (dibenzoacridine)	279	279(100) 277(42) 140(30) 280(26) 139(21) 278(18)	2.0
12	3874	$C_{21}H_{13}N$ (dibenzoacridine)	279	279(100) 278(27) 138(27) 280(25) 126(17) 249(15)	1.5
15	4282	$C_{23}H_{11}N$[b]	301	301(100) 150(31) 302(25) 300(25) 151(24) 152(22)	1.0

[a] Nitrogen PAH probably equivalent to idenopyrene.

[b] Nitrogen PAH probably equivalent to methylcholanthrene.

MW – Molecular weight.

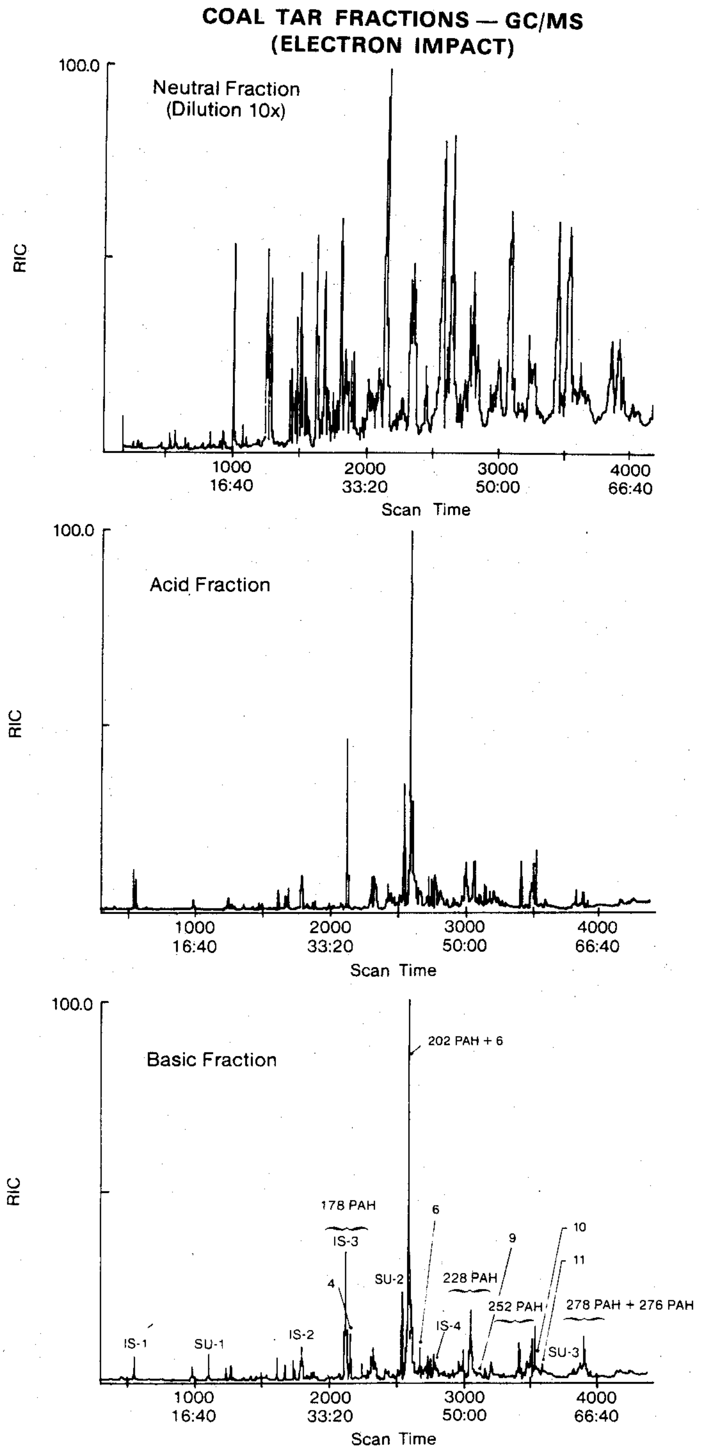


Figure 3 Reconstructed ion chromatogram of the neutral extract (top) acid extract (middle) and base extract (bottom) of the methylene chloride-soluble fraction of coal tar. Temperature program was as follows: 30 °C (4 min) to 300 °C (8 min) at 4 °C/min. For peak assignments refer to Table 2.

indicated excellent separation of compounds into the three groups (bases, acids, neutrals) with recoveries greater than 90 to 95 percent. One exception was 9H-carbazole which remained in the neutral fraction (approximately 90 percent) and a small fraction of it was found in the acid fraction.

The azaarenes were not detected in the neutral fraction of the coal tar; however, the detection limit for the neutral fraction was 10 times as high as for the base or acid fractions, because of dilution needed to bring compound concentrations within the dynamic range of our mass spectrometer. Furthermore, only a few azaarenes could be detected in the base fraction because of interferences from PAHs, especially phenanthrene/anthracene, fluoranthene/pyrene, benzo(a)anthracene, and benzofluoranthenes.

To separate the azaarenes from PAHs and other interfering compounds, we eluted the base fraction through a neutral alumina column and collected five fractions. Fraction 1 contained the PAHs listed in Table 1 for the base fraction. Fractions 2, 4 and 5 did not contain any PAHs or azaarenes. Fraction 3 contained the azaarenes. A RIC for Fraction 3 is shown in Figure 4 and Table 2 lists all of the azaarene compounds detected in Fraction 3. In addition to the approximate concentration values, we have include in Table 2 the mass-to-charge ratios (m/z) and the relative intensities of five to seven most abundant ions in the electron impact mass spectra of the azaarene compounds detected in the coal tar.

The fragmentation of the acridine and alkylacridines under electron impact has been reported.[26] These types of compounds tend to give strong molecular ions. Fragment ions due to loss of a hydrogen $(M\text{-}1)^+$, methyl $(M\text{-}15)^+$ and doubly charged ions M^{2+}, $(M\text{-}2)^{2+}$, $(M\text{-}26)^{2+}$, $(M\text{-}27)^{2+}$ have been reported.[26] The fragment ions at m/z 83 and m/z 97 for compounds labeled as peak no. 5 in Figure 4 are those corresponding to $(M\text{-}27)^{2+}$ and M^{2+}. Among the four methylacridine isomers at scans 2321, 2337, 2359 and 2384 we assigned the one at scan 2384 as being 9-methylacridine. Our identification is based on the fact that in 9-methylacridine the $(M\text{-}1)^+$ ion was larger than any other fragment ions in the mass spectrum, the $(M\text{-}2)^{2+}$ fragment at m/z 96 is more intense than M^{2+} (m/z 97), and the $(M\text{-}27)^+$ fragment at m/z 83 is less abundant than the M^{2+}.

The other azaarenes in Table 2 exhibit similar fragmentation

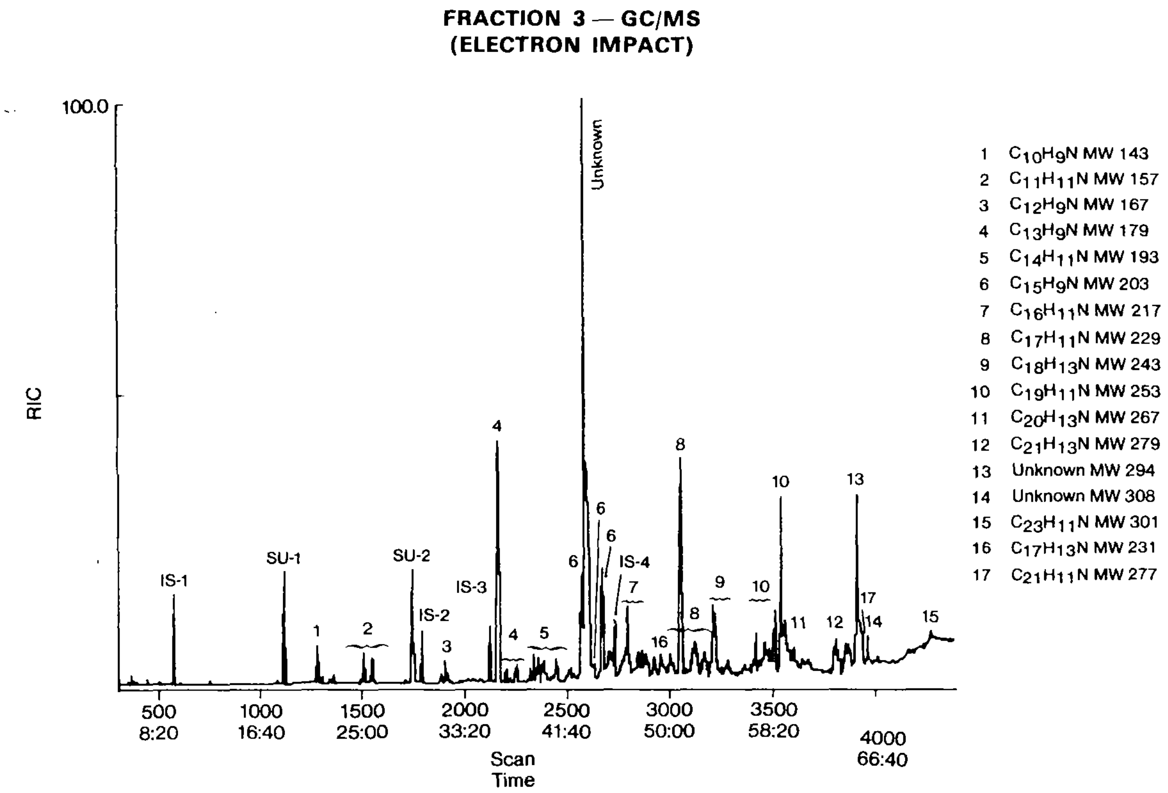


Figure 4 Reconstructed ion chromatogram of Fraction 3 of the methylene chloride-soluble fraction of coal tar. Temperature program was as follows: 30 °C (4 min) to 300 °C (8 min) at 4 °C/min. For peak assignments refer to Table 2.

patterns. For example, we observed strong molecular ions, presence of a double charged M^{2+} (e.g. azapyrene has the M^{2+} fragment ion at m/z 101 and azachrysene has the M^{2+} fragment ion at m/z 115), and the presence of $(M\text{-}1)^+$ ions (e.g. fragment ions at m/z 202 for azapyrene, m/z 228 for azachrysene, m/z 252 for azabenzopyrene, etc.).

We regarded the azaarenes' identifications as tentative because of the lack of authentic standards. However, we confirmed the molecular weights of all compounds listed in Table 2 with ammonia chemical ionization. Under ammonia chemical ionization conditions all azaarene compounds gave strong protonated molecular ions. We did not observe any adduct ions $(M+18)^+$. This is not surprising as the azaarene compounds are tertiary amines and such compounds do not form adduct ions.[27]

Thermospray MS

Both thermospray direct MS and thermospray LC/MS were used in conjunction with the thermospray technique to analyze for the azaarene in Fraction 3 of the coal tar extract. Figure 5 shows an averaged mass spectrum (number of scans is 6) obtained from 10 μl of Fraction 3 extracted by thermospray direct MS with the filament on. Figure 6 shows a reconstructed ion chromatogram of the Fraction 3 extract introduced into the mass spectrometer via the thermospray LC inlet. Separation of azaarenes was achieved with the C_{18} bonded reverse phase column and acetonitrile/water solvent at 1.2 ml/min.

The direct thermospray MS analysis does not allow any structural information other than the confirmation of the molecular weights of azaarenes from the protonated molecular ions. For example, the ions at m/z 144, 158, 168, 180, 194, 204, 218, 230, 244, 254, 268, 280 and 302 were those of azaarene compounds 1 through 12, and 15 in Figure 4, respectively. The ions at m/z 137, 180 and 151 were those of the deuterated compounds spiked prior to alumina chromatography: naphthalene-$^2H_8$, acridine-$^2H_9$, and 2-naphthylamine-$^2H_7$, respectively. The presence of the alkyl-substituted azaarenes was suspected as the ions at m/z 172, 208, 232 and 258 were observed. The parent compounds had masses at 157, 193, 217 and 243 amu.

Separation of the azaarenes by high pressure LC and their

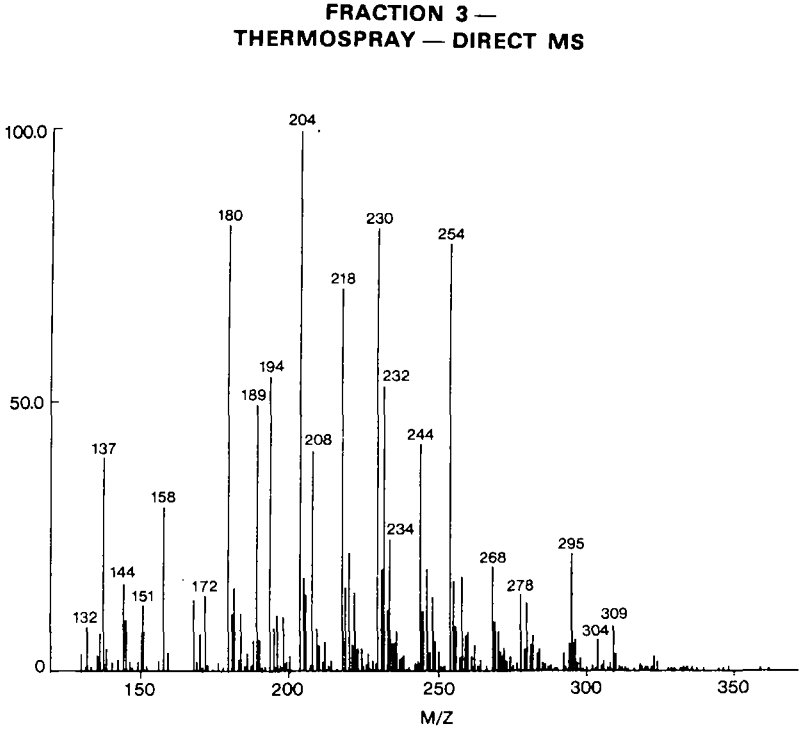


Figure 5 Thermospray direct MS of Fraction 3. The spectrum is an averaged mass spectrum of six scans.

identification by MS is shown in Figure 6. The major components are the azaarenes with molecular weights of 179, 203 and 229 amu. This is in agreement with the direct MS analysis. The azaarenes with molecular weights of 157, 193, 217, 243 and 253 amu which were relatively abundant in Figure 5 are still present but they were resolved into several isomers as we have shown in Figure 7.

It is interesting to note the good agreement between the GC/MS information and the thermospray LC/MS information for the azabenzopyrene isomers. Seven isomers with molecular weights of 253 amu were retrieved from the electron impact data using mass

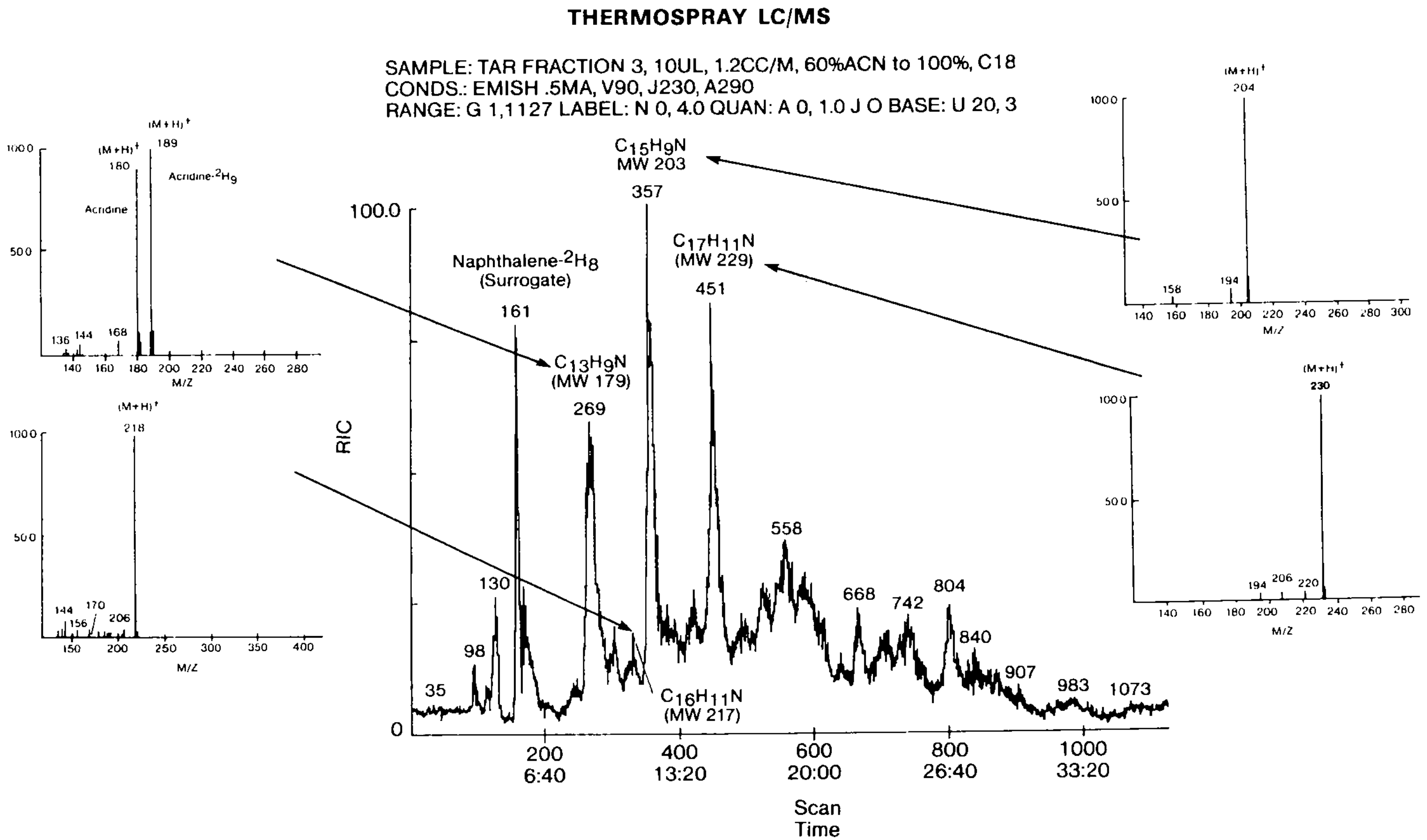
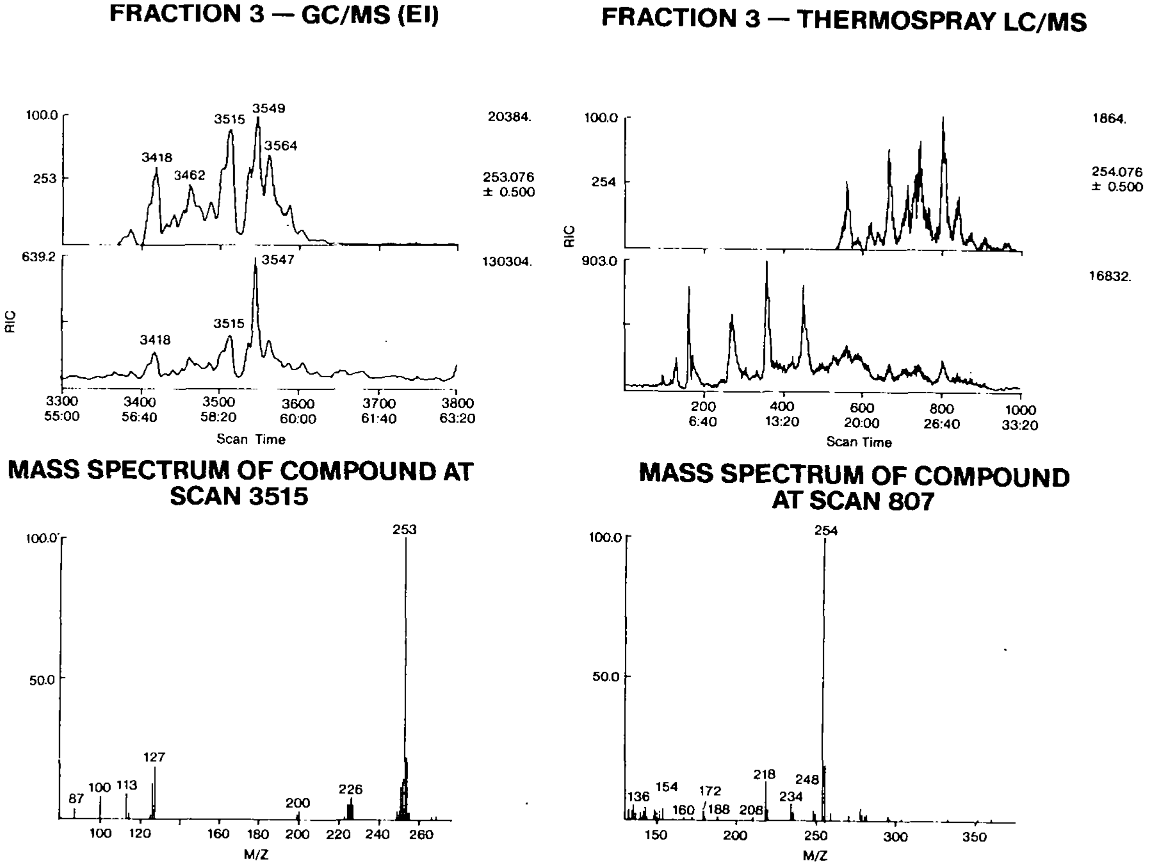


Figure 6 Thermospray LC/MS of Fraction 3. LC conditions: C_{18}-bonded reverse phase column; gradient elution from 60 percent acetronitrile in water to 100 percent acetonitrile at 1.2 ml/min.



FRACTION 3 — GC/MS (EI)

FRACTION 3 — THERMOSPRAY LC/MS

MASS SPECTRUM OF COMPOUND AT SCAN 3515

MASS SPECTRUM OF COMPOUND AT SCAN 807

Figure 7 Extracted ion current profiles for m/z 253 and m/z 254 for Fraction 3 analyzed by electron impact GC/MS and thermospray LC/MS and mass spectra of azabenzopyrene isomer at scan 3515 for GC/MS analysis and scan 807 for the thermospray LC/MS analysis.

chromatograms or extracted ion current profiles (EICPs). Likewise, we retrieved at least seven isomers of azabenzopyrene by searching the thermospray LC/MS files for the protonated molecular ions at m/z 254. The electron impact mass spectrum and the spectrum obtained by thermospray LC/MS for one of the azabenzopyrenes are also shown in Figure 7.

Environmental impact

In order to assess the environmental impact of the azaarenes detected in the coal tar, we obtained well water samples from ten wells located on the site of a former coal tar distillation plant and its vicinity in the city of St. Louis Park, Minnesota (Figure 1). These samples were analyzed specifically for the Environmental Protection Agency's priority pollutant compounds (semivolatile fraction) and 25 other target compounds. The results of these analyses and details of sample preconcentration on resin cartridges including a breakthrough study are given elsewhere.[28] Table 3 shows the results for three azaarenes: quinoline, acridine, and 9H-carbazole which were among the 25 target compounds. The "less than" concentrations

Table 3 Concentration of compounds identified in the well samples (dissolved phase) and quantitated by isotope dilution GC/MS

Well no.	*Volume sampled (litre)*	*Concentration (μg/l)*		
		Quinoline	*Acridine*	*9H-Carbazole*
W-48	8; 8[a]	<1.15	<0.175	<0.550
SLP-8	257; 236	<0.019	<0.012	<0.002
SLP-15	16.9; 19.2	<0.295	<0.189	<0.035
W-23	7.4[a]	<1.24	2.76	12.2
W-24	22.9; 19.5	<0.227	<0.146	0.330; 0.290[b]
SLP-6	268; 257	<0.019	<0.012	<0.002
SLP-4	139; 124	<0.036	<0.023	0.070; 0.074[b]
W-14	22.0; 25.3	<0.227	<0.146	<0.027
W-40	143; 163	<0.035	<0.022	<0.004
W-133	15.7[a]	<0.586	<0.089	<0.280

[a] Grab sample; not filtered.

[b] Values given represent duplicate measurements.

given in Table 3 were derived from our method detection limit and the volume of sample collected for each well. Acridine and 9H-carbazole were detected in the well W-23 at 2.76 μg/l and 12.2 μg/l, respectively. 9H-Carbazole was also detected in wells W-24 and SLP-4. We have not found any of the other azaarenes listed in Table 2 in the ten well water samples. Although we have not determined the detection limits of the compounds listed in Table 2, we anticipate that they will be comparable to those of acridine. The extent of groundwater contamination by the azaarene compounds present in the coal tar should be investigated since many of the compounds are carcinogens and mutagens[29] and concentrations much higher than those found by us have been reported for acridine and benzo-(h)quinoline at another well.[21,22] For example, Steinheimer and Ondrus[22] reported acridine at 107 μg/l in a fluid sample taken from well W-13 located 205 m south of the site. Pereira and co-workers[21] reported 106 μg/l for acridine and 7 μg/l for benzo(h)quinoline in the same sample.

Because the coal tar contains several other azaarenes, it is possible that these compounds are present in the groundwater at concentrations lower than our method detection limit. Further work using this methodology should address the feasibility of detecting low-part-per-trillion levels of azaarenes in groundwater.

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