

DISCRIMINATION OF CRITICAL POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) ISOMERS IN WATER SAMPLES BY SBSE-TD-GC-MS USING TWO JOINTED COMPLEMENTARY-PHASE CAPILLARY COLUMNS

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Polycyclic aromatic hydrocarbons (PAHs) represent a major environmental and health concern, for the carcinogenic and/or mutagenic properties of some of their members, and their concentrations in air, waters, food, beverages and soil are strictly regulated by local and/or national and international laws. Their determination and quantitation can be achieved by HPLC with fluorimetric detection or by GC-MS or GC-MS/MS techniques. Currently, not all PAH congeners can be separated at once with a single GC-chromatographic column. Chrysene and triphenylene (Mw 228) and benzo [b,j,k] fluoranthene (Mw 252) isomers require different columns for their separation.

Is it possible to separate all PAH congeners in a single GC-MS run and quantitate them accordingly in water samples at ppt level?

Experimental

Instrumentation

Agilent 5975C MSD spectrometer with Gerstel MPS2 XL equipped with TDU-CIS 4 injection system and twister option

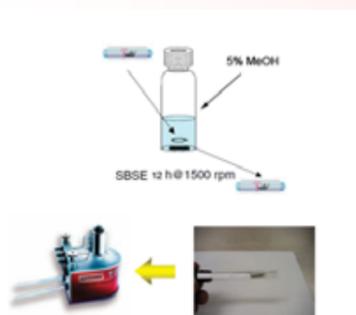


Chromatographic conditions

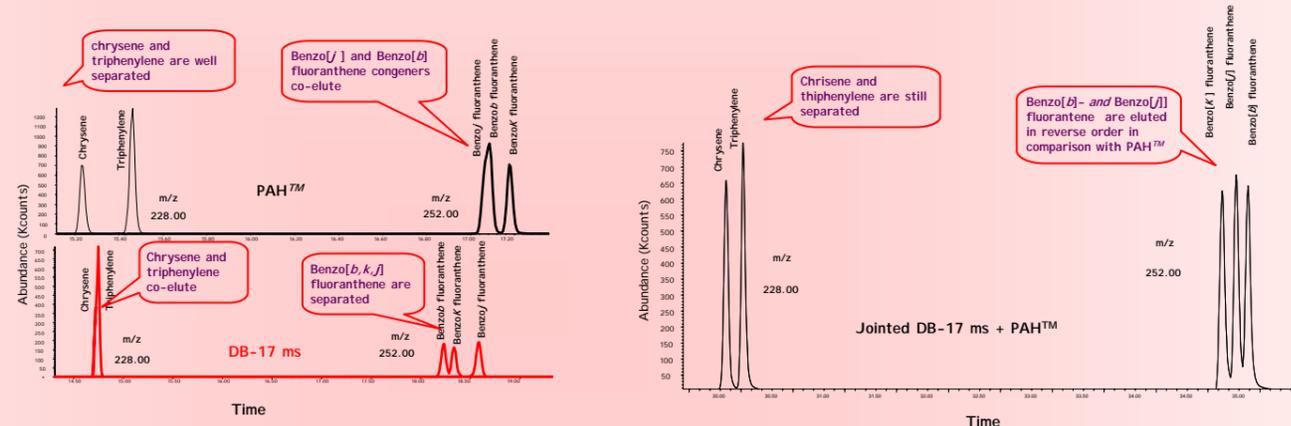
- Restek RTX PAHTM column (12 m, 0.25 mm i.d. x 0.25 µm d.f.) - liquid crystalline silica
- J&W DB 17 column (20 m, 0.25 mm i.d. x 0.25 µm d.f.) - (50% phenyl) methylpolysiloxane silicone
- Jointed Restek RTX PAHTM + J&W DB 17 column

SBSE extraction conditions & calibration

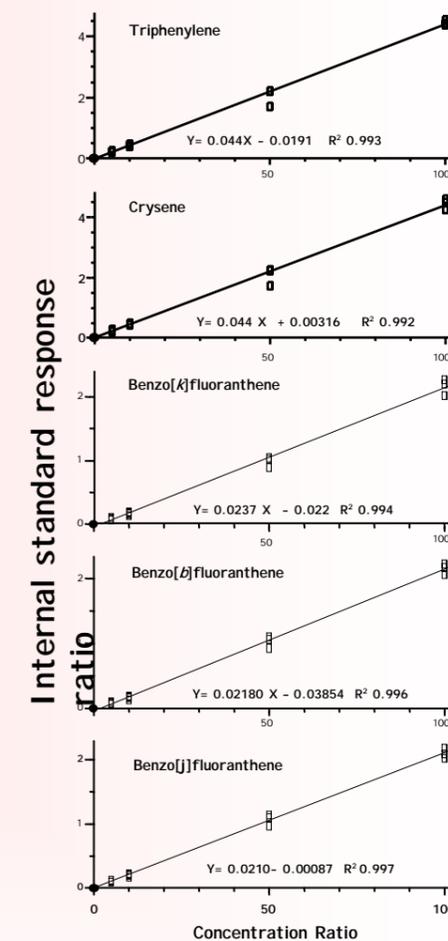
100-ml aliquot of drinking water spiked with internal standard (ISTD) mix (final concentration 100 ng L⁻¹) and STD mix (final concentration ranging from 10 to 2000 ng L⁻¹) supplemented with 5 ml of MeOH in 100 ml glass jars 10 mm, 0.5 mm PDMS Twister, T° = 20 °C, extraction time: 12 h



Results



Linear calibration curves in the range 5-100 ng L⁻¹



Chromatographic parameters of PAHs and labelled PAHs used as internal standard

compound	K'	a	m/z	LOQ	rt
naphthalene d8*	6,61445783		136	0,83	6,32
naphthalene	6,6686747	1,00819672	128	100	6,365
acenaphthene	11,6385542	1,74525745	153	10	10,49
biphenylene	12,626506	1,08488613	152	10	11,31
acenaphthene d10*	13,060241	1,03435115	164	10	11,67
fluorene	15,5783133	1,19280443	166	10	13,76
anthracene d10*	21,0927711	1,35398299	188	10	18,337
phenanthrene	21,2168675	1,00588336	178	10	18,44
anthracene	21,4036145	1,00880182	202	10	18,595
fluoranthene	28,1084337	1,3132564	202	10	24,16
pyrene	29,686747	1,05615088	202	10	25,47
benz[a]anthracene	36,7228916	1,23701299	228	10	31,31
triphenylene	37,0722892	1,00951444	228	10	31,6
chrysene d12*	37,1084337	1,00097498	240	10	31,63
chrysene	37,2650602	1,00422078	252	10	31,76
benzo[b]fluoranthene	42,8795181	1,15066279	252	10	36,42
benzo[k]fluoranthene	43,0361446	1,00365271	252	10	36,55
benzo[j]fluoranthene	43,1686747	1,00307951	252	10	36,66
benzo[a]pyrene	44,7349398	1,03628244	252	10	37,96
perylene	45,1807229	1,00996499	252	10	38,33
perylene d12*	45,6024096	1,00933333	264	10	38,68
benzo[ghi]perylene	53,686747	1,17727873	276	10	45,39
dibenz[a,h]anthracene	54,060241	1,00695691	278	10	45,7
indeno[1,2,3-cd]pyrene	56,8650602	1,05188322	276	10	48,028
dibenzo[a]pyrene	74,6024096	1,31192	302	50	62,75
dibenzo[a,e]pyrene	83,3578313	1,11736111	302	50	70,017
dibenzo[a,h]pyrene	90,7108434	1,08821021	302	50	76,12
dibenzo[a,i]pyrene	93,9036145	1,03519724	302	50	78,77

Conclusions

- ✓ Satisfactory chromatographic separation of all PAH isomers was achieved (including the critical congeners) by jointed Restek RTX PAH + J&W DB 17 columns.
- ✓ PAH quantitation in water samples was achieved at 10 - 50 ppt threshold level (depending on PAH compounds) using the 10 mm x 0.5 mm PDMS twister.
- ✓ Quantitation at lower concentrations requires a more selective detection, i.e. the coupling with a MS/MS detector.