Electronic Supplementary Material (ESI) for Analytical Methods.

A rapid gas chromatography quadrupole time-of-flight mass spectrometry method for the determination of polycyclic aromatic hydrocarbons and sulfur heterocycles in spilled crude oils

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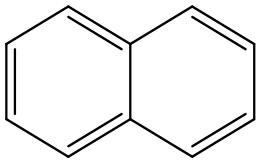
Supplementary Data:

GC-MS/MS run parameters:

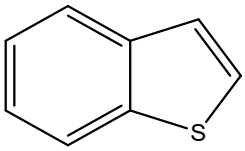
GC separation was performed on a Restek Rtx-5MS with an Integra-guard column (30 m x 0.25 mm id x 0.25 µm film thickness). The analysis was performed using an injection volume of 1 µL in pulsed splitless mode with both inlet temperature and GC-MS transfer line temperature of 280 °C. The helium carrier gas flow rate was set at 1 mL/min. The temperature programming began at 50 °C, held for 2 minutes, followed by an increase of 6 °C/min until a temperature of 310 °C was reached and held for 15 minutes. MS acquisition was carried out in electron impact ionization positive (EI+) mode with Pseudo Multiple Reaction Monitoring (pMRM).[1,4-6] The source and quadrupole temperature were at 280 °C and 150 °C, respectively, and helium quench gas was set at 4.0 mL/min. Agilent's MassHunter software was used for data acquisition and processing. The total run time was 60.333 minutes.

Comparison between structures of some PAHs with PASHs:

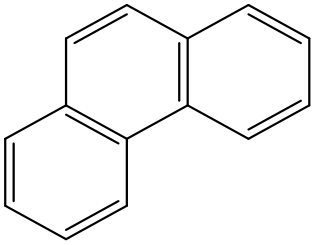
Naphthalene



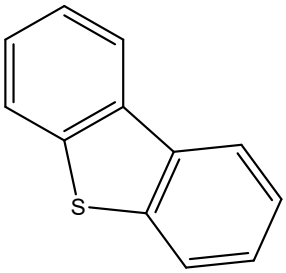
Benzothiophene



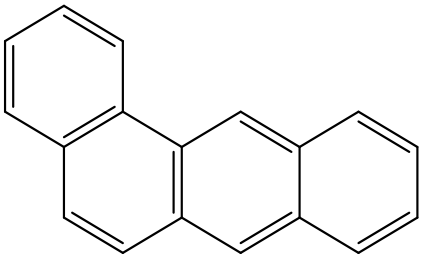
Phenanthrene



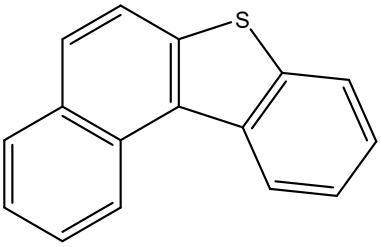
Dibenzothiophene



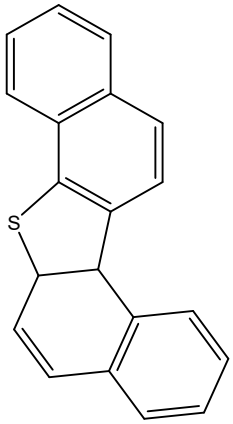
Benzo(a)anthracene



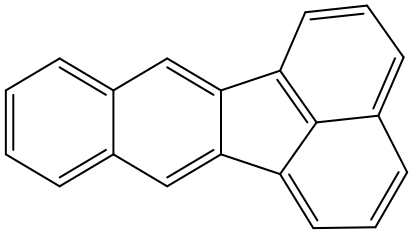
Benzonaphthothiophene



Dinaphthothiophene



Benzo(k)fluoranthene



Determination of LOD and LOQ:

Eight blanks of DCM containing no PASH/APASH stock were analyzed using the PAC method. These blanks were taken from multiple analytical sequences completed over various days (Table S8). The average values for each of the compounds was determined along with the standard deviation (STD). Equations 1 and 2 were then used to determine the LOD and LOQ for the PAC method. The largest value for the LOD and LOQ for the compounds was taken as the maximum allowed value which resulted in a LOD of 3.6 µg/L and a LOQ of 6.4 µg/L.

$$LOD = \bar{x} + (3.3 \times STD)$$

(Equation 1)

$$LOQ = \bar{x} + (10 \times STD)$$

(Equation 2)

Determination of %RSD:

Six samples of the same crude oil were analyzed using the PAC method over multiple analytical sequences (Table S9). The average value of the concentrations was determined along with the standard deviation for each of the compounds. These values were then used in Equation 3 to determine the %RSD for each of the compounds. This resulted in all of the compounds having a %RSD of <15%.

$$\%RSD = \left(\frac{\bar{x}}{STD}\right) \times 100\%$$

(Equation 3)

Tables:

Table S1: Specific details for crude oils used for reporting results

Crude Oil	Crude Oil Type	Location Collected	Year Collected	Source of Spill	Year of Spill
HFO 6303	Heavy Fuel Oil (Bunker C)	Imperial Oil Ltd., Nova Scotia, Canada	2012/11/22	n/a	n/a
BK C 1994	Heavy Fuel Oil	Cape Town, South Africa	2017/04/06	Ship sinking	1994/06/22
CLWB 1.1	Heavy Crude, bitumen and condensate	Canadian National Resources Ltd Primrose South Plant	2017/09/22	n/a	n/a
ANS 2015	Crude oil/ process water	Milne Point Tract 14 Production Line	2017/09/22	Production line rupture	2015/02/28
BOS 2007	Heavy Synthetic Crude Oil	Trans Mountain Pipeline between Burnaby Tank Farm and Westridge Marine Terminal	2007	Pipeline puncture	2007/07/24

Table S2: Comparison of the PAH and APAH concentrations (µg/mL) for crude oil samples determined by the GC-QToF and the GC-MS/MS

	HFO 6303		BKC 1994		CLWB 1.1		ANS 2015		BOS 2007	
PAH/APAH	GC-MS/MS	GC-QToF	GC-MS/MS	GC-QToF	GC-MS/MS	GC-QToF	GC-MS/MS	GC-QToF	GC-MS/MS	GC-QToF
Naphthalene	443.32	368.88	520.57	472.20	38.32	36.15	542.94	613.35	51.85	41.00
Acenaphthylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acenaphthene	72.62	93.67	61.65	83.62	0.00	9.80	11.13	43.99	5.72	7.95
Fluorene	96.10	117.57	135.51	122.63	14.39	18.50	51.02	76.73	12.48	11.35
Anthracene	46.93	42.41	17.22	25.09	0.00	6.00	0.00	7.27	0.00	3.04
Phenanthrene	446.86	392.25	328.54	283.23	59.57	50.64	158.12	175.49	58.04	54.50
Pyrene	201.12	207.60	145.10	181.65	0.00	9.77	5.78	11.38	190.49	189.63
Fluoranthene	23.73	29.79	23.44	28.89	0.00	2.65	0.00	2.37	15.44	14.54
Chrysene	326.11	238.46	414.16	363.70	23.08	14.57	39.26	29.58	92.87	77.21
Benzo(a)anthracene	150.20	111.10	111.81	129.80	0.00	3.20	0.00	1.95	32.08	32.18
Benzo(b)fluoranthene	51.84	37.53	64.57	51.89	0.00	3.89	4.58	4.15	35.92	27.26
Benzo(k)fluoranthene	12.16	4.30	11.16	5.74	0.00	0.80	0.00	0.00	8.95	6.25
Benzo(e)pyrene	75.06	73.55	120.03	108.97	0.00	4.52	8.03	6.89	82.49	79.29
Benzo(a)pyrene	79.32	65.64	90.70	78.15	0.00	2.14	0.00	1.58	41.07	45.70
Perylene	42.48	19.96	48.70	39.55	0.00	9.94	4.76	5.19	27.29	26.92
Indeno(1,2,3-cd)pyrene	0.00	3.62	0.00	5.24	0.00	1.17	0.00	0.00	18.92	14.91
Benzo(g,h,i)perylene	34.61	22.27	45.00	35.41	0.00	2.84	0.00	2.45	103.00	101.38
Dibenzo(a,h)anthracene	10.87	13.66	23.36	20.93	0.00	0.57	0.00	0.81	18.62	17.05
c1-Naphthalene	2414.69	2652.01	2969.28	2709.07	129.77	142.49	1838.14	2246.99	265.70	202.05
c2-Naphthalene	4069.24	3877.62	4376.34	3753.20	352.45	333.36	2562.48	2710.33	442.40	391.54
c1-Acenaphthene	797.10	2213.72	637.13	2078.89	168.57	490.54	465.21	1340.85	159.23	465.99
c1-Biphenyl	254.01	738.69	333.34	649.42	16.34	94.69	254.14	417.45	30.05	76.32
c3-Naphthalene	6504.34	4134.49	6825.03	3835.84	1049.04	631.11	4071.64	2702.22	801.94	542.84
c1-Fluorene	819.37	712.73	650.76	677.21	177.54	154.25	396.90	442.46	122.32	111.72
c2-Biphenyl	311.60	430.77	196.16	273.56	24.17	45.88	38.47	78.60	20.02	45.77
c4-Naphthalene	1081.20	638.03	1572.13	439.84	500.01	179.69	713.49	384.88	197.88	120.36
c1-Phenanthrene/Anthracene	2109.33	1883.78	1503.44	1551.46	276.95	263.80	627.07	749.98	334.70	357.83
c2-Fluorene	1690.52	1339.57	1228.02	1105.34	432.25	366.03	757.91	770.11	302.32	329.24
c1-Dibenzothiophene	817.33	597.19	615.97	476.39	297.83	223.63	437.15	390.75	241.99	178.14
c5-Naphthalene	1100.45	1213.30	793.52	1064.35	416.25	405.01	535.78	834.39	278.38	495.37
c2-Phenanthrene/Anthracene	4227.19	3200.50	3417.29	2924.25	591.14	469.79	1085.54	982.01	590.17	653.52
c3-Fluorene	266.94	241.20	171.74	174.78	69.34	66.93	103.09	110.03	50.89	57.27
c2-Dibenzothiophene	1574.62	882.97	1138.06	773.13	649.54	335.98	790.29	534.30	542.98	384.30
c1-Fluoranthene	3720.57	4551.59	3337.78	5238.79	205.43	335.14	178.73	382.29	1627.11	2447.71
c3-Phenanthrene/Anthracene	4655.71	3267.63	3838.84	3155.60	716.99	461.38	902.78	740.45	774.37	613.93
c4-Fluorene	500.85	351.63	250.21	314.18	138.56	110.90	204.70	119.09	126.32	121.47
c3-Dibenzothiophene	2047.65	1667.17	1671.09	1618.17	936.33	804.70	879.90	826.13	660.19	757.64
c2-Fluoranthene/Pyrene	5964.40	3011.94	6938.90	3802.12	353.31	274.30	330.20	312.96	1814.42	1030.96
c4-Phenanthrene/Anthracene	3006.99	2077.25	2520.88	2201.91	367.03	360.40	385.64	373.03	515.93	803.83
c4-Dibenzothiophene	919.87	435.70	743.81	441.67	462.06	182.26	305.89	148.50	313.74	163.59
c1-Benzo[a]anthracene/chrysene	1998.39	3767.19	2078.62	5430.32	132.63	170.32	153.58	221.47	961.21	1337.36
c3-Fluoranthene/Pyrene	1595.84	2167.07	1743.12	2771.98	130.61	280.52	112.69	289.67	334.96	818.10
c5-Phenanthrene/Anthracene	1920.77	449.02	3122.19	725.16	483.49	76.92	512.60	77.46	542.20	106.06
c2-Benzo[a]anthracene/chrysene	1195.10	4905.66	1367.15	6469.18	512.97	300.00	515.25	373.30	2930.83	2068.80
c4-Fluoranthene/Pyrene	968.78	697.68	1061.68	876.99	145.07	64.02	137.67	82.09	314.69	182.22
c1-Benzopyrene/Perylene	605.71	564.44	691.79	725.62	21.55	58.76	26.41	51.08	290.56	418.08
c3-Benzo[a]anthracene/chrysene	854.92	4270.46	909.14	5089.61	470.95	609.43	337.78	559.98	2664.57	2078.26
c5-Fluoranthene/Pyrene	432.44	285.44	408.83	339.98	98.81	43.14	78.98	45.88	378.04	119.94
c2-Benzopyrene/Perylene	814.08	492.09	804.04	732.17	36.29	49.61	29.95	49.20	282.63	273.74
c4-Benzo[a]anthracene/chrysene	1947.35	1565.10	1805.09	1836.70	254.89	149.60	221.77	155.43	784.19	776.25
c3-Benzopyrene/Perylene	737.77	821.75	631.16	975.88	38.77	119.65	40.99	126.35	218.11	519.20
c5-Benoz[a]anthrancene	429.15	82.23	478.73	119.58	66.55	16.66	70.22	16.53	393.78	48.84
c4-Benzopyrene/Perylene	81.89	113.58	65.37	259.86	0.00	41.59	5.25	33.09	28.23	157.28
c5-Benzopyrene/Perylene	74.07	100.15	44.11	112.63	0.00	40.23	8.49	35.57	46.13	116.05

Table S3: Concentrations (µg/mL) for the PASHs and APASHs for crude oil samples determined by the newly developed GC-QToF PAC method

PASH/APASH	HFO 6303	BK C 1994	CLWB 1.1	ANS 2015	BOS 2007
Benzothiophene	9.44	12.58	2.95	<LOQ	1.31
Dibenzothiophene	68.48	60.10	18.79	81.84	18.91
Benzonaphthothiophene	128.16	167.79	23.43	26.23	29.38
Dinaphthothiophene	28.65	29.18	6.82	6.94	14.18
c1-Benzothiophene	54.38	43.54	9.99	3.18	6.35
c2-Benzothiophene	114.34	75.69	27.72	24.63	22.18
c3-Benzothiophene	128.29	81.82	55.13	73.30	55.43
c4-Benzothiophene	65.23	44.14	55.87	51.57	50.80
c1-Dibenzothiophene	229.88	183.53	71.96	164.05	82.92
c2-Dibenzothiophene	492.19	383.60	197.60	245.58	186.57
c3-Dibenzothiophene	496.20	478.63	222.35	198.86	182.41
c4-Dibenzothiophene	385.62	354.65	184.62	117.11	130.99
c1-Benzonaphthothiophene	347.17	437.77	56.60	53.82	81.73
c2-Benzonaphthothiophene	526.48	677.87	106.05	91.53	143.25
c3-Benzonaphthothiophene	489.16	564.11	110.06	82.73	116.87
c4-Benzonaphthothiophene	193.79	230.52	48.34	37.54	64.15
c1-Dinaphthothiophene	70.12	83.86	14.44	12.73	38.38
c2-Dinaphthothiophene	102.40	117.50	24.46	19.71	59.46
c3-Dinaphthothiophene	63.72	65.59	18.67	15.39	35.38
c4-Dinaphthothiophene	61.53	64.17	28.38	22.45	59.50

Table S4: Concentrations (µg/mL) for PASHs and APASHs for crude oil samples determined using the authentic PASH and APASH standards

PASH/APASH	HFO 6303	BK C 1994	CLWB 1.1	ANS 2015	BOS 2007
Benzothiophene	14.30	20.47	4.56	1.04	2.25
2-Phenylthiophene	4.08	2.98	1.10	0.77	0.94
Dibenzothiophene	126.85	115.74	37.66	134.53	34.99
Benzonaphthothiophene	31.54	42.49	6.98	10.09	6.62
1,2,3,4-tetrahydrobenzo(b)naphthol(1,2-d)thiophene	8.67	7.09	4.83	6.10	24.83
2-naphthalen-2-yl-benzo(b)thiophene	3.60	6.63	1.60	2.73	1.56
Dinaphthothiophene	1.25	2.60	0.63	0.66	1.74
c1-Benzothiophene	87.14	73.38	17.54	6.09	12.77
c2-Benzothiophene	340.73	174.66	76.89	69.89	71.52
c1-Dibenzothiophene	481.30	425.32	157.78	317.65	164.19
c2-Dibenzothiophene	865.31	709.92	336.69	407.75	321.61
c4-Dibenzothiophene	944.39	922.48	452.62	351.16	406.62

Table S5: PASH and APASH concentration (µg/mL) comparisons between the GC-MS/MS and the GC-QToF for crude oil samples. Data generated from the run using authentic PASH and APASH standards.

PASH/APASH	HFO 6303		BK C 1994		CLWB 1.1		ANS 2015		BOS 2007	
	GC-MS/MS	GC-QToF	GC-MS/MS	GC-QToF	GC-MS/MS	GC-QToF	GC-MS/MS	GC-QToF	GC-MS/MS	GC-QToF
Benzothiophene	18.52	14.30	26.05	20.47	6.28	4.56	7.60	1.04	4.18	2.25
2-Phenylthiophene	7.37	4.08	7.97	2.98	3.19	1.10	3.82	0.77	2.21	0.94
Dibenzothiophene	144.27	126.85	132.47	115.74	42.36	37.66	151.02	134.53	37.53	34.99
Benzonaphthothiophene	23.76	31.54	32.50	42.49	5.21	6.98	5.79	10.09	5.70	6.62
1,2,3,4-tetrahydrobenzo(b)naphthol(1,2-d)thiophene	27.41	8.67	24.59	7.09	3.60	4.83	5.48	6.10	37.97	24.83
2-naphthalen-2-yl-benzo(b)thiophene	32.49	3.60	23.71	6.63	2.43	1.60	3.36	2.73	21.00	1.56
Dinaphthothiophene	48.36	1.25	52.93	2.60	2.28	0.63	2.41	0.66	15.51	1.74
c1-Benzothiophene	121.70	87.14	115.29	73.38	26.95	17.54	15.08	6.09	18.76	12.77
c2-Benzothiophene	603.88	340.73	383.63	174.66	131.14	76.89	120.16	69.89	110.26	71.52
c1-Dibenzothiophene	763.16	481.30	582.27	425.32	237.27	157.78	414.24	317.65	226.91	164.19
c2-Dibenzothiophene	1675.24	865.31	1189.66	709.92	594.15	336.69	783.42	407.75	548.72	321.61
c4-Dibenzothiophene	1654.97	944.39	1440.05	922.48	833.25	452.62	476.87	351.16	727.77	406.62

Table S6: PASH and APASH concentration (µg/mL) comparisons between the GC-MS/MS and the GC-QToF for crude oil samples using the PAC method

PASH/APASH	HFO 6303		BK C 1994		CLWB 1.1		ANS 2015		BOS 2007	
	GC-MS/MS	GC-QToF	GC-MS/MS	GC-QToF	GC-MS/MS	GC-QToF	GC-MS/MS	GC-QToF	GC-MS/MS	GC-QToF
Benzothiophene	34.19	9.44	36.27	12.58	0.00	2.95	67.75	<LOQ	27.36	1.31
Dibenzothiophene	331.34	68.48	279.42	60.10	85.22	18.79	261.44	81.84	72.19	18.91
Benzonaphthothiophene	3476.54	128.16	3145.08	167.79	809.06	23.43	818.01	26.23	1159.55	29.38
Dinaphthothiophene	1128.82	28.65	851.04	29.18	120.25	6.82	83.61	6.94	344.95	14.18
c1-Benzothiophene	313.46	54.38	342.19	43.54	113.06	9.99	369.86	3.18	157.70	6.35
c2-Benzothiophene	220.24	114.34	152.71	75.69	55.88	27.72	37.20	24.63	30.79	22.18
c3-Benzothiophene	392.22	128.29	284.43	81.82	182.40	55.13	122.82	73.30	109.35	55.43
c4-Benzothiophene	101.95	65.23	72.90	44.14	99.93	55.87	58.43	51.57	53.47	50.80
c1-Dibenzothiophene	1125.93	229.88	838.69	183.53	401.42	71.96	518.21	164.05	288.01	82.92
c2-Dibenzothiophene	1926.45	492.19	1930.17	383.60	1102.38	197.60	1305.20	245.58	764.96	186.57
c3-Dibenzothiophene	2171.22	496.20	1919.33	478.63	1309.10	222.35	1143.53	198.86	1095.04	182.41
c4-Dibenzothiophene	1246.73	385.62	988.51	354.65	619.02	184.62	318.89	117.11	355.79	130.99
c1-Benzonaphthothiophene	1658.76	347.17	2170.29	437.77	846.17	56.60	790.35	53.82	1402.92	81.73
c2-Benzonaphthothiophene	2204.81	526.48	2969.72	677.87	542.84	106.05	470.68	91.53	736.64	143.25
c3-Benzonaphthothiophene	1542.26	489.16	1919.33	564.11	445.54	110.06	340.42	82.73	528.52	116.87
c4-Benzonaphthothiophene	949.11	193.79	898.88	230.52	203.67	48.34	165.10	37.54	296.41	64.15
c1-Dinaphthothiophene	658.30	70.12	583.52	83.86	144.93	14.44	84.76	12.73	450.55	38.38
c2-Dinaphthothiophene	145.67	102.40	143.27	117.50	30.38	24.46	22.80	19.71	83.52	59.46
c3-Dinaphthothiophene	120.43	63.72	101.89	65.59	39.49	18.67	25.85	15.39	73.37	35.38
c4-Dinaphthothiophene	40.25	61.53	34.35	64.17	0.00	28.38	22.62	22.45	68.74	59.50

Table S7: Concentration (µg/mL) comparisons between the response factors applied to the PAC method (RCF) and the authentic PASH and APASH standards (APS) for crude oil samples

PASH/APASH	HFO 6303		BK C 1994		CLWB 1.1		ANS 2015		BOS 2007	
	RCF	APS	RCF	APS	RCF	APS	RCF	APS	RCF	APS
Benzothiophene	13.80	14.30	20.15	20.47	4.04	4.56	0.59	1.04	1.77	2.25
Dibenzothiophene	144.27	126.85	130.02	115.74	37.62	37.66	154.24	134.53	34.76	34.99
Benzonaphthothiophene	30.98	31.54	42.69	42.49	8.19	6.98	7.71	10.09	6.06	6.62
Dinaphthothiophene	2.40	1.25	2.87	2.60	2.01	0.63	1.00	0.66	2.76	1.74
c1-Benzothiophene	99.12	87.14	80.56	73.38	16.42	17.54	5.37	6.09	11.74	12.77
c2-Benzothiophene	406.90	340.73	266.02	174.66	80.93	76.89	72.40	69.89	74.37	71.52
c1-Dibenzothiophene	644.51	481.30	512.89	425.32	189.54	157.78	369.11	317.65	198.50	164.19
c2-Dibenzothiophene	1066.67	865.31	846.12	709.92	397.84	336.69	497.48	407.75	377.23	321.61
c4-Dibenzothiophene	1199.85	944.39	1166.38	922.48	614.90	452.62	421.13	351.16	541.55	406.62

Table S8: Concentration (µg/L) of the eight blanks analyzed over multiple analytical sequences used to determine the LOD and LOQ.

PASH/APASH	Blank 1	Blank 2	Blank 3	Blank 4	Blank 5	Blank 6	Blank 7	Blank 8
Benzothiophene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dibenzothiophene	0.86	0.44	0.62	0.20	0.42	0.00	0.51	0.02
Benzonaphthothiophene	0.88	0.79	0.56	0.66	0.61	0.51	0.60	0.52
Dinaphthothiophene	1.61	1.57	1.14	1.15	1.18	1.00	1.17	1.03
c1-Benzothiophene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
c2-Benzothiophene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
c3-Benzothiophene	0.60	0.59	0.61	0.65	0.35	0.30	0.71	0.43
c4-Benzothiophene	0.89	0.72	0.91	0.88	0.45	0.28	0.96	0.60
c1-Dibenzothiophene	0.59	0.50	0.22	0.59	0.01	0.02	0.12	0.10
c2-Dibenzothiophene	0.85	0.68	0.41	1.30	0.12	0.11	0.32	0.32
c3-Dibenzothiophene	0.93	0.78	0.63	1.51	0.26	0.20	0.59	0.54
c4-Dibenzothiophene	0.79	0.70	0.54	1.29	0.26	0.17	0.54	0.39
c1-Benzonaphthothiophene	0.98	0.87	0.53	1.11	0.51	0.52	0.56	0.60
c2-Benzonaphthothiophene	1.21	0.97	0.67	1.75	0.63	0.63	0.78	0.77
c3-Benzonaphthothiophene	1.32	1.20	1.12	2.19	0.87	0.89	1.08	1.13
c4-Benzonaphthothiophene	1.12	1.02	1.00	1.39	0.84	0.77	0.88	0.93
c1-Dinaphthothiophene	1.32	1.22	0.38	0.31	0.47	0.28	0.65	0.52
c2-Dinaphthothiophene	1.64	1.43	0.67	0.67	0.73	0.50	0.88	0.68
c3-Dinaphthothiophene	1.49	1.31	0.79	0.54	0.57	0.42	0.75	0.60
c4-Dinaphthothiophene	2.81	2.43	2.49	1.97	1.87	1.51	2.34	2.02

Table S9: Sample concentrations (µg/mL) of the six BK C 1994 analyzed over multiple analytical sequences used to determine the %RSD.

PASH/APASH	BK C 1994 (1)	BK C 1994 (2)	BK C 1994 (3)	BK C 1994 (4)	BK C 1994 (5)	BK C 1994 (6)
Benzothiophene	13.13	13.21	13.37	13.60	13.78	13.83
Dibenzothiophene	62.48	63.20	66.94	68.90	74.48	76.45
Benzonaphthothiophene	197.74	193.55	204.31	195.71	207.72	207.50
Dinaphthothiophene	34.40	38.98	34.52	33.22	37.13	38.16
c1-Benzothiophene	51.06	48.91	47.66	46.67	44.71	44.45
c2-Benzothiophene	89.20	86.27	81.95	80.26	73.61	73.28
c3-Benzothiophene	104.15	104.46	94.32	91.18	83.56	83.01
c4-Benzothiophene	57.15	57.50	52.01	49.62	41.04	41.76
c1-Dibenzothiophene	191.08	192.36	208.69	207.91	228.12	228.46
c2-Dibenzothiophene	368.00	369.78	385.90	390.52	438.69	440.66
c3-Dibenzothiophene	484.96	489.24	508.14	513.70	561.69	566.69
c4-Dibenzothiophene	368.18	368.93	375.68	377.83	393.38	397.11
c1-Benzonaphthothiophene	525.54	517.49	533.25	514.71	517.48	521.95
c2-Benzonaphthothiophene	741.40	739.56	732.11	707.61	718.36	717.16
c3-Benzonaphthothiophene	595.96	591.30	581.22	556.28	572.73	575.47
c4-Benzonaphthothiophene	266.32	263.40	262.85	257.23	269.09	274.05
c1-Dinaphthothiophene	95.35	98.44	95.24	93.90	108.54	112.25
c2-Dinaphthothiophene	129.22	133.62	122.63	128.26	150.26	151.80
c3-Dinaphthothiophene	77.61	81.83	82.37	83.02	92.95	98.23
c4-Dinaphthothiophene	59.76	77.26	61.28	62.32	69.22	66.43

Figures:

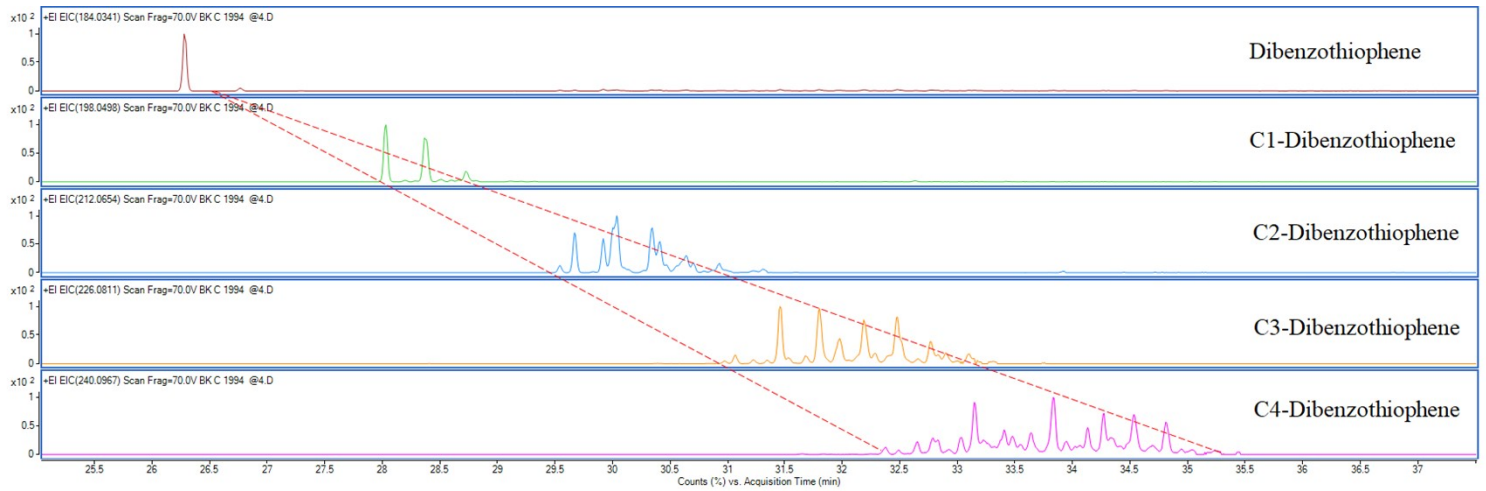


Fig. S1: Chromatograms for Dibenzothiophene and C1-C4 Dibenzothiophene for BK C 1994 extracted at 10 µg/mL.

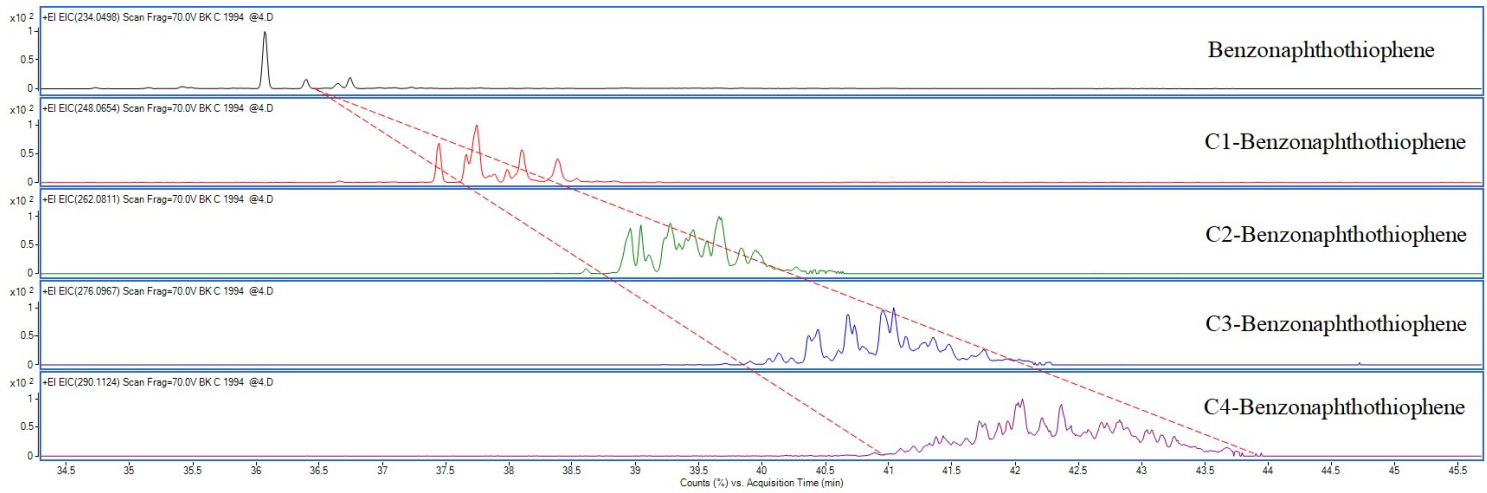


Fig. S2: Chromatograms for Benzonaphthothiophene and C1-C4 Benzonaphthothiophene for BK C 1994 extracted at 10 µg/mL.

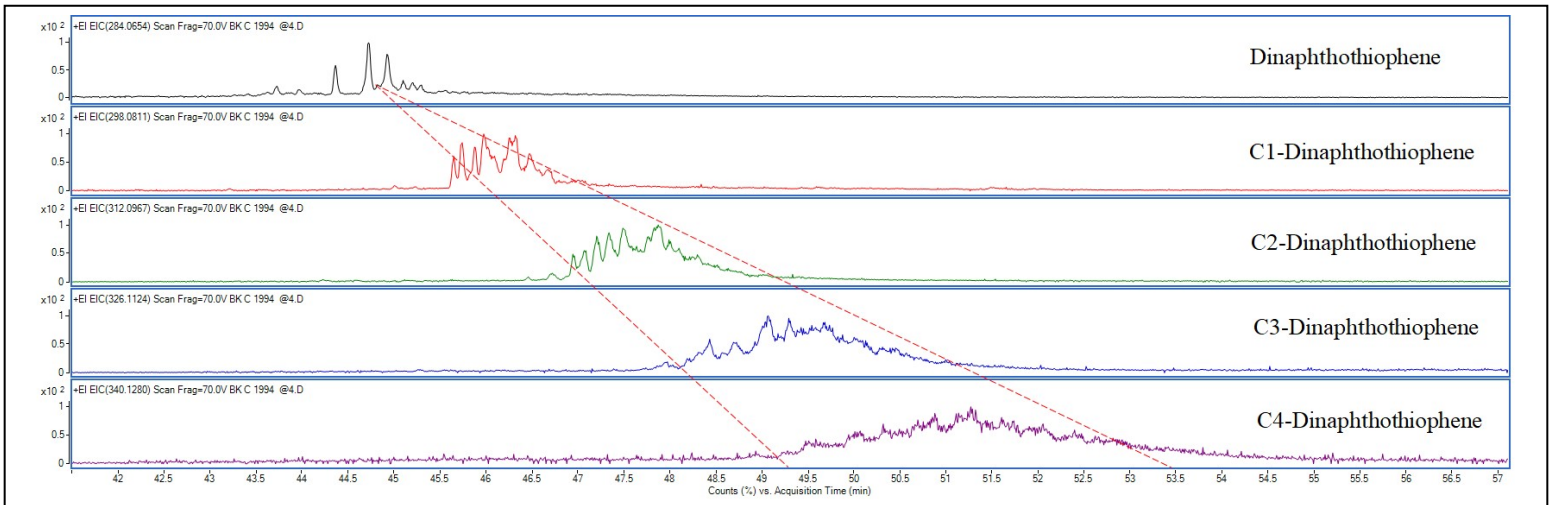


Fig. S3: Chromatograms for Dinaphthothiophene and C1-C4 Dinaphthothiophene for BK C 1994 extracted at 20 µg/mL.

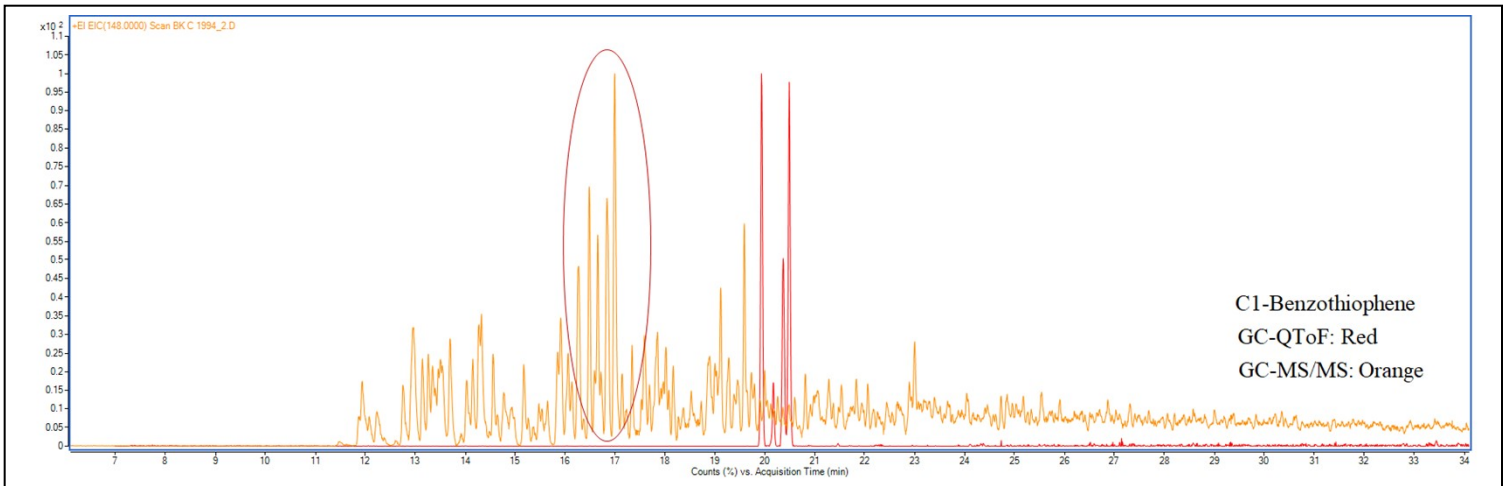


Fig. S4: Overlapping chromatograms for C1-Benzothiophene for the GC-QToF and GC-MS/MS extracted at 0.5000 m/z. Note, there is a retention time shift due to two different instruments with similar GC columns but different trimming being used and the matching peaks are circled for reference.

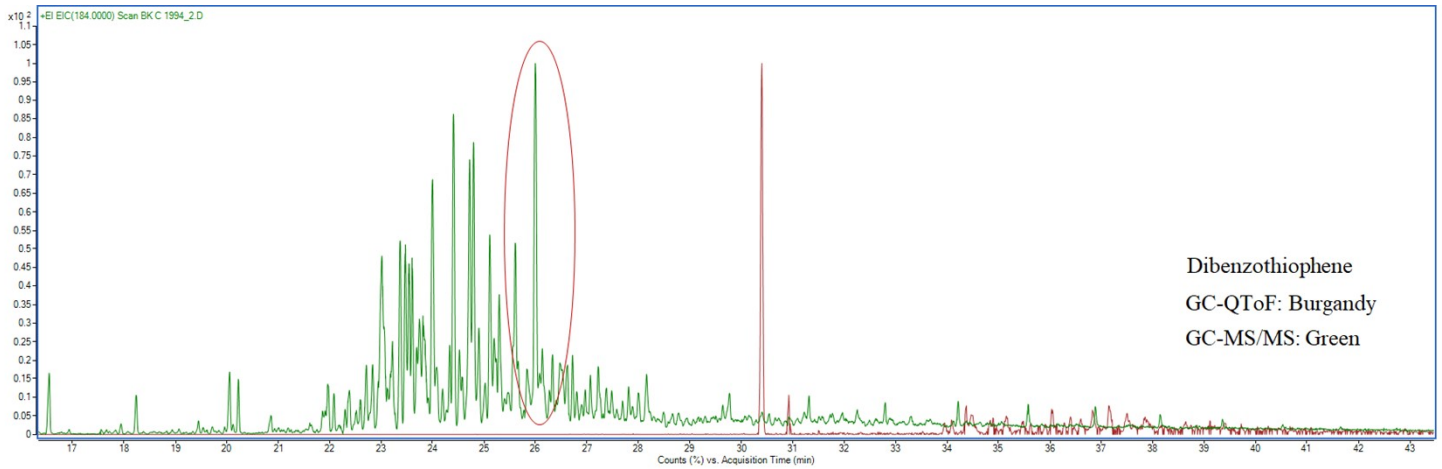


Fig. S5: Overlapping chromatograms for Dibenzothiophene for the GC-QToF and GC-MS/MS extracted at 0.5000 m/z. Note, there is a retention time shift due to two different instruments with similar GC columns but different trimming being used and the matching peaks are circled for reference.

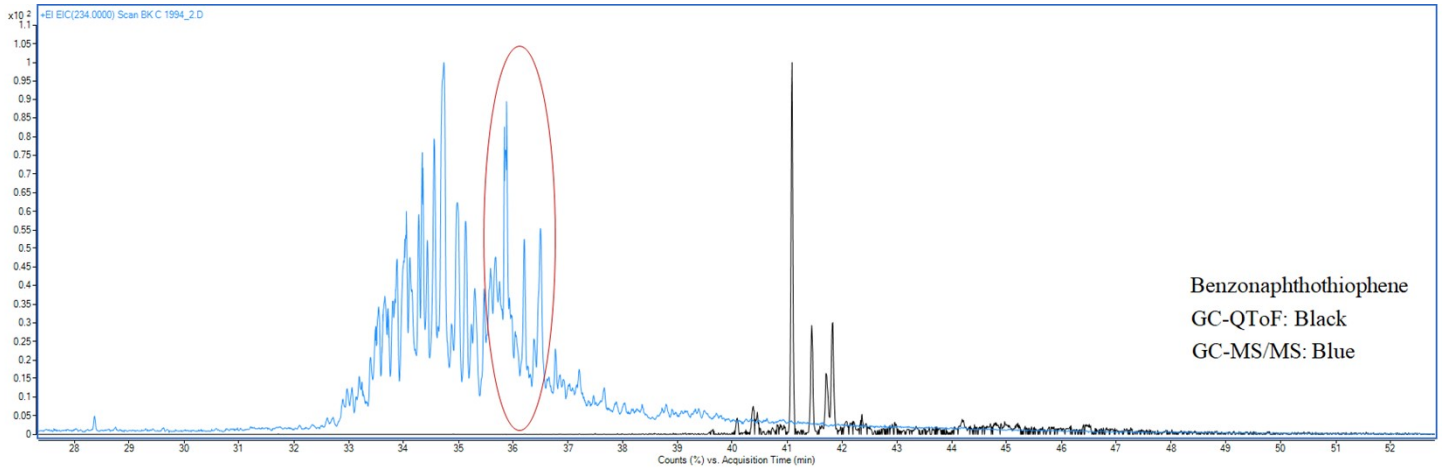


Fig. S6: Overlapping chromatograms for Benzonaphthothiophene for the GC-QToF and GC-MS/MS extracted at 0.5000 m/z. Note, there is a retention time shift due to two different instruments with similar GC columns but different trimming being used and the matching peaks are circled for reference.

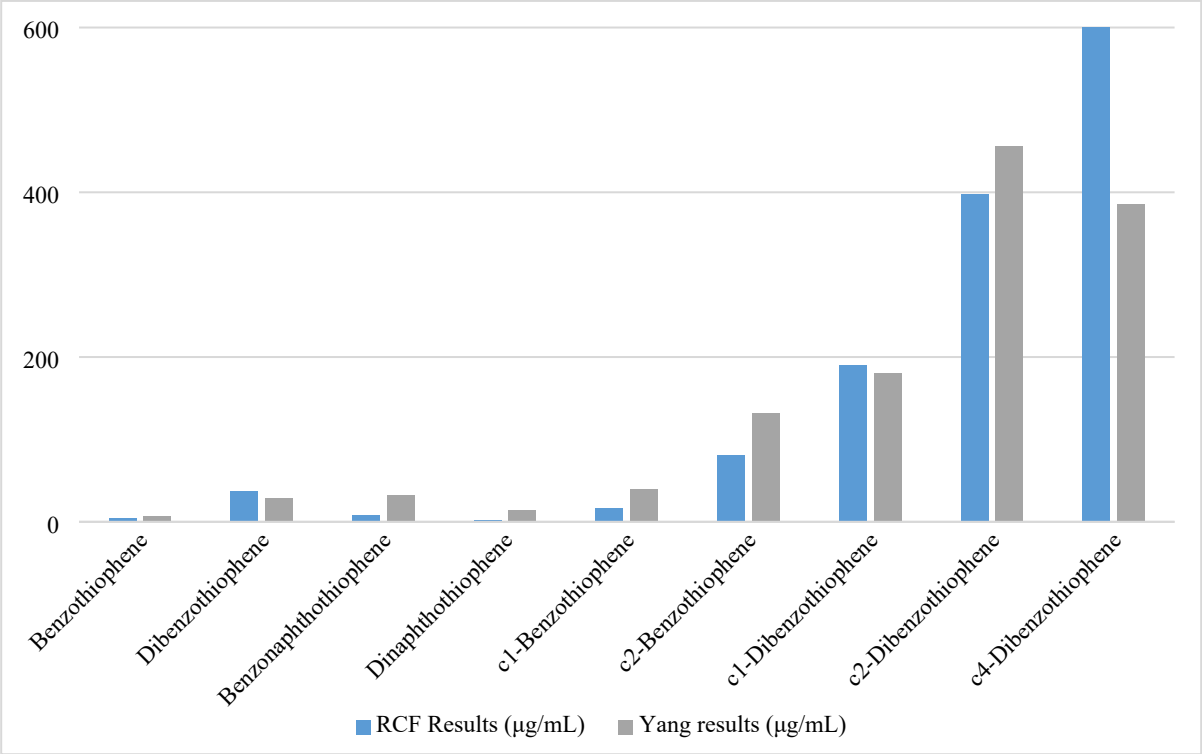


Fig. S7: Comparison of cold lake dilbit PASH and APASH concentration results from Yang et *al*.[7] and the developed PAC method.