

A Dissolved / Particulate Baseline Study of PAH's (Poly Aromatic Hydrocarbons) in Particulate Laden Water

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Introduction

Poly Aromatic Hydrocarbons are of great environmental concern due to their carcinogenic impact. When water samples are extracted and analyzed for the PAH's, many methods require the water sample to first be filtered, such that the particulate matter is removed. Filtration is required when conventional Solid Phase Extraction (SPE) cartridges are used for extracting the sample because SPE cartridges will easily plug when any particulate matter is present. With Liquid Liquid Extraction (LLE) techniques, emulsions typically create problems which could adversely impact the proper extraction of the suspended material.

However, compounds such as PCB's and PAH's will come out of the dissolved phase and adsorb onto the surface of the suspended particulate matter in the water column. Therefore, to determine the actual concentration of PAH's in the water sample, the "whole" water sample with the suspended particulate matter should be processed. As many water samples extracted for PAH's are surface water, river water, ground water, waster water, or water with suspended material, it is desirable to have a analytical method that can handle the "whole" water sample. SPE in a 47mm "disk" format is a proven extraction method for extracting particulate laden water samples. SPE disks provide fast flow rates with no breakthrough of analytes. Aqueous samples of 1 liter and greater can be processed quickly and effectively, providing excellent recoveries of PAH compounds at lower detection limits.

The International Organization for Standardization (ISO), a worldwide federation of national standards solicited their technical committees to develop a new ISO method for analyzing PAH's in particulate laden water. The IWW Water Centre Institute, located in Muelheim an der Ruhr, Germany, offered to participate in the development of a method to explore the possibilites of using SPE disks for the analysis of 16 PAH's in drinking water, ground water, waste water, and surface water. This study conducted by IWW had several goals which are listed below:

- Develop an SPE disk method that could handle "whole" water samples (including particulates and suspended matter).
- Due to possible partitioning of PAH's between the dissolved and particulate phase of the water column, to determine the effectiveness of the extraction technique for PAH's when the particulate matter and the SPE disk are both extracted and eluted with the SPE extracting solvent.
- Determine the total amount of particulate matter that can be handled by the SPE disk.
- Determine the best non-halogenated solvent to be used for extracting the SPE disk.
- Determine if a method could be developed that did not require a solvent concentration step.
- Develop a fully automated SPE disk method.

Experiments were carried out using both spiked drinking water and spiked surface water coming from natural water bodies (river water). These experiments would examine the ability of "whole" water samples to be extracted, and confirm if SPE would be sufficient to properly extract the sediment particles, and remove any PAH's adsorbed onto the sediment particles.

The best recoveries for this work were achieved with reverse phase C18 JT Baker Speedisks and the Horizon SPE-DEX[®] 4790 Automated Extractor System. This combination worked well for many surface water samples spiked with natural sediments up to a level of 1000 mg/l. Even with this level of suspended material, 1000 ml samples could still be processed in less than 20 minutes, without ever plugging a disk.

Before starting the planned work on surface water samples spiked with natural sediments, the following preliminary work was done:

- Calculate recoveries of PAH spiked drinking water samples not containing any suspended particulate matter (without any solvent concentration step).
- Explore potential adverse effects of solvent extract concentration; i.e. potential losses of target compounds.
- Determine PAH recoveries from the extraction of certified dried natural sediments (not spiked to the water sample).

Instrumentation

- Horizon Technology SPE-DEX[®] 4790 Automated Extractor System
- JT Baker C18 Speedisk
- Agilent 6890 GC/MS

Method Summary

- 1) 1000 ml water samples were used.
- 2) Spiked sample to 0.10 ug/l concentration.
- 3) Place the sample bottle onto the 4790 Extractor.
- 4) Start the method.
- 5) After 20 minutes, approximately 9 ml of extract are collected.
- 6) Some extracts were concentrated and others were not, to determine the impact of the concentration step.
- 7) Analyze by GC/MS.

Results

Spiked Drinking Water Samples:

All water samples were processed using the following method:

Step	Solvent	Soak Time	Dry Time
Prewet 1	Acetone	20 sec	20 sec
Prewet 2	Acetone	20 sec	20 sec
Prewet 3	Reagent Water	20 sec	20 sec
Prewet 4	Reagent Water	20 sec	20 sec
Process Sample			
Wash 1	Reagent Water	10 sec	10 sec
Air Dry			7:00 min
Rinse 1	Acetone	1:00 min	30 sec
Rinse 2	Acetone	5:00 min	30 sec
Rinse 3	Acetone	1:00 min	1:00 min

One litre drinking water samples were spiked at a concentration of 0.1 ug/l, and extracted. To maintain consistent conditions, a set water sample flow rate of 50 ml/min was maintained by adjusting the vacuum level. As one of the goals was to examine the impact of solvent evaporation, the rinse solvent volumes was adjusted so each solvent rinse delivered approximately 3 ml of solvent. With three rinses, this gave a final solvent volume of approximately 9 ml. The final volume was adjusted to 10 ml, and the extract analyzed.

The results from these experiments (see Table 1) show high recoveries for the 16 PAH's under investigation. Even Naphthalene showed recoveries of 75% and a low repeatability coefficient of variation, however, minor losses could be traced back to the 7 minute air dry time of the SPE disk. A long air dry time can lead to volatilization and oxidation of the PAH compounds.

Table 1: Recovery of PAH spiked drinking water, not containing any suspended matter (starting volume: 1000ml, conc = 0.1 ug/l, conditioning and elution with acetone, final volume 10 ml, no solvent concentration).

substance	recovery (%)	repeatability coefficient of variation (n = 4) CV _r
naphthalene	75	0.8
acenaphthylene	83	5.1
acenaphthene	85	3.2
fluorene	85	1.5
phenanthrene	93	5.1
anthracene	93	4.8
fluoranthene	93	5.1
pyrene	93	6.1
benzo(a)anthracene	88	3.6
chrysene	94	4.1
benzo(b)fluoranthene	89	7.6
benzo(k)fluoranthene	80	3.7
benzo(a)pyrene	81	7.7
indeno(1,2,3,c,d)pyrene	85	7.2
dibenzo(a,h)anthracene	82	7.6
benzo(g,h,i)perylene	91	7.0

Impact of Solvent Concentration:

To determine if there could be substantial losses of individual analytes during the solvent concentrating process, several non-halogenated solvents were spiked with all 16 PAH's. The concentrating process was carried out with a 10 ml sample (starting) volume spiked to a concentration level of 0.005

ug/ml, using a gentle stream of nitrogen and temperatures below 20C. The final solvent volume was 1 ml. Both acetone and hexane containing 5% (v/v) ethyl acetate appeared to provide the best results.

Results from these experiments with a final volume of 1 ml are shown in Table 2. It can be seen from these results, that if concentration to 1.0 ml is necessary, that better recoveries can be achieved by using hexane / 5% ethyl acetate.

Table 2: Recovery of concentration procedure using different solvents (starting volume: 10 ml, conc = 0.005 ug/ml, final volume 1 ml, a: acetone, b: hexane / 5% ethyl acetate).

Substance	- a - recovery (%)	repeatability coefficient of variation (n = 4) CV _r	- b - recovery (%)	repeatability coefficient of variation (n = 4) CV _r
Naphthalene	58	9.7	76	4.2
Acenaphthylene	77	3.0	79	4.5
Acenaphthene	82	3.5	81	4.7
Fluorene	81	13.4	83	5.1
Phenanthrene	67	1.0	92	3.1
Anthracene	64	2.0	92	4.0
Fluoranthene	83	2.4	101	2.8
Pyrene	85	1.8	99	3.4
benzo(a)anthracene	71	1.6	104	1.8
Chrysene	79	2.7	99	1.4
benzo(b)fluoranthene	66	1.5	105	2.2
benzo(k)fluoranthene	74	5.9	101	0.7
benzo(a)pyrene	61	2.3	103	3.0
indeno(1,2,3,c,d)pyrene	70	2.1	101	2.6
dibenzo(a,h)anthracene	71	4.3	105	2.3
benzo(g,h,i)perylene	66	3.9	105	3.1

To determine the impact on recoveries of stopping the concentration at a final volume of 5 ml rather than 1.0 ml, another set of experiments were run. Each experiment was carried out four times and the results are shown in Table 3. The results include the repeatability coefficient of variation.

Table 3: Recoveries of concentration procedure using different solvents (starting volume: 10 ml, conc = 0.005 ug/l, final volume 5 ml, a: acetone, b: hexane/5% ethyl acetate).

Substance	- a - recovery (%)	repeatability coefficient of variation (n = 4) CV _r	- b - recovery (%)	repeatability coefficient of variation (n = 4) CV _r
Naphthalene	88	2.0	99	2.0
Acenaphthylene	90	1.7	102	0.7
Acenaphthene	82	2.7	97	1.8
Fluorene	84	1.5	95	1.0
Phenanthrene	88	2.3	99	0.6
Anthracene	91	4.0	99	1.3
Fluoranthene	87	2.5	99	1.6
Pyrene	87	0.8	97	2.7
benzo(a)anthracene	88	1.2	100	1.6
Chrysene	92	3.5	100	3.6
benzo(b)fluoranthene	91	4.2	104	3.3
benzo(k)fluoranthene	88	5.5	97	2.6
benzo(a)pyrene	89	6.4	103	5.1
indeno(1,2,3,c,d)pyrene	94	6.8	96	2.7
dibenzo(a,h)anthracene	101	2.8	102	5.9
benzo(g,h,i)perylene	100	2.8	106	5.7

It can be seen from the results of Table 2 and Table 3 that high recoveries will be achieved for all analytes under investigation. However, by stopping the concentration at 5 ml, rather than 1.0 ml, there is a significant improvement in the recovery values. As great care is essential to avoid losses of the readily volatile naphthalene and acenaphthylene during the concentration step, eliminating the solvent concentration step was chosen. In addition, temperatures during the concentration step should not exceed 20C and the final volume of the concentration step should not go below the 5 ml mark. In those cases, both solvents can be used.

Extraction of Certified Dried Natural Sediments (not spiked into water sample):

Table 4 shows the results of direct extraction of dried natural sediment by using acetone and hexane / 5% ethyl acetate. The extractions were performed in vessels fitted with a magnetic stirrer, with 0.5 g sediment, and each with 5 ml of each solvent. The sediment used was EC-3 (A Lake Ontario Sediment for Toxic Organics) – National Water Research Institute, Canada 1999 certified reference values (see Table 4). It can be seen from the results that both solvents lead to acceptable extraction yields. Most measured values lie exactly within deviations of EC-3 uncertainty limits, or at least within a range of 15% above or below. However, the measured amount of PAH using acetone is a bit higher than when using hexane / 5% ethyl acetate. The EC-3 natural dried sediment was later used for spiking purposes as described below.

Table 4: PAH extraction yields calculated from the direct extraction of 0.5 g of the dried certified sediment of Lake Ontario (EC-3) by using 5 ml of both acetone and hexane containing 5% ethyl acetate. Deviations from the certified reference value are given as a percentage (!: deviation within EC-3 uncertainty limits).

substance	EC-3 certified reference value, uncertainty based on just 1 measurement		acetone		hexane containing 5% ethyl acetate	
	(ng/g) informative	uncertainty (± ng/g)	found (ng/g)	deviation from EC-3 uncertainty limits (± %)	found (ng/g)	deviation from EC-3 uncertainty limits (± %)
naphthalene	35	20	94	+111	48	
acenaphthylene	25	8	44	+44	28	
acenaphthene	22	9	20		20	
fluorene	42	21	16	-12	16	-12
phenanthrene	293	33	130	-44	170	-31
anthracene	59	11	45	-5	42	-10
fluoranthene	558	46	455	-10	387	-22
pyrene	436	47	406		342	-11
benzo(a)anthracene	312	28	269	-5	215	-22
chrysene	458	59	379	-4	294	-23
benzo(b)fluoranthene	505	88	538		411	
benzo(k)fluoranthene	271	104	270		207	
benzo(a)pyrene	386	50	403		311	-6
indeno(1,2,3,c,d)pyrene	359	36	430	+10	259	-18
dibenzo(a,h)anthracene	109	17	69	-21	44	-44
benzo(g,h,i)perylene	348	70	411		270	-2

Extraction of Surface Water Samples Spiked with Dried Natural Sediment (EC-3):

The next set of experiments added 500 mg of sediment (EC-3) to 1000 ml surface water samples. The experiments were carried out four times, and acetone was used as the extracting solvent. The goal was to explore the use of a strong, water soluble extracting solvent like acetone to sufficiently extract the particulate matter and the SPE disk, even when the SPE disk was still slightly wet with residual water. The results show that the selected seven minute air dry time for the filtered disk was sufficient for sediment amounts up to 750 mg. For greater sediment loadings, a longer air dry time would be better. This will be explained later in this study.

Table 5 shows the results from a 500 mg spiking experiment of a 1000 ml surface water sample (both including and not including a solvent concentration step). The sample with no solvent concentration step had the final extract volume brought to 10 ml, while the other extract was concentrated to 5.0 ml. The results show basically very similar recovery values.

Table 5: PAH extraction yields calculated from surface water (1000 ml) spiked with 500 mg of certified sediment EC-3 of Lake Ontario. Procedure used acetone (a: without solvent concentration, b: including solvent concentration – final volume = 5 ml). PAH concentrations calculated as both water sample (ug/l) and sediment (ng/g). Deviations from the certified reference value are calculated as a percentage (!: deviation within EC-3 uncertainty limits of Table 4).

substance	spiked with 500 mg sediment (EC-3) (without solvent concentration)				spiked with 500 mg sediment (EC-3) (final volume: 5 ml)			
	found concentration µg/l	calc. as ng/g	repeatable coefficient of variation (n = 4) CV _r	deviation from EC-3 uncertainty limits (± %)	found concentration µg/l	calc. as ng/g	repeatable coefficient of variation (n = 4) CV _r	deviation from EC-3 uncertainty limits (± %)
naphthalene	0.036	72	7.9	+49	0.032	64	8.5	+25
acenaphthylene	0.016	31	10.1		0.016	33	7.3	
acenaphthene	0.010	20	9.4		0.010	19	2.4	
fluorene	0.009	18	9.9	-7	0.007	15	4.1	-14
phenanthrene	0.110	220	10.8	-14	0.087	173	2.2	-30
anthracene	0.028	56	6.8		0.021	42	5.0	-10
fluoranthene	0.178	356	3.2	-28	0.184	367	1.8	-26
pyrene	0.165	329	7.0	-14	0.160	319	1.9	-16
benzo(a)anthracene	0.110	220	7.8	-21	0.121	243	5.4	-13
chrysene	0.139	279	9.7	-26	0.142	284	3.4	-25
benzo(b)fluoranthene	0.193	385	4.7	-6	0.179	358	7.0	-12
benzo(k)fluoranthene	0.152	304	8.3		0.147	294	11.2	
benzo(a)pyrene	0.220	440	4.8	+1	0.182	363	4.4	
indeno(1,2,3,c,d)pyrene	0.195	390	8.2		0.190	380	3.7	
dibenzo(a,h)anthracene	0.038	77	5.4	+14	0.029	58	12.8	-31
benzo(g,h,i)perylene	0.147	294	8.2		0.150	300	2.5	

The study then examined the recovery of samples with both 250 mg and 750 mg of certified sediment added to water samples. The results are shown in Table 6, and also indicate good extraction recoveries. It should also be noted that all extracts were concentrated to 5.0 ml.

Table 6: PAH extraction yields calculated from surface water (1000 ml) spiked with various amounts of certified sediment EC-3 of Lake Ontario (a: 250 mg and b: 750 mg). Procedure used acetone and a concentration step (final volume: 5 ml). PAH concentrations calculated as both water sample (ug/l) and sediment (ng/g). Deviations from the certified reference value are given as a percentage (!: deviation within EC-3 uncertainty limits of Table 4).

substance	spiked with 250 mg sediment (EC-3) (final volume: 5 ml)				spiked with 750 mg sediment (EC-3) (final volume: 5 ml)			
	found concentration µg/l	calc. as ng/g	repeatable coefficient of variation (n = 4) CV _r	deviation from EC-3 uncertainty limits (± %)	found concentration µg/l	calc. as ng/g	repeatable coefficient of variation (n = 4) CV _r	deviation from EC-3 uncertainty limits (± %)
naphthalene	0.015	61	6.1	+17	0.051	68	2.1	+37
acenaphthylene	0.006	24	6.1		0.026	35	9.3	+8
acenaphthene	0.004	17	6.2		0.014	18	6.1	
fluorene	0.003	11	9.6	-24	0.011	15	7.1	-14
phenanthrene	0.044	176	2.8	-29	0.131	175	6.2	-29
anthracene	0.009	36	3.4	-20	0.039	52	5.4	
fluoranthene	0.082	327	3.3	-33	0.277	369	5.8	-26
pyrene	0.073	292	3.4	-22	0.242	323	5.5	-15
benzo(a)anthracene	0.048	193	5.3	-29	0.179	239	10.6	-14
chrysene	0.063	252	4.9	-32	0.216	288	6.9	-24
benzo(b)fluoranthene	0.072	289	1.8	-25	0.268	357	10.1	-12
benzo(k)fluoranthene	0.060	239	8.1		0.204	272	6.3	
benzo(a)pyrene	0.073	293	7.5	-11	0.285	381	8.3	
indeno(1,2,3,c,d)pyrene	0.052	208	7.1	-32	0.197	263	12.8	-17
dibenzo(a,h)anthracene	0.016	63	4.5	-26	0.042	56	10.8	-33
benzo(g,h,i)perylene	0.061	245	8.1	-9	0.199	265	8.2	-4

Table 7 shows the recovery values when a 1000 ml sample was extracted that contained 1000 mg of certified sediment. As can be seen with the recovery data, these values were lower than desired. It was later determined that the 7 minute air dry time, after the water sample had filtered through the SPE disk was

insufficient to completely remove most of the residual water from the disk surface. To improve these recoveries, the air dry time should be increased, but care must be taken to ensure that not too long of a dry time is used. Due to the volatility and the likelihood of oxidizing the PAH's, the proper air dry time should be determined.

With the Horizon Technology automated SPE system used for this work, an approach to solve this problem would be as follows. First, visually inspect the sample bottle and estimate the amount of suspended material present. If the amounts appears to be less than the 1000 mg limit, than to use the normal method with the 7 minute air dry time. If the amount appears to approach, or be greater than 1000 mg, than to use an SPE method that stops the extraction process after the established 7 minute air dry time.

The operator would than visually examine the SPE disk with the suspended matter retained on the SPE disk surface, and empirically determine the additional air dry time that might be required. This new method would be downloaded and run. As an example, there could be a series of methods the operator would choose from that would have additional air dry times; 2 minute, 4 minute, 6 minute, etc. Each of these methods would also include the solvent extraction portion of the method. This type of sample handling would definitely improve the recovery of these compounds.

Table 7: PAH extraction yields calculated from surface water (1000 ml) spiked with 1000 mg of certified sediment EC-3 of Lake Ontario (insufficient disk drying time). Procedure used acetone and a solvent concentration step (final volume: 5 ml). PAH concentrations calculated as both water sample (µg/l) and sediment (ng/g). Deviations from the certified reference value are given as a percentage (!: deviation within EC-3 uncertainty limits of Table 4).

substance	spiked with 1000 mg sediment (EC-3) (final volume: 5 ml)			
	found concentration µg/l	calc. as ng/g	repeatable coefficient of variation (n = 4) CVr	deviation from EC-3 uncertainty limits (± %)
naphthalene	0,046	46	4,3	!!
acenaphthylene	0,016	16	8,6	-4
acenaphthene	0,011	11	5,7	-9
fluorene	0,010	10	6,9	-26
phenanthrene	0,128	128	7,8	-45
anthracene	0,031	31	8,4	-29
fluoranthene	0,212	212	7,1	-53
pyrene	0,183	183	7,6	-47
benzo(a)anthracene	0,126	126	8,0	-51
chrysene	0,152	152	6,6	-54
benzo(b)fluoranthene	0,170	170	8,7	-49
benzo(k)fluoranthene	0,124	124	8,3	-16
benzo(a)pyrene	0,203	203	8,9	-34
indeno(1,2,3,c,d)pyrene	0,099	99	6,4	-62
dibenzo(a,h)anthracene	0,030	30	8,3	-57
benzo(g,h,i)perylene	0,116	116	5,5	-47

Conclusions

This study shows that the SPE-DEX[®] 4790 Automated Extractor system, a fully automated SPE system, can process water samples containing suspended particulate matter up to 1000 mg, for the analysis of PAH's. As PAH's are found in both the dissolved and particulate phase of the water sample, it is important to be able to handle "whole" water samples, such that the particulate matter in the water sample is retained on the surface of the SPE disk and extracted, along with the SPE disk. This filtration method ensures that PAH's found in the dissolved phase, and those PAH's adsorbed onto the particulate matter are properly extracted.

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