Simultaneous determination of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in waste oils by gas chromatography- mass spectrometry- ion trap

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ABSTRACT

A capillary gas chromatographic mass spectrometry with ion trap was applied for the simultaneous determination of nine polychlorinated biphenyl (PCB) congeners and sixteen polycyclic aromatic hydrocarbons (PAHs) in waste oils (used hydraulic oils, automotive oil, machine oil, cutting oil and transformer oil). The optimized procedure involves solvent extraction using dimethyl sulfoxide (DMSO) in first step and mixture of ethyl acetate and hexane in second step. Extraction efficiency was monitored by using pyrene-d10 as surrogate standard. The separation of PCBs and PAHs was done in VF-5MS (30 m x 0.25 mm x 0.25 μm) capillary column and analysed on GC-MS using selective ion monitoring (SIM) mode. The method was calibrated using phenanthrene-d10 as an internal standard. Correlation coefficients ranged from 0.9993 to 0.9999 for PCBs and 0.9941 to 0.9995 for PAHs. Recoveries of PCBs and PAHs are over 87.0 % and 70.0 % respectively. The average concentration of total PAH in all waste oil samples was 1997.8 mg kg^{-1}. The trends of the concentrations of the total PAH found in present study were machine oil > automotive oil > transformer oil > cutting oil > hydraulic oil. The average percentage of total PAH based on the rings was 78.32% (2 ring), 8.26 % (3 ring), 6.74 % (4 ring), 4.80 % (5 ring) and 1.56 % (6 ring).
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INTRODUCTION

One important area of modern environmental analysis is the determination of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) both of which commonly occur in the environment. They are highly toxic, mutagenic and persistent in the environment, and therefore are on the US Environmental Protection Agency (IEPA) list of priority pollutants.[1]

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. Mixtures of PCBs tend to be chemically stable, non-flammable and elec-

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trically 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. The Indian Environmental Protection Agency (EPA), 2008 have proposed a limit of less than 2.0 mg kg^{-1} for PCBs in waste oils.

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.[2] In general, low molecular weight 2- and 3-ringed PAHs have a significant acute toxicity, whereas 4- to 6-ringed PAHs tend to display a greater carcinogenicity.[3] 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.[4] In specific locations there may also be a petrogenic contribution of PAHs from crude oil, coal and various refinery products. Many hundreds of PAHs exist in the environment, but the US Environmental Protection Agency (USEPA) has listed sixteen as "Consent Decree" priority pollutants such as; naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)-perylene. The Indian Environmental Protection Agency (EPA), 2008 have proposed a limit of maximum 6% for PAHs in waste oils. The literature survey shows few studies on simultaneous determination of PCBs and PAHs in waste oils. The analytical methods for PCBs are currently based on their separation by gas chromatography (GC) using capillary columns with specific detectors such as electron capture detector (ECD)[5,6] and mass spectrometry (MS).[7-9] Analysis of PAHs, in most of the cases, is performed using gas

chromatography (GC),[10] gas chromatography-mass spectrometry (GC-MS),[11,12] and high performance liquid chromatography (HPLC) techniques.[13] This investigation was undertaken in order to establish a solvent extraction method for simultaneous determination of PCBs and PAHs in waste oils (used hydraulic oil, automotive oil, machine oil, cutting oil and transformer oil) and their analysis by GC-MS with ion trap analyser.

EXPERIMENTAL

Reagents

The solvents ethyl acetate, hexane and dimethyl sulfoxide (DMSO) were HPLC grade and sulphuric acid (98 %) was A. R. grade used in the present work. Silica gel (100–200 mesh, Sigma–Aldrich) activated at 200 ^{0}C for 6 h. and anhydrous sodium sulphate (A. R. grade) were used in the clean-up stage. Water was purified with a Milli-Q plus system (Millipore).

Standard solutions

The mixture of nine PCBs containing 2-chlorobiphenyl, 2,3-dichlorobiphenyl, 2,4,5-trichlorobiphenyl, 2,2',4,6-tetrachlorobiphenyl, 2,2',3,4,5'-pentaclhorobipheny, 2,2',4,4',5,6'-hexachlorobiphenyl, 2,2',3,4',5,6,6'-heptachlorobiphenyl, 2,2',3,3',4,5',6,6'-octachlorobiphenyl and 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl and sixteen PAHs containing naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)-anthracene, and benzo(g,h,i)perylene was purchased from AccuStandard (M-680A) and AccuStandard (Z-013-17) respectively. Phenanthrene-d10 from AccuStandard (M-680-IS-10X) and pyrene-d10 from Sigma Aldrich were used as an internal standard and surrogate standard respectively. All the solutions were prepared in 1:1 ethyl acetate and hexane mixture. Mix standard solutions of 0.015-12.50 mg kg^{-1} concentrations of PCBs and 0.30-9.60 mg kg^{-1} concentrations of PAHs were prepared from the stock solution for calibration and 0.3 mg kg^{-1} of internal standard was added to each.

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Instrumental analysis of PCBs and PAHs

The analysis of PCBs and PAHs was carried out by an integrated system of gas chromatography, equipped with automatic injection system and coupled to a mass spectrometric system with ion trap analyser. Varian CP-3800 GC, Saturn-2200 mass spectrometer with auto injector CP-8410 was used for analysis. The separations of PCBs and PAHs were done in a 30 meter length, 0.25 mm internal diameter and 0.25 µm film thickness coated with 5% phenyl-95% methylpolysiloxane Varian VF-5MS column. Helium was used as the carrier gas at 9.6 psi pressure and 1 ml min^{-1} flow. The injector was used at constant temperature and 280 ^{0}C. The initial oven temperature was 80 ^{0}C (4 min. isothermal) to 180 ^{0}C (at 20 ^{0}C min.$^{-1}$) to 250 ^{0}C (at 2 ^{0}C min.$^{-1}$) to 280 ^{0}C (at 10 ^{0}C min.$^{-1}$) isothermal for 4 minutes. The injection volume was 1 µL in splitless mode. The temperature of ion trap, manifold and transference line was 220 ^{0}C, 50 ^{0}C and 280 ^{0}C respectively.

Samples

The waste oils/used oils of hydraulic, automotive, machine, cutting and transformer were stored in 250 ml pre-cleaned dark glass bottles with teflon caps at a maximum temperature of 4 ^{0}C. Moisture determinations were made according to ASTM D 3976.[14] The concentrations of PCBs and PAHs were calculated on dry weight basis.

Extraction procedure

Portion of about 0.5 g of sample was accurately weighed in a glass centrifuge tube and 1 ml of 2.5 mg kg^{-1} of pyrene-d10 was added. The first extraction was carried out by 10 ml DMSO (HPLC grade) and deionised water (95:5) then repeated the same with 8 ml and finally 5 ml after keeping the tubes into centrifuge machine (3500 rpm) for 10 minutes. Then 10 ml water was added in extraction portion. This was further extracted with 10 ml ethyl acetate and hexane (1:1) mixture, repeated the same with 8 ml and finally with 5 ml after keeping in centrifuge machine for 10 minutes. The extracted portion was reduced in rotary evaporator and made up in 5 ml after adding 1.5 µg internal standard and finally injected 1 µL into GC.

Sample clean-up

A variety of substances in waste oil can be simulta-neously extracted and cause interference in the determination of PCBs and PAHs by GC-MS. Therefore the extraction was purified using silica gel column. The clean-up procedure was as follows: The concentrated extract was applied to open glass column (0.45 m, 1 cm i.d.) filled with (from bottom to top) glass wool, silica gel (100-200 mesh) and water free sodium sulphate (2 cm). The extract was eluted using 20 ml hexane subsequently 30 ml hexane: dichloromethane (95:5) mixture, both the solutions mixed together and reduced the volume in rotary evaporator. Finally the solution was made up in 5 ml after adding 1.5 µg internal standard and injected 1 µL into GC.

RESULT AND DISCUSSION

Chromatographic separation

The chromatographic conditions used yielded an adequate resolution of the target compounds in less than 51 min. Figure 1 shows a total ion chromatogram (TIC) with the 0.015-0.078 mg kg^{-1} of PCBs, 0.3 mg kg^{-1} of
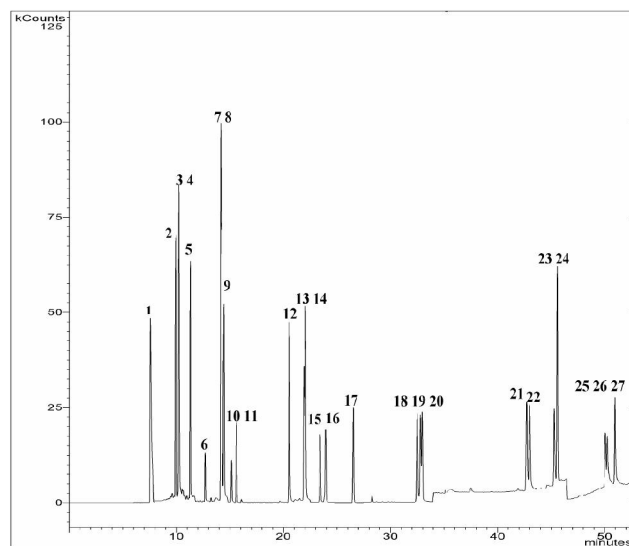
Peaks: 1. Naphthalene, 2. Acenaphthylene, 3. Acenapthene, 4. PCB 1, 5. Fluorene, 6. PCB 5, 7. Phenanthrene-d10, 8. Phenanthrene, 9. Anthracene, 10. PCB 29, 11. PCB 50, 12. Fluoranthene, 13. Pyrene-d10, 14. Pyrene, 15. PCB 87, 16. PCB 154, 17. PCB 188, 18. Benz(a)anthracene, 19. Chrysene, 20. PCB 201, 21. Benzo(b)fluoranthene, 22. Benzo(k)fluoranthene, 23. Benzo(a)pyrene, 24. PCB 209, 25. Indeno(1,2,3-cd)pyrene, 26. Dibenzo(a,h)anthracene and 27. Benzo(g,h,i)perylene.

Figure 1 : TIC chromatogram of PCBs M-680A AccuStandard (0.015-0.078 mg kg^{-1}), PAHs Z-013-17 AccuStandard (0.3 mg kg^{-1}), Phenanthrene-d10 (0.3 mg kg^{-1}) and Pyrene-d10 (2.5 mg kg^{-1})

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PAHs, 0.3 mg kg⁻¹ phenanthrene-d10 and 2.5 mg kg⁻¹ pyrene-d10 spiked in PCBs and PAHs free waste oil followed by optimized procedure. Using the NIST-2.0 library search and Varian Workstation-MS data review version 6.6 software, twenty seven compounds were identified in the mixture; nine PCBs, sixteen PAHs, one phenanthrene-d10 internal standard and one pyrene-d10 surrogate standard under the chromatographic conditions described in the experimental section. All calculations were done using quantitation ion abundance.

Validation of the analytical method

The method validation is an important issue of overall quality associated with analytical data. The following parameters are those currently considered more important in quantitative analytical methods validation.

Linearity

In the present work, the linearity of the method was determined by injecting 1 µL of spiked blank matrix extracts. Linear calibration graphs were constructed by least squares regression of concentration versus peak area and height ratio (analyte / I.S.) of the calibration standards. The calibration graphs obtained for 0.015-2.50 mg kg⁻¹ for PCBs 1, 5 and 29, 0.031-5.00 mg kg⁻¹ for PCBs 50, 87 and 184, 0.046-7.50 mg kg⁻¹ for PCBs 188 and 201 and 0.078-12.50 mg kg⁻¹ for PCB 209 and 0.30-9.60 mg kg⁻¹ of PAHs were linear over the concentration range examined. Correlation coefficients of all studied PCB congeners were ranged from 0.9993 to 0.9999 and for PAHs 0.9941 to 0.9995 as can be seen in TABLE 1.

Limits of detection and limits of quantification

LoDs and LoQs values are specified in TABLE 2 were calculated through the definition based on the standard deviation of the signal of the blank injections following IUPAC recommendations.[15] The limits calculated for PCBs are LoDs 0.10-0.13 µg kg⁻¹ and LoQs 0.30-0.42 µg kg⁻¹ and for PAHs 0.17-2.1 µg kg⁻¹ LoDs and 0.51-6.3 µg kg⁻¹ LoQs.

Recovery

Waste oil (PCBs and PAHs free) was spiked with a known amount PCBs and PAHs. The extraction procedure was followed, the extracts were subjected to GC-MS and the recoveries of total PCB and PAH were

calculated by reference to the calibration graphs. The TABLE 2 illustrates that recovery results which shows within the commonly accepted range 84.0-91.4% recovery and 1.0-3.5 % RSD for PCBs and 70.0-96.8 % recovery and 1.8-10.2 % RSD for PAHs.

TABLE 1 : IUPAC number of PCBs, ring of PAHs, quantitation ion, confirmation ion, retention time, and correlation coefficients of PCBs and PAHs

PCBs and PAHs	IUPAC no. of PCBs	Ring of PAHs	Quantitation ion	Confirmation ion	RT (min.)	Correlation coefficients
2	1	-	188	152	10.28	0.9995
2,3	5	-	222	224	12.70	0.9997
2,4,5	29	-	256	258	15.16	0.9996
2,2',4,6	50	-	292	294	15.62	0.9999
2,2',3,4,5'	87	-	326	324	23.44	0.9993
2,2',4,4',5,6'	154	-	360	362	23.96	0.9994
2,2',3,4',5,6,6'	188	-	394	396	26.55	0.9997
2,2',3,3',4,5',6,6'	201	-	430	428	32.98	0.9996
2,2',3,3'4,4',5,5',6,6'	209	-	498	500	45.60	0.9994
NAP	-	2	128	76	07.66	0.9993
ACY	-	3	152	76	09.93	0.9949
ACE	-	3	154	153	10.22	0.9952
FLU	-	3	165	166	11.29	0.9994
PHE	-	3	178	152	14.24	0.9990
ANT	-	3	178	152	14.43	0.9977
FLT	-	4	202	200	20.53	0.9992
PYR	-	4	202	200	22.05	0.9985
B(a)A	-	4	228	226	32.45	0.9993
CHR	-	4	228	226	32.78	0.9993
B(b)F	-	5	252	250	42.70	0.9986
B(k)F	-	5	252	250	42.97	0.9995
B(a)P	-	5	252	250	45.26	0.9941
IP	-	6	276	274	50.03	0.9976
D(a,h)A	-	5	278	276	50.22	0.9993
B(g,h,i)P	-	6	276	274	50.94	0.9964

NAP: Naphthalene, ACY: Acenaphthylene, ACE: Acenapthene, FLU: Fluorene, PHE: Phenanthrene, ANT: Anthracene, FLT: Fluoranthene, PYR: Pyrene, B(a)A: Benz(a)anthracene, CHR: Chrysene, B(b)F: Benzo(b)fluoranthene, B(k)F: Benzo(k)fluoranthene, B(a)P: Benzo(a)pyrene, IP: Indeno(1,2,3-cd)pyrene, D(a,h)A: Dibenzo(a,h)anthracene, B(g,h,i)P: Benzo(g,h,i)perylene.

Reproducibility

The reproducibility of the extraction procedure and

TABLE 2 : Recovery, limits of detection (LoDs) and limits of quantification (LoQs) of PCBs and PAHs in waste oil

PCBs & PAHs	% Recovery	% RSDs	LoDs[a] (μg kg^{-1})	LoQs[b] (μg kg^{-1})
1	89.5	2.5	0.13	0.42
5	90.1	1.5	0.13	0.42
29	91.4	1.0	0.13	0.42
50	87.9	2.5	0.10	0.32
87	90.2	2.0	0.10	0.32
154	90.2	1.0	0.10	0.32
188	89.9	3.5	0.12	0.40
201	84.0	1.5	0.12	0.40
209	85.0	1.0	0.10	0.30
NAP	87.5	4.1	0.29	0.85
ACY	90.8	3.9	0.39	1.80
ACE	92.2	3.5	0.32	0.96
FLU	87.5	3.0	0.53	1.62
PHE	95.5	4.0	0.29	0.85
ANT	95.6	3.4	0.31	0.92
FLT	88.0	3.2	0.17	0.51
PYR	96.8	3.8	0.17	0.51
B(a)A	86.8	2.1	1.50	4.70
CHR	96.0	1.8	1.50	4.70
B(b)F	82.0	7.8	1.20	3.60
B(k)F	79.5	5.3	0.19	0.57
B(a)P	82.6	5.9	1.30	3.90
IP	79.0	6.8	1.10	3.60
D(a,h)A	70.0	10.2	1.50	4.70
B(g,h,i)P	79.0	7.5	2.10	6.30

$\text{LoDs}^a = \dfrac{So \times 3}{S}$, $\text{LoQs}^b = \dfrac{So \times 10}{S}$, **So: Standard deviation of noise, S: Detector response.**

Varian CP-3800 GC, Saturn-2200 mass spectrometer CP-8410 with VF-5MS column was studied for six replicate spiked samples containing 0.015-0.078 mg kg^{-1} of PCBs and 0.3 mg kg^{-1} of PAHs (TABLE 3). The RSD in area counts for all PCBs and PAHs was less than 3 % (two sets of six replicate injections). The RSD of extraction procedure and retention times were 2.5 to 10.5 % and 0.012 to 0.048 % respectively which is below the CLP maximum allowable RSD of 15 %.[16]

DETERMINATION OF PCBS AND PAHS IN ACTUAL SAMPLES

Five samples of used hydraulic oil, automotive oil, machine oil, cutting oil and transformer oil were treated

TABLE 3 : Reproducibility of PCBs and PAHs analysis

PCBs and PAHs	PCBs and PAHs (mg kg^{-1}) spiked	% RSD	R.T. (min.) mean	% RSD	Area counts mean	% RSD
1	0.015	5.8	10.28	0.047	17529	1.82
5	0.015	8.2	12.70	0.047	5092	1.65
29	0.015	5.9	15.16	0.017	4121	1.65
50	0.031	9.8	15.62	0.025	8005	1.75
87	0.031	5.8	23.44	0.025	6794	1.95
154	0.031	7.8	23.96	0.048	6772	1.95
188	0.045	2.5	26.55	0.048	7381	2.07
201	0.045	9.2	32.98	0.016	7421	2.05
209	0.078	4.5	45.60	0.016	15660	1.97
NAP	0.31	4.2	07.66	0.028	53003	1.98
ACY	0.31	5.6	09.93	0.048	22254	2.05
ACE	0.31	5.9	10.22	0.012	17927	2.50
FLU	0.31	6.2	11.29	0.015	13682	2..10
PHE	0.31	9.2	14.24	0.018	52209	1.75
ANT	0.31	8.5	14.43	0.017	16919	2.15
FLT	0.31	4.7	20.53	0.019	20458	2.45
PYR	0.31	5.9	22.05	0.048	20657	2.85
B(a)A	0.31	5.8	32.45	0.017	10609	2.54
CHR	0.31	5.2	32.78	0.026	97936	1.45
B(b)F	0.31	3.2	42.70	0.031	8144	2.54
B(k)F	0.31	8.5	42.97	0.027	7552	1.55
B(a)P	0.31	9.2	45.26	0.027	5298	2.85
IP	0.31	10.5	50.03	0.032	3501	2.98
D(a,h)A	0.31	10.0	50.22	0.017	1997	2.85
B(g,h,i)P	0.31	9.8	50.94	0.016	5273	2.89

and analysed using the optimized procedure. The figure 2 shows the SIM chromatogram PAHs of actual waste oil sample. None of samples were found PCBs. The average standard deviation of individual PAH concentrations measured are presented in TABLE 4. The total PAH concentrations were 354.2, 2140.9, 5088.7, 717.6 and 1687.8 mg kg^{-1} in hydraulic oil, lubricating oil, machine oil, cutting oil and transformer oil respectively. The mean concentration of total PAH was 1997.8 mg kg^{-1} for all samples together. The trends of the concentrations of the total PAH found in present study were machine oil > automotive oil > transformer oil > cutting oil > hydraulic oil. The average percentage of total PAH based on the rings was 78.32% (2 ring), 8.26 % (3 ring), 6.74 % (4 ring), 4.80 % (5 ring) and 1.56 % (6 ring). The figure 3 also illustrates that 2-ring and 3-ring PAHs were found to be
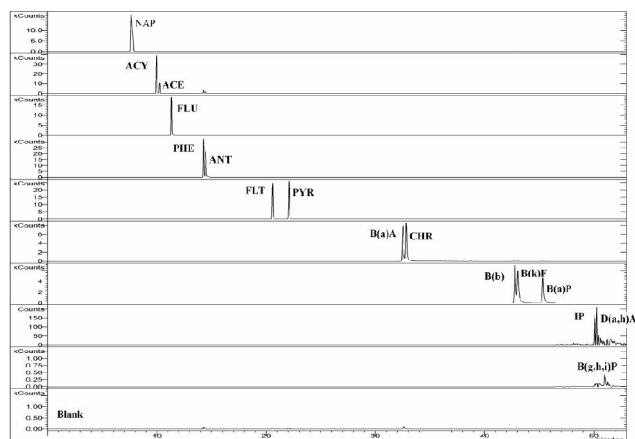
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Figure 2 : SIM chromatogram of actual waste oil sample shows presence of sixteen PAHs.

TABLE 4 : Average concentrations of PCBs and PAHs in different waste oils samples (mg kg⁻¹)

PCBs & PAHs	Hydraulic oil Mean ± RSD %	Automotive oil Mean ± RSD %	Machine oil Mean ± RSD %	Cutting oil Mean ± RSD %	Transformer oil Mean ±RSD %
1	Nd	Nd	Nd	Nd	Nd
5	Nd	Nd	Nd	Nd	Nd
29	Nd	Nd	Nd	Nd	Nd
50	Nd	Nd	Nd	Nd	Nd
87	Nd	Nd	Nd	Nd	Nd
154	Nd	Nd	Nd	Nd	Nd
188	Nd	Nd	Nd	Nd	Nd
201	Nd	Nd	Nd	Nd	Nd
209	Nd	Nd	Nd	Nd	Nd
NAP	300.0±10	1575.0±12	4000.0±15	600.00±7	1200.0±11
ACY	1.0±2	33.0±2	70.2±5	4.0±2	6.8±2
ACE	1.2±1	7.0±4	90.2±6	10.2±2	30.2±5
FLU	2.5±1	40.2±8	15.0±4	3.5±1	38.2±5
PHE	19.0±5	90.0±7	110.0±8	23.3±2	89.2±6
ANT	2.0±1	35.0±7	45.0±5	5.0±2	31.1±4
FLT	2.0±2	20.5±5	26.0±4	7.2±2	19.2±3
PYR	3.0±2	65.0±5	90.0±5	8.2±2	31.2±2
B(a)A	1.0±2	25.0±4	90.0±6	5.2±1	22.2±2
CHR	13.0±3	68.2±2	100.9±9	23.2±3	61.4±3
B(b)F	9.0±2	60.0±10	100.2±8	20.0±3	61.0±3
B(k)F	Nd	20.0±7	98.0±7	3.5±1	17.6±2
B(a)P	Nd	35.0±7	90.0±7	1.2±1	20.1±2
IP	0.5±1	19.0±5	45.0±4	1.0±2	17.2±2
D(a,h)A	Nd	8.0±3	20.2±4	1.0±1	4.2±1
B(g,h,i)P	Nd	40.0±4	98.0±7	1.1±2	38.2±3
Total PAHs	354.2	2140.9	5088.7	717.6	1687.8

dominant in the samples having 78.32 % and 8.26 % of the total PAH where as 5-ring compounds including benzo(a)pyrene (considered to be most carcinogenic) and 6-ring compounds contributes 4.8 % and 1.56 % respectively of the total PAHs. It is also illustrates from the present work that hydraulic oil is the least contaminated by PAHs, as expected since this application does not required a heating process at high temperature and it is well known that PAHs are mainly formed in high temperature applications where organic compound are involved.[17] The machinery oil and automotive oil are the most contaminated, with a high number of PAHs than the other oil samples.

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