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GC/MS analysis of polynuclear aromatic hydrocarbons in sediment samples from the Niger Delta region

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Abstract

Thirteen sediment samples from different locations in the Niger Delta region of Nigeria were analyzed for the presence of 16 polynuclear aromatic hydrocarbons (PAHs) via gas chromatography/mass spectrometry. The specific target compounds for this study included naphthalene, acenaphthylene, acenaphthene, flourene, phenanthrene, anthracene, flouranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]flouranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene, dibenz[*a*,*h*]anthracene, and indeno[1,2,3-*cd*]pyrene. Four isotopically labeled polynuclear aromatic hydrocarbons (acanaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} and perylene- d_{12}) were used for internal standardization. All 16 PAHs were found in most of the thirteen samples with concentration ranging from 0.1 µg/kg to 28 µg/kg. It was also found that the 5 and 6-ring PAHs were present in higher concentrations than all the other compounds, indicating their high resistance to microbial degradation.

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1. Introduction

PAHs are a class of compounds composed of two or more aromatic rings. They are a component of crude and refined petroleum and coal, and persist in soil and sediments. Hundreds of PAHs have been identified and these usually are found as complex mixture (Mottier et al., 2000). Fig. 1 shows the structures of sixteen priority PAHs. They are all volatilizable and as such GC/MS is a viable analytical approach. PAHs may also be generated as prod-

* Corresponding author. Tel.: +234 8023131333. *E-mail address:* chimezie@email.com (C. Anyakora). ucts of incomplete combustion processes such as forest fires and volcanic eruptions (Grova et al., 2002). Anthropogenic sources such as industrial production, transportation and waste incineration generate significant levels of PAHs (Lorber et al., 1994; Yang et al., 1998).

PAHs are classified as environmentally hazardous organic compounds due to their known or suspected carcinogenicity and are included in the European Community (EC) and United States Environmental Protection Agency (US EPA) priority pollutant list (Nieva-Cano et al., 2001). They are ubiquitous in the environment largely due to the extensive use of fossil fuels. Several PAHs are known to be potential human carcinogens; these include benz[*a*]anthracene, chrysene, benzo[*b*]flouranthene, benzo[*a*]pyrene and benzo[*ghi*]perylene (Guillen et al.,

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Fig. 1. The chemical structures for 16 priority PAHs.

2000). The health hazards posed by these compounds have been studied extensively by several authors (Perera et al., 1988; Schoket et al., 1993). The presence of these compounds in environmental samples (sediment, water and fish) has also been studied by numerous authors (Xu and Fang, 1988; Speer et al., 1990).

Soil samples from industrial sites involved with the production and disposal of fossil fuels and fossil fuel derived products usually contain PAHs at higher levels than background levels (Van Brummelen et al., 1996). The Niger Delta region of Nigeria has an extensive petroleum production activity, which has gone on for several decades, and as a result there is a strong possibility of elevated PAH concentrations in sediments in this area. The purpose of this work is to investigate the types and levels of PAHs in this area.

Various methods have been employed in the analysis of PAH such as high performance liquid chromatography (HPLC) with photometric (UV/VIS) or fluorimetric (FL) detection (Kiyali-Sayadi et al., 1999), gas chromatography with flame ionization detection (Guerin, 1999), micellar electrokinetic capillary chromatography with ultraviolet (UV) detection (Moy et al., 1998). Most of these methods lack specificity in their detection method and may give false positives when used to analyze complex mixtures. Given the complexity of the crude oil, which is the primary pollutant of the environment under study, we employed GC/MS using isotopically labeled internal standards to ensure unambiguous identification and more reliable quantification of PAHs.

2. Materials and method

Sediment samples were collected from thirteen different sites in the Niger Delta (hereafter referred to as SD-01, SD-02, SD-03, SD-04, SD-05, SD-06, SD-07, SD-08, SD-09, SD-10, SD-11, SD-12 and SD-13). Table 1 gives the sample information. These were air dried and stored at low temperature prior to sample workup and analysis. The sediment samples were collected from locations that have some history of oil pollution or are close to some oil production facilities. The sediments were collected from the riverbed, with the exception of two (SD-06 and SD-12), which were collected from a burrow pit and a water well facility. The texture of the sediments ranged from sandy to loamy.

A PAH (SRM 1647c) standard mixture (NIST, Baltimore, MD) containing naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]flouranthene, benzo[k]flouranthene, benzo[a]pyrene, benzo[ghi]perylene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene was used in this study. A mixture containing four isotopically labeled PAHs (ChemService, Westchester, PA) namely acenaphthene- d_{10} , chrysene d_{12} , phenanthrene- d_{10} and perylene- d_{12} was used as an internal standard. HPLC grade dichloromethane (Fischer Scientific, New Jersey) used for the extraction.

Soxhlet extractions were carried out using a modified form of the EPA 3540 (1994). The Soxhlet apparatus consisted of a 250 ml round bottom flask, condenser

Table 1 Sample information

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ID no.	Sample description	Analysis method	Extraction method		
SD-01	Sediment sample	GC/MS—US EPA method TO 13A	EPA method 3540		
SD-02	Sediment sample	GC/MS—US EPA method TO 13A	EPA method 3540		
SD-03	Sediment sample	GC/MS—US EPA method TO 13A	EPA method 3540		
SD-04	Sediment sample	GC/MS—US EPA method TO 13A	EPA method 3540		
SD-05	Sediment sample	GC/MS—US EPA method TO 13A	EPA method 3540		
SD-06 ^a	Sediment sample	GC/MS—US EPA method TO 13A	EPA method 3540		
SD-07	Sediment sample	GC/MS—US EPA method TO 13A	EPA method 3540		
SD-08	Sediment sample	GC/MS—US EPA method TO 13A	EPA method 3540		
SD-09	Sediment sample	GC/MS—US EPA method TO 13A	EPA method 3540		
SD-10	Sediment sample	GC/MS—US EPA method TO 13A	EPA method 3540		
SD-11	Sediment sample	GC/MS—US EPA method TO 13A	EPA method 3540		
SD-12 ^a	Sediment sample	GC/MS—US EPA method TO 13A	EPA method 3540		
SD-13	Sediment sample	GC/MS—US EPA method TO 13A	EPA method 3540		

^a Samples that are not from the river bed.

and extractor tube, seated in a temperature-controlled heating mantle. A 20 g portion of the air-dried sediment sample was extracted with 150 ml of HPLC grade dichloromethane for 16 h.

2.1. Preparation of calibration standards

Five standard solutions each containing 16 target compounds were prepared by diluting the standard mix (1647c mix from NIST) to desired concentrations with dichloromethane. To these were added $0.5 \,\mu g$ (volumetric equivalent) of the four internal standards namely acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene d_{12} and perylene- d_{12} . These were transferred to a capped and sealed vial until ready for analysis.

2.2. GC/MS instrumentation and conditions

GC/MS analysis was carried out on a Finnigan Magnum instrument equipped with a CTC A200S autosampler and a 30 m, 0.25 ID DB-5 ms fused silica capillary column (J & W Scientific, Folson CA). Helium was used as the carrier gas and the column head pressure was maintained at 10 psi to give an approximate flow rate of 1 ml/min. The injector and transfer line were maintained at 290 °C and 250 °C respectively. All injection volumes were 1 μ l in the splitless mode. The column temperature was initially held at 70 °C for 4 min, ramped to 300 °C at a rate of 10 °C/min, then temperature was held at 300 °C for 10 min. The mass spectrometer was used in electron ionization mode and all spectra were acquired using a mass range of *m*/*z* 50– 400 and automatic gain control (AGC).

2.3. Identification and quantification

The PAHs in the sample were identified by a combination of a retention time match and mass spectral match against the calibration standards. Quantitation was performed by the method of internal standardization using acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} and perylene- d_{12} . Acenaphthene- d_{10} was used as the internal standard for naphthalene, acenaphthylene, acenaphthene and flourene. Phenanthrene- d_{10} was used as the internal standard for phenanthrene, anthracene, flouranthene and pyrene. Chrysene- d_{10} was used for benz[*a*]anthracene and chrysene. Perylene- d_{10} was used for the rest of the PAHs.

3. Results and discussion

3.1. Analytical characteristics

Calibration curves were obtained using a series of standard solution. All 16 calibration curves were linear with correlation coefficients from the linear regression ranging from 0.994 to 1.000. The relative standard deviations (n = 3) were mostly below 10% as shown in Table 2. Limits of detection and quantitation (LODs and LOQs) are provided in Table 3. The lowest LOD was 0.02 µg/ml for lower molecular weight compounds while indeno(1,2,3-cd)pyrene has the highest at $1.7 \,\mu$ g/ml. To evaluate the extraction efficiency for the target compounds, recovery studies were carried out using 4 isotopic PAH to represent 2 and 3 ring, 4 ring, 5 ring and 6 ring PAHs respectively. The recoveries ranged from 90.58% to 118%. Tables 4 and 5 show the retention time and important ions for 16 PAHs used in the quantification and the internal standards respectively.

3.2. GC-MS separation and identification

Prior to analyzing the samples, the efficiency of GC/ MS for analysis of the target compounds was tested with a standard mixture of 16 PAH (target compounds).

 Table 2

 Calibration parameters of the PAH compounds

Compound	Linear range (µg/ml)	Slope	Intercept	Regression coefficient	RSD (%)
Naphthalene	0.503-5.033	3.28	1.143	0.994	4.76
Acenaphthylene	0.387-3.888	6.93	0.074	0.997	1.7
Acenaphthene	0.519-5.193	4.653	0.342	0.996	0.89
Flourene	0.119-1.188	4.024	0.084	0.997	6.2
Phenanthrene	0.086-0.855	5.063	0.105	0.997	7.17
Anthracene	0.020-0.198	5.272	0.01	0.997	4.92
Flouranthene	0.191-1.910	6.108	0.243	0.998	2.48
Pyrene	0.212-2.118	6.269	0.664	0.998	4.4
Benz[a]anthracene	0.102-1.023	5.354	-0.134	0.999	5.36
Chrysene	0.092-0.918	5.388	0.089	0.996	4.26
Benzo[b]flouranthene	0.104-1.043	10.249	-0.159	0.997	1.69
Benzo[k]flouranthene	0.118-1.180	13.24	-0.417	0.999	2.71
Benzo[a]pyrene	0.123-1.228	6.884	-0.411	0.995	2.11
Benzo[ghi]perylene	0.354-0.885	1.377	-0.167	0.995	10.16
Dibenz[a,h]anthracene	0.368-0.920	0.922	-0.108	0.997	15.79
Indeno[1,2,3-cd]pyrene	0.428-1.070	1.307	-0.122	1	4.77

Table 3 List of LODs and LOQs for the 16 PAHs

Compound	Mol. mass	No. of rings	Ret. time (min)	LOD (µg/ml)	LOQ (µg/ml)
Naphthalene	128	2	8.46	0.06	0.2
Acenaphthylene	152	3	13	0.02	0.06
Acenaphthene	154	3	13.26	0.02	0.06
Flourene	166	3	14.49	0.02	0.06
Phenanthrene	178	3	17.14	0.03	0.09
Anthracene	178	3	17.22	0.02	0.06
Flouranthene	202	4	20.16	0.04	0.12
Pyrene	202	4	20.49	0.04	0.12
Benz[<i>a</i>]anthracene	228	4	23.55	0.06	0.2
Chrysene	228	4	24	0.06	0.2
Benzo[b]flouranthene	252	5	26.3	0.1	0.3
Benzo[k]flouranthene	252	5	26.35	0.15	0.5
Benzo[a]pyrene	252	5	27.18	0.15	0.5
Benzo[ghi]perylene	276	6	30.06	0.75	2.5
Dibenz[a,h]anthracene	278	6	30.17	0.9	2.7
Indeno[1,2,3-cd]pyrene	276	6	30.55	1.7	5

Fig. 2 shows the total ion chromatogram for this analysis. A good separation was achieved using the EPA method TO 13A (1999) in 37 min. The identities of these compounds were established by combining the retention time data and the individual mass spectra.

Since the target compounds are numerous and have significantly different chemical properties and retention times, four isotopic internal standards were used to monitor the 16 compounds. Acenaphthene- d_{10} with a retention time of 13.23 min was used for the 2 and 3 aromatic ring-containing PAHs within the retention time window of 8–15 min. Phenanthrene- d_{10} with a retention time of 17.10 min was used for the PAHs within the retention time range of 17–21 min. Chrysene- d_{12} was used for chrysene and benz[*a*]anthracene. Perylene- d_{12} was used for the remaining PAHs. Figs. 3 and 4 show the selected ion chromatograms illustrating how the internal standards effectively cover the different PAH compounds. The separation and quantitation of PAHs in the sediment samples was achieved using the same GC/MS conditions as the standards. Fig. 5 shows the total ion chromatogram of an extracted sediment sample. PAHs were quantified using internal standardization.

3.3. PAH distribution

The concentrations of PAHs in the sediment samples from the locations studied are reported in Table 6. In

Table 4 List of m/z values for the 16 PAHs

Compound	m/z
Naphthalene	128, 115, 102, 87, 75, 63, 51
Acenaphthylene	152, 126, 98, 87, 76, 63, 50
Acenaphthene	154, 126, 102, 87, 77, 63, 50
Flourene	166, 139, 115, 83, 63, 50
Phenanthrene	178, 152, 126, 111, 99, 89, 76, 63, 50
Anthracene	178, 152, 126, 89, 76, 63
Flouranthene	202, 174, 150, 122, 101, 87, 74, 50
Pyrene	202, 174, 150, 101, 88, 74, 50
Benz[a]anthracene	228, 200, 150, 113, 88, 63, 50
Chrysene	228, 202, 176, 150, 113, 101, 63
Benzo[b]flouranthene	252, 224, 174, 150, 126, 113, 86
Benzo[k]flouranthene	252, 224, 198, 150, 126, 74
Benzo[a]pyrene	252, 225, 161, 126, 74
Benzo[ghi]perylene	276, 248, 225, 207, 191, 138,
	125, 97, 73
Dibenz[a,h]anthracene	278, 248, 225, 207, 191, 138, 125,
	83, 73, 57
Indeno[1,2,3-cd]pyrene	276, 248, 225, 207, 191, 138,
	111, 97, 73, 57

most of the samples, all 16 priority PAHs were detected with concentration ranging from as low as $0.1 \ \mu g/kg$ to as high as 28 $\mu g/kg$. It is interesting to note that there is a certain pattern followed by the compounds in the studied samples. Lower molecular mass PAHs with two to four rings tend to have low concentration as shown in Fig. 6. A good explanation for this is the fact the microorganisms degrade these compounds much easily (Yun et al., 2003). The compounds with five and six rings namely Benzo[ghi]perylene, Dibenz[a,h]anthra-

Table 5 List of m/z value for the four internal standards

Compound	mlz
D-acenaphthene	164, 132, 108, 84, 66, 51
D-phenanthrene	188, 160, 132, 94, 80, 66, 51
D-chrysene	240, 208, 156, 120
D-perylene	264, 236, 207, 180, 132, 118, 86

cene and Indeno[1,2,3-cd]pyrene are more difficult to degrade giving rise to this observed trend (Yun et al., 2003). Dibenz[a,h]anthracene with a molecular weight of 278 was consistently the most abundant in all the samples with very few exceptions.

In one of the sediment samples (SD-05), Benzo [ghi]perylene, Dibenz[a,h]anthracene and Indeno[1,2,3*cd*]pyrene were not detected. This is consistent with the relatively low amount of the other PAHs found in that sample. Since these three compounds with higher number of aromatic rings have very high limit of detection (Table 3) comparatively, it means that the sample has in general low concentration of PAH giving rise to the inability to detect the compounds with high LOD. The samples were collected from wide area with some samples collected as far as 300 km from one another. Hence one should expect different types of microbial and selective degradation, other sources of PAHs contamination and so on. Most of the low molecular weight PAHs have relatively high vapour pressure (from 1.04 to 2.71× 10^{-5} Pa) compared to less volatile compounds such as Indeno[1,2,3-cd]pyrene with a vapour pressure of 2.6×10^{-9} Pa (Mackay et al., 1992). Light compounds with four or fewer aromatic rings have higher water



Fig. 2. Total ion chromatogram of 16 PAH standards namely naphthylene, acenaphthylene, acenaphthylene, flourene, phenanthrene, anthracene, flouranthene, pyrene, benz[a]anthracene, chrysene, benz[b]flouranthene, benz[a]flouranthene, benz[a]pyrene, benz[a]pyrene, benz[a]nthracene and inden[1,2,3-cd]pyrene.



Fig. 3. The selected ion chromatogram of sixteen priority PAHs. The first window shows the peak for naphthylene, acenaphthylene, acenaphthene and flourene. The second window show peaks for phenanthrene, anthracene, flouranthene and pyrene. The third window shows the peaks for benz[a]anthracene and chrysene. The fourth window shows the peaks for benz[b]flouranthene, benzo[k]flouranthene, benzo[a]pyrene, benzi[b]flouranthene, dibenzo[a,h]anthracene and indeno[1,2,3-cd]pyrene.



Fig. 4. The selected ion chromatogram of the internal standards illustrating how the internal standards effectively cover the different PAH compounds. The first window shows the peak for acenaphtene- d_{10} [the internal standard for naphthylene, acenaphthylene, acenaphthene and flourene]. The second window shows the peak for phenanthrene- d_{10} [the internal standard for phenanthrene, anthracene, flouranthene and pyrene]. The third window shows the peak for chrysene- d_{12} [the internal standard for benz[a]anthracene and chrysene]. The fourth window shows the peak for perylene- d_{12} [the internal standard for benz[b]flouranthene, benzo[k]flouranthene, benzo[k]flouranthene]flouranthene,

solubility and bind less strongly to soil disposing them to easy transportation to other locations by natural cause such as rain and intense sunshine which are typical of the sampling location. These factors can account for very little variation in the distribution such as benz[a]anthracene and chrysene not being detected in



Fig. 5. The total ion chromatogram of an extracted sediment sample.

some samples. Naphthalene being disproportionately higher in some samples like SD-05, SD-06, SD-10 and SD-12. Flourene was also found to be disproportion-

Table 6 Concentration of PAH in the studied sample [in μ g/kg]

ately high in some samples. Another interesting pattern in the PAH distribution is that phenanthrene and anthracene (which are isomers) maintained a certain proportion. In future work we are going to look at this pattern to ascertain whether it has to do with stability of a particular isomer and susceptibility of degradation.

Sediment is a major sink for PAHs. The level of PAHs found depends on the level and duration of influx of PAH contamination. The range of PAH found in a given environment sometimes vary quite widely, for instance the total PAH concentration in bottom sediment from the main stem of the Chesapeake Bay were reported to range from 45 to 8920 μ g/kg for samples collected from 16 stations in 1986 (Huggett et al., 1988). Average concentrations of total PAHs in sediments from three coastal South Carolina marinas were reported to range from 35.6 to 352.3 μ g/kg (Marcus et al., 1988). In our study a range of 3.15–144.89 μ g/kg of total PAH (16 priority PAH) was observed. Apart

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	SD-01	SD-02	SD-03	SD-04	SD-05	SD-06 ^a	SD-07	SD-08	SD-09	SD-10	SD-11	SD-12 ^a	SD-13
NA	1.25	1.62	0.7	1.05	0.39	3.5	0.41	1.75	2.46	4.24	4.34	4.77	1.23
ACY	0.32	1.71	0.33	0.35	0.18	0.52	0.09	0.13	0.46	0.35	0.31	0.35	0.23
ACE	0.37	0.75	0.24	0.18	0	0.15	0.09	0.42	0.54	0.68	0.63	0.69	0.65
FL	0.66	4.27	0.4	0.22	0.19	0.45	0.16	3.2	4.68	4.8	4.64	4.26	4.59
PH	1.99	10.99	0.67	1.09	0.3	0.98	0.2	0.99	2.63	1.74	2.05	1.57	0.85
AN	1.07	7.66	0.28	0.31	0.1	0.16	0.11	0.23	0.48	0.45	0.44	0.45	0.35
FLR	1.65	5.71	0.36	1.22	0.16	0.15	0.15	0.36	1.32	0.82	1.57	0.82	0.44
PY	1.53	11.65	0.33	1.09	0.11	0.57	0.18	0.33	1.18	0.95	1.28	1.25	0.49
BaA	1.28	4.85	0.59	1.28	0	0.55	0.19	0	2.45	2.8	0	0	0
CH	1.17	6.59	0.55	1.27	0	0.61	0.22	0	2.53	0	3.54	0	0
BbF	3.88	5.48	1.97	2.4	0.6	1.1	0.86	4.54	1.99	0.85	1.25	0.77	0.57
BkF	2.88	3.19	1.14	1.77	0.3	0	0.54	1.13	1.38	1.19	0.77	0.77	0.82
BaP	5.91	7.71	5.18	2.49	0.82	1.05	1.79	4.68	9.22	6.9	3.54	2.33	1.37
DA	18.3	24.81	14.9	3.95	0	3.55	4.66	5.54	5.71	4.07	3.33	3.78	3.69
BP	21.3	28.28	17.7	2.97	0	2.64	6.54	15.8	10.3	8.72	8.96	6.92	10.4
IP	11.5	19.59	13.9	2.65	0	4.16	4.27	4.33	6.09	4.12	3.87	7.42	2.98

^a Samples that are not from the river bed.



Fig. 6. The profile of PAHs in the studied samples.

from the sample with the total PAH of $3.15 \,\mu$ g/kg other samples can be considered to be very polluted.

4. Conclusion

This study has provided new insights into the distribution pattern of PAHs in sediment samples with a history of crude oil contamination. It also lends support to the fact that some PAHs are more complex and stable hence resist microbial attack more than the others. Also low volatility and higher solubility of the lower molecular mass PAHs account for the relatively low concentration of these compounds in the studied samples. With this study we have open up numerous research directions such as the factors affecting the degradability of PAHs, the reason for certain pattern in PAH distribution and the possibility of developing a biomarker for determining the age of a particular pollution.

References

- Grova, N., Feidt, C., Crepineau, C., Laurent, C., Lafargue, P.E., Hachimi, A., Rychen, G., 2002. Detection of polycyclic aromatic hydrocarbon level in milk collected near potential contamination sources. J. Agricult. Food Chem. 50, 4640–4642.
- Guerin, T.F.J., 1999. The extraction of aged polycyclic aromatic hydrocarbon (PAH) residues from a clay soil using sonication and a soxhlet procedure: a comparative study. Environ. Monit. 1, 63–67.
- Guillen, M.D., Sopelana, P., Partearroyo, M.A., 2000. Determination of polycyclic aromatic hydrocarbons in commercial liquid flavouring of different compositions by gas chromatography-mass spectrometry. J. Agricult. Food Chem. 48, 126–131.
- Huggett, R.J., Defur, P.O., Bieri, R.H., 1988. Organic compounds in Chesapeake Bay sediments. Mar. Pollut. Bull. 19 (9), 454–458.
- Kiyali-Sayadi, M.N., Rubio-Barroso, S., Cuesta-Jimenez, M.P., Polo-Diez, L.M., 1999. A new method for the determination of selected PAH in coffee brew samples by HPLC with flourimetric detection and solid phase extraction. J. Liquid Chromatogr. Relat. Technol. 22, 615–627.
- Lorber, M., Cleverly, D., Schaum, J., Phillips, L., Schweer, G., Leighton, T., 1994. Development and validation of an air to beef food chain model for dioxin-like compounds. Environ. Sci. Technol. 156, 39–65.
- Mackay, D., Shin, W.Y., Ma, K.C., 1992. Illustrated Handbook of Physical Chemical Properties and Environmental

Fate of Organic Chemicals, vol. 2. Lewis Publishers, Boca Raton, FL.

- Marcus, J.M., Swearingen, G.R., Williams, A.D., Heizer, D.D., 1988. Polynuclear aromatic hydrocarbons and heavy metal concentrations in sediment at South Carolina marinas. Arch. Environ. Contam. Toxicol. 17 (1), 103– 114.
- Mottier, P., Parisod, R.J., Turesky, J., 2000. Quantitative determination of polycyclic aromatic hydrocarbons in barbecued meat sausages by gas chromatography coupled to mass spectrometry. J. Agricult. Food Chem. 48, 1160– 1166.
- Moy, T.W., Ferguson, P.L., Grange, A.H., Matchett, W., Kelliher, V.A., Brumley, W.C., Glassman, J., Farlay, J.W., 1998. Development of separation systems for polynuclear aromatic hydrocarbon environmental contaminants using micellar electrokinetic chromatography with molecular micelles and free zone electrophoresis. Electrophoresis 19, 2090–2094.
- Nieva-Cano, M.J., Rubio-Barroso, S., Santos-Delgado, M.J., 2001. Determination of PAH in food samples by HPLC with flourimetric detection following sonication extraction without sample clean-up. The Analyst 126, 1326– 1331.
- Perera, F.P., Hemminki, K., Young, T.L., 1988. Detection of polycyclic aromatic-DNA adduct in white blood cell of foundry workers. Cancer Res. 48, 2288–2291.
- Schoket, b., Doty, W.A., Vincze, I., 1993. Increased sensitivity for determination of polycyclic hydrocarbon-DNA adducts in human DNA samples by dissociation—enhanced lanthanide flouroimmunoassay (DELFIA). Cancer Epidemol. Biomarker Prevent. 2, 349–353.
- Speer, K., Steeg, E., Horsetmann, P., Kuhn, Th., Mantang, A., 1990. Determination and distribution of PAH in native vegetable oils, smoked fish products, mussels and oysters, and bream from the river Elbe. J. High Resolut. Chromatogr. 13, 104–111.
- US EPA, 1994. Soxhlet Extraction-Method 3541.
- US EPA, 1999. Method TO-13A, Compendium of Methods for Toxic Air Pollutants.
- Van Brummelen, T.C., Verweij, R.A., Wedzinga, S.A., Van Gestel, C.A.M., 1996. Enrichment of polycyclic aromatic hydrocarbons in forest soils near a blast furnace plant. Chemosphere 32, 293–314.
- Xu, B.X., Fang, Y.Z., 1988. Determination of polynuclear aromatic hydrocarbons in water by floatation enrichment and HPLC. Talanta 35 (11), 891–894.
- Yun, T., Tianling, Z., Xinhong, W., 2003. PAH contamination and PAH-degrading bacteria in Xiamen Western Sea. Chem. Speciat. Bioavail. 14, 25–34.
- Yang, H.H., Lee, W.J., Chen, S.J., Lai, S.O., 1998. PAH emission from various industrial stacks. J. Hazard. Mater. 60, 159–174.