Appendix 1: Polycyclic Aromatic Compounds: Nomenclature and Analysis

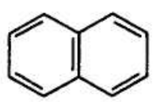
This appendix provides an explanation for and definition of the terms that have been used to describe polycyclic aromatic compounds. A general discussion is also included on the analysis of polycyclic aromatic compounds and a detailed description and commentary is given on the individual methods described in the reports reviewed by the PAC Task Group (TG).

A1.1 Nomenclature

For purposes of clarity and consistency, the PAC TG has used the definitions of the following terms throughout this project.

Polycyclic Aromatic Hydrocarbon (PAH)

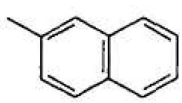
A fused aromatic-ring compound consisting only of carbon and hydrogen. Similar compounds include chrysene, pyrene, benzo[a]pyrene, perylene, etc. Naphthalene, the simplest PAH consists of two fused benzene rings:



The "ultimate" PAH is graphite, an inert material comprised of parallel sheets of fused benzene rings in an "infinite" array (API, 2002).

PAHs most commonly encountered in the environment contain two to seven fused benzene rings, although PAHs with a greater number of rings are also found in most PAH-containing materials, though usually at lower levels than the 2-6 membered ring species. The majority of the PAHs found in crude oil and petroleum streams have alkyl-substituents, with from one to twenty carbons, or even higher, depending on the boiling range of the petroleum stream (Altgelt et al., 1994; Milton et al., 1981).

These compounds are referred to as "branched" or "alkylated" PAHs. Methylnaphthalene is the simplest example of an alkylated PAH: there are two possible isomers, 1-methyl and 2-methyl. 2-

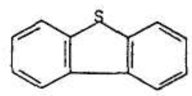


methylnaphthalene is shown below:

Polycyclic aromatic compound (PAC)

PAC is a more inclusive term than PAH. PAC includes PAHs, alkylated PAHs, and those multi-ringed aromatic molecules in which one or more atoms of a heteroatom such as nitrogen, oxygen or sulfur replaces a corresponding number of carbon atoms in a ring system. The PACs with heteroatoms can be grouped according to the heteroatom they contain. In general, the PAC categories contain only one heteroatom, although some having more than one type of heteroatom can be found at very low levels in some materials. As with PAHs, the majority of the PACs found in crude oil and petroleum streams have alkyl-substituents, with from one to twenty carbons, or even higher, depending on the boiling range of the petroleum stream.

S-PACs – are unalkylated and alkylated PACs in which the heteroatom is sulfur. These include the thiophenes and their benzologues (with additional aromatic rings fused to the thiophene structure).
Dibenzothiophene is an example of an S-PAC:



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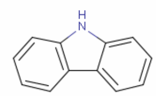
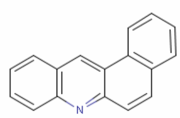
(API, 2002)

N-PACs- are unalkylated and alkylated PACs in which the heteroatom is nitrogen. These are the pyrrolic (five-membered ring aromatic) and pyridinic (six-member ring aromatic) structures and their benzologues. Carbazoles, referred to as non-basic N-PACs, are N-PACs with a dibenzopyrrole system:



Due to their behavior as weak bases, N-PACs containing a quinoline nucleus are referred to as "basic N-PACs". Benz[a]acridine is an example of a basic N-PAC:



If the heteroatom is oxygen, the part of the structures containing the heteroatom is usually either a furan or a dioxane. Certain keto-structures, such as quinones, also can be found in some crude oils.

<u>Polynuclear Aromatic (PNA)</u>

This term is an obsolete term that is not recognized as valid by either the International Union on Pure and Applied Chemistry or the American Chemical Society. Historically, the term was used to describe the multi-ringed aromatic hydrocarbons now called PAHs. The term was used in company reports of Method 2 analyses to describe compounds that were later referred to as PACs in a publication (Feuston et al., 1994) by the sponsoring company.

References

Altgelt, K.H. and Boduszynski, M.M. (1994)
Composition and analysis of heavy petroleum fractions.
Marcel Dekker.

API, (2002)
A Guide to Polycyclic Aromatic Hydrocarbons for the Non-Specialist;
Publication No. 4714, February 2002; Washington, D.C.).

A1.2 Analytical Methods Used in the Compositional Reports Reviewed by the Task Group

One hundred and fifty-three (153) analytical reports were made available to the TG and these included data that had been derived from 70 samples by a variety of different methods. Not all the samples had been characterized by all methods. Five analytical methods were used to determine PAC concentrations. The analytical method used for each sample is shown in the **Table A1-1**.

Table A1-1. Analytical Methods Used for Each Sample

Sample No.	Method 1			Method 2	Method 3	Method 4	Method 5	Calculation [1]
	1-5 Ring Aromatics	S-PACS (Measured)	N-PACs (Calculated)	1-7 Ring Aromatics	24 Individual PAH/PAC (measured)	16 Individual PAH and two methyl-naphthalenes (Measured)	Carbazoles (Measured)	1-7 Ring PAC (Calculated)
F-115								√
F-127						√		√
F-128						√		√
F-129						√		√
F-130						√		√
F-131						√		√
F-132						√		√
F-134						√		√
F-179	√	√		√		√	√	√
F-184						√		√
F-185						√		√
F-186						√		√
F-187						√		√
F-188						√		√
F-193	√	√		√		√	√	√
F-194	√	√		√		√	√	√
F-195	√	√		√		√	√	√
F-196	√	√		√		√	√	√
F-197	√	√		√		√	√	√
F-199	√	√		√		√	√	√
F-200	√	√		√		√	√	√
F-201	√	√		√		√	√	√
F-202						√	√	√
F-213				√		√	√	√

Sample No.	Method 1			Method 2	Method 3	Method 4	Method 5	Calculation [1]
	1-5 Ring Aromatics	S-PACS (Measured)	N-PACs (Calculated)	1-7 Ring Aromatics	24 Individual PAH/PAC (measured)	16 Individual PAH and two methyl-naphthalenes (Measured)	Carbazoles (Measured)	1-7 Ring PAC (Calculated)
F-215				√		√	√	√
F-220				√		√	√	√
F-221	√	√		√		√	√	√
F-222	√	√		√		√	√	√
F-225	√	√		√			√	
F-227	√	√		√			√	
F-228	√	√		√			√	
F-229	√	√		√			√	
F-233	√	√		√				
F-236	√			√				
F-274	√	√		√				
F-275	√	√		√				
F-276	√	√		√				
F-277				√				
F-73								√
89645				√				
89646	√	√	√	√				
86271	√	√	√	√				
86270	√	√	√	√	√			
86268	√	√	√					
90062	√	√	√					
85244	√	√	√	√	√			
86193	√	√	√	√				
86192	√	√	√					
8281	√	√	√	√	√			
86001	√			√	√			
86484	√	√	√	√				
87213	√	√	√	√	√			
83366	√	√	√	√	√			
86181	√	√	√	√				
86272	√	√	√	√				

Sample No.	Method 1			Method 2	Method 3	Method 4	Method 5	Calculation [1]
	1-5 Ring Aromatics	S-PACS (Measured)	N-PACs (Calculated)	1-7 Ring Aromatics	24 Individual PAH/PAC (measured)	16 Individual PAH and two methyl-naphthalenes (Measured)	Carbazoles (Measured)	1-7 Ring PAC (Calculated)
87438	Benzo(a)pyrene only measured on this sample							
89106	√	√	√	√				
88614				√				
87058	√	√	√					
86525	√	√	√					
87293	√	√	√					
86187	√	√	√	√				
86045	√		√	√				
82191				√				
91490				√				
89040	√	√	√					
84152					√			
84095	A limited analysis was conducted on this sample but the methods used were not comparable with any other methods summarized in this table.							

[1] Data shown in this column were calculated and were not measured. For this reason they were not used in any evaluation.

The five principal analytical methods differ in the following important respects:

- **Method 1** is a combination of analytical methods that provided actual and estimated measurements of various PAC classes of compounds, such as number of rings (1-5), S-PACs, and N-PACs. The method used for measuring ring classes relies on the separation of the sample into an aromatic and a non-aromatic fraction followed by GC separation coupled with MS analysis of the components in the aromatic fraction. Components in the aromatic fraction include unalkylated and alkylated aromatics and PACs. The term Method 1 used elsewhere in the report generally refers to the 1 – 5-ring classes.
- **Method 2** is a single analytical method that involves solvent extraction (DMSO) and an analysis of the DMSO-extracted concentrate of PACs by gas chromatography with an FID or MS detector. The DMSO extraction procedure is selective for the less polar PAC species, so that highly alkylated PACs are excluded from measurement. The term Method 2 used elsewhere in the report refers to the 1 – 7-ring classes.
- **Method 3** is a combination of analytical methods used to identify the quantities of 24 specific unalkylated PAHs present in the petroleum stream being examined, limiting its utility. The method relies on the separation of the petroleum substance into six fractions followed by the identification of individual compounds within each fraction.
- **Method 4** is a single analytical method that identifies 16 specific unalkylated PAHs present in the petroleum substance being examined, limiting its utility.
- **Method 5** is a combination of analytical methods that provided actual measurements of pyrrole benzologues. Carbazole and it alkylated derivatives are only one of several in a series of pyrrole benzologues measured.

A brief description of the five principal methods for measuring PAC/PAH and the parameters reported by each of the laboratory reports is described in **Table A1-2**.

Table A1-2. Summary of Analytical Methods Used and the Parameters Reported

PAC Analysis Method	Compositional Information Reported
Method 1 The aromatic and non-aromatic fractions of the test material were separated by silica gel elution chromatography. The aromatics fraction was then analyzed by electron impact mass spectrometry to quantify and partially identify components based on the number of aromatic rings present (1- to 5-ring PAC), S -PAC and unidentified aromatics. Basic nitrogen was determined by a perchloric acid-potentiometric titration method. Quantitation of total nitrogen was accomplished by chemiluminescence. Non-basic nitrogen was estimated by taking the difference between the total nitrogen and the basic nitrogen. In some cases elemental sulfur was determined by oxidizing the sulfur to sulfur dioxide and then determining the concentration by iodate titration. Estimation of non-basic N-PACs was obtained assuming an average MW of 150 for the nitrogen PACs and calculating the theoretical wt % based on elemental analysis findings.	Total sulfur (%) Total nitrogen (ppm) Basic nitrogen (ppm) Nonaromatics (wt. %) Total aromatics (wt. %) Monoaromatics (wt. %) • Alkyl benzenes(wt. %) • Napthene benzenes (wt. %) • Dinapthene benzenes (wt. %) Diaromatics (wt. %) • Napthalenes (wt. %) • Acenapthenes (biphenyls) (wt. %) • Fluorenes (wt. %) 3-Ring PACs (wt. %) • Phenanthrenes (wt. %) • Napthene phenathrenes, (wt. %) 4-Ring PACs (wt. %) • Pyrenes (fluoranthenes) (wt. %) • Chrysenes, (wt. %) 5-Ring PACs(wt. %) • Benzofluoranthenes(wt. %) • Perylenes(wt. %) • Dibenzanthracenes(wt. %) Sulfur-PACs (wt. %) • Benzothiophenes (wt. %) • Dibenzothiophenes (wt. %) • Naphthobenzothiophenes (wt. %) Unidentified aromatics (wt. %) Nitrogen-PAC (Estimated) • Non-basic carbazole-type (wt. %) • Basic quinoline-type (wt. %)
Method 2 Samples were diluted with cyclohexane, fortified with anthracene d10 and perylene-d12 as internal standards, and extracted twice with DMSO. The combined DMSO extracts were diluted with water	Total wt. % of PACs reported for 2 replicates PAC content profile reported according to the number of ring classes • Group I (wt. %)

Table A1-2. Summary of Analytical Methods Used and the Parameters Reported

PAC Analysis Method	Compositional Information Reported
and extracted three times with pentane. The pentane fraction was recovered and evaporated to approximately 5 ml and then extracted with water to remove any residual DMSO. The pentane fraction was recovered, dried over anhydrous sodium sulfate and finally concentrated to 2 ml for analysis by gas chromatography with flame ionization detection (GC/FID) and mass spectrometric analysis (GC/MS) for determination of 1-7-ring content (separated by ring number but not speciated). Following GC/FID and GC/MS analyses, the remaining extract concentrates were dried under nitrogen and the residues weighed for determination of the various 1-7 ring fractions or their combinations, such as 3-7 or 4-6, of PAC compounds (Feuston et al., 1994; Roy et al., 1985; Roy et al., 1988)	• Group II (wt. %) • Group III (wt. %) • Group IV (wt. %) • Group V (wt. %) • Group VI (wt. %) • Group VII (wt. %) The groups each represented the number of ring e.g. Group VII was the group of 7-Ring PNAs. The TG noted that the results using this method used the term PNA rather than PAC
<u>Method 3</u> Samples were separated into six fractions by liquid chromatography using a range of solvents. Specific components and groups of components within each fraction were then characterized by GC-MS and measured using GC-FID.	The fractions separated and components identified and measured were: Fraction 1 C10 to C32 Paraffinic hydrocarbons Fraction 2 Diaromatics & dibenzothiophenes Fraction 3 Three-ring PAC Fraction 4 3-ring and 4-ring PAC Fraction 5 4-Ring PAC Fraction 6 Alkylcarbazoles/alkylbenzocarbazoles
<u>Method 4</u> Both preparative liquid chromatography (Prep LC) and gas chromatography/mass spectroscopy (GC/MS) techniques were used to isolate and quantify the polynuclear aromatics present in the sample. The carbon black oils were first fractionated into saturates, mono-aromatics and a 2-ring+ carbon fraction by the preparative LC method. The saturates and mono-aromatics fractions were discarded. The 2 ring+ fraction was then recovered and analyzed by GC/MS. (For a detailed description of the conditions of analysis refer to the reports). The GC/MS method for PAH analysis utilized standards obtained for EPA method 610M and lab-	The following PAH were quantified (mg/kg) • Naphthalene • 2-Methylnaphthalene • 1-Methylnaphthalene • Acenaphthylene • Acenaphthene • Fluorene • Phenanthrene • Anthracene • Fluoranthene • Pyrene • Benzo(a)anthracene • Chrysene

Table A1-2. Summary of Analytical Methods Used and the Parameters Reported

PAC Analysis Method	Compositional Information Reported
prepared standards blended from pure samples of the individual polynuclear aromatics. A qualitative analysis for the presence of carbazoles was also made by GC/MS after dilution of the neat sample. Quantitative analysis was not possible because recovery efficiency of carbazoles in the sample preparation procedure (Prep LC) was unknown. Isolation procedures involving acid-base extractions and liquid chromatography separations showed little or no recovery of carbazole spikes from the carbon black oil matrix. Carbazole spectral searches were based on literature spectra, spectra from a carbazole spike and assumptions that simple substituted carbazoles would show a similar spectra with the parent mass shifted up 14 amu (atomic mass units) for each additional methyl substitution. No carbazoles were detected in the samples at the detection limits reported for the analytical procedures. Classes of aromatics were quantified with GC-FID.	• Benzo(b)fluoranthrene • Benzo(k)fluoranthene • Benzo(a)pyrene • Dibenzo(a,h)anthracene • Benzo(g,h,i)perylene • Indeno(1,2,3-cd)pyrene A simulated distillation curve was included in the report MS analysis using method ASTM D-2789 was used to identify and quantify the following • Paraffins • Monocycloparaffins • Dicycloparaffins • Alkylbenzenes • Indanes/tetralins • Naphthalenes n-Paraffin distribution of the following was also reported • N-Nonane • N-Decane • N-Undecane The following metals were measured and reported (mg/kg) • Lead • Copper • Iron • Nickel • Sodium • Vanadium • Arsenic • Chromium
Method 5 (Benzologues) Quantification by elemental analyses of total nitrogen and basic nitrogen (using the methods described above for Method 1) to estimate amounts of carbazole compounds. Isolation of pyrrole benzologues (PB) fraction by silica gel, separation GC, quantification by NPD, FID and MS.	Total nitrogen Basic nitrogen Carbazoles and alkyl-substituted carbaozoles Benzocarbazoles and alkyl-substituted benzocarbazoles 4H/11-dibenzocarbazole and 4H-naphthocarbazole and alkyl-substituted 4H/11-dibenzocarbazoles and 4H-naphthocarbazoles Phenanthrocarbzole and alkyl-substituted phenanthrocarbazoles Dibenzocarbazole/Napthocarbazole and alkyl-substituted dibenzocarbazoles/ napthocarbazoles

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Estimation of mutagenic and dermal carcinogenic activities of petroleum fractions based on polynuclear aromatic hydrocarbon content. In: Polynuclear Aromatic Hydrocarbons: A decade of Progress. Ed. Cooke, M and Dennis, A. J., Batelle Press

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