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THE USE OF GC-MSMS AS A TOOL TO ANALYSE DIFFERENT SOOT FOR POSSIBLE POPS EMITTED FROM ENGINES AND STOVES

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Introduction

The mean of this study is to give us an estimation of POPS in soot particles from different sources. The methods used were based on In-house methods, EPA 16131 and SFS-EN 1948:Part 1-32. The soot was collected from a small stoves chimney burning wood. The diesel particulate used was the old NIST SRM 1650 and the urban dust sample used was NIST SRM 1649 (original old material from 1982). The measured POPS where PAH, PCB, PCDD/F and for some samples some PBDEE congeners.

Materials and methods

Both soot and diesel particulate samples were extracted using toluene and ASE extraction³. The urban dust sample was extracted using hexane:acetone (75:25 V/V). All corresponding C13-labelled internal standards were added before the extraction, (P48-S6, P48-S7, P48-M-ES, P48-W-ES, deuterated PAH (Naphthalene, Anthracene, Chrysene and Dibenzo[ah]anthracene) and C13PBDEE). The extracts were concentrated to about 4 ml. Then 1 ml was taken for PAH analysis. To the rest of the extracts 50µl of tetradecane was added and then concentrated to dryness. They were redissolved in a small amount of n-hexane and then cleaned by CAPE Technology⁴ columns. The silica and active carbon column set was cleaned by 20 ml of n-hexane before the sample was added on the top. Fraction 1 was eluted with 30 ml of n-hexane, fraction 2 was eluted with 6 ml of n-hexane:toluene 50:50 V/V and the third fraction containing the PCDD/F compounds was eluted in reverse mode using 20 ml of toluene.

PAH The PAH compounds were analyzed from a portion of the same extract and then analyzed on a AGILENT 7000QQQ running in SRM mode. The column used was a 15m HP-5 (0,25mm, 0,25µm) and 60 m DB-5ms capillary column (60m, 0.25mm, 0.25µm): Injector temperature 280 °C, split-less-injection 1.0 minute, transfer line temperature 290 °C, detector temperature 250 °C. Carrier gas He 4.6 and pressure 32.4 psi (at 80 °C). The oven temperature program used was:80 °C (1 min)-10 °C/min-200 °C (0 min)-10 °C/min-235 °C (0 min)- 10 °C/min-3250 °C (26 min).

PCDD/F⁵ The volume was reduced to 20 µl and then analyzed on an AGILENT 7000QQQ running in SRM mode. The column used was a 15m + 60 m DB-5ms capillary column (60m, 0.25mm, 0.25µm): Injector temperature 300 °C, split-less-injection 1.0 minute, transfer line temperature 290 °C, detector temperature 250 °C. Carrier gas He 4.6 and pressure 34.6 psi (at 180 °C). The oven temperature program used was:180 °C (1 min)-10 °C/min-200 °C (16min)-5 °C/min-235 °C (7 min)- 5 °C/min-325 °C (9 min). PCB: The PCB:s were analyzed from fraction 1 and 2. The final volume 50µl dodecane, on the AGILENT 7000QQQ running in SRM mode.. Same columns and temperatures were used as for the PCDD/F analyzes³.

PBDEE: The PPDEE:s were analyzed from fraction 1 and 2. The final volume 50µl dodecane, on the AGILENT 7000QQQ running in SRM mode.. Same columns and temperatures were used as for the PCB analyzes but the quadrupole rods were at 180 °C.

Results and discussion

From the data we can see that the method is robust and produce reproducible results. This is demonstrated using SRM 1650 and the PAH compounds that are certified, Table 1. The content in these different matrixes are shown by analyzing one unknown soot sample and two known NIST reference materials (SRM1650 and SRM1649).

The PAH, PCDD/F, PCB and PBDEE compounds analysed are shown in the tables 1-5.

We can draw the conclusion that NST1649 and soot have similar composition^{6,7}, see also table 5. The chimney soot is more toxic and this should be acknowledged when deciding where to put the soot from chimney cleaning. It has the highest TEQ values of all matrixes tested, including CIND4 materials. This was something that we had not anticipated. We will have more samples tested in the final poster.

Acknowledgements

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References:

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3. ASE 300 Dionex Application Note 352
4. TN-005 Carbon Column Fractionation and Analysis of Samples for PCB-TEQ 3/8/06, Cape Technologies, B. Harrison
5. E. Sandell, Polykloorattujen dibentsodioksiinien ja -furaanien määrittäminen maa-, sedimentti-, lentotuhka-, vesi-, pyyhkäisy- ja päästönäytteistä kaasukromatografia-massaspektrometrisesti. R-K-142, In-house Method.
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7. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition, Mark B. Yunkera,* , Robie W. Macdonald, Roxanne Vingarzac, Reginald, H. Mitchell, Darcy Goyette, Stephanie Sylvestre, Organic Geochemistry 33 (2002) 489–515

Table 1. The results for the PAH-compounds from the diesel particulate NIST SRM 1650.

Compound Method	Retention	SRM1650						Recoveries	
		1650 a2	1650 a1	1650 a	mean	St dev	St dev	indicative	
Name	Time	µg/g	µg/g	µg/g	µg/g	µg/g	%	µg/g	%
Naphthalene	10.805	33.9	31.6	29.2	31.56	2.34	7.40		
Methylnaphthalene, 2-	12.358	34.3	33.2	34.0	33.87	0.57	1.68		
Methylnaphthalene, 1-	12.595	20.3	20.3	19.8	20.13	0.25	1.25		
1,1-biphenyl	13.448	67.0	66.0	58.7	63.89	4.53	7.10		
Fluorene	16.223	16.4	16.9	11.6	14.94	2.95	19.72		
Dibenzo thiophene	18.268	8.2	8.1	7.8	8.04	0.19	2.38		
Phenanthrene	18.578	73.4	72.9	72.0	72.78	0.72	0.99	71	103
Anthracene	18.702	9.3	9.7	9.3	9.44	0.22	2.33		
Fluoranthene	21.524	45.4	44.9	44.0	44.77	0.70	1.57	47	95.3
Pyrene	22.091	50.2	49.1	48.5	49.26	0.89	1.81	48	103
Benz[a]anthracene	25.038	5.9	5.9	5.8	5.88	0.04	0.71	6.5	90.4
Chrysene	25.132	15.2	15.3	15.7	15.4	0.27	1.76	22	70.0
Benzo[b]fluoranthene	27.734	3.6	4.4	4.3	4.12	0.42	10.21		
Benzo[k]fluoranthene	27.749	2.8	1.9	2.3	2.32	0.46	19.74	2.1	111
Benzo[j]fluoranthene	27.801	1.9	2.5	2.0	2.14	0.33	15.44		
Benzo[e]pyrene	28.49	5.6	5.8	6.0	5.80	0.21	3.54	9.6	60.4
Benzo[a]pyrene	28.641	0.8	0.9	0.8	0.86	0.03	3.62	1.2	71.7
Perylene	28.87	0.1	0.0	0.1	0.07	0.02	32.70	0.13	51.9
Dibenzo[a,h]anthracene	32.174	0.6	0.7	0.9	0.70	0.14	20.04		
Indeno[1,2,3-cd]pyrene	32.175	2.5	2.6	2.8	2.64	0.13	4.78	2.3	115
Benzo[g,h,i]perylene	33.183	3.6	3.6	3.9	3.68	0.19	5.23	2.4	153

Table 2. The PAH content in three different particle materials, mg/kg.

Compound Method	Retention	NIST	NIST	Soot	NIST	NIST	Chimney
		1650	1649		1650	1649	Soot
Name	Time	µg/g	µg/g	µg/g			
Naphthalene	10.805	34	1.4	84			
Methylnaphthalene, 2-	12.358	34	1.4	3.3			
Methylnaphthalene, 1-	12.595	20	0.70	1.1			
1,1-biphenyl	13.448	67	0.70	1.3			
Dibenzofuran	15.359	33	0.40	2.9			
Fluorene	16.223	16	0.30	1.9			
Dibenzo thiophene	18.268	8.2	0.20	0.08			
Phenanthrene	18.578	73	3.3	106	An/178	An/178	An/178
Anthracene	18.702	9.3	0.40	13	0.11	0.11	0.11
Fenylapthalene, 2-	20.485	7.2	0.30	21	Fl/Fl+Py	Fl/Fl+Py	Fl/Fl+Py
Fluoranthene	21.524	45	4.0	130	0.47	0.53	0.56
Pyrene	22.091	50	3.6	103	BaA/228	BaA/228	BaA/228
Benz[a]anthracene	25.038	5.9	1.5	38	0.28	0.39	0.43
Chrysene	25.132	15	2.3	50			
Benzo[b]fluoranthene	27.734	3.6	4.1	32			
Benzo[k]fluoranthene	27.749	2.8	2.0	24			
Benzo[j]fluoranthene	27.801	1.9	1.3	16			
Benzo[e]pyrene	28.49	5.6	3.2	27			
Benzo[a]pyrene	28.641	0.80	2.0	24			
Perylene	28.87	0.10	0.6	4.3			
Dibenzo[a,h]anthracene	32.174	0.60	0.40	3.7	IP/IP+Bghi	IP/IP+Bghi	IP/IP+Bghi
Indeno[1,2,3-cd]pyrene	32.175	2.5	1.6	18	0.41	0.40	0.49
Benzo[g,h,i]perylene	33.183	3.6	2.4	19			

The three last columns contains information about sources described in the reference 5.

Table 3. The PCDD/F compounds found in the different matrixes studied.

	Method	SOOT	NIST1649	NIST1650
	Blanc	blanc ded	blanc ded	blanc ded
Dioxins and Furans	pg/g	pg/g	pg/g	pg/g
2,3,7,8-TCDD	< 0.01	128	12	< 0.01
1,2,3,7,8-PeCDD	< 0.01	334	81	< 0.01
1,2,3,4,7,8-HxCDD	< 0.01	230	247	< 0.01
1,2,3,6,7,8-HxCDD	< 0.01	743	730	< 0.01
1,2,3,7,8,9-HxCDD	< 0.01	556	600	< 0.01
1,2,3,4,6,7,8-HpCDD	< 0.01	2902	18301	939
1,2,3,4,6,7,8,9-OCDD	< 0.01	5237	173338	3781
2,3,7,8-TCDF	< 0.01	633	42	360
1,2,3,7,8-PeCDF	< 0.01	279	93	362
2,3,4,7,8-PeCDF	< 0.01	302	279	330
1,2,3,4,7,8-HxCDF	< 0.01	131	488	0.00
1,2,3,6,7,8-HxCDF	< 0.01	134	356	0.00
2,3,4,6,7,8-HxCDF	< 0.01	203	692	758
1,2,3,7,8,9-HxCDF	< 0.01	60	50	0.00
1,2,3,4,6,7,8-HpCDF	< 0.01	821	3253	40170
1,2,3,4,7,8,9-HpCDF	< 0.01	70	562	0.00
1,2,3,4,6,7,8,9-OCDF	< 0.01	416	6617	60244
Summa PCDD ja PCDF	< 0.01	13180	205740	106944
WHO TEQ SUM (Ubp)		870	775	652

Table 4. PCB compounds found in the different matrixes studied.

	Soot	NIST 1649	NIST 1650
PCB-DL	pg/g	pg/g	pg/g
PCB 81	129	140	135
PCB 77	730	1536	1286
PCB 123	55	1058	940
PCB 118	1243	22167	19886
PCB 114	32	732	837
PCB 105	247	1926	7785
PCB 126	173	416	317
PCB 167	219	2226	795
PCB 156	327	5334	1692
PCB 157	74	1107	388
PCB 169	18	85	10
PCB 189	62	1354	315
TEQ(PCB-DL)	17.99	45.41	33.1
TEQ(PCDD/F+PCB-DL)	888.4	820.3	685.2
Marker PCB ICES-6	ng/g	ng/g	ng/g
PCB 28	0.53	10	195
PCB 52	0.45	15	386
PCB 101	2.6	49	386
PCB 153	4.4	89	170
PCB 138	3.6	61	175
PCB 180	2.4	74	79
PCB 170	1.2	29	20
Total PCB ICES-6	14	299	1391
TEQ TOTAL(PCDD/F+PCB+PAH)	31879	3419	3872

Table 5. The PBDEE in the sample

BDE# native	Soot	NIST1649	SRM sediment CZ-7006
	ng/g	ng/g	ng/g
17	< 0.01	0.03	0.64
28	0.02	0.10	1.0
47	2.7	16	31
66	< 0.01	0.36	1.7
49	4.4	0.51	2.7
85	0.12	0.86	4.5
99	4.3	27	34
100	1.1	6.8	8.4
138	0.01	< 0.01	0.84
153	0.15	0.83	3.2
154	0.31	2.4	0.55
183	< 0.01	< 0.01	5.1
190	< 0.01	< 0.01	0.27
Summa PBDEE	13	55	94