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Original Review Article

Importance of Polycyclic Aromatic Hydrocarbons as a Chemical Marker in Forensic Studies

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Abstract

Introduction: Polycyclic aromatic hydrocarbons (PAHs) are omnipresent micro-pollutants. They are ubiquitous and carcinogenic in nature and found in the environment. They are obtained from Petrogenic and Pyrogenic sources and hence found everywhere. **Medicolegal aspects:** In recent studies, they are used as chemical markers in source identification. When petroleum products and organic materials are burned they produce a specific and unique type of PAHs which are used as chemical markers in the source apportionment. In the present study importance of polycyclic aromatic hydrocarbons is explored in several fields of forensic science such as forensic toxicology, Environmental Forensics, Food Forensics, Petroleum Forensics, and in fire investigation. **Conclusion:** Polycyclic aromatic hydrocarbons are important in the different fields of forensic science such as forensic toxicology, environmental forensics, food forensic and petroleum forensic etc.

1. Introduction

Polycyclic aromatic hydrocarbons are omnipresent micro-pollutants (**Fig. no. 1**).[1, 2] They are two to five rings of hydrophobic organic aromatic compounds, oleophilic in nature. Pure chemical PAHs are colorless, or pale-yellowish color solid. On the basis of molecular weight classification, they are classified into two categories i.e. low molecular weight (LMW) and High molecular weight (HMW).[3,4]They are classified on the basis of its origin as Digenic, Pyrogenic and Petrogenic. Digenic when it is produce thorough the volcanic eruption and degradation of organic matter. When they are produce through the incomplete combustion of organic matter like wood, oil, vehicular emission, industrial emission then it is considered as pyrogenic and when they are produce due to contamination with petroleum product then it is considered as petrogenic PAHs (**Table 1**). Petrogenic PAHs are also called natural sources because they are produce from the erosion of petroliferous shales.[5,6]

2. Importance of Polycyclic Aromatic Hydrocarbons in Forensic Investigation

2.1 Forensic Toxicology

Modern toxicology deals with the identification of unknown chemicals that are found in living organisms.[7] PAHs consists of the largest class of cancer-causing chemicals and ranked 9th among chemical compounds threatening humans. It has the ability to accumulate in living soft tissues.

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They are not directly carcinogenic instead of that they act as a synergist. Its carcinogenic effect is due to its ability to bind DNA thereby causing disruptive effects that can result in tumor initiation. Most of them show genotoxic, mutagenic, teratogenic, and carcinogenic effects. It is a persistent organic pollutant more than hundreds of PAH compounds were identified however out of these only 16 was classified and identified by EPA as priority-listed carcinogenic PAHs. In one study on toxicity of benzo(a)pyrene (Bap) on mice conducted, it was found that it causes carcinomas distal to the point of application, 70% or more than that incidence of gastric tumors were found in mice fed 50-250 ppm for 4-6 months. In another study, tumors were observed in the forestomach, esophagus and larynx of rat who are ingested Benzo(a)pyrene. It was also found that 90% of contribution of BaP ingestion is due to food in non-smokers and only 1% contribution is due to air inhalation and to drinking water. Benzo (a)pyrene causes lung and liver tumor. They are found in urine, blood and tissues. They are enzymatically converted in mammalian cells to polar reactive intermediates, capable of covalently binding to cellular macromolecules.[8]

Exposure to benzo(a)pyrene at the celluar level leads to the formation of DNA adducts N^2-deoxyguanosine and N^6-deoxyadenosine with guanine and adenine nucleotides respectively.[9] One study conducted on analysis of PAHs associated with terrorist attack at world trade center (WTC), wherein pregnant women who were present at the time of attack at WTC were studied and it was found that women in the first trimester of pregnancy delivered infants with significantly shorter gestation (-3.6 days) and a smaller head circumference (-0.48 cm) compared with women at later stages of pregnancy, regardless of the distance of their residence or work sites from the WTC.[10]

Fig. no.1: Chemical Structure of United Nation Environmental Protection Agency Listed 16 PAHs

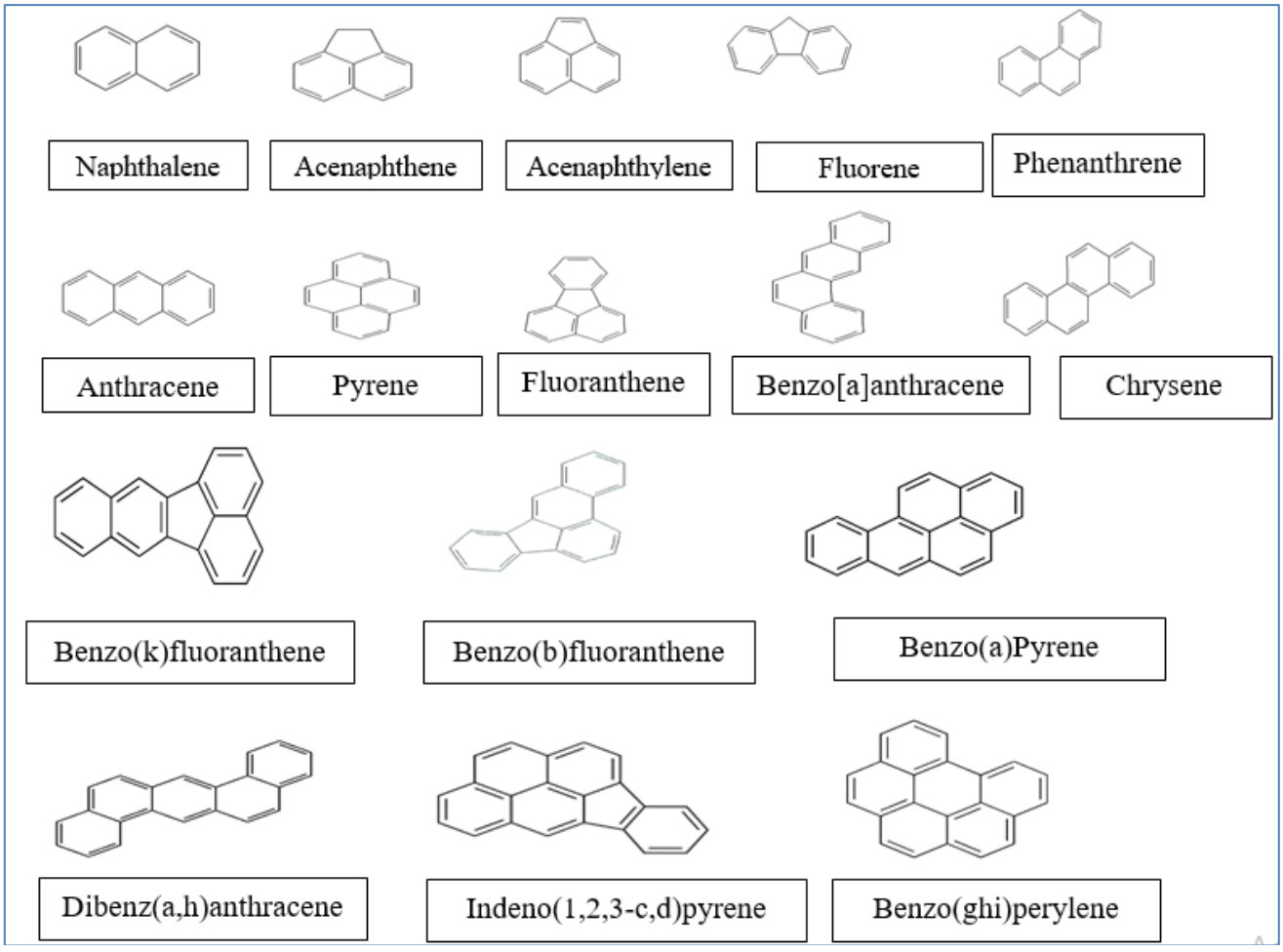

Table No. 1: Chemical Properties of United Nation Environmental Protection Agency Listed 16 PAHs

Sr. No.	PAHs	Abbreviation	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Flash Point (°C)	Relative Molecular mass	IUPAC name
1	Naphthalene	Nap	C_2H_8	80.2	217.9	79	128	Bicyclo[4.4.0]deca-1,3,5,7,9-pentaene
2	Acenaphthene	Ace	$C_{12}H_{10}$	93.4	279	125	154	1,2-dihydroacenaphthylene
3	Acenaphthylene	Acy	$C_{12}H_8$	92.5	280	122	152	Acenaphthylene
4	Fluorene	Fle	$C_{13}H_{10}$	114.8	295	151	166	9*H*-fluorene
5	Phenanthrene	Ph	$C_{14}H_{10}$	99.2	340	171	178	phenanthrene
6	Anthracene	An	$C_{14}H_{10}$	215	339.9	121	178	Anthracene
7	Pyrene	Py	$C_{16}H_{10}$	151.2	404	151.2	202	Pyrene
8	Fluoranthene	Fla	$C_{12}H_{10}$	107.8	384	198	202	fluoranthene
9	Benzo[a]anthracene	B[a]A	$C_{18}H_{12}$	155-157	437.6	209.1	228	benzo[a]anthracene
10	Chrysene	Chr	$C_{18}H_{12}$	258.2	448	-	228	chrysene
11	Benzo(k)fluoranthene	B(k)F	$C_{20}H_{12}$	217	480	-	252.3	benzo[k]fluoranthene
12	Benzo(b)fluoranthene	B(b)F	$C_{20}H_{12}$	168	481	-	252.3	pentacyclo[10.7.1.$0^{2,7}$.$0^{8,20}$.$0^{13,18}$]icosa-1(19),2(7),3,5,8(20),9,11,13,15,17-decaene
13	Benzo(a)pyrene	B(a)P	$C_{20}H_{12}$	176.5	495	-	252.3	benzo[a]pyrene
14	Dibenz(a,h)anthracene	DBahA	$C_{22}H_{14}$	269.5	524	-	278.3	naphtho[1,2-b]phenanthrene
15	Indeno(1,2,3-c,d)pyrene	IP	$C_{22}H_{12}$	163.6	536	-	276.3	hexacyclo[16.3.1.$0^{2,7}$.$0^{8,21}$.$0^{11,20}$.$0^{14,19}$]docosa-1(22),2,4,6,8(21),9,11(20),12,14(19),15,17-undecaene
16	Benzo(ghi)perylene	B(g,h,i)P	$C_{22}H_{12}$	278	550	-	276.3	hexacyclo[12.8.0.$0^{2,11}$.$0^{3,8}$.$0^{4,21}$.$0^{17,22}$]docosa-1(14),2(11),3(8),4,6,9,12,15,17(22),18,20-undecaene

In human PAHs absorb through three main routes i.e. inhalation of polluted air, skin contact and ingestion of contaminated food. In lungs absorption is depends on structure of the PAH, the size and chemical nature of the particles. Through skin coal cooking, petroleum refining and road paving associated PAHs absorbed in the body. PAH metabolism involves oxidation to a range of primary (epoxides, phenols and dihydrodiols) and secondary metabolites followed by conjugation with glutathione, glucuronic acid or sulfate.[9,11] Paver and roofers along with aluminium smelter also produces PAHs. Fluoranthene, Acenaphthene and Fluorene also produces commercially as an intermediate product in pharmaceutical industry.[12]

2.2 Environment Forensics

Subsequent to its production PAHs are exposed to various environmental matrices like air, water, soil and food.[12,13] Phenanthrene and some chrysene PAHs originated near-shore marine sediments, adjacent to forested shorelines they are produced due to diterpenoid, abietic acid, pimaric acid and triterpenoid degradation abundant in pine resin, terrestrial plants and wood ash. Typically forest soil consist of 5 µg to 100 µg/Kg. Rural area soil consists of 10-100 µg/Kg and urban soil consist of 600-3000 µg/Kg carcinogenic PAHs.[14] Large cargo ships carry petroleum products in the sea that contaminated sea water through the process of drilling activity, runoff water, oil spills and atmospheric fallout. Through that PAHs absorbs in the fish, quantic plants etc.[15] In water concentration

of PAHs found in ground water up to 1 ppt and in sewage water it is found around 1 ppm.[10]

Water also contaminated with PAHs due to leaching from linings of water storage tanks/distribution lines, and deposition from air. Most commonly found PAHs in water are fluoranthene, Benzo [b]fluoranthene, Benzo [k] fluoranthene, Benzo [a] pyrene, benzo[ghi]perylene and indebo[1,2,3-cd]pyrene collectively their concentration did not exceed 0.1µg/litre. A study conducted in Federal republic of Germany in 1981 estimated that 56% of 18 tons of air contamination were caused by heating with coal, 30% caused by coke production, 13% by motor vehicle and 0.5% by combustion of heating oil and coal-fired power generation.[14] Main indoor sources of PAHs are cigarette smoke, fuel and wood combustion and cooking and outdoor sources are vehicle exhaust, coal combustion, biomass burning, power plant, sewage plant, Burning of garbage, volcanic erruption and industrial facilities.[9,16]

2.3 Food Forensics

They are found in meat and meat products like poultry and eggs, Bacon, Sausages, smoked meat/beat/chicken, grilled sausages/duck.[17] They enter in the food through the soil contamination and through food chain. Through the contaminated water PAHs are absorb in mussels, fish, and shellfish. PAHs in food also produce through the thermal treatment like grilling, roasting, baking and frying.[5, 8, 13, 15] PAHs forms during grilling and roasting are due to pyrolysis of edible oil and fat at the surface of food and they burnt at the temperature of 150°C-400°C. process of frying takes less time than roasting and grilling hence produces lower amount of PAHs.[15] The presence of PAHs in food is result of time and temperature of burning, humidity, type of food processing, type of control and smoke used and the design and types of kilns.

2.4 Fire Investigation

Fire investigation conducted under the forensic chemistry sub branch of forensic science.[18, 19] PAHs are produce after combustion and fire is based on combustion process. In fire investigation PAHs are used as a source identifier. A study conducted wherein atmospheric PAHs are used as source identifier in forest fire detection.[20] During fire investigation presence of other combustion material affect the identification of accelerant. Hence in another study author used PAHs as a source identifier in detection of fire ignitable residues on different burned plastic carpets. Fluorene, anthracene, phenanthrene, methyl anthracene, methyl phenanthrene, fluoranthene, pyrene as a main component found in gasoline mixed combustion smoke of PVC plastic carpet.[21]

2.5 Petroleum Forensic

Petroleum forensic is a new emerging field of forensic science that deals with application of scientific knowledge of petroleum and related products to help in court of law. In the crude oil analysis, PAHs are considered as a biomarker to reflect the terrestrial source of the original organic material.[6] Natural activities such as offshore drilling, tanker leakage and ship leakage leads to contamination of sea water with petroleum oil that affect marine biota and they enter in to the food chain. PAHs are one of the contaminant found in petroleum oil which has bioaccumulation property. Diesel fuel contains significant levels of PAHs of smaller molecular size, the 2 to 3 ring PAH predominating. It was found that greater the number of rings, that the poorer the PAH destruction percent and destruction percent decreases with increasing alkylation.[22] Petroleum chemical fingerprinting techniques was used in Exxon vldaez oil spill cases wherein PAHs were characterized and differentiated among different petroleum sources in the Prince William Sound region after the spill.[23]

3. Conclusion:

Polycyclic aromatic hydrocarbons are important in the different fields of forensic science such as forensic toxicology, environmental forensics, food forensic and petroleum forensic etc. as discussed above. Hence in detail and enhanced characterization and identification of PAHs are required to incorporate its uses in different fields of forensic science.

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