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Simultaneous Determination of PAHs and PCBs by GCMS Analysis.

BGS Laboratory Technique Development (E2156S67)

Internal Report IR/07/045

BRITISH GEOLOGICAL SURVEY

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Simultaneous Determination of PAHs and PCBs by GCMS Analysis.

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Foreword

This report is the published product of a study by the British Geological Survey (BGS) into the development of a technique for the simultaneous determination of PAHs and PCBs by GCMS analysis.

A multiple component mixture of PAH and PCB analytes together with their respective internal standards were used to establish GC method for their separation. It was also used to develop the supporting software to automatically identify the compounds.

Acknowledgements

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Summary

A method for the simultaneous separation and identification of PAHs and PCBs by GCMS was successfully developed by this laboratory.

The programming of associated software to identify and differentiate between similar compounds was an integral part of this development.

1. Introduction

1.1 GENERAL

Public concern over contamination of the built environment has grown rapidly as the potential health hazards of past and present industrialisation have become recognised. Under the Environmental Protection Act 1990 and the Environment Act 1995, there is a requirement for each local authority to inspect its own area for contaminated land and monitor air quality. Structural planning strategies within built areas are required to optimise the use of land resources for new development. Since the Industrial Revolution vast quantities of hydrocarbons have been, and still are, contaminating the environment. Past and present use of land on which fossil fuels are utilised include: power generation, transport, oil refineries, gasworks, mining, chemical industries, landfill sites and scrap yards. Over time these activities have resulted in varying levels of topsoil contamination by direct spillage and fall out. With the expansion of conurbations and changes of land use these sites are now often located within residential areas. The dereliction of industrial sites, brownfield-site redevelopment and increased road traffic are all potential sources of air-borne particle pollution (Department for Environment, Food and Rural Affairs, 2001).

1.2 POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

The abbreviation PAHs denotes polycyclic aromatic hydrocarbons, which are a class of organic compounds, characterised by two or more fused aromatic rings. Occurring in the environment, they give cause for concern because some display toxic, mutagenic and carcinogenic activity (Menzie *et al.*, 1992). In general, low molecular weight two- and three-ringed PAHs have a significant acute toxicity, whereas four- to six-ringed PAHs tend to display a greater carcinogenicity (Witt, 1995).

The presence of PAHs in the environment is the result of a variety of anthropogenic and biogenic activities with incomplete combustion and pyrolysis of fossil fuels serving as the major source (McCready *et al.*, 2000). This pyrolitic input may be supplemented by PAHs originating from grass and forest fires. In specific locations there may also be a petrogenic contribution of PAHs from crude oil, coal and various refinery products. Frequently, anthropogenic in origin and commonly arising from run-off, industrial and sewage discharges, spillage, shipping activities *etc.* this source can in some cases though be natural as, for instance, oil seepage from depth. Additionally, but to a lesser extent, petrogenic PAHs in sediments can originate from the diagenesis of natural precursors like terpenes, pigments and steroids.

Many hundreds of PAHs exist in the environment, but the US Environmental Protection Agency (USEPA) has listed sixteen as “Consent Decree” priority pollutants chosen because:

- most information is available on these PAHs
- they are suspected of being more harmful than most other PAHs
- they exhibit harmful effects representative of PAHs
- chance of exposure to these is greater than to other PAHs
- these PAHs had the highest concentrations at hazardous waste sites.

Normally, it is the USEPA 16 PAHs that are selected in the majority of publications that focus upon environmental PAH pollution. However, information arising from knowledge of these does not usually provide sufficient detail on PAH distributions to permit definitive links to be made to specific sources of contamination. Their principle value is in providing an estimate of total and individual PAH concentrations.

1.3 POLYCHLORINATED BIPHENYLS (PCBs)

The class of organic compounds known as Polychlorinated Biphenyls (PCBs) are known to cause cancer and affect immune, reproductive, nervous and as well as endocrine systems in animals. Studies on humans confirm their potential carcinogenic and non-carcinogenic effects. Mixtures of PCBs tend to be chemically stable, non-flammable and electrically insulating with high boiling points. These properties made PCBs ideal for use in the electricity and mining industries as cooling, insulating and hydraulic fluids. With the exception of production and disposal sites the main sources of PCB emissions include power transformers, capacitors, hydraulic oils, thermal and lubricating oils. Alternative sources include release from paints, printing inks, sealants and adhesives as well as rubber plasticizers. An estimated 40,000 t of total PCBs were commercially manufactured in the UK from 1954 onwards, peak production was achieved in mid-1960's before declining throughout the 1970's due to restrictions and an eventual UK sales ban in 1977. The most common formulations were Aroclors which are comprised of congeners 28, 52, 101, 138, 153 and 180. The commercial and industrial manufacture of these toxic compounds, were, subject to eventual ban in 1985 under the OSPAR convention (OSPAR 1997).

PCBs are persistent in the environment and accumulate in soils, marine sediments, seawater, sewage sludge and vegetation as well as the fatty tissues of animals. The river systems receive polluted waste from shipbuilding, textile, paper and engineering industries (Edgar et al., 1999; Edgar et al., 2003). Additional sources of anthropogenic contaminants such as PCBs include effluent and accidental discharges from military bases and from sewage sludge disposal (Kelly 1995). The combination of high population density and heavy industry has consequently created the issue of PCB pollution. After entering the environment PCBs accumulate in sediments and/or biological tissues as compared to water because of physiochemical factors such as low vapour pressures and low solubility.

1.4 THE NEED FOR THIS STUDY

The scope of this method, and hence its validation, is the determination of 16 individual USEPA PAHs and 8 individual PCBs in sediments. Currently these analyses require 2 separate determinations. It is proposed to combine the 2 methods to enable us to offer one unit analysis to determine both PAH and PCB concentrations simultaneously. The ability to do this will be dependent on the relative concentrations PCBs to PAHs in any one sample because PCBs are usually in much lower concentrations compared to PAHs (i.e. PAHs may require dilution so as not to over load the GCMS and thus dilute the PCBs below their limit of quantification).

2. Methods

2.1 MATERIALS AND REAGENTS

All standards and stock solutions were stored in a 5mL vial fitted with a Mininert^{TM} valve at 4°C in darkness.

PAH Standards. All internal standard PAH compounds were purchased from Sigma Aldrich Chemical Co. (Gillingham, Dorset, UK). PAH analytes were purchased as a mixture from LGC PromoChem (Teddington, Middlesex, U.K.), these are listed in **Table 1**.

PCB Standards. All PCB internal standards, sample evaluation / preparation standards (SES/SPS), recovery determination standard (RDS) and retention time window PCBs were purchased as individual compounds from LGC PromoChem (Teddington, Middlesex, U.K.). PCB analytes were purchased as a mixture (7 PCB Mix CERTAN, 10µg/mL in iso-octane) from the same supplier, these are listed in **Table 2**.

2.2 GCMS ANALYSIS

The GCMS used was a Varian 1200L GC-MS-MS. Mass range: full scan ion monitoring (m/z: 40-600), scan time was 0.5 second, with electron impact and quadrupole analyser. Split/splitless injection (1:25 at 250°C) was onto a DB-1 column (60m length x 0.32 mm i.d. x 0.25 µm film thickness). Oven temperature programme: 60°C (1 min. isothermal) to 200°C (at 5°C / min.) to 280°C (at 2.6°C / min.) to 320°C (at 20°C / min.) and isothermal at 320°C for 10 minutes. Carrier gas: helium at 1mL/min.

3. Results and Discussion

3.1 CHROMATOGRAPHY AND SOFTWARE

A 40 component mixture was made **(Table 1 and Table 2)** excluding retention time window PCBs. The mixture was analysed in the full-scan mode (**Figure 1**). The retention times and the mass spectra of the compounds were identified using the NIST-MS library search.

The instrument software '*Varian MS Workstation – MS Data Review, version 6.5*' was used to automatically identify these compounds which involved programming in an extensive list of specific qualifying ion ratios and retention time windows **(Table 1 and Table 2).**

The chromatogram presented in **Figure 1** shows the elution of all compounds and their separation. The ratio PAH : PCB concentrations in this standard was 10:1 which represents the higher proportion of PAHs relative to PCB which is encountered in many environmental matrices (e.g. soils and sediments).

When viewed as a single ion chromatogram, excellent resolution of closely eluting compounds is clearly seen as between Py-d10:Py and B[a]A:Ch-d10. The isomers B[b]F and B[k]F are 80% resolved by 2 seconds. Some slight peak tailing is noticeable after 55 minutes retention time. Peak width increases with retention time (RT), this is observed where the naphthalene peak width is 10 seconds (RT = 15.85 minutes) and increases to 20 seconds for B[ghi]Per (RT = 64.00 minutes). Column bleed becomes noticeable after 60minutes (>280°C), this does not affect the peak-height : background ratio of the analytes in this region when the quantitative ions are viewed as a single ion chromatogram (i.e. Ind[1,2,3,-cd]Py and B[ghi]Per at m/z 276 give well defined peak shapes). In **Figure 1** it is noted that there seems to be chromatographic discrimination of the high boiling point compounds after 40 minutes retention time. This can be improved by using a splitless injection technique combined with a higher injector temperature.

GCMS vs. HPLC: The higher chromatographic resolution of GCMS is possible to separate alkylated PAHs such as the alkylated phenanthrenes, this is particularly important for petrogenic / pyrogentic source determination. Secondly, HPLC can only detect 15 of the 16 USEPA PAHs, because the fluorescence detector is unable to detect acenaphthylene, which has a negligible fluorescence.

Simultaneous chromatography of PAH and PCB pollutants is achievable using current instrumentation with in the BGS labs. It is envisaged that once proven to work on certified reference materials and selected reference materials the novel method outlined in this study will be offered as an analytical service to external and internal customers.

4. Conclusions

A method for the simultaneous separation and identification of PAHs and PCBs by GCMS was successfully developed by this laboratory.

The programming of associated software to identify and differentiate between similar compounds was an integral part of this development.

Further work could include application of the method to determine limits of quantification, response factors and subsequent determination of PAHs and PCBs in certified reference materials (CRMs). When proven to work with CRMs this method will be offered as an analytical service to external and internal customers.

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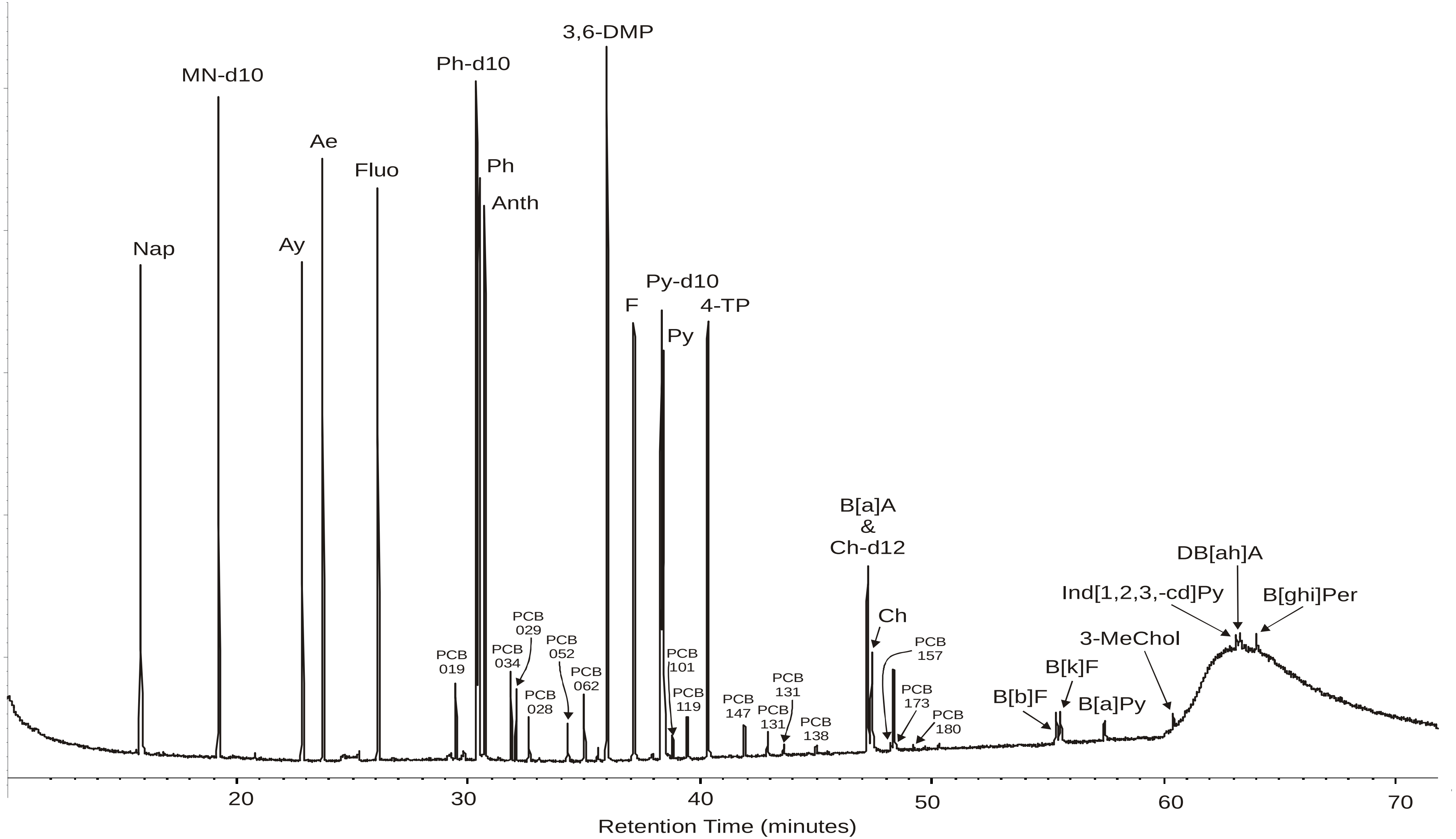
Table 1. PAHs used and respective analytical ions used for quantification; RT = retention time; FW = formula weight

Name	**Abbreviation**	**RT (min.)**	**Rings**	**Type**	**FW**	**Formula**	**CAS**	**1° ion**	**Analytical ion**	**Qualifying ions**	**Conc$^{\underline{n}}$ (ng/μL)**	**Notes**
naphthalene	Nap	15.886	2	analyte	128.17	C10H8	91-20-3	128.0	128.3	127.5,102.0,129.1		
1-methylnaphthalene-d10	MN-d10	19.255	2	internal std.	152	C10D7(CD3)	38072-94-5	152.0	152.0	152.1,122.0,151.1	0.593	
acenaphthylene	Ay	22.875	2.5	analyte	152	C12H8	208-96-8	152.4	152.4	151.4,150.0,76.0	0.500	
acenaphthene	Ae	23.766	2.5	analyte	154	C12H10	83-32-9	153.0	153.0	154.1,152.0,76.0	0.500	
fluorene	Fluo	26.143	2.5	analyte	166	C13H10	86-73-7	166.0	166.0	163.0,164.0,82.2	0.500	
phenanthrene-d10	Ph-d10	30.405	3	internal std.	188	C14D10	1517-22-2	188.4	188.4	184.1,189.2,158.1	0.623	
phenanthrene	Ph	30.500	3	analyte	178	C14H10	85-01-8	178.3	178.3	176.0,179.0,151.0	0.500	
anthracene	Anth	30.750	3	analyte	178	C14H10	120-12-7	178.3	178.3	176.0,179.0,151.0	0.500	
3,6-dimethylphenanthrene	3,6-DMP	36.044	3	RDS	206	C14H8(CH3)2	1576-67-6	206.3	206.3	191.0,205.3,102.0	0.580	
fluoranthene	F'anth	37.201	4	analyte	202	C16H10	206-44-0	202.4	202.4	201.4,200.0,101.0	0.500	
pyrene-d10	P-d10	38.384	4	internal std.	212	C16D10	1718-52-1	212.3	212.3	211.3,106.0,208.1	0.608	
pyrene	Py	38.481	4	analyte	202	C16H10	129-00-0	202.4	202.4	201.4,200.0,101.0	0.500	
4-terphenyl	4-TP	40.391	3	internal std.	230	C6H5C6H4C6H5	92-94-4	230.0	230.0	231.2,115.0,228.0	0.632	
benzo[a]anthracene	B[a]A	47.268	4	analyte	228	C18H12	56-55-3	228.0	228.0	226.0,229.1,113.9	0.500	co-elutes with Ch-d12
chrysene-d12	Ch-d12	47.304	4	internal std.	240	C18D12	1719-03-5	240.1	240.1	236.1,241.2,120.0	0.577	co-elutes with B[a]A
chrysene	Ch	47.483	4	analyte	228	C18H12	218-01-9	228.0	228.0	226.0,229.1,113.9	0.500	
benzo[b]fluoranthene	B[b]F	55.447	5	analyte	252	C20H12	205-99-2	252.0	252.0	250.0,126.0,113.0	0.500	also called: benz[e]acephenanthrylene
benzo[k]fluoranthene	B[k]F	55.619	5	analyte	252	C20H12	207-08-9	252.0	252.0	250.0,126.0,113.0	0.500	
benzo[a]pyrene	B[a]Py	57.516	5	analyte	252	C20H12	50-32-8	252.0	252.0	250.0,126.0,113.0	0.500	
3-methylcholanthrene	3-MeChol	60.470	5	internal std.	268	C21H16	56-49-5	268	268	252.0,253.0,126.0	0.604	
indeno[1,2,3-cd]pyrene	I[1,2,3-cd]Py	63.199	6	analyte	276	C22H12	193-39-5	276	276	274.0,137.4,138.3	0.500	unresolved from DB[ah]A
dibenz[ah]anthracene	DB[ah]A	63.340	5	analyte	278	C20H12	53-70-3	278	278	139.0,279.0,276.0	0.500	unresolved from I[1,2,3-cd]Py
benzo[ghi]perylene	B[ghi]Per	64.059	7	analyte	276	C22H12	191-24-2	276	276	138.0,137.0,274.0	0.500	

Table 2. PCBs used and respective analytical ions used for quantification. SES / SPS = sample evaluation / preparation standard; RDS = recovery determination standard; RT = retention time; FW = formula weight

Name	Abbreviation	RT (min.)	Cl atoms	Type	FW	Formula	CAS No.	1° ion	Analytical ion	Qualifying ions	Conc$^{\underline{n}}$ (ng/μL)	Notes
2,2',6-trichlorobiphenyl	PCB 019	29.508	3	SES/SPS	257.5	C12H7Cl3	038444-73-4	186	256	257.9,186.0,150.0	0.39	
2',3,5-trichlorobiphenyl	PCB 034	31.888	3	IS	257.5	C12H7Cl3	037680-98-5	186	256	258,186,150	0.48	
2,2',6,6'-tetrachlorobiphenyl	PCB 054	31.916	4	first tetra	292.0	C12H6Cl4	015968-05-5		292			co-elutes just after PCB 034
2,4,5-trichlorobiphenyl	PCB 029	32.107	3	RDS	257.5	C12H7Cl3	01586-07-4	186	256	258,186,150	0.41	
2,4,4'-trichlorobiphenyl	PCB 028	32.671	3	analyte	257.5	C12H7Cl3	7012-37-5	186	258	258,256,150	0.50	
2,2',5,5'-tetrachlorobiphenyl	PCB 052	34.336	4	analyte	292.0	C12H6Cl4	35693-99-3	220	292	290,222,150	0.50	
2,3,4,6-tetrachlorobiphenyl	PCB 062	35.058	4	IS	292.0	C12H6Cl4	054230-23-7	220	292	222,150	0.47	
2,2',4,6,6',-pentachlorobiphenyl	PCB 104	35.183	5	first penta	326.5	C12H5Cl5	056558-16-8		326			
2,2',4,4',6,6'-hexachlorobiphenyl	PCB 155	38.543	6	first hexa	361.0	C12H4Cl6	033979-03-2		360			
2,2',4,5,5'-pentachlorobiphenyl	PCB 101	38.867	5	analyte	326.5	C12H5Cl5	37680-73-2	325.8	325.8	327.7,184.0,109.0	0.50	
2,3',4,4',6-pentachlorobiphenyl	PCB 119	39.505	5	IS	326.5	C12H5Cl5	056558-17-9	325.8	326	327.7,184.0,109.0	0.47	
3,3',4,4'-tetrachlorobiphenyl	PCB 77	40.612	4	last tetra	292.0	C12H6Cl4	032598-13-3		292			
2,2',3,4',5,6-hexachlorobiphenyl	PCB 147	41.963	6	SES/SPS	361.0	C12H4Cl6	068194-13-8	289.8	359.7	361.7,217.9,144.9	0.50	
2,3',4,4',5-pentachlorobiphenyl	PCB 118	42.727	5	analyte	326.5	C12H5Cl5	31508-00-6	325.8	325.8	327.7,184.0,109.0		not in PCB-Mix 7
2,2',3,3',4,6,-hexachlorobiphenyl	PCB 131	42.981	6	IS	361.0	C12H4Cl6	091798-70-7	289.8	360	361.7,217.9,144.9	0.46	
2,2',3,4',5,6,6'-heptachlorobiphenyl	PCB 188	43.368	7	first hepta	395.5	C12H3Cl7	074487-85-7		394			
2,2',4,4',5,5',-hexachlorobiphenyl	PCB 153	43.692	6	analyte	361.0	C12H4Cl6	35065-27-1	359.8	359.8	361.7,217.9,144.9	0.50	
2,2',3,4,4',5'-hexachlorobiphenyl	PCB 138	45.085	6	analyte	361.0	C12H4Cl6	35065-28-2	359.7	359.7	361.7,217.9,144.9	0.50	
3,3',4,4',5-pentachlorobiphenyl	PCB 126	45.522	5	last penta	326.5	C12H5Cl5	057465-28-8		326			
2,3,3',4,4',5'-hexachlorobiphenyl	PCB 157	48.308	6	RDS	361.0	C12H4Cl6	069782-90-7	359.7	359.7	361.7,217.9,144.9	0.39	
2,2',3,3',4,5,6-heptachlorobiphenyl	PCB 173	48.443	7	IS	395.5	C12H3Cl7	068194-16-1	393.7	393.7	395.7,161.8	0.45	
2,2',3,4,4',5,5'-heptachlorobiphenyl	PCB 180	49.275	7	analyte	395.5	C12H3Cl7	35065-29-3	393.7	393.7	395.7,161.8	0.50	
3,3',4,4',5,5'-hexachlorobiphenyl	PCB 169	50.388	6	last hexa	361.0	C12H4Cl6	032774-16-6		360			
2,3,3',4,4',5,5'-heptachlorobiphenyl	PCB 189	52.680	7	last hepta	395.5	C12H3Cl7	039635-31-9		394			



<u>Figure 1</u> **Total Ion Chromatogram (TIC) showing simultaneous analysis of PAH (10ng) and PCB (1ng) standards. A key to the peak labels is presented in Table 1 and Table 2**