The Grimmer Method – determination of parent and alkylated PAH profiles in crude oil and refined-petroleum products by GC/MS (SIM)

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Grimmer method

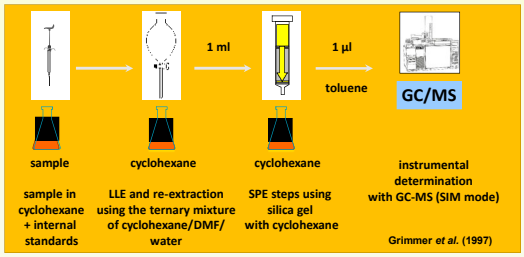
The Grimmer method (SOP PAH-0397) is based on a stable isotope dilution principle using GC-MS with selected ion monitoring (SIM mode) and allows the quantification of the PAH content in the sub-ppb range. The method has been validated for various matrices during the work of BIU for the Environmental Specimen Bank (ESB) of the German Federal Environment Agency (UBA) and is published (Grimmer *et al.* (1997)).

Method description

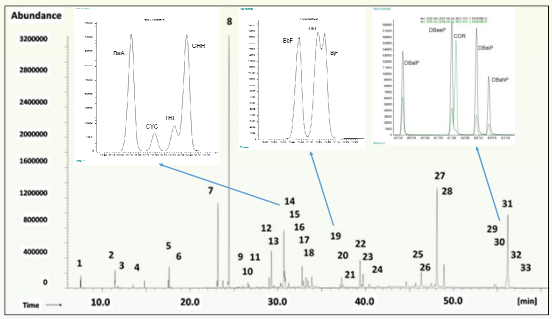
- GC-MS analysis is performed using an Agilent 6890N connected to an Agilent 5973N quadrupole mass spectrometer (SIM mode).
- Separation of the PAH profile is carried out on an Agilent DB-35MS capillary (Agilent Technologies, 30 m × 0.25 mm i.d. × 0.25 µm film thickness, virtually equivalent to a (35%-phenyl)methylpolysiloxane) using helium (purity 99.999%) as carrier gas (flow rate 1 mL/min).
- Calibration is performed for each individual PAH compound with linear curve fitting in a working range of 0.03 to 10 ng/µL.
- Limits of quantification (LOQ) and limits of detection (LOD) are determined using the signal-to-noise ratios (S/N; LOQ is determined by a S/N ratio of 10:1).
- Identification of PAH is conducted based on relative retention times and molecular ions compared to reference materials.
- Quantification is achieved via the PAH applied as internal standards (stable isotope dilution method). The system is operated by Agilent Enhanced ChemStation Software (G1701DA Version D.00.00.38).

Sample preparation

- Sample preparation depends on the matrix to be analysed and is adjusted accordingly.
- If the matrix is soluble in cyclohexane, an aliquot is dissolved in this solvent for further sample preparation.
- In order to remove almost all matrix components, the solution of the crude material (or extract) is subjected to LLE (liquid-liquid extraction) and subsequent SPE steps using silica gel.
- Before subjected to instrumental analysis the sample volume is reduced via evaporation under vacuum or diluted if needed.



GC-MS chromatogram of PAH



Peak	Compound	Peak	Compound	Peak	Compound
1	Naphthalene *	12	Benzo[*ghi*]fluoranthene	23	Benzo[*a*]pyrene
2	Acenaphthylene	13	Benzo[*c*]phenanthrene	24	Perylene
3	Acenaphthene	14	Benzo[*a*]anthracene	25	Indeno[1,2,3-*cd*]pyrene
4	Fluorene	15	Cyclopenta[*cd*]pyrene	26	Dibenzo[*a,h*]anthracene
5	Phenanthrene	16	Triphenylene	27	Benzo[*ghi*]perylene
6	Anthracene	17	Chrysene	28	Anthanthrene
7	Fluoranthene	18	5-Methylchrysene	29	Dibenzo[*a,l*]pyrene
8	Pyrene	19	Benzo[*b*]fluoranthene	30	Dibenzo[*a,e*]pyrene
9	Benzo[c]fluorene	20	Benzo[*k*]fluoranthene	31	Coronene
10	1-Methylpyrene ***	21	Benzo[*j*]fluoranthene	32	Dibenzo[*a,i*]pyrene
11	BNT **	22	Benzo[*e*]pyrene	33	Dibenzo[*a,h*]pyrene

* Standard Grimmer method covers in total 26 environmentally relevant PAH including the 16 US EPA PAH.

** Benzo[*b*]naphtho[*2,1-d*]thiophene is the lead compound for the group of heterocyclic PAH (N,O,S-PAH) (Schwartz *et al.* (2016)).

*** 1-Methylpyrene - measurement at workplace recommended by MAK (DFG) and included in the regulation of Standard 100 by OEKO-TEX®, Annex 5, limit value for 24 PAH.

PAH Analysis of distillate aromatic extract (DAE)

mg/kg	Grimmer *	MAK/DFG *	REACH *	mg/kg	Grimmer *	MAK/DFG *	REACH *
Naphthalin		0,823		Benzo[j]fluoranthen	4,472	4,472	4,472
Phenanthren	3,838	3,838		Benzo[k]fluoranthen	8,028	8,028	8,028
Anthracen	0,137			Benzo[e]pyren	103,273		103,273
Fluoranthen	1,121			Benzo[a]pyren	13,046	13,046	13,046
Pyren	10,382	10,382		Perylen	7,195		
1-Methylpyren		32,784		Indeno[1,2,3-cd]pyren	4,811	4,811	
Benzo[b]naphtho [2,1-d]thiophen	35,115	35,115		Dibenzo[a,h]anthracen	5,326	5,326	5,326
Benzo[ghi]fluoranthen	1,895			Benzo[ghi]perylen	51,428		
Benzo[c]phenanthren	1,479			Anthanthren	2,773	2,773	
Benzo[a]anthracen	25,018	25,018	25,018	Dibenzo[a,l]pyren		3,079	
Cyclopenta[cd]pyren	0,370	0,370		Dibenzo[a,e]pyren		9,797	
Triphenylen	108,352			Coronen	11,604		
Chrysen	91,541	91,541	91,541	Dibenzo[a,i]pyren		0,392	
Benzo[b]fluoranthen	34,917	34,917	34,917	Dibenzo[a,h]pyren		0,188	
				Sum	526,121	286,700	285,621

PAH Analysis of treated distillate aromatic extract (TDAE)

mg/kg	Grimmer *	MAK/DFG *	REACH *	mg/kg	Grimmer *	MAK/DFG *	REACH *
Naphthalin		0,485		Benzo[j]fluoranthen	0,017	0,017	0,017
Phenanthren	0,369	0,369		Benzo[k]fluoranthen	0,026	0,026	0,026
Anthracen	0,014			Benzo[e]pyren	0,694		0,694
Fluoranthen	0,022			Benzo[a]pyren	0,094	0,094	0,094
Pyren	0,165	0,165		Perylen	0,062		
1-Methylpyren		0,195		Indeno[1,2,3-cd]pyren	0,058	0,058	
Benzo[b]naphtho [2,1-d]thiophen	0,105	0,105		Dibenzo[a,h]anthracen	0,046	0,046	0,046
Benzo[ghi]fluoranthen	0,005			Benzo[ghi]perylen	0,629		
Benzo[c]phenanthren	0,005			Anthanthren	0,025	0,025	
Benzo[a]anthracen	0,050	0,050	0,050	Dibenzo[a,l]pyren		0,023	
Cyclopenta[cd]pyren	<0,001	<0,001		Dibenzo[a,e]pyren		0,079	
Triphenylen	0,306			Coronen	0,190		
Chrysen	0,255	0,255	0,255	Dibenzo[a,i]pyren		0,004	
Benzo[b]fluoranthen	0,141	0,141	0,141	Dibenzo[a,h]pyren		<0,001	
				Sum	3,278	2,137	1,323

*Grimmer list (22 PAH compounds), monitoring of environmental PAH in Germany (ESB). *PAH-list recommended by the MAK commission for monitoring at workplaces in Germany. * 8 EU priority PAH used for regulatory purposes.

Typical PAH profile of a medicinal white oil

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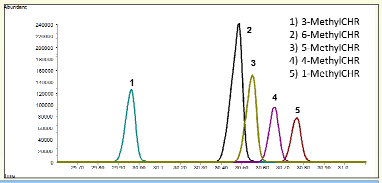
Limits:	
Benzo[a]pyrene (limit ≤ 1,0 µg/kg)	<0,042
Dibenzo[a,h]anthracene (limit ≤ 1,0 µg/kg)	<0,011
Dibenzo[a,e]pyrene (limit ≤ 1,0 µg/kg)	<0,019
Dibenzo[a,l]pyrene (limit ≤ 0,1 µg/kg)	<0,019
Dibenzo[a,i]pyrene (limit ≤ 0,1 µg/kg)	<0,019
Dibenzo[a,h]pyrene (limit ≤ 0,1 µg/kg)	<0,019
Sum I PAHs [1] (limit ≤ 5 µg/kg)	0,068
Sum II PAHs [2] (limit ≤ 20 µg/kg)	0,078
Sum III PAHs [3] (limit ≤ 100 µg/kg)	0,593

PAH	µg/kg
Phenanthrene[3]	0,292
Anthracene[3]	<0,005
Fluoranthene[3]	0,151
Pyrene[3]	0,123
Benzo[c]fluorene [2]	<0,027
Benzo[b]naphtho[2,1-d]thiophene [2]	<0,016
Benzo[ghi]fluoranthene[3]	<0,033
Benzo[c]phenanthrene[3]	<0,015
Benzo[a]anthracene [2]	0,039
Cyclopenta[cd]pyrene [2]	<0,032
Triphenylene[3]	<0,016
Chrysene [2]	0,039
5-Methylchrysene [2]	<0,016
Benzo[b]fluoranthene [1]	0,036
Benzo[k]fluoranthene [1]	0,015
Benzo[j]fluoranthene [1]	0,017
Benzo[e]pyrene[3]	0,027
Benzo[a]pyrene	<0,042
Perylene[3]	<0,024
Indeno[1,2,3-cd]pyrene [1]	<0,027
Dibenzo[a,h]anthracene	<0,011
Benzo[ghi]perylene [2]	<0,019
Anthanthrene [1]	<0,019
Dibenzo[a,l]pyrene	<0,019
Dibenzo[a,e]pyrene	<0,019
Dibenzo[a,i]pyrene	<0,019
Dibenzo[a,h]pyrene	<0,019
Coronene[3]	<0,019

Alkylated PAH

Separation of monomethyl chrysenes on GC capillary ZB 35 MS (Phenomenex, supplier)



Method strengths and conclusions

- ✓ The Grimmer method is based on a stable isotope dilution principle using GC-MS with SIM mode.
- ✓ The method is very well suited for the characterisation and determination of PAH and alkylated PAH in crude oil (Grimmer *et al.* (1983)), refined petroleum products and vacuum residues (bitumen) (Robertus *et al.* (2016)).
- ✓ Due to the high specificity and sensitivity, the method allows the determination of a wide range of PAH and alkylated PAH in several matrices from the sub-ppb range (e.g. medicinal white oils) to the high-ppm level (e.g. DAE, heavy fuel oils etc.).
- ✓ Availability of in-house synthesis lab facilities allows to prepare reference materials and internal standards of unknown PAH and alkylated as well as heterocyclic PAH (N,O,S-PAH).

References

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