



## Characterization for Types and Percents of Polycyclic Aromatic Hydrocarbons in Sera of Workers at Fuels Stations at Baghdad

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### **Abstract**

All polycyclic aromatic hydrocarbons (PAHs) have a high toxicity, and/or carcinogenic and/or mutagenic to most microorganisms and humans.

Main aim to this study is to provide contemporary information (quantitative and qualitative) PAHs in sera of fuel stations, workers whom exposure with petroleum products.

The study includes 60 male petrol-filling workers in 5 petrol stations around Baghdad. Their ages were between (20 – 50) years. For compared the results a 30 sera samples from healthy individuals was collected with corresponding age-matched as control group. The samples were collected from October 2017 until April 2018. The BMI was calculated for all subjects.

Technique of High performance liquid chromatography (HPLC) was used to detect the presence of PAHs quantitatively and qualitatively in the sera of all subjects.

The mean level of total PAHs in sera of workers was  $1275.65 \pm 934.267$  higher than that for healthy subjects  $67.380 \pm 46.16$  with significant value  $p=0.033$ . Also the types and percent of PAHs in the sera of workers were differ. For studying the epidemiologic, no correlation between the percent of % PAHs in sera of workers who exposure to petroleum without affected with their age and BMI.

**Keywords:** PAHs, Environmental pollution, Gasoline, petrol, toxic and carcinogenic compounds

## توصيف الى انواع والنسب المنوية للمركبات الاروماتية متعددة الحلقات في امصال العاملين في محطات تعبئة الوقود في بغداد

### الخلاصة

ان الكثير من المركبات الاروماتية متعددة الحلقات ذات سمية عالية وتسبب طفرات الجينية ومسرطنة للكائنات الحية الدقيقة وللإنسان.

هدفت الدراسة الى التحري عن النسب الكمية والنوعية للمركبات الاروماتية المتعددة الحلقات في امصال عمال محطات الوقود الذين يتعرضون للمنتجات النفطية ومن ثم ايجاد علاقتها مع اعمار ومعدل كتلة الجسم للعمال.

تضمنت الدراسة الحالية 60 عينة من امصال الذكور العاملين في 5 محطات وقود في بغداد، تراوحت اعمارهم ما بين 20-50 سنة ولغرض مقارنة النتائج جمعت 30 عينة من الذكور الاصحاء وبنفس المدى من العمر. جمعت العينات ابتداء من تشرين الاول 2017 الى نيسان 2018. تم حساب معامل كتلة الجسم من قياس كتلة وطول كل شخص. استخدمت تقنية كروموتوغرافيا السائل العالي الاداء لتشخيص وجود المركبات الاروماتية متعددة الحلقات (نوعيا وكميا) في امصال العمال والاصحاء.

وجد ان معدل المركبات الاروماتية متعددة الحلقات في امصال العمال ( $934.267 \pm 1275.65$ ) اعلى مما للاصحاء ( $46.16 \pm 67.380$ ) وبصورة ملحوظة ( $P=0.033$ ). واختلفت نسب ونوع المركب في المصل. ولاتوجد هناك علاقة ما بين النسبة المئوية لكل مركب مع اعمار العاملين و BMI في محطات التعبئة وانما مع الفترة الزمنية للتعرض.

### 1. Introduction

Gasoline is derived from petroleum; a mixture of volatile hydrocarbons used as fuel for internal-combustion engines, enhanced with different additives [1, 2]. The main primary pollutants in the motor vehicle exhaust can be carbon oxides, nitrogen oxides, alcohols, aldehydes, ketones, sulfur compounds, and hydrocarbons. In those hydrocarbons may include mono-aromatic composition on the exhaust emissions, including direct comparison of petroleum gas passenger emissions from similar liquefied (LPG) and unleaded petrol [3].

Polycyclic aromatic hydrocarbons (PAHs) present as particles in urban air pollution, which are derived from fueled vehicles (diesel and gasoline). Exhaust emission is able to cause several health problems in human such as mutagenicity and carcinogenicity [2].

More than 500 types of hydrocarbons are a formed complex mixture called gasoline these hydrocarbons may have between 5 to 12 carbons. Straight chain or branched alkanes are

consist of the greatest amounts, while gasoline consist of small amounts of cyclic and aromatic alkane compounds [4].

Benzene and other known carcinogens are present in gasoline [5, 6]. From leakage and handling during production, transport and delivery gasoline can also enter the environment uncombusted, both as liquid and as vapor, (e.g., from storage tanks, from spills, etc.) [1].

The oxidative degradation of gasoline during long-term storage produces Gummy, sticky harmful resin deposits. By adding 5–100 ppm of the antioxidants such as phenylenediamines, substituted phenols and other amines it could be prevented this degradation through this addition [7].

At the workplace people can be exposed to the toxic gasoline by swallowing it, breathing in vapors, skin contact, and eye contact. The gasoline has designated as a carcinogen furthermore its toxicity by the National Institute for Occupational Safety and Health (NIOSH) [8, 9].

In some weak communities and indigenous groups Australia, Canada, New Zealand, and some Pacific Islands the inhalation of gasoline has become epidemic [10]. The practice is thought to cause severe damage to organ, including mental retardation [11].

A process of thermal decomposition called (pyrolysis) and subsequent recombination (pyrosynthesis) of organic molecules form the most of PAH are formed. The PAHs enter the environment through various routes and are usually found as a mixture containing two or more of these compounds, e.g., soot. Through various toxic actions the PAHs affect organisms. The mechanism of this toxicity is considered to be interacted and interference with the normal function of cellular membranes and with the systems of enzyme associated with the membrane. They have been noted to cause carcinogenic and mutagenic effects and are potent suppression the immunity. Their impacts have been documented with respect to develop the immune system, humeral immunity, and host resistance [12]. Reduction the sulfur present in the diesel bring about reduced emissions of PAHs, the biodiesel is free from aromatic compounds and sulfur used to blend with the diesel fuel to reduce the emissions of PM, HC, and CO and optimization of hydrocarbon compositions of gasoline to reach a lowest exhaust emission [13]. The aim of the present study is to provide complimentary information (quantitative and qualitative) PAHs in sera of fuel stations, workers whom exposure with petroleum products.

## **2. Materials and Methods**

### **Subjects**

Thirty men working in 5 petrol stations around Baghdad the capital of Iraq were enrolled in this study. The ages were between (20 – 50) years from January to June 2018, named the first group. The second group consists of 30 healthy subjects (20 – 50) as control group.

### **Anthropometric measurements**

The value of body mass index (BMI) was calculated by dividing the weight (kg) on the height<sup>2</sup> (m<sup>2</sup>). People were taken as obese if their body mass index was 29.9 or more [14].

### **Specimen collection**

Samples of five ml blood were drawn from men workers in petrol stations and healthy control by venipuncture using disposable syringe were placed into plane tubes. After that, each tube was centrifuged at 1500×g for about 10 min to collect the serum and store it at -20C° until use for determining polycyclic aromatics Hydrocarbons.

### **Methods**

The instrument gas chromatography supplied from Shimadzu company (2010, Japan) was used in the detection of PAHs in the laboratories of the Ministry of Science and Technology, column separation was carried out in a (30 m × 0.25mm i.d.) DB-5 column (J&W Scientific, Folsom, CA) coated with a 0.25-µm thick film of 5% diphenyl–polydimethylsiloxane. Each sample was injected in the split mode at an injection temperature of 280 °C. The column temperature was initially held at 40 °C for 1 min, raised to 120 °C at the rate of 25 °C/min, then to 160 °C at the rate of 10 °C/min, and finally to 300 °C at the rate of 5 °C/min, held at final temperature for 15 min. By using a detector (FID) the temperature was kept at 330 °C. Gas of Helium was used as a carrier gas at a constant flow rate of 5 mL/min [15].

### **Statistical analysis**

Data are analyzed through the use of SPSS (Statistical Process for Social Sciences) version 22 application statistical analysis system and Excel (statistical package). The statistical data analysis including mean, Standard deviation (SD) and score values of Confidence interval (95%) for population mean were used in order to analyze and assess the results of this study.

### 3. Results and Discussion

The present study achieved on 30 individuals who were working at petroleum stations in Baghdad city and 30 healthy individuals who were consider as control group matched in their ages. Table (1) explain their characterization including the age and the BMI. Both of them had a non-significant alterations for the workers in compare with the control group.

**Table (1) Statistical analysis of Age, weight, height, BMI measurements distributed among workers at petroleum stations and control groups.**

Parameters	Workers (N=30) Mean $\pm$ SD	Control (N=30) Mean $\pm$ SD	P value
Age years	33.367 $\pm$ 9.49	33.375 $\pm$ 4.405	NS*
Weight kg	77.500 $\pm$ 13.125	74.250 $\pm$ 9.177	NS*
Height m <sup>2</sup>	1.703 $\pm$ 0.072	1.723 $\pm$ 0.035	NS*
BMI Kg/m <sup>2</sup>	27.232 $\pm$ 4.448	25.111 $\pm$ 3.767	NS*

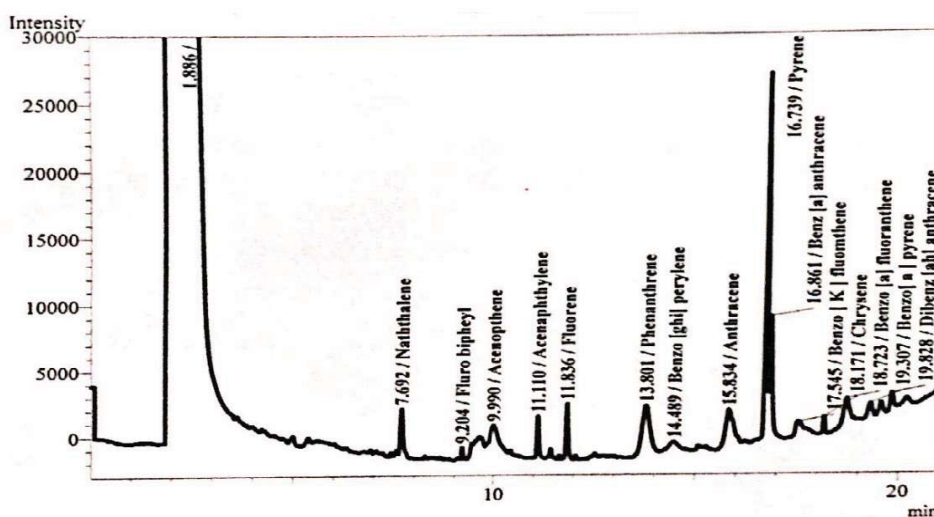
NS: no significant

The influences of gasoline fuel on the emission of polycyclic aromatic hydrocarbons (PAHs) from gasoline engine were investigated. To investigate the status of PAH in the serum of the workers quantitatively and qualitatively by using atomic absorption spectroscopy technique was used twice. First one for standard compounds, then for each worker's serum. Table (2) illustrates the concentrations for each standard with their calculated Rt values, while Table (3) includes the concentration of PAH in the sera of the workers.

**Table (2) Measurements of Polycyclic Aromatics Hydrocarbons in standard sample**

PAHs	Rt	Concentration of PAHs (ppm)
Naphthalene	7.692	59.27
Biphenyl	9.204	58.27
Tetraphenylene	9.990	59.38
Acenaphthylene	11.110	59.56
Fluorene	11.836	59.36
Phenanthrene	13.801	58.49
Benzo [c] Phenanthrene	14.489	56.63
Anthracene	15.834	58.76
Pyrene	16.739	59.70
Benz[a]anthracene	16.861	140.07
Ovalene	17.545	58.70
Chrysene	18.171	59.37
Benzo[a]fluoranthene	18.723	59.78
Dibenz[a,h]anthracene	19.828	55.34

The calculation for each concentration of each PAH had calculate depending on the chromatogram gas chromatography specified to each PAH as shown in Figure (1) using standard PAH compoundsto calculate their Rt then determined the PAHs in the serum of each worker depending on the standard Rt value Table (4).



**Fig. (1) Chromatogram gas chromatography of polycyclic aromatics Hydrocarbons in standard sample.**

Table (3) Concentrations of each PAH serum of each worker.

W	PAHs Compoundppm													
	Nap	Fbp	Ace	Any	Fln	Phe	B(c)P	Ant	Py	B(a)A	B(K)F	Chr	B(a)F	DahA
W1	-	-	-	-	-	-	-	7.13	3.07	20.92	-	86.18	-	31.92
W2	-	-	-	-	-	-	-	431.1 6	8.84	60.24	48.06	-	19.58	-
W3	-	-	-	-	-	-	48.15	0.66	2.84	19.34	277.48	98.38	-	-
W4	7.07	-	-	-	-	-	36.12	6.28	2.70	18.41	194.85	108.76	-	26.77
W5	-	23.71	-	6.14	-	-	9.122	2.81	1.140	7.76	-	29.45	-	-
W6	31.67	-	-	-	-	-	11.71	-	6.14	41.80	-	221.14	-	45.23
W7	-	-	-	-	-	-	-	6.54	2.95	20.10	819.99	161.90	-	-
W8	-	-	-	-	-	22.15	-	31.67	-	-	211.54	421.45	-	-
W9	18.63	-	-	-	-	-	-	-	-	-	1353.8 9	-	-	-
W10	-	-	-	-	-	-	-	-	23.89	162.79	854.56	-	310.68	-
W11	12.12 3	-	-	-	-	-	-	-	-	-	338.64	-	-	-
W12	-	63.90	-	10.46	-	-	14.10	-	1.25	8.49	-	-	-	-
W13	-	-	-	-	-	12.49	-	-	-	-	-	-	-	-
W14	-	-	-	10.73	-	-	8.70	-	1.41	9.62	-	-	-	-
W15	-	-	-	-	-	-	-	-	-	-	35.04	-	-	-
W16	-	-	-	1784. 06	136 9.95	13.40	-	-	-	-	1040.6 5	-	-	-
W17	-	-	-	-	148. 871	-	-	6.54	2.95	20.10	819.99	161.90	-	-
W18	-	-	-	-	-	22.15	-	31.67	-	-	211.54	421.45	-	-
W19	-	-	-	-	-	-	15.16	3.93	-	-	56.53	-	-	19.36
W20	-	-	-	21.85	-	-	-	2.33	-	-	726.06	-	-	-
W21	31.43	-	-	13.72	-	-	52.60	4.26	-	-	38.96	58.95	-	-
W22	-	32.85	-	-	-	-	-	-	-	-	107.83	68.56	-	-
W23	-	211.4 7	81. 76	-	-	-	-	-	-	-	70.36	-	-	-
W24	-	46.54	-	-	-	-	-	4.48	1.57	10.73	-	52.60	-	20.83

**Table (4): the mean concentration of each compound that present in sera of worker**

PAHs	No.of workers	%	Mean of Compounds Conc.(ppm)
Nap	5	20.8	20.33
Fbp	6	25	158.93
Ace	1	4.16	81.76
Any	6	25	307.83
Fln	2	8.33	759.41
Phe	4	16.67	48.92
B(c)P	8	33.33	900.75
Ant	12	50	44.955
Py	13	54.17	4.51
B(a)A	13	54.17	30.79
B(K)F	17	70.83	423.35
Chr	11	45.83	171.07
B(a)F	2	8.33	165.13
DahA	5	20.83	28.82

In a previous study the concentration of 21 individual PAHs in the engine exhaust, original gasoline were determined and analyzed by a gas chromatography/mass spectrometer (GC/MS). The results of this were summarized as follows. The mean total-PAH (summation of 21 PAHs), among nine Lead-free fuel, the highest one is that C95-LFG (60.6 mg/L), secondly is T92-LFG (45.5 mg/L), C92-LFG (42.1 mg/L), C98-LFG (35.5 mg/L) T95-LFG(20.8 mg/L). The main PAHs evaluate effects of aromatic contents in gasoline on air pollutant emissions from a four-stroke motorcycle engine [13], The previous studies had focused on the PAHs emission from three types, i.e. 2-stroke carburetor (2-Stk/Cb), 4-stroke carburetor (4-Stk/Cb) and 4-stroke fuel injection (4-Stk/FI) motorcycles and the toxicity also studied by total BaP equivalent [16], and the size distribution of PAHs in emission of a two-stroke carburetor motorcycle [17] showed that most of the 21 analyzed PAHs have two significant modes that peak at  $< 0.1$  and  $0.18\text{--}0.32\mu\text{m}$ , it imply that those emitted particulates rise a high health risk for that particulates smaller than  $2.5\mu\text{m}$  traverse easily through the upper analyzed by (GC/MS). A gas chromatography/mass spectrometer lungs [16].



Yan Miguel *et al.*, concluded that the concentration of PAHs levels were safe for human consumption of mussels in Cienfuegos Bay. These results contribute to the database of the Caribbean region because the information about the contamination for PAHs is scarce in bivalves, in Cuba [18]. In previous study the PAH were determined in diesel and gasoline particulate extracts and DNA binding to CT DNA. A high difference in content of 14 PAHs in diesel and gasoline extracts was shown, observed an increase in the concentration of 14 PAHs, 6 carcinogenic PAHs, benzo[a] pyrene (B[a]P) in diesel more than in gasoline extracts. The CT DNA adduct formation was higher for diesel extracts in compare to gasoline extracts [12].

The Government of Australia and BP Australia began the usage of Opal fuel in remote areas prone to petrol sniffing in the year 2005 [19].

To evaluate the occupational exposure to particulate and volatile PAH concentrations, they were used personal air samples and lymphocyte DNA adducts as markers of exposure.

Only in winter samples of exposed workers, the extraction of butanol revealed a significant increase for adduct levels in compare with those of control persons. While in summer, no differences had seen in adduct levels between exposed and control persons. The total concentrations of particulate and volatile PAHs measured in eight workplaces in winter showed a good significant correlation with total DNA adducts analyzed in workers' lymphocytes [12].

When the PAHs containing up to four rings they are refer as light PAHs while those that contain more than four rings are heavy PAHs. All heavy PAHs are more stable and more toxic than the light PAHs [20, 21, 22].

### **Conclusion**

All sera of the studied workers had different types and concentrations of PAHs. The Types of PAHs in the serum of the Iraqi workers are fourteen. The ratio of these types ranged between 8.33 to 70.83 for B(a)F, Fln and B(K)F respectively with a concentration 165.13, 759.41 and 423.35 ppm respectively. The concentration of each type of PAHs in the stander samples ranged between 55.34 ppm to 140.07 ppm for Dibenz [a, h] anthracene and Benz[a]anthracene respectively. In studying the relationship among the height, weight, BMI values and the PAHs, it found there was no correlation among them.

**List of Symbols:**

No.	Key	Symbol
1	Acenaphthene	Ace
2	Acenaphthylene	Any
3	Anthracene	Ant
4	Benzo[a]anthracene	B(a)A
5	Benzo[a]fluoranthene	B(a)F
6	Benzo[k]fluoranthene	B(K)F
7	Benzo [c] Phenanthrene	B(c)P
8	Body Mass Index	BMI
9	Chrysene	Chr
10	Concentration	Conc.
11	Dibenzo[a,h]anthracene	DahA
12	Fluorene	Fln
13	2-Fluorobiphenyl	Fbp
14	High performance liquid chromatography	HPLC
15	Naphthalene	Nap
16	Part per million ( $\mu\text{g/L}$ )	ppm
17	Percentage	%
18	Phenanthrene	Phe
19	polycyclic aromatic hydrocarbons	PAHs
20	Pyrene	Py
21	Standard deviation	SD

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