BACKUP DATA REPORT
NIOSH Method No. 5528

Title: Polynuclear aromatic hydrocarbons in air by GC-MS SIM

Analyte: Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene, Benzo[g,h,i]perylene

Author: Dawn Farwick

Developer: Method developed by DataChem under contract CDC-200-2001-0800

Date: October 6, 2021

I. INTRODUCTION AND BACKGROUND

Polynuclear Aromatic Hydrocarbons (PAHs) are some of the most widespread environmental contaminants. PAHs are formed by virtually all types of combustion, with possible sources of PAH exposure including automobile exhaust, factory smokestack exhaust, and even the family backyard barbecue.

Most exhaust contains a whole host of various PAH compounds, and for this reason it has historically been difficult to use epidemiological data to determine toxicity of individual polynuclear aromatic hydrocarbons. Not all PAHs have the same toxicity; some are relatively harmless compared to others. Recent science has focused on benzo[a]pyrene as perhaps the most toxic of these 16 PAHs. Benzo[a]pyrene is metabolized in mammalian tissue to a highly carcinogenic bay-region diol epoxide [1]. Much work has yet to be done on the toxicity of individual PAHs, but it is nonetheless clear that exposure to PAHs is detrimental to human health. Because of their different toxic natures, it is important to have analytical methods which can reliably detect and differentiate PAHs.

There are several published methods for the analysis of PAHs in air. NIOSH Method 5506 uses a filter and an XAD-2 sorbent tube followed by HPLC with fluorescence and/or UV detection [2]. NIOSH Method 5515 uses the same sampling device followed by gas chromatography with an FID detector [3].

The introduction of the OSHA Versatile Sampler (OVS) in the 1980's provided an opportunity for easier sampling of workplace exposures and a greater capacity for trapping organic vapors and submicron particles [4]. The sampling device used in NIOSH Methods 5506 and 5515 is a filter cassette, spacer ring, and sorbent tube, all connected in series. This multi-part device is somewhat bulky and inconvenient to use compared to the one-piece OVS sampler. Furthermore, the sorbent tube of Method 5506/5515 contains about one-third the sorbent of the OVS tube [2,3].

Due to the relatively broader peaks inherent in HLPC (when compared to GC), it is sometimes more difficult to properly resolve isomeric pairs when analyzing by HPLC. Benzo[e]pyrene, for example, was included in the Method 5506 target compound list not because it was an analyte of concern, but rather because it was necessary to demonstrate that the HPLC system could separate the relatively innocuous benzo[e]pyrene from its highly toxic cousin benzo[a]pyrene. GC analysis has sharper peaks and does not have this problem with peak resolution, making it a preferred choice in analytical instrumentation for this class of compounds. HPLC was used because of the sensitivity using fluorescence detection. Since then, GC/MS advances have allowed comparable limits of detection.

Considering the above-mentioned issues, a method using the more compact OVS sampling device with more specific analytical analysis was investigated. Gas chromatography/mass spectrometry (GC/MS) was chosen for study because of its ability to use the mass-spectral fingerprint for reliable identification even in the most complex of matrices. The use of selected-ion monitoring (SIM), scanning as many as ten ions at a time, could give detection limits rivaling those of Methods

5506/5515 while still collecting enough mass spectral data to obtain a reliable mass spectrum for identity confirmation. The remainder of this report documents the development of a method for analysis of PAHs using an OVS sampler followed by GC/MS SIM analysis. This method has been assigned the number NIOSH 5528 [5].

II. REAGENTS AND MATERIALS

Presented in Table 1 is the list of reagents and solvents used for this method development.

Table 1. List of Chemicals

Chemical	Vendor	CAS #	Purity	Lot #
Methylene Chloride	Burdick & Jackson	75-09-2	High Purity	C0173
Naphthalene-D_8	Cambridge Isotope Labs	1146-65-2	99%	P-7172
Acenaphthene-D_{10}	MSD Isotopes	15067-26-2	98.7%	5693-M
Phenanthrene-D_{10}	Cambridge Isotope Labs	1517-22-2	98%	P-7101
Chrysene-D_{12}	Cambridge Isotope Labs	1719-03-5	98%	P-6241
Perylene-D_{12}	Cambridge Isotope Labs	1520-96-3	98%	P-8438
PAH mixture	Absolute Standards (10007)	Various	N/A	111804

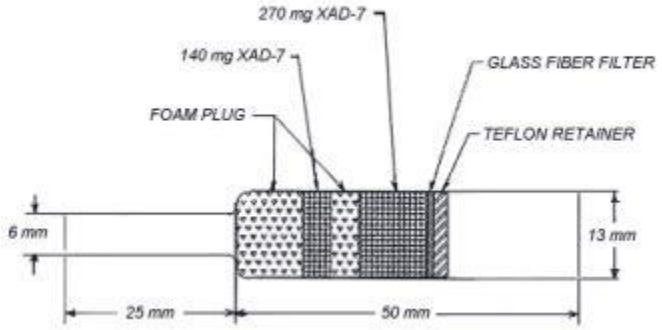
III. SELECTION OF SAMPLING MEDIA

After some preliminary laboratory studies of samplers using various media (XAD-2, Chromosorb-6, Florisil®, XAD-7, and Tenax), it was determined that an OVS sampler with XAD-7 would be the most appropriate sampler [6].

OVS Sampler

The OVS device used has a glass fiber filter (GFF) of 13-mm diameter with front and backup sections of sorbent separated by polyurethane foam. Devices used in the study were purchased from SKC (OVS-7, catalog number 226-57). Figure 1 is a picture of this device [7].

Figure 1. OVS-7 Sampler



Most published analytical methods for PAHs do not specify the use of XAD-7, favoring instead XAD-2 or polyurethane foam (PUF). The XAD-2 resin is a styrene divinylbenzene polymer, and the XAD-7 resin is an acrylate-based polymer. XAD-2 has polyphenyl alkane breakdown products which can interfere with the detection of PAHs, especially alkyl substituted PAHs. XAD-7, however, presented a cleaner chromatographic background than the XAD-2 and showed good desorption efficiency. XAD-7 has a dipole moment of 1.8, pore size of 90 Angstroms (mesh 20 to 60), and a surface area of 450 m^2/gram.[8]

IV. USE OF SELECTED ION MONITORING (SIM) AND INSTRUMENT CONDITIONS

This GC/MS method can be run in full-scan mode, monitoring every ion ranging from mass-to-charge 35 through 500. In fact, full scan mode would be the most desirable approach if there is a need to identify PAH components outside the target-compound list. There are some instances in which alkyl-substituted PAHs may be of more concern than the parent PAH. As more toxicity data become available over the coming years, it may be needed to expand the analyte list or at least to use mass-spectral data for tentative identifications of non-target analytes. The only disadvantage to running in full-scan mode would be a higher limit of detection, but this method is written with the assumption that the emphasis lies on obtaining the lowest reasonable detection limit and that there is no need to identify PAH components outside the list of target analytes.

This method specifies the use of SIM and the monitoring of as many as ten ions in a single scan. The extra ions are included so that an abbreviated mass spectrum may be obtained to provide additional data for confirmation (or rejection) of the PAH identification. It is often assumed by analysts that this choice to monitor more ions represents a major trade-off in terms of sensitivity versus the alternative of monitoring one ion only. This assumption seems logical. If the mass spectrometer spends half a second scanning ten ions, then it ought to be able to give a ten-fold increase in sensitivity if it were to spend that same half-second scanning a single ion instead of ten. The assumption is logical, but it is not supported by the data, at least not on the instrumentation used for method development (Agilent 5972 and 5973). In truth, there is no significant difference in sensitivity between monitoring a single ion versus ten.

A test was performed to see what degree of sensitivity improvements can be made by running in SIM mode over full scan. A PAH standard at 2 µg/mL was injected four times at each of three different operating conditions. The three operating conditions were full scan, SIM mode monitoring one ion only, and SIM mode monitoring about 9 ions. The samples were injected in random, interspersed order.

The results, displayed in Table 2 below, show that a two-fold increase in sensitivity can be gained by using SIM mode over full scan, as measured by peak areas. It further shows that it does not make any difference in dropping to one ion versus nine; an interesting result because one would

expect that a greater dwell time (or the same dwell time but many more cycles per second) would result in greater sensitivity. It does not.

Table 2. Areas of Naphthalene Peaks in Three SIM/Scan Conditions

	Full Scan Mode	**SIM Mode 1 ion**	**SIM Mode 9 ion**
Replicate	1.53 scans/sec	20 cycles/sec	2.4 cycles/sec
#1	325,088	856,985	726,988
#2	376,578	649,654	717,072
#3	382,163	794,097	637,035
#4	298,324	573,070	793,673
Average	345,538	718,452	718,692

An additional experiment was performed to measure sensitivity variations in a slightly different manner. It was theorized that using peak areas to measure sensitivity was the best approach. To test for this, consecutively lower concentration standards were analyzed to check for a difference in sensitivity. No difference was observed. There was no concentration level at which the one-ion analysis showed a peak when the 9-ion analysis did not. Both sets of SIM parameters reached the point where signal-to-noise levels were less than two at the same concentration level. This experiment confirmed that there is no increase in sensitivity by monitoring a single ion rather than nine.

A few experiments were performed in which the dwell time was varied from 10 to 800 milliseconds (ms). No significant difference in sensitivity was noted from one parameter to another. The only notable difference was the extreme case of 800-ms dwell times resulted in poor peaks shapes from too few scans to define the GC peak. The 30-ms dwell time gave the best peak shapes, which agrees with the manufacturer's recommendation for SIM analysis of more than three ions.

Instrument Conditions

The systems used consisted of an Agilent Technologies Model 5890 gas chromatograph with a Model 5972 mass spectrometer or an Agilent Technologies Model 6890 gas chromatograph with a Model 5973 mass spectrometer. The column used was a fused silica capillary column (DB-5ms, 30m × 0.32mm I.D., 0.5 µm film).

GC programming was as follows:

- Temperature program: 50 °C for one minute; 25 °C/minute until 130 °C; 13 °C/minute until 240 °C; 22 °C/minute until 300 °C; hold for 7 minutes
- Injector temperature: 280 °C
- MS transfer line: 310 °C
- Injection volume: 1 µL; splitless time of 0.5 minutes
- constant pressure at 1.3 mL/minute

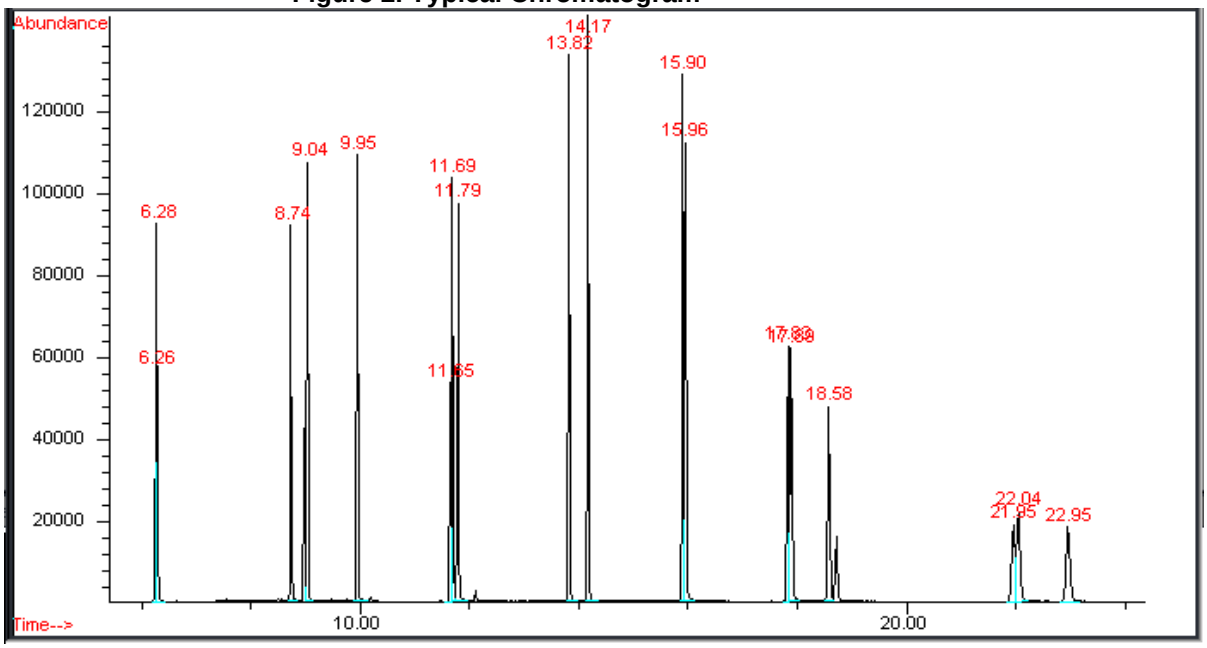
Chromatogram Analysis

A list of typical retention times using the conditions described above is shown in Table 3. Figure 2 displays a typical chromatogram when the previously described conditions are employed. Refer to Table 3 for elution order of the peaks. The retention times will vary according to the age of the individual GC columns. For example, a proper injection port maintenance normally includes trimming a few inches from the front of the column, thus an older column will be somewhat shorter than a new column and will have earlier elution times.

Table 3. Typical Retention Times.

Compound	Approximate Retention Time (minutes)
Naphthalene	6.28
Acenaphthylene	8.74
Acenaphthene	9.04
Fluorene	9.95
Phenanthrene	11.69
Anthracene	11.79
Fluoranthene	13.82
Pyrene	14.17
Benz[a]anthracene	15.90
Chrysene	15.96
Benzo[b]fluoranthene	17.83
Benzo[k]fluoranthene	17.89
Benzo[a]pyrene	18.58
Indeno[1,2,3-cd]pyrene	21.95
Dibenz[a,h]anthracene	22.04
Benzo[ghi]perylene	22.95

Figure 2. Typical Chromatogram



The mass spectrometer is operated in Selected-Ion Monitoring (SIM) mode using a dwell time of 30 ms for each ion. Six different SIM windows are used as shown in Table 4. Table 5 lists ions to use for quantitation, ions for spectral confirmation and internal standard references.

Table 4. SIM Parameters.

	Start Time (minutes)	Dwell Time (ms)	Ions to monitor
Group 1	1 minute before naphthalene (~5.5 min)	30	136, 128, 129, 126, 64
Group 2	1 minute after naphthalene (~7.5 min)	30	164, 152, 150, 153, 76, 154, 166, 165, 167, 82
Group 3	1 minute after fluorene (~11 min)	30	188, 178, 179, 176, 89, 202, 200, 203, 101
Group 4	1 minute before fluoranthene (~13 min)	30	240, 202, 200, 203, 101, 228, 229, 226, 114
Group 5	1 minute after chrysene (~17.3 min)	30	264, 252, 253, 250, 126
Group 6	1.5 min after benzo[a]pyrene (~21 min)	30	276, 277, 274, 138, 278, 279, 139

Table 5. Quantitation Ions, Secondary Ions and Internal Standard References.

Compound	Quantitation ion	Secondary Ions	Internal Standard Ref.
Naphthalene	128	129, 127, 126, 64	Naphthalene-D_8
Acenaphthylene	152	153, 150, 76	Acenaphene-D_{10}
Acenaphthene	153	154, 152, 150, 76	Acenaphene-D_{10}
Fluorene	166	167, 165, 164, 82	Acenaphene-D_{10}
Phenanthrene	178	179, 176, 89	Phenanthrene-D_{10}
Anthracene	178	179, 176, 89	Phenanthrene-D_{10}
Fluoranthene	202	203, 200, 101	Phenanthrene-D_{10}
Pyrene	202	203, 200, 101	Chrysene-D_{12}
Benz[a]anthracene	228	229, 226, 114	Chrysene-D_{12}
Chrysene	228	229, 226, 114	Chrysene-D_{12}
Benzo[b]fluoranthene	252	253, 250, 126	Perylene-D_{12}
Benzo[k]fluoranthene	252	253, 250, 126	Perylene-D_{12}
Benzo[a]pyrene	252	253, 250, 126	Perylene-D_{12}
Indeno[1,2,3-cd]pyrene	276	277, 274, 138	Perylene-D_{12}
Dibenz[a,h]anthracene	278	279, 276, 139	Perylene-D_{12}
Benzo[ghi]perylene	276	277, 274, 138	Perylene-D_{12}
Naphthalene- D_8	136	N/A	N/A
Acenaphene-D_{10}	164	N/A	N/A
Phenanthrene-D_{10}	188	N/A	N/A
Chrysene-D_{12}	240	N/A	N/A
Perylene-D_{12}	264	N/A	N/A

V. CALIBRATION AND SAMPLE PREP

Preparation of Primary Stock and Internal Standard Solutions

The desorption fluid was methylene chloride (high purity). Standards were prepared by spiking the appropriate volume of Absolute Standards mixture 10007 (or a dilution of this solution). An internal standard solution consisting of naphthalene-D_8, acenaphthene-D_{10}, phenanthrene-D_{10}, chrysene-D_{12}, and perylene-D_{12} was prepared at a concentration of 2000 µg/mL in methylene chloride. Analysis presumably could be performed using a single internal standard rather than five, but with so many analytes there is a benefit in having an internal standard for each section of the chromatogram. These deuterated internal standards are readily available commercially.

Calibration

To quantify the concentrations of target analytes present in samples, a calibration curve is constructed with nine working standards (six concentration levels, with two replicates for each of the lower three levels) covering the anticipated concentration range of the samples. The working standards are prepared by spiking known amounts of the PAH mixture (or a dilution of it) onto the

filter and front resin of a fresh OVS tube. Two milliliters of methylene chloride are added, and the working standards are desorbed for at least thirty minutes in an ultrasonic bath. An aliquot of the desorbate is placed in a GC vial and spiked with the internal standard solution to yield a concentration of 1.0 µg/mL for each internal standard. After analyzing the standards, a calibration graph is generated for each analyte by plotting the normalized analyte response (peak area of analyte divided by the peak area of the internal standard on the same chromatogram) on the y-axis vs. concentration of analyte on the x-axis.

Since this method specifies the use of media standards, there is no need to perform desorption efficiency studies.

Sample Preparation

The filter and front section of the OVS-7 tube are placed into an amber 4-mL screw-top vial. The backup resin (including foam plug which separates the front resin from the back) is placed in a separate vial. Two milliliters of methylene chloride are then added to each vial and the vials are desorbed in an ultrasonic bath for at least 30 minutes.

VI. SAMPLER CAPACITY AND BREAKTHROUGH STUDY

The OVS devices are recommended for a sampling rate of 1 liter per minute, which differs from the 2-liter-per-minute rate specified in other NIOSH PAH methods. It was felt there was some benefit in keeping the same sample volume used in other methods to allow for a comparison of the methods/samplers. The OVS tubes were therefore sampled at 1 liter per minute for 4, 8, 12, 16, 20, and 24 hours.

It is recommended that the spiking level be equal to twice the PEL [9]. Currently, there are not PEL values for all PAHs, but several of them have a PEL of 0.2 mg/m^3. Assuming this PEL applies for all analytes, and further assuming a typical air volume for this method would be about 1000 liters of air (8 hours × 2 L/min × 60 min/hr = 960 L), the amount to spike on each filter was determined to be 400 µg of each PAH.

400 µg/ 1000 L × 1000 L / m^3 × 1 mg / 1000 µg = 0.4 mg/m^3.

This was accomplished by spiking 200 µL of the Absolute Standards mix #10007 which was at a concentration of 2000 µg/mL. It was not advisable to spike more than 25 µL because of potential problems with the spiking solution pooling around the edge of the filter and being aspirated around the filter, resulting in anomalous breakthrough numbers, so spiking was accomplished by spiking 25 µL at a time, then waiting for the solvent to dry before spiking again, 8 times, until the full amount was delivered. Six replicates were made at each level.

Figures 3 through 7 show graphical representations of the breakthrough characteristics of the first five analytes. A tabular summary of the entire study is presented in Tables 6-11.

Figure 3. Naphthalene on OVS with XAD-7.

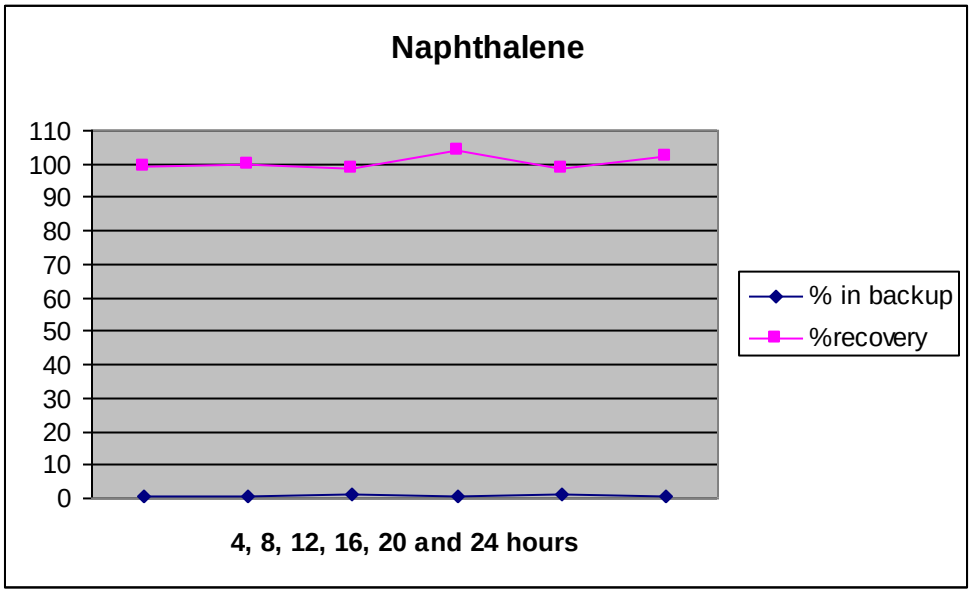


Figure 4. Acenaphthylene on OVS with XAD-7.

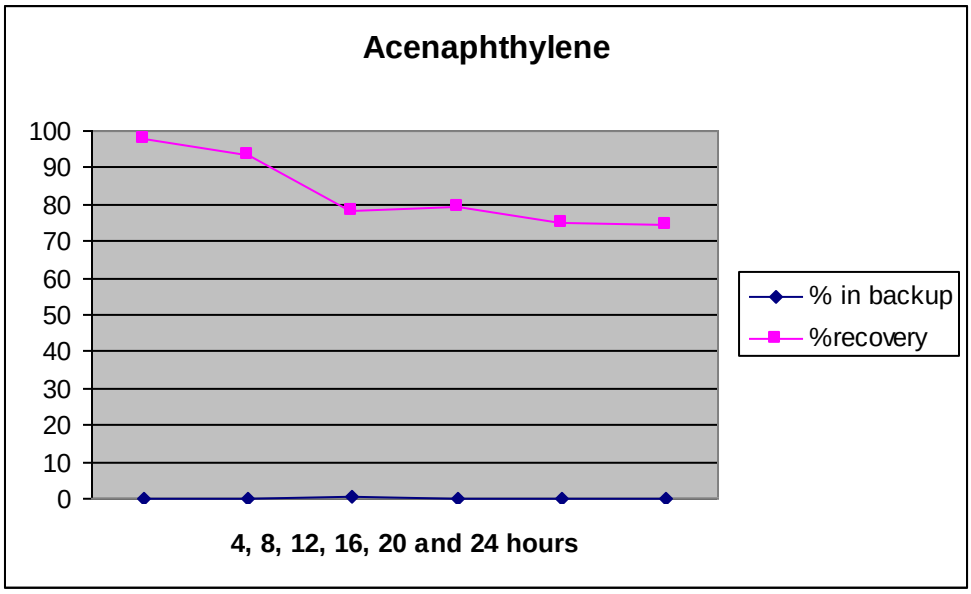


Figure 5. Acenaphthene on OVS with XAD-7.

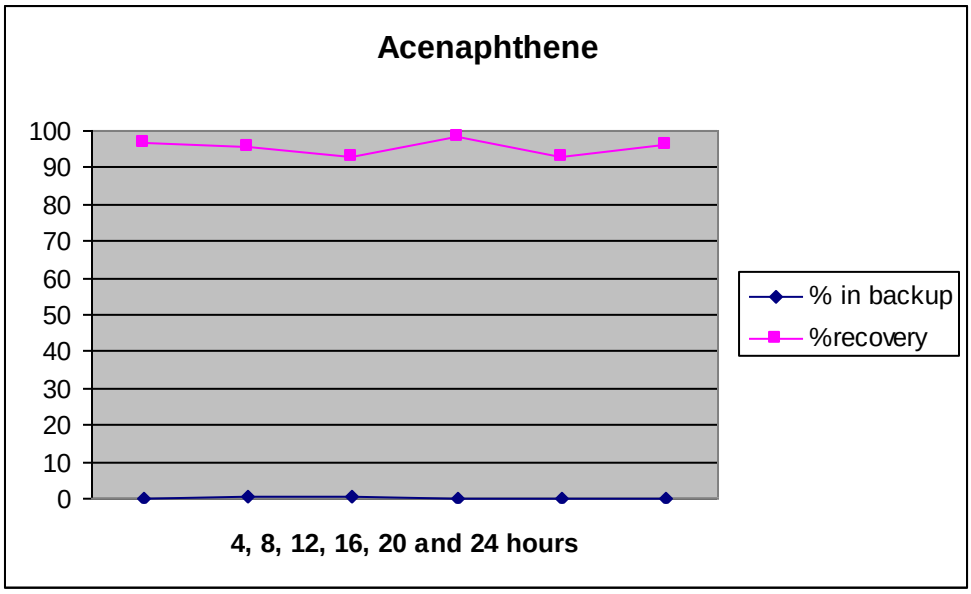


Figure 6. Fluorene on OVS with XAD-7.

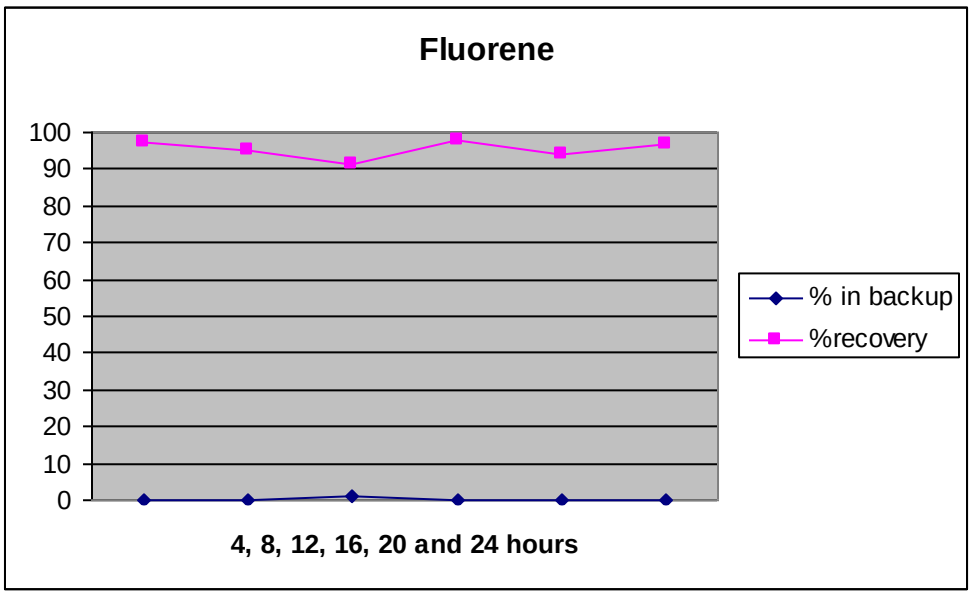


Figure 7. Phenanthrene on OVS with XAD-7.

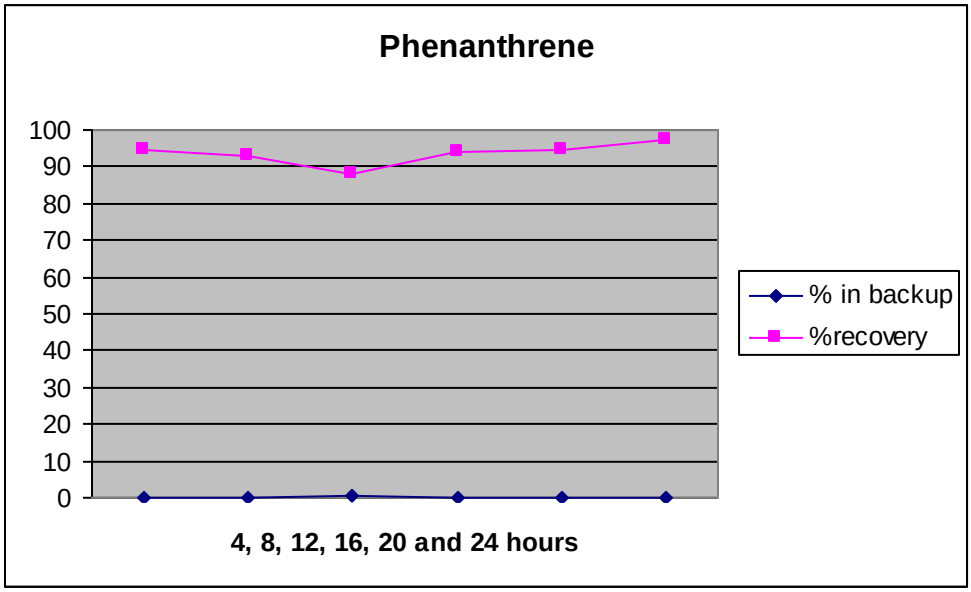


Table 6. Breakthrough at Four Hours
(average of 6 replicates; units of concentration are µg/sampler)

Analyte	Filter	Front resin	Back resin	cassette	total	% in backup	%rec
Naphthalene	1.95	394	1.07	0.0740	397	0.3	99.3
Acenaphthylene	3.78	387	0.616	0.0543	392	0.2	97.9
Acenaphthene	4.87	381	0.754	0.0743	386	0.2	96.6
Fluorene	63.1	324	0.694	1.88	390	0.2	97.5
Phenanthrene	127	247	0.548	3.15	378	0.1	94.4
Anthracene	200	178	0.412	4.79	383	0.1	95.7
Fluoranthene	201	195	0.460	4.99	401	0.1	100
Pyrene	173	163	0.435	4.54	341	0.1	85.3
Benzo[a]anthracene	185	140	0.211	4.06	329	0.1	82.2
Chrysene	225	173	0.541	6.33	405	0.1	101
Benzo[b]fluoranthene	191	144	0.232	3.80	339	0.1	84.6
Benzo[k]fluoranthene	205	155	0.445	4.74	365	0.1	91.4
Benzo[a]pyrene	195	145	0.273	4.22	345	0.1	86.3
Indeno[1,2,3-cd]pyrene	210	154	0.316	4.11	369	0.1	92.2
Dibenz[a,h]anthracene	218	159	0.241	4.52	382	0.1	95.5
Benzo[ghi]perylene	221	163	0.326	4.77	389	0.1	97.3

Table 7. Breakthrough at Eight Hours
(average of 6 replicates; units of concentration are µg/sampler)

Analyte	Filter	Front resin	Back resin	cassette	total	% in backup	%rec
Naphthalene	1.26	396	1.40	0.134	399	0.4	99.7
Acenaphthylene	3.86	368	0.871	0.193	373	0.2	93.3
Acenaphthene	5.30	375	1.07	0.280	382	0.3	95.4
Fluorene	54.5	325	0.869	1.15	381	0.2	95.3
Phenanthrene	115.	255	0.668	1.71	372	0.2	93.1
Anthracene	204.	172	0.506	2.71	380	0.1	95.0
Fluoranthene	207	191	0.586	2.83	401	0.1	100
Pyrene	178	162	0.545	2.59	343	0.2	85.7
Benzo[a]anthracene	191	129	0.244	1.83	322	0.1	80.4
Chrysene	242	165	0.678	3.95	411	0.2	103
Benzo[b]fluoranthene	202	136	0.257	1.84	340	0.1	85.0
Benzo[k]fluoranthene	221	147	0.511	2.74	372	0.1	92.9
Benzo[a]pyrene	207	136	0.348	2.22	345	0.1	86.2
Indeno[1,2,3-cd]pyrene	221	144	0.388	2.46	368	0.1	92.1
Dibenz[a,h]anthracene	231	148	0.286	2.19	382	0.1	95.4
Benzo[ghi]perylene	232	152	0.427	2.47	387	0.1	96.7

Table 8. Breakthrough at Twelve Hours
(average of 6 replicates; units of concentration are µg/sampler)

Analyte	Filter	Front resin	Back resin	cassette	total	% in backup	%rec
Naphthalene	0.888	389	3.57	0.328	394	0.9	98.5
Acenaphthylene	1.97	310	2.21	0.116	314	0.7	78.5
Acenaphthene	2.84	366	2.90	0.159	372	0.8	93.0
Fluorene	34.0	327	3.17	1.51	365	0.9	91.3
Phenanthrene	78.5	269	2.91	3.18	353	0.8	88.3
Anthracene	170	173	1.53	5.56	350	0.4	87.6
Fluoranthene	156	191	1.66	5.43	355	0.5	88.7
Pyrene	150	168	1.60	5.56	326	0.5	81.4
Benzo[a]anthracene	172	131	0.966	4.80	308	0.3	77.0
Chrysene	199	151	1.50	7.76	359	0.4	89.8
Benzo[b]fluoranthene	201	149	1.08	5.30	357	0.3	89.3
Benzo[k]fluoranthene	206	153	1.32	6.64	368	0.4	91.9
Benzo[a]pyrene	191	144	1.19	5.94	343	0.3	85.7
Indeno[1,2,3-cd]pyrene	194	154	1.35	5.86	355	0.4	88.6
Dibenz[a,h]anthracene	197	151	1.22	6.02	355	0.3	88.6
Benzo[ghi]perylene	199	156	1.45	6.48	363	0.4	90.8

Table 9. Breakthrough at Sixteen Hours
(average of 6 replicates; units of concentration are µg/sampler)

Analyte	Filter	Front resin	Back resin	cassette	total	% in backup	%rec
Naphthalene	1.22	413	1.38	0.147	415	0.3	104
Acenaphthylene	2.83	315	0.122	0.102	319	0.0	79.6
Acenaphthene	4.47	389	0.194	0.157	394	0.0	98.5
Fluorene	39.30	350	0.189	2.34	392	0.0	97.9
Phenanthrene	84.1	288	0.228	4.44	376	0.1	94.1
Anthracene	183	181	0.169	8.71	373	0.0	93.1
Fluoranthene	162	207	0.200	8.17	378	0.1	94.4
Pyrene	159	179	0.228	8.06	346	0.1	86.6
Benzo[a]anthracene	181	136	0.089	8.86	325	0.0	81.3
Chrysene	216	160	0.269	11.5	388	0.1	97.1
Benzo[b]fluoranthene	216	163	0.120	10.5	389	0.0	97.4
Benzo[k]fluoranthene	227	167	0.213	11.3	405	0.1	101
Benzo[a]pyrene	203	153	0.140	10.5	367	0.0	91.7
Indeno[1,2,3-cd]pyrene	215	165	0.215	11.0	391	0.1	97.7
Dibenz[a,h]anthracene	217	159	0.133	11.0	388	0.0	97.0
Benzo[ghi]perylene	222	170	0.242	11.7	404	0.1	101

Table 10. Breakthrough at Twenty Hours
(average of 6 replicates; units of concentration are µg/sampler)

Analyte	Filter	Front resin	Back resin	cassette	total	% in backup	%rec
Naphthalene	1.87	389	3.67	0.191	394	0.9	98.6
Acenaphthylene	1.72	297	0.431	0.288	300	0.1	75.0
Acenaphthene	2.80	368	0.585	0.439	371	0.2	92.9
Fluorene	35.0	340	0.213	1.05	377	0.1	94.2
Phenanthrene	75.4	301	0.0973	1.58	378	0.0	94.6
Anthracene	180	196	0.0587	3.18	378	0.0	94.6
Fluoranthene	163	225	0.0480	3.18	391	0.0	97.9
Pyrene	151	189	0.0460	3.07	343	0.0	85.8
Benzo[a]anthracene	182	149	0.0137	3.11	335	0.0	83.7
Chrysene	219	172	0.0470	5.21	396	0.0	99.0
Benzo[b]fluoranthene	197	166	0.0237	3.57	367	0.0	91.7
Benzo[k]fluoranthene	210	170	0.0690	4.51	385	0.0	96.2
Benzo[a]pyrene	197	159	0.0403	3.88	360	0.0	90.1
Indeno[1,2,3-cd]pyrene	228	202	0.0783	4.31	434	0.0	109
Dibenz[a,h]anthracene	234	196	0.0550	4.46	434	0.0	109
Benzo[ghi]perylene	237	208	0.0847	4.91	450	0.0	112

Table 11. Breakthrough at Twenty-Four Hours
(average of 6 replicates; units of concentration are µg/sampler)

Analyte	Filter	Front resin	Back resin	cassette	total	% in backup	%rec
Naphthalene	0.537	405	2.82	0.0937	409	0.7	102
Acenaphthylene	0.923	296	0.139	0.0280	297	0.0	74.2
Acenaphthene	1.66	382	0.223	0.0467	384	0.1	96.1
Fluorene	34.6	350	0.110	1.32	386	0.0	96.6
Phenanthrene	77.5	310	0.0810	2.61	390	0.0	97.5
Anthracene	184.	197	0.0400	5.04	387	0.0	96.6
Fluoranthene	162	235	0.0730	5.04	402	0.0	101
Pyrene	154	197	0.0733	4.87	356	0.0	89.1
Benzo[a]anthracene	187	150	0.0237	4.82	338	0.0	84.5
Chrysene	229	172	0.0833	7.45	408	0.0	102
Benzo[b]fluoranthene	201	167	0.0350	5.44	373	0.0	93.3
Benzo[k]fluoranthene	217	170	0.116	6.63	394	0.0	98.5
Benzo[a]pyrene	202	158	0.0517	5.91	365	0.0	91.4
Indeno[1,2,3-cd]pyrene	244	199	0.120	6.65	450	0.0	112
Dibenz[a,h]anthracene	252	193	0.0837	7.01	452	0.0	113
Benzo[ghi]perylene	258	207	0.132	7.63	474	0.0	118

A noteworthy observation is the fact that recovery of acenaphthylene on the overall sampler drifts downward over time to below 80%. The subsequent section addresses this observation in more detail.

VII. THE TROUBLE WITH ACENAPHTHYLENE

As can be seen in Figure 4 above, recovery of acenaphthylene on the OVS-7 sampler decayed over time to less than 80%. Recovery of 70-75% is beyond the range of what one would expect to be written off as experimental error.

Since there is no appreciable amount (above the LOD) of analyte showing up in the backup section, it is assumed that the acenaphthylene is not being drawn out the back end of the sampler. A more logical hypothesis is that this analyte is undergoing oxidation or photolysis over time. A full-scan analysis of the desorbate from the front resin section from one of the 24-hour samplers shows evidence that oxidation reactions are indeed taking place.

Figure 8 shows the structure of acenaphthylene. Figure 9 shows the probable chemical structure of one of the observed breakdown products. The identity of this breakdown product is based on interpretation of the mass spectral data utilizing a library search of the NBS spectral database. The chromatogram is presented in Figure 10.

Figure 8. Chemical Structure of Acenaphthylene.

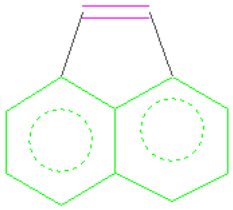


Figure 9. Structure of Degradation Product at RT 10.780 minutes (Acenaphthenone)

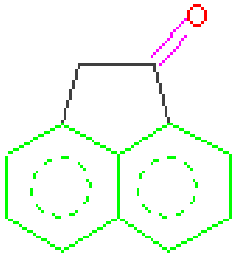
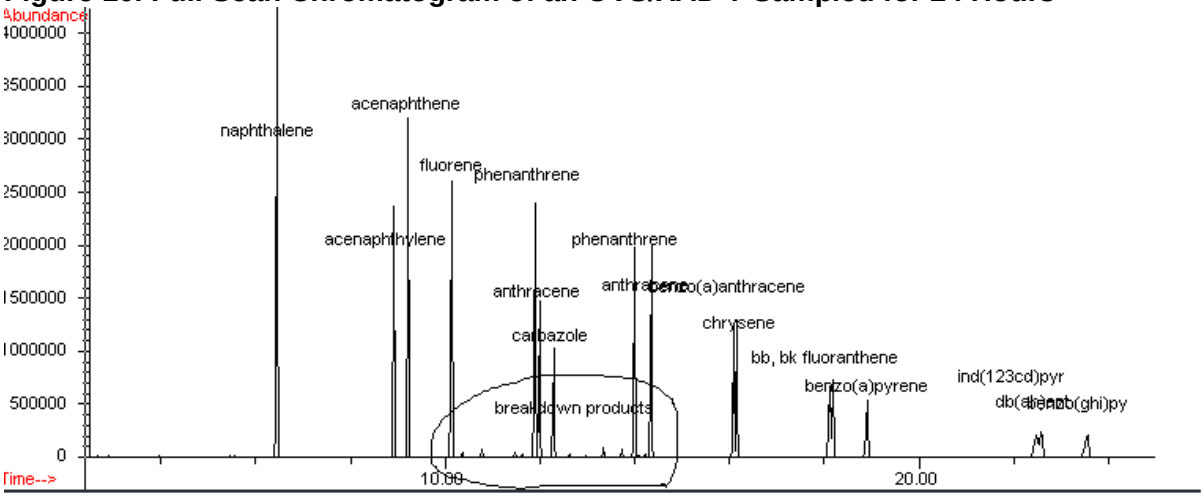


Figure 10. Full Scan Chromatogram of an OVS/XAD-7 Sampled for 24 Hours



An examination of these full scan data gives evidence that acenaphthylene may in fact be degrading to one or more reaction products during sampling. The evidence is not conclusive; for example, some of these breakdown products appear to be fluorene derivatives, yet fluorene recovery is not significantly inhibited over time. The presence of acenaphthenone as a breakdown product does, however, provide substantiation that acenaphthylene loss may be a result of degradation

reactions during the sampling event even though the precise nature of the acenaphthylene degradation remained unknown. A brief experiment was conducted to determine whether the degradation of acenaphthylene could be avoided by protecting the sampler from light. Six OVS-7 tubes were spiked with acenaphthylene and sampled for 24 hours under the same conditions used in the breakthrough study. Another six devices were then spiked with acenaphthylene and protected from light for the 24-hour sampling time. The results were somewhat inconclusive, with the protected tubes showing slightly better acenaphthylene recovery (about 14% better); however, both batches showed evidence of breakdown. For example, reaction product acenaphthenone was detected in both the protected and the unprotected sampling devices.

Regardless of the impact of light, it is not realistic to expect that an industrial hygienist in the field would be able to protect the OVS tube from light during a sampling event, and for this reason no further investigation into the causes of acenaphthylene degradation was undertaken. End users of the data should understand that breakdown of this analyte does occur during sampling and that reported concentrations of acenaphthylene will likely be biased somewhat low.

Because of these results/observations, an 8-hr sampling time is the maximum recommended.

VIII. LIMIT OF DETECTION AND QUANTITATION STUDY

The limit of detection (LOD) for this method lies somewhere between 0.08 and 0.4 µg/sample. It is possible to see GC peaks for most analytes at a level below 0.08 µg/sample, but there are some problems inherent with going too low in the calibration range. One results from the ubiquitous nature of PAHs; namely that some PAHs will often be detected in the media blanks at levels very much below 0.08 µg/sample. Another problem is that peak shapes tend to deteriorate at extremely low concentration levels. This poses a problem particularly for isomeric pairs that elute closely together. These include benzo[b]- and benzo[k]fluoranthene as well as benz[a]anthracene and chrysene. The worst of these is the benz[a]anthracene/chrysene pair, which becomes increasingly difficult to separate at the lower levels and increasingly distorted in terms of peak-area proportionality. Indeno[1,2,3-cd]pyrene is also problematic because its peak (base peak of m/z = 276) has a hump produced by the dibenz[a,h]anthracene peak, which has a 276 ion as one of the minor ions in its spectrum. At the higher levels this hump can be distinguished and excluded from the integrated area. In the lower levels it cannot.

Figures 11 through 14 demonstrate some of these problems, which arise from calibrating at too low a concentration level.

Figure 11. Benz[a]anthracene and Chrysene in a High Standard

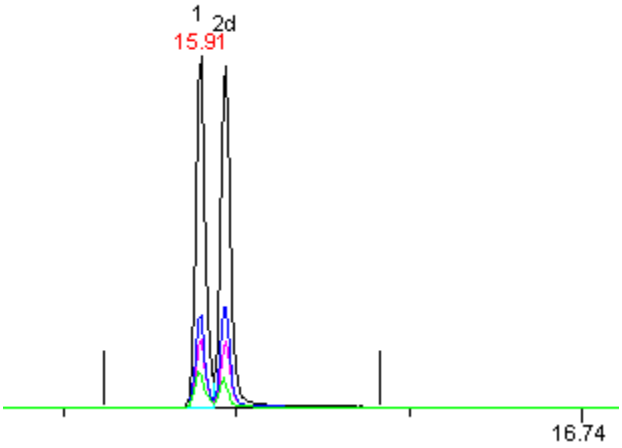


Figure 12. Benz[a]anthracene and Chrysene in a Low Standard

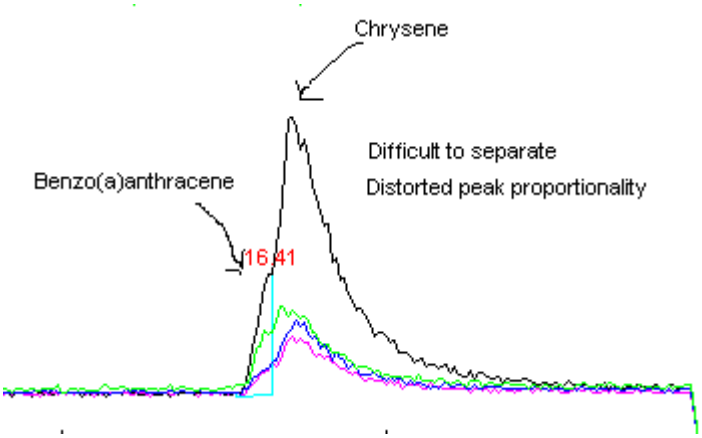


Figure 13. Indeno[1,2,3-cd]pyrene in a High Standard

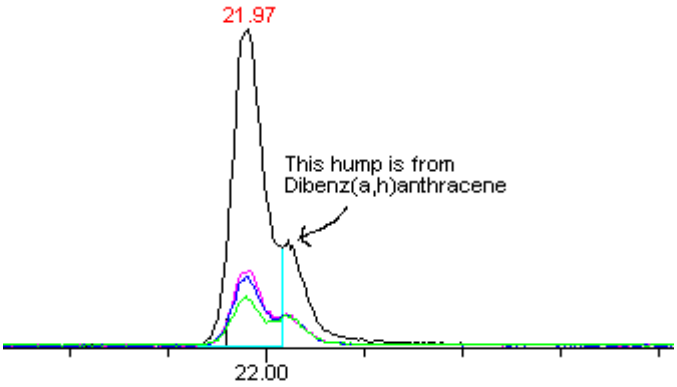
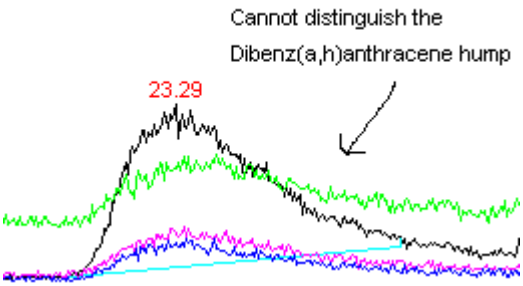


Figure 14. Indeno[1,2,3-cd]pyrene in a Low Standard



Based upon the experience gained from method development experiments and from analysis of a moderate number of field samples submitted by NIOSH during the term of the method development, it has been determined that the optimal LOD target is about 0.1 µg/sample for most of the PAHs on the target analyte list. Using calibration standards prepared at concentrations of 0.08, 0.12, 0.4, 4, 10 and 40 µg/sample and applying the Burkart Method [10] for statistical calculations, an LOD ranging from 0.08 to 0.4 µg/sample is generally obtainable for the various analytes. The resulting limit of quantitation (LOQ) is defined as 3.33 times the LOD, with results in LOQ values ranging from 0.3 to 1 µg/sample. The LOD and LOQ will vary from batch to batch depending on the statistics of each individual calibration curve.

IX. LONG-TERM STABILITY STUDY

This experiment is designed to assess the stability of target analytes over time. Forty-three OVS tubes were spiked with 4.0 µL of the PAH mixture (Absolute Standards mix 10007 at 2000

µg/mL), which corresponded to a level of about 30 times the LOQ, or about 8 µg/sample. Seven of these samplers were desorbed immediately and analyzed the same day. The remaining samplers were divided into two groups. One group was stored at room temperature and the other refrigerated at 4 °C.

After seven days, six of the refrigerated samples and six of the ambient-stored samples were desorbed and analyzed. On Days 10, 14, and 21, three of each were desorbed and analyzed, and on Day 30, six of each were desorbed and analyzed.

The results are shown in Tables 12-24. All analytes are stable for up to thirty days from sampling as all average recoveries are greater than 80%. Refrigeration is not required for stability. However, it should be noted that at nearly every sampling point, the recovery from the refrigerated samples is a bit better. Therefore, it is recommended that the samples be refrigerated upon arrival at the laboratory.

Even the problematic acenaphthylene was shown to be stable under storage for up to thirty days. Unlike the precision and accuracy study (discussed in the subsequent section) in which air was drawn through the samplers for four hours prior to analysis, these stability-study samplers were spiked and then immediately capped for storage. The fact that acenaphthylene exhibits good storage stability gives evidence that it is the passage of air through the sampler which is the likely cause of degradation seen in other experiments. Acenaphthylene does not appear to degrade under anaerobic storage.

Table 12. Sample Storage Stability on Day Zero (as % recovery)

Analyte	#1	#2	#3	#4	#5	#6	#7	Average
Naphthalene	91.9	93.4	97.3	94.6	91.6	90.0	108	95.2
Acenaphthylene	92.1	87.5	91.4	93.7	88.4	86.9	108	92.6
Acenaphthene	91.6	89.8	94.6	94.6	86.2	91.3	108	93.7
Fluorene	92.3	88.7	90.3	94.8	83.1	85.3	107	91.7
Phenanthrene	94.1	88.5	91.9	92.1	89.5	83.8	106	92.3
Anthracene	92.7	94.1	90.5	90.7	89.4	89.8	107	93.5
Fluoranthene	90.8	90.8	92.8	85.8	89.5	88.3	108	92.3
Pyrene	90.0	84.0	87.6	97.3	95.5	86.9	110	93.0
Benzo[a]anthracene	90.1	88.9	92.1	92.3	91.9	83.5	109	92.6
Chrysene	95.6	88.5	92.8	101.7	90.0	86.1	105	94.2
Benzo[b]fluoranthene	91.7	93.4	97.3	90.7	87.7	87.7	109	93.9
Benzo[k]fluoranthene	93.3	90.1	95.7	90.0	89.8	87.9	107	93.3
Benzo[a]pyrene	91.4	95.0	94.1	92.0	91.8	91.6	109	94.9
Indeno[1,2,3-cd]pyrene	88.8	93.4	90.4	89.5	91.5	84.2	113	92.9
Dibenz[a,h]anthracene	90.3	93.3	91.9	86.7	94.7	87.8	110	93.5
Benzo[ghi]perylene	87.2	95.0	90.3	92.9	97.0	89.9	113	95.0

Table 13. Sample Storage Stability at Ambient Temperature on Day Seven
(as % recovery)

Analyte	#1	#2	#3	#4	#5	#6	Average
Naphthalene	89.4	84.3	89.0	89.8	88.5	91.6	88.8
Acenaphthylene	82.1	87.0	83.0	88.2	86.5	91.8	86.4
Acenaphthene	82.4	87.1	81.6	89.1	88.9	93.6	87.1
Fluorene	85.8	86.6	86.2	93.7	84.7	87.0	87.3
Phenanthrene	88.0	85.2	92.1	88.7	89.0	91.1	89.0
Anthracene	93.7	92.5	94.4	98.1	93.4	94.4	94.4
Fluoranthene	85.4	86.1	92.6	89.4	87.9	83.6	87.5
Pyrene	91.5	97.7	96.0	92.2	93.9	98.0	94.9
Benzo[a]anthracene	86.5	85.9	92.8	85.3	85.5	87.7	87.3
Chrysene	85.3	92.2	93.6	89.9	92.7	91.5	90.8
Benzo[b]fluoranthene	91.5	90.0	98.4	96.3	92.3	91.0	93.3
Benzo[k]fluoranthene	93.2	94.6	97.1	93.5	92.9	96.8	94.7
Benzo[a]pyrene	92.5	90.5	95.9	93.6	90.5	95.5	93.1
Indeno[1,2,3-cd]pyrene	88.2	93.0	99.1	89.4	93.6	94.9	93.0
Dibenz[a,h]anthracene	87.1	90.7	99.2	88.6	89.8	93.3	91.4
Benzo[ghi]perylene	93.0	96.3	105	93.8	93.5	99.5	96.8

Table 14. Sample Storage Stability under Refrigeration on Day Seven
(as % recovery)

Analyte	#1	#2	#3	#4	#5	#6	Average
Naphthalene	91.6	89.9	87.4	86.0	93.2	93.1	90.2
Acenaphthylene	87.5	94.7	91.9	86.2	91.0	95.0	91.1
Acenaphthene	88.3	91.8	90.2	85.1	92.5	92.7	90.1
Fluorene	83.8	88.2	87.5	84.4	90.9	92.8	87.9
Phenanthrene	88.9	96.7	91.0	88.4	89.5	90.7	90.9
Anthracene	98.4	101	96.6	94.9	92.3	96.7	96.7
Fluoranthene	88.4	94.1	91.8	89.1	88.7	92.0	90.7
Pyrene	96.6	91.7	91.0	91.6	99.2	96.8	94.5
Benzo[a]anthracene	89.9	86.8	87.0	86.3	92.8	91.7	89.1
Chrysene	92.4	91.6	87.9	89.1	94.9	95.9	91.9
Benzo[b]fluoranthene	92.2	93.1	95.3	87.7	92.7	93.4	92.4
Benzo[k]fluoranthene	95.6	93.9	105	89.9	97.8	101	97.1
Benzo[a]pyrene	95.3	95.4	97.8	91.6	99.9	99.3	96.5
Indeno[1,2,3-cd]pyrene	92.7	94.3	97.9	87.2	97.8	101	95.1
Dibenz[a,h]anthracene	95.7	94.4	95.7	86.1	95.6	100	94.6
Benzo[ghi]perylene	98.8	97.3	100	85.4	100	107	98.1

Table 15. Sample Storage Stability at Ambient Temperature on Day Ten (as % recovery)

Analyte	#1	#2	#3	Average
Naphthalene	87.2	84.5	82.3	84.6
Acenaphthylene	84.4	80.9	77.8	81.0
Acenaphthene	84.5	80.6	80.0	81.7
Fluorene	86.0	83.1	82.2	83.8
Phenanthrene	86.1	83.4	81.3	83.6
Anthracene	84.9	81.8	82.3	83.0
Fluoranthene	86.2	80.8	82.1	83.0
Pyrene	86.0	86.4	85.9	86.1
Benzo[a]anthracene	83.7	82.1	81.4	82.4
Chrysene	84.8	82.3	80.0	82.4
Benzo[b]fluoranthene	94.3	83.9	84.8	87.7
Benzo[k]fluoranthene	91.6	81.8	84.7	86.0
Benzo[a]pyrene	84.2	80.6	80.2	81.7
Indeno[1,2,3-cd]pyrene	72.2	93.1	82.7	82.6
Dibenz[a,h]anthracene	70.0	94.3	78.3	80.9
Benzo[ghi]perylene	66.6	95.4	80.7	80.9

Table 16. Sample Storage Stability under Refrigeration on Day Ten (as % recovery)

Analyte	#1	#2	#3	Average
Naphthalene	88.7	86.9	91.4	89.0
Acenaphthylene	85.6	87.5	89.9	87.7
Acenaphthene	86.7	88.8	91.0	88.8
Fluorene	89.0	86.3	89.9	88.4
Phenanthrene	86.2	87.3	91.9	88.4
Anthracene	84.0	87.1	90.6	87.2
Fluoranthene	83.0	85.6	89.6	86.1
Pyrene	91.5	95.1	90.3	92.3
Benzo[a]anthracene	88.2	87.3	88.0	87.8
Chrysene	86.3	88.9	91.5	88.9
Benzo[b]fluoranthene	92.0	89.1	92.7	91.2
Benzo[k]fluoranthene	90.4	90.5	93.7	91.5
Benzo[a]pyrene	85.5	86.0	91.1	87.5
Indeno[1,2,3-cd]pyrene	87.2	84.8	86.1	86.0
Dibenz[a,h]anthracene	84.1	86.0	87.8	86.0
Benzo[ghi]perylene	83.9	88.6	92.1	88.2

Table 17. Sample Storage Stability at Ambient Temperature on Day Fourteen (as % recovery)

Analyte	#1	#2	#3	Average
Naphthalene	77.9	101	73.6	84.1
Acenaphthylene	83.4	107	77.3	89.2
Acenaphthene	82.4	108	78.1	89.6
Fluorene	80.0	108	76.4	88.0
Phenanthrene	81.6	108	76.3	88.7
Anthracene	81.5	108	72.9	87.4
Fluoranthene	81.7	106	74.7	87.3
Pyrene	76.6	102	87.0	88.7
Benzo[a]anthracene	81.6	104	72.0	85.8
Chrysene	78.4	107	77.9	87.7
Benzo[b]fluoranthene	79.1	119	64.8	87.6
Benzo[k]fluoranthene	76.6	127	65.7	89.6
Benzo[a]pyrene	79.0	113	73.1	88.4
Indeno[1,2,3-cd]pyrene	73.1	123	89.0	95.2
Dibenz[a,h]anthracene	75.6	122	88.1	95.2
Benzo[ghi]perylene	76.1	119	85.2	93.4

Table 18. Sample Storage Stability under Refrigeration on Day Fourteen (as % recovery)

Analyte	#1	#2	#3	Average
Naphthalene	83.9	78.3	106	89.5
Acenaphthylene	89.7	82.9	110	94.1
Acenaphthene	89.5	82.2	108	93.2
Fluorene	88.5	81.6	99.5	89.9
Phenanthrene	89.3	81.9	104	91.8
Anthracene	89.0	80.7	94.3	88.0
Fluoranthene	89.5	81.7	104	91.7
Pyrene	87.2	79.3	101	89.0
Benzo[a]anthracene	88.9	81.3	79.9	83.4
Chrysene	87.9	79.3	83.9	83.7
Benzo[b]fluoranthene	74.4	78.8	90.5	81.2
Benzo[k]fluoranthene	71.4	80.7	98.1	83.4
Benzo[a]pyrene	80.4	81.3	88.0	83.2
Indeno[1,2,3-cd]pyrene	69.8	88.3	91.9	83.3
Dibenz[a,h]anthracene	69.9	88.0	98.1	85.3
Benzo[ghi]perylene	70.4	81.3	114	88.7

Table 19. Sample Storage Stability at Ambient Temperature on Day Twenty One (as % recovery)

Analyte	#1	#2	#3	Average
Naphthalene	85.8	87.0	88.8	87.2
Acenaphthylene	90.7	92.4	94.0	92.3
Acenaphthene	94.5	88.5	92.5	91.8
Fluorene	97.0	91.6	96.3	94.9
Phenanthrene	94.5	95.1	94.9	94.8
Anthracene	93.8	94.4	91.8	93.3
Fluoranthene	84.3	88.5	84.2	85.7
Pyrene	92.3	94.9	91.4	92.8
Benzo[a]anthracene	85.9	88.3	85.9	86.7
Chrysene	93.8	95.6	94.6	94.7
Benzo[b]fluoranthene	94.3	86.5	88.4	89.7
Benzo[k]fluoranthene	101	94.3	96.4	97.2
Benzo[a]pyrene	95.3	91.3	93.0	93.2
Indeno[1,2,3-cd]pyrene	92.9	81.3	86.7	87.0
Dibenz[a,h]anthracene	93.6	87.8	88.2	89.9
Benzo[ghi]perylene	98.8	86.6	90.8	92.1

Table 20. Sample Storage Stability under Refrigeration on Day Twenty One (as % recovery)

Analyte	#1	#2	#3	Average
Naphthalene	93.0	87.9	96.3	92.4
Acenaphthylene	99.4	94.8	92.7	95.6
Acenaphthene	98.0	91.1	93.1	94.1
Fluorene	103	93.7	96.2	97.7
Phenanthrene	103	96.1	95.3	98.0
Anthracene	103	94.6	93.9	97.0
Fluoranthene	105	94.8	93.6	97.9
Pyrene	101	95.3	94.5	97.0
Benzo[a]anthracene	93.5	90.3	86.2	90.0
Chrysene	99.9	93.6	98.3	97.3
Benzo[b]fluoranthene	95.4	95.2	95.5	95.4
Benzo[k]fluoranthene	106	101	97.1	102
Benzo[a]pyrene	99.8	96.5	95.5	97.3
Indeno[1,2,3-cd]pyrene	93.3	89.7	88.3	90.4
Dibenz[a,h]anthracene	97.8	88.0	91.8	92.5
Benzo[ghi]perylene	101	92.0	92.2	95.1

Table 21. Sample Storage Stability at Ambient Temperature on Day Thirty (as % recovery)

Analyte	#1	#2	#3	#4	#5	#6	Average
Naphthalene	85.2	86.1	88.6	94.8	87.6	90.7	88.8
Acenaphthylene	92.4	98.2	95.0	101	97.4	96.7	96.7
Acenaphthene	92.7	97.8	94.8	99.5	96.3	98.1	96.5
Fluorene	92.4	103	93.7	102	98.9	102	98.5
Phenanthrene	95.6	99.4	97.2	102	92.8	101	98.1
Anthracene	95.9	97.0	97.0	104	95.2	98.7	97.9
Fluoranthene	97.8	101	86.1	102	94.9	101	97.2
Pyrene	90.6	97.1	95.0	95.0	90.0	97.6	94.2
Benzo[a]anthracene	91.2	96.0	86.3	97.4	88.0	93.6	92.1
Chrysene	90.9	94.4	96.1	101	95.6	98.2	96.0
Benzo[b]fluoranthene	90.0	95.1	92.5	102	89.2	97.1	94.2
Benzo[k]fluoranthene	95.1	99.5	99.2	101	93.2	98.1	97.6
Benzo[a]pyrene	90.7	97.2	96.6	101	92.8	96.2	95.8
Indeno[1,2,3-cd]pyrene	90.9	96.3	92.7	98.4	93.9	93.5	94.3
Dibenz[a,h]anthracene	89.2	94.1	90.9	98.8	91.1	96.4	93.4
Benzo[ghi]perylene	89.7	97.4	94.2	101	91.3	95.6	94.9

Table 22. Sample Storage Stability under Refrigeration on Day Thirty (as % recovery)

Analyte	#1	#2	#3	#4	#5	#6	Average
Naphthalene	87.2	88.9	89.4	98.5	92.7	87.3	90.6
Acenaphthylene	94.2	95.0	94.0	105	96.4	98.2	97.1
Acenaphthene	94.3	95.8	95.1	104	96.3	95.4	96.9
Fluorene	96.5	98.4	98.4	109	96.3	98.1	99.5
Phenanthrene	91.5	93.9	96.2	107	101	101	98.4
Anthracene	94.4	93.3	98.2	106	99.0	101	98.5
Fluoranthene	86.1	84.3	96.6	108	96.7	88.9	93.3
Pyrene	88.9	89.7	92.2	99.6	93.2	96.0	93.3
Benzo[a]anthracene	90.8	90.7	89.9	99.9	94.1	91.6	92.8
Chrysene	91.3	96.3	96.5	105	97.7	97.1	97.4
Benzo[b]fluoranthene	93.4	95.1	96.0	108	94.1	93.2	96.6
Benzo[k]fluoranthene	95.3	95.1	103	105	100	102	100
Benzo[a]pyrene	96.0	95.4	97.4	106	96.4	97.4	98.1
Indeno[1,2,3-cd]pyrene	92.5	91.3	94.4	104	93.9	97.3	95.5
Dibenz[a,h]anthracene	96.1	94.8	95.4	104	92.7	96.4	96.6
Benzo[ghi]perylene	93.7	93.2	97.2	108	95.1	99.8	97.8

Table 23. Average Storage Stabilities Relative to Day Zero Recoveries At Ambient Temperature (as % recovery)

Analyte	0 day	7 day	10 day	14 day	21 day	30 day
Naphthalene	100	93.3	88.9	88.3	91.6	93.3
Acenaphthylene	100	93.3	87.5	96.3	99.7	104
Acenaphthene	100	93.0	87.2	95.6	98.0	103
Fluorene	100	95.2	91.4	96.0	104	107
Phenanthrene	100	96.4	101	96.1	103	106
Anthracene	100	101	99.5	93.5	99.8	105
Fluoranthene	100	94.8	101	94.6	92.8	105
Pyrene	100	91.3	103	95.4	99.8	101
Benzo[a]anthracene	100	94.3	89.0	92.7	93.6	99.5
Chrysene	100	96.4	87.5	93.1	101	102
Benzo[b]fluoranthene	100	99.4	93.4	93.3	95.5	100
Benzo[k]fluoranthene	100	102	92.2	96.0	104	105
Benzo[a]pyrene	100	98.1	86.1	93.2	98.2	101
Indeno[1,2,3-cd]pyrene	100	100	88.9	103	93.6	102
Dibenz[a,h]anthracene	100	97.8	86.5	102	96.1	99.9
Benzo[ghi]perylene	100	102	85.2	98.3	96.9	99.9

Table 24. Average Long-Term Storage Stabilities Relative to Day Zero Recoveries at Refrigerated Temperature (as % recovery)

Analyte	0 day	7 day	10 day	14 day	21 day	30 day
Naphthalene	100	94.7	93.5	94.0	97.1	95.2
Acenaphthylene	100	98.4	94.7	102	103	105
Acenaphthene	100	96.2	94.8	99.5	100	103
Fluorene	100	95.9	96.4	98.0	107	109
Phenanthrene	100	98.5	95.8	99.5	106	107
Anthracene	100	103	93.3	94.1	104	105
Fluoranthene	100	98.3	93.3	99.3	106	101
Pyrene	100	102	99.2	95.7	104	100
Benzo[a]anthracene	100	96.2	94.8	90.1	97.2	100
Chrysene	100	97.6	94.4	88.9	103	103
Benzo[b]fluoranthene	100	98.4	97.1	86.5	102	103
Benzo[k]fluoranthene	100	104	98.1	89.4	109	107
Benzo[a]pyrene	100	102	92.2	87.7	103	103
Indeno[1,2,3-cd]pyrene	100	102	92.6	89.7	97.3	103
Dibenz[a,h]anthracene	100	101	92.0	91.1	98.9	103
Benzo[ghi]perylene	100	103	92.8	93.4	100	103

IX. PRECISION, ACCURACY, AND BIAS STUDY

A study was performed to determine the precision, accuracy, and bias of the method. Concentration levels ranging from this study's LOQ to 300× LOQ were used. Seven samplers at each of the following levels were spiked with target compounds to produce the desired concentrations: 0.25 µg/sample, 0.75 µg/sample, 2.50 µg/sample, 7.50 µg/sample, 25.0 µg/sample, and 75.0 µg/sample. The OVS-7 tubes were then placed in an environmental chamber and air was drawn through each sampler at a rate of 1 liter per minute for four hours. The samples were prepared and analyzed according to the method. Table 25 displays the average recoveries of the analytes over the ranges studied. Following Table 25 are tables for each analyte (Tables 26-41). These tables contain the recoveries for each replicate for each of the six concentration levels used. The recoveries are given in µg/sample (sample being 1 mL) and in percent recovery.

Table 25. Average percent recoveries over various levels

Analyte (by retention time)	0.25 (µg/sample)	0.75 (µg/sample)	2.50 (µg/sample)	7.5 (µg/sample)	25.0 (µg/sample)	75.0 (µg/sample)	Pooled CV
Naphthalene	110	96.3	101	87.6	95.1	85.7	0.0305
Acenaphthylene	**64.7**	**71.0**	**57.9**	**67.5**	87.0	78.3	0.0340
Acenaphthene	97.1	92.6	96.1	87.6	93.8	83.8	0.0258
Fluorene	95.7	92.3	98.2	90.8	97.4	85.0	0.0309
Phenanthrene	97.1	92.3	99.6	90.1	98.6	86.3	0.0249
Anthracene	75.7	83.1	89.0	86.3	97.4	84.1	0.0323
Fluoranthene	95.1	92.6	97.8	91.9	105	87.4	0.0367
Pyrene	92.3	91.4	92.7	89.3	99.1	86.2	0.0474
Benz[a]anthracene	86.7	86.1	94.7	92.1	103	86.4	0.0352
Chrysene	96.9	92.5	99.7	86.4	94.3	85.3	0.0315
Benzo[b]fluoranthene	92.8	91.6	95.7	91.7	104	87.4	0.0294
Benzo[k]fluoranthene	83.0	86.3	101	91.0	97.5	86.7	0.0387
Benzo[a]pyrene	**70.1**	76.5	85.8	87.4	102	85.1	0.0370
Indeno[1,2,3-c,d]pyrene	80.5	81.4	86.1	90.9	103	91.0	0.0545
Dibenz[a,h]anthracene	86.7	87.3	105	102	109	89.0	0.0463
Benzo[ghi]perylene	87.9	86.0	104	102	109	91.7	0.0493

(1) Recoveries less than 75% are highlighted in bold numerals. (See comments in following text.)
(2) This table summarizes data in Tables 26-42

TABLE 26. ACENAPHTHENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

Int Std: Acenaphthene-D_{10}; Quant. ion (*m/z*): 153

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.242	96.8	0.666	88.8	2.36	94.2	6.92	92.2	22.7	90.6	65.6	87.5
2	0.254	102	0.688	91.7	2.48	99.0	6.39	85.2	22.9	91.8	60.4	80.5
3	0.242	96.8	0.684	91.2	2.49	99.5	6.66	88.8	23.0	92.1	62.3	83.1
4	0.238	95.2	0.716	95.5	2.39	95.8	6.61	88.2	24.0	96.1	61.4	81.9
5	0.240	96.0	0.716	95.5	2.30	91.9	6.40	85.3	24.0	96.0	62.3	83.1
6	0.242	96.8	0.682	90.9	2.36	94.3	6.92	92.2	23.5	94.1	64.4	85.9
7	0.242	96.8	0.710	94.7	2.44	97.5	6.10	81.3	23.9	95.8	63.5	84.6
average =	0.243	97.1	0.695	92.6	2.40	96.1	6.57	87.6	23.4	93.8	62.8	83.8
std dev =	0.00515	2.06	0.0195	2.60	0.0696	2.79	0.299	3.99	0.570	2.28	1.78	2.38

TABLE 27. ANTHRACENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

Int Std: Phenanthrene-D_{10}; Quant. ion (*m/z*):178

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.196	78.4	0.646	86.1	2.20	87.92	6.90	92.00	23.8	95.15	64.8	86.4
2	0.196	78.4	0.600	80.0	2.31	92.32	6.39	85.23	23.6	94.50	60.5	80.7
3	0.180	72.0	0.632	84.3	2.30	91.84	6.41	85.47	23.6	94.55	62.5	83.4
4	0.198	79.2	0.604	80.5	2.21	88.32	6.55	87.36	24.9	99.59	62.3	83.1
5	0.176	70.4	0.644	85.9	2.11	84.64	6.28	83.79	25.1	100.25	62.5	83.4
6	0.192	76.8	0.608	81.1	2.19	87.60	6.69	89.20	24.7	98.78	64.9	86.5
7	0.186	74.4	0.630	84.0	2.25	90.00	6.09	81.20	24.8	99.15	64.0	85.3
average =	0.189	75.7	0.623	83.1	2.22	88.95	6.47	86.32	24.4	97.43	63.1	84.1
std dev =	0.00863	3.45	0.0192	2.56	0.0667	2.6667	0.267	3.5636	0.641	2.5634	1.56	2.08

TABLE 28. ACENAPHTHYLENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

Int Std: Acenaphthene-D_{10}; Quant. ion (*m/z*): 152

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.180	**72.0**	0.548	**73.1**	1.42	**57.0**	5.49	**73.3**	20.2	80.7	61.4	81.8
2	0.162	**64.8**	0.456	**60.8**	1.55	**61.9**	4.97	**66.3**	21.5	85.9	56.2	74.9
3	0.156	**62.4**	0.574	**76.5**	1.56	**62.5**	5.12	**68.2**	21.5	85.9	58.5	78.0
4	0.160	**64.0**	0.496	**66.1**	1.51	**60.6**	5.22	**69.6**	21.9	87.7	57.5	76.7
5	0.148	**59.2**	0.522	**69.6**	1.22	**48.9**	4.77	**63.7**	22.4	89.5	58.1	77.5
6	0.164	**65.6**	0.554	**73.9**	1.44	**57.5**	5.19	**69.2**	22.1	88.4	60.5	80.7
7	0.162	**64.8**	0.576	76.8	1.43	**57.0**	4.68	**62.4**	22.7	90.6	58.9	78.6
average =	0.162	**64.7**	0.532	**71.0**	1.45	**57.9**	5.06	**67.5**	21.7	87.0	58.7	78.3
std dev =	0.00969	3.88	0.0440	5.87	0.115	4.61	0.278	3.71	0.814	3.25	1.77	2.36

TABLE 29. BENZ[a]ANTHRACENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

Int Std: Chrysene-D_{12}; Quant. ion (*m/z*): 228

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.224	89.6	0.644	85.9	2.35	94.1	7.15	95.3	24.37	97.5	66.4	88.6
2	0.230	92.0	0.634	84.5	2.49	99.5	6.70	89.4	24.9	99.4	62.1	82.8
3	0.216	86.4	0.622	82.9	2.41	96.3	6.84	91.3	25.2	101	62.6	83.5
4	0.212	84.8	0.632	84.3	2.31	92.4	7.13	95.0	26.5	106	65.1	86.8
5	0.204	81.6	0.672	89.6	2.33	93.0	6.79	90.6	26.7	107	64.1	85.5
6	0.218	87.2	0.634	84.5	2.38	95.1	7.18	95.7	26.3	105	67.2	89.7
7	0.214	85.6	0.682	90.9	2.32	92.6	6.54	87.2	26.6	107	66.0	88.1
average =	0.217	86.7	0.646	86.1	2.37	94.7	6.90	92.1	25.8	103	64.8	86.4
std dev =	0.00840	3.36	0.0225	3.00	0.0635	2.54	0.251	3.34	0.956	3.82	1.96	2.61

TABLE 30. BENZO[b]FLUORANTHENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

Int Std: Perylene-D_{12}; Quant. ion (*m/z*): 252

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.232	92.8	0.664	88.5	2.39	95.6	7.06	94.2	24.3	97.4	67.7	90.2
2	0.244	97.6	0.676	90.1	2.46	98.3	6.71	89.5	25.2	101	63.3	84.4
3	0.234	93.6	0.694	92.5	2.46	98.6	6.87	91.6	25.4	101	63.6	84.8
4	0.228	91.2	0.682	90.9	2.32	93.0	6.97	93.0	26.8	107	64.6	86.1
5	0.224	89.6	0.704	93.9	2.44	97.5	6.66	88.8	27.1	108	65.0	86.6
6	0.226	90.4	0.668	89.1	2.36	94.4	7.25	96.7	26.2	105	67.7	90.2
7	0.236	94.4	0.720	96.0	2.32	92.6	6.64	88.5	27.4	110	66.9	89.3
average =	0.232	92.8	0.687	91.6	2.39	95.7	6.88	91.7	26.1	104	65.5	87.4
std dev =	0.00683	2.73	0.0203	2.70	0.0620	2.48	0.231	3.08	1.12	4.50	1.86	2.48

TABLE 31. BENZO[k]FLUORANTHENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

Int Std: Perylene-D_{12}; Quant. ion (*m/z*): 252

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.214	85.6	0.642	85.6	2.49	99.6	6.95	92.7	23.0	91.9	67.2	89.7
2	0.230	92.0	0.640	85.3	2.59	104	6.71	89.4	23.8	95.2	62.4	83.2
3	0.204	81.6	0.642	85.6	2.57	103	6.95	92.7	23.9	95.8	63.7	85.0
4	0.208	83.2	0.656	87.5	2.41	96.4	6.93	92.4	24.5	98.1	65.3	87.1
5	0.206	82.4	0.660	88.0	2.56	102	6.56	87.5	25.0	100	62.7	83.6
6	0.190	76.0	0.634	84.5	2.57	103	7.14	95.2	25.0	100	67.6	90.1
7	0.200	80.0	0.658	87.7	2.46	98.5	6.55	87.3	25.4	101	66.5	88.6
average =	0.207	83.0	0.647	86.3	2.52	100	6.83	91.0	24.4	97.5	65.1	86.7
std dev =	0.0124	4.97	0.0103	1.37	0.0679	2.71	0.224	2.99	0.849	3.39	2.14	2.86

TABLE 32. BENZO[ghi]PERYLENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

Int Std: Perylene-D_{12}; Quant. ion (*m/z*): 276

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.236	94.4	0.628	83.7	2.63	105	8.00	107	25.5	102	69.8	93.0
2	0.226	90.4	0.644	85.9	2.61	104	7.79	104	25.7	103	65.5	87.3
3	0.212	84.8	0.618	82.4	2.61	104	7.58	101	26.0	104	69.5	92.6
4	0.216	86.4	0.612	81.6	2.59	104	7.78	104	28.8	115	66.1	88.2
5	0.200	80.0	0.712	94.9	2.47	98.6	7.61	101	28.2	113	66.9	89.3
6	0.244	97.6	0.634	84.5	2.71	108	8.02	107	27.7	111	73.3	97.7
7	0.204	81.6	0.668	89.1	2.66	106	6.66	88.9	28.7	115	70.6	94.2
average =	0.220	87.9	0.645	86.0	2.61	104	7.64	102	27.2	109	68.8	91.7
std dev =	0.0164	6.54	0.0348	4.63	0.0744	2.98	0.461	6.15	1.45	5.78	2.78	3.70

TABLE 33. BENZO[a]PYRENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

Int Std: Perylene-D_{12}; Quant. ion (*m/z*): 252

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.188	75.2	0.576	76.8	2.16	86.4	6.76	90.1	24.1	96.4	65.6	87.5
2	0.190	76.0	0.560	74.7	2.26	90.3	6.56	87.5	24.8	99.2	61.1	81.5
3	0.172	**68.8**	0.584	77.9	2.20	88.2	6.63	88.4	25.3	101	62.6	83.4
4	0.178	**71.2**	0.556	74.1	2.02	81,0	6.78	90.4	26.3	105	63.2	84.3
5	0.162	**64.8**	0.616	82.1	2.11	84.2	6.33	84.4	26.7	107	62.7	83.6
6	0.176	**70.4**	0.556	74.1	2.17	86.8	6.80	90.7	26.1	104	66.5	88.7
7	0.160	**64.0**	0.566	75.5	2.10	83.8	6.03	80.4	26.8	107	65.1	86.9
average =	0.175	**70.1**	0.573	76.5	2.15	85.8	6.55	87.4	25.7	103	63.8	85.1
std dev =	0.0116	4.64	0.0215	2.87	0.0771	3.08	0.284	3.78	1.01	4.04	1.95	2.60

TABLE 34. CHRYSENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

INT STD: Chrysene-D_{12}; Quant. ion (*m/z*): 228

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.244	97.6	0.656	87.5	2.50	100	7.02	93.6	22.5	89.9	66.4	88.5
2	0.254	102	0.708	94.4	2.55	102	6.57	87.6	22.8	91.4	61.9	82.6
3	0.238	95.2	0.686	91.5	2.52	101	6.74	89.8	23.1	92.4	62.5	83.4
4	0.240	96.0	0.690	92.0	2.40	96.0	6.70	89.3	24.1	96.3	63.0	84.1
5	0.234	93.6	0.712	94.9	2.45	97.9	6.40	85.3	24.1	96.4	630	84.0
6	0.240	96.0	0.698	93.1	2.48	99.4	7.05	940	24.2	96.7	66.0	87.9
7	0.246	98.4	0.708	94.4	2.54	102	6.46	86.1	24.3	97.3	64.8	86.4
average =	0.242	96.9	0.694	92.5	2.50	99.7	6.70	89.4	23.6	94.3	63.9	85.3
std dev =	0.00647	2.59	0.0194	2.59	0.0538	2.15	0.255	3.40	0.752	3.01	1.75	2.33

TABLE 35. DIBENZ[a,h]ANTHRACENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

Int Std: Perylene-D_{12}; Quant. ion (*m/z*): 278

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.224	89.6	0.660	88.0	2.65	106	8.10	108	25.1	100	68.2	90.9
2	0.222	88.8	0.680	90.7	2.60	104	7.77	104	26.8	107	63.8	85.1
3	0.218	87.2	0.604	80.5	2.59	104	7.58	101	26.0	104	66.9	89.2
4	0.206	82.4	0.554	73.9	2.64	106	7.80	104	28.8	115	64.9	86.6
5	0.186	74.4	0.736	98.1	2.47	98.7	7.66	102	27.8	111	64.0	85.3
6	0.2400	96.0	0.646	86.1	2.75	110	7.99	107	27.3	109	70.9	94.6
7	0.222	88.8	0.704	93.9	2.68	107	6.81	90.8	28.3	113	68.3	91.1
average =	0.217	86.7	0.655	87.3	2.63	105	7.67	102	27.2	109	66.7	89.0
std dev =	0.0169	6.75	0.0612	8.16	0.0872	3.49	0.422	5.63	1.30	5.21	2.62	3.49

TABLE 36. FLUORANTHENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

Int Std: Phenanthrene-D_{10}; Quant. ion (*m/z*): 202

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.244	97.6	0.698	93.1	2.38	95.4	7.37	98.3	26.6	106	68.2	91.0
2	0.246	98.4	0.696	92.8	2.57	103	6.81	90.9	25.0	100	63.5	84.7
3	0.236	94.4	0.682	90.9	2.48	99.0	7.05	94.1	25.8	103	64.8	86.4
4	0.248	99.2	0.674	89.9	2.42	96.9	6.87	91.7	26.7	107	64.2	85.7
5	0.222	88.8	0.692	92.3	2.38	95.0	6.66	88.8	26.5	106	64.1	85.5
6	0.234	93.6	0.672	89.6	2.38	95.2	7.11	94.8	26.6	106	67.8	90.4
7	0.234	93.6	0.748	99.7	2.51	100	6.39	85.2	25.7	103	65.9	87.9
average =	0.238	95.1	0.695	92.6	2.45	97.8	6.90	91.9	26.1	105	65.5	87.4
std dev =	0.00905	3.62	0.0257	3.43	0.0762	3.05	0.320	4.27	0.629	2.52	1.85	2.46

TABLE 37. FLUORENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

Int Std: Phenanthrene-D_{10}; Quant. ion (*m/z*): 166

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.244	97.6	0.674	89.9	2.42	97.0	7.26	96.8	23.9	95.7	66.0	88.1
2	0.246	98.4	0.702	93.6	2.56	103	6.62	88.2	23.6	94.5	61.3	81.8
3	0.238	95.2	0.678	90.4	2.52	101	6.86	91.4	23.8	95.2	63.2	84.3
4	0.240	96.0	0.694	92.5	2.43	97.2	6.86	91.4	24.8	99.0	62.9	83.9
5	0.226	90.4	0.704	93.9	2.37	95.0	6.69	89.3	25.1	101	63.2	84.3
6	0.238	95.2	0.678	90.4	2.38	95.0	7.08	94.4	24.6	98.3	65.3	87.1
7	0.242	96.8	0.714	95.2	2.49	99.5	6.31	84.1	24.7	98.7	63.9	85.2
average =	0.239	95.7	0.692	92.3	2.45	98.2	6.81	90.8	24.4	97.4	63.7	85.0
std dev =	0.00652	2.61	0.0155	2.07	0.0729	2.91	0.311	4.14	0.576	2.30	1.57	2.09

TABLE 38. INDENO[1,2,3-c,d]PYRENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

Int Std: Perylene-D_{12}; Quant. ion (*m/z*): 276

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.214	85.6	0.592	78.9	2.17	86.9	7.14	95.2	23.8	95.4	69.7	92.9
2	0.212	84.8	0.642	85.6	2.14	85.7	6.89	91.9	25.3	101	64.9	86.6
3	0.198	79.2	0.578	77.1	2.14	85.4	6.86	91.5	24.7	98.8	67.9	90.5
4	0.196	78.4	0.530	70.7	2.09	83.4	6.95	92.6	27.2	109	66.5	88.6
5	0.180	72.0	0.654	87.2	2.08	83.3	6.87	91.7	26.1	105	66.4	88.5
6	0.216	86.4	0.644	85.9	2.28	91.2	7.15	95.3	25.6	102	72.2	96.3
7	0.192	76.8	0.632	84.3	2.17	86.9	5.90	79.0	27,0	108	70.7	94.2
average =	0.201	80.5	0.610	81.4	2.15	86.1	6.82	91.0	25.7	103	68.3	91.1
std dev =	0.0134	5.34	0.0454	6.05	0.0668	2.67	0.426	5.68	1.21	4.83	2.63	3.51

TABLE 39. NAPHTHALENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

Int Std: Naphthalene-D_8; Quant. ion (*m/z*): 128

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.272	109	0.682	90.9	2.45	98.2	6.88	91.7	22.9	91.7	66.7	88.9
2	0.278	111	0.720	96.0	2.57	103	6.45	86.1	23.3	93.2	61.3	81.8
3	0.266	106	0.698	93.1	2.58	103	6.67	88.9	23.4	93.8	63.5	84.7
4	0.272	109	0.730	97.3	2.51	100	6.64	88.5	24.3	97.2	63.0	84.0
5	0.262	105	0.740	98.7	2.41	96.6	6.36	84.8	24.4	97.7	64.0	85.3
6	0.304	122	0.716	95.5	2.54	102	6.90	92.0	23.9	95.7	65.7	87.6
7	0.272	109	0.772	103	2.53	101	6.08	81.1	24.1	96.6	65.4	87.3
average =	0.275	110	0.723	96.3	2.51	101	6.57	87.6	23.8	95.1	64.2	85.7
std dev =	0.0137	5.48	0.0292	3.89	0.0614	2.45	0.292	3.90	0.568	2.27	1.84	2.45

TABLE 40. PHENANTHRENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

Int Std: Phenanthrene-D_{10}; Quant. ion (*m/z*): 178

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.246	98.4	0.680	90.7	2.46	98.3	7.08	94.4	23.7	94.6	66.7	88.9
2	0.252	101	0.690	92.0	2.54	102	6.71	89.5	24.1	96.2	62.4	83.2
3	0.240	96.0	0.672	89.6	2.55	102	6.73	89.7	24.1	96.3	64.0	85.3
4	0.242	96.8	0.694	92.5	2.48	99.3	6.82	91.0	25.2	101	64.2	85.6
5	0.230	92.0	0.710	94.7	2.40	96.0	6.56	87.4	25.3	101	64.1	85.4
6	0.248	99.2	0.688	91.7	2.49	99.5	7.09	94.6	24.9	99.7	66.7	88.9
7	0.242	96.8	0.710	94.7	2.52	101	6.33	84.4	25.3	101	65.4	87.2
average =	0.243	97.1	0.692	92.3	2.49	99.6	6.759	90.1	24.6	98.6	64.8	86.3
std dev =	0.00701	2.80	0.0142	1.90	0.0514	2.05	0.273	3.64	0.698	2.79	1.58	2.10

TABLE 41. PYRENE RECOVERY FROM SPIKED MEDIA (Weathered for 4 hours at 1 L/min)

Int Std: Chrysene-D_{12}; Quant. ion (*m/z*): 202

	Applied 0.250 (µg/sample)		Applied 0.750 (µg/sample)		Applied 2.50 (µg/sample)		Applied 7.50 (µg/sample)		Applied 25.0 (µg/sample)		Applied 75.0 (µg/sample)	
	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent	Found	Percent
Replicate	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery	µg/sample	Recovery
1	0.238	95.2	0.634	84.5	2.31	92.4	6.82	91.0	23.0	92.0	66.4	88.5
2	0.246	98.4	0.676	90.1	2.45	98.0	6.53	87.0	24.9	99.5	620	82.7
3	0.220	88.0	0.658	87.7	2.38	95.3	6.81	90.8	25.2	101	63.9	85.1
4	0.244	97.6	0.758	101	2.26	90.6	6.82	91.0	25.3	102	61.6	82.1
5	0.218	87.2	0.700	93.3	2.27	91.0	6.37	84.9	24.8	99.2	64.5	86.0
6	0.224	89.6	0.714	95.2	2.31	92.5	7.28	97.0	24.8	99.3	67.5	90.0
7	0.226	90.4	0.660	88.0	2.24	89.4	6.24	83.3	25.4	102	66.7	89.0
average =	0.231	92.3	0.686	91.4	2.32	92.7	6.70	89.3	24.8	99.1	64.6	86.2
std dev =	0.0116	4.64	0.0417	5.56	0.0744	2.98	0.347	4.63	0.812	3.25	2.33	3.11

Method for Processing the Data

Recovery data less than 75% were not used in any statistical analysis. Overall precision, accuracy, and bias (Sr^2) were calculated using the relationships described in Bartley [11], using the data from Tables 26-42. Identical calculations were made for Method precision, accuracy, and bias (Sr^1) using data only from the user check. A description of the user check and the data tables are presented in Appendix A at the end of this report.

As noted in Bartley [11, p. 363] the relationship between bias (B), accuracy (A), and precision (S_{rT}) may formulated as

$$\alpha = \Phi\left[\frac{B+A}{S_{rT}}\right] - \Phi\left[\frac{B-A}{S_{rT}}\right] \qquad (1)$$

where Φ is the standard normal distribution function and S_{rT} (a measure of precision) is the true relative standard deviation. Accuracy was computed with α = 0.95 and was estimated using the formula presented in Bartley [11, p. 359]

$$A = \begin{Bmatrix} u_{(1+\alpha)/2} \cdot \left[B^2 + S_{rT}^2\right]^{\frac{1}{2}}, & |B| < \dfrac{S_{rT}}{u_\alpha} \\ |B| + u_\alpha \cdot S_{rT}, & otherwise \end{Bmatrix}$$

Specifically, for $u_{(1+\alpha)/2} = u_{0.975} = 1.96$ and for $u_\alpha = u_{0.95} = 1.645$ as presented in (A3) in NIOSH [12], the estimate of accuracy, $\hat{A}$, was computed as

$$\hat{A} = \begin{Bmatrix} 1.96 \cdot \left[\hat{B}^2 + \hat{S}_{rT}^2\right]^{\frac{1}{2}}, & |\hat{B}| < \dfrac{\hat{S}_{rT}}{1.645} \\ |\hat{B}| + 1.645 \cdot \hat{S}_{rT}, & otherwise \end{Bmatrix} \qquad (2)$$

The estimated precision, $\hat{S}_{rT}$, was calculated as in NIOSH [12, p. 57]

$$\hat{S}_{rT} = \hat{S}_{pool} = \sqrt{\sum_{i=1}^{k} \frac{(n_i - 1)\left(\dfrac{\hat{S}_i}{C_i}\right)^2}{\sum_{i=1}^{k}(n_i - 1)}} = \sqrt{\sum_{i=1}^{k} \frac{(n_i - 1)\left(\hat{S}_{rTi}\right)^2}{\sum_{i=1}^{k}(n_i - 1)}} \qquad (3)$$

if Bartlett's test did not reject homogeneity of the true relative standard deviations $\left(\dfrac{\hat{S}_i}{C_{Ti}}\right)$ over the *k* concentrations where

n_i = number of observations for i^{th} concentration,

k = number of concentrations,

$\hat{S}_i$ = standard deviation of observations at i^{th} concentration, and

C_{Ti} = known i^{th} concentration.

If, on the other hand, Bartlett's test did reject homogeneity of the true relative standard deviations are set

$$\hat{S}_{rT} = \max\left\{\hat{S}_{ri}\right\}.$$

To calculate the bias, *B,* the bias for each measurement, y_{ij}, was computed as

$$y_{ij} = \frac{x_{ij} - C_{Ti}}{C_{Ti}}$$

where x_{ij} = the j^{th} measurement for the i^{th} concentration (run). Letting $\overline{y}_{i.} = \frac{\sum_{j=1}^{j=n} y_{ij}}{n_i}$ calculate the sum of squares within each concentration as $SS_{within} = \sum_{i=1}^{i=k}\sum_{j=1}^{j=n}\left(y_{ij} - \overline{y}_{i.}\right)^2$ and the error mean square = $MSE = \frac{SS_{within}}{\left(\sum_{i=1}^{i=k} n_i\right) - k}$. Next, calculate the sum of squares between concentrations as $SS_{between} = \sum_{i=1}^{i=k} n_i\left(\overline{y}_{i.} - \overline{y}_{..}\right)^2$ and the treatment (concentration) mean square = $MSTR = \frac{SS_{between}}{k-1}$. Then use a straightforward ANOVA, as shown in [12, p.51] and Neter Wasserman, Kutner [13], calculating $F = \frac{MSTR}{MSE}$ with (k – 1) and $\left(\sum_{i=1}^{i=k} n_i\right) - k$ degrees of freedom using SAS PROC GLM. If different concentrations were judged to have equivalent biases, then

$$\hat{B} = \overline{y}_{..} = \frac{\sum_{i=1}^{i=k} \overline{y}_{i.}}{k}.$$

However, if the different concentrations were judged not to have equivalent biases, then $\overline{y}_{i.}$ was chosen such that $\left|\overline{y}_{i.}\right| = \max\left\{\left|\overline{y}_{1.}\right|,...,\left|\overline{y}_{k.}\right|\right\}$ and set $\hat{B} = \overline{y}_{i.}$.

Note that the value of bias was chosen based on it having the largest absolute value, but the actual of $\hat{B}$ could be negative or positive. The 95% upper confidence limit of accuracy was calculated according to the formula (A4) given in NIOSH [12, p. 44]. These results are presented in Tables 42 and 43.

Table 42. Overall Bias, Accuracy and Precision ($\bar{S}_{rT}$)[1,2]

Compound (alphabetically)	Range For Calculation[3] (µg/sample)	Bias (B)	Overall Precision ($\overline{S_{rT}}$)	Accuracy (A)	95% Upper Confidence Limit of Accuracy
Acenaphthene	0.25 - 75	-0.162	0.057	0.256	0.284
Acenaphthylene	25 - 75	-0.217	0.058	0.312	0.370
Anthracene	0.25 - 75	-0.243	0.058	0.338	0.367
Benz[a]anthracene	0.25 - 75	-0.139	0.059	0.236	0.265
Benzo[b]fluoranthene	0.25 - 75	-0.126	0.059	0.223	0.252
Benzo[k]fluoranthene	0.25 - 75	-0.170	0.060	0.268	0.298
Benzo[ghi]perylene	2.5 - 75	-0.140	0.072	0.258	0.293
Benzo[a]pyrene	0.75 - 75	-0.235	0.060	0.334	0.367
Chrysene	0.25 - 75	-0.147	0.057	0.241	0.269
Dibenz[a,h]anthracene	0.25 - 75	-0.133	0.076	0.257	0.295
Fluoranthene	0.25 - 75	-0.126	0.060	0.225	0.254
Fluorene	0.25 - 75	-0.151	0.057	0.245	0.273
Indeno[1,2,3-cd]pyrene	0.25 - 75	-0.195	0.070	0.310	0.344
Naphthalene	0.25 - 75	-0.143	0.062	0.245	0.275
Phenanthrene	0.25 - 75	-0.137	0.056	0.229	0.257
Pyrene	0.25 - 75	-0.138	0.065	0.245	0.277

(1) Data was not included where desorption was <75% or >125%; therefore:
Acenaphthylene: Omits 4 lower levels (0.25-7.5)
Benzo[a]pyrene: Omits lowest level (0.25)
(2) Data includes 5% pump error correction
(3) Range for calculation is the range over which the precision, bias, and accuracy were calculated. Range studied was 0.25 to 75.0 µg/sample for all 16 PAHs.

Table 43. Method Bias, Accuracy and Precision (S_r)[1,2]

Analyte	Range For Calculation[2] (µg/sample)	Bias (B)	Precision (S_r)	Accuracy (A)	95% Upper Confidence Limit of Accuracy
Acenaphthene	0.5-20	-0.012	0.066	0.131	0.178
Acenaphthylene	0.5-20	-0.113	0.077	0.240	0.295
Anthracene	0.5-20	-0.207	0.0972	0.367	0.436
Benzo[a]anthracene	0.5-20	-0.207	0.095	0.363	0.431
Benzo[a]pyrene	2-20	-0.141	0.081	0.273	0.343
Benzo[b]fluoranthene	0.5-20	-0.207	0.080	0.338	0.395
Benzo[ghi]perylene	0.5-20	-0.018	0.062	0.127	0.172
Benzo[k]fluoranthene	0.5-20	-0.042	0.062	0.144	0.188
Chrysene	0.5-20	0.019	0.057	0.117	0.159
Dibenz[a,h]anthracene	0.5-20	-0.097	0.118	0.290	0.374
Fluoranthene	0.5-20	-0.16	0.087	0.302	0.364
Fluorene	0.5-20	0.025	0.105	0.212	0.287
Indeno[1,2,3-cd]pyrene	0.5-20	-0.217	0.144	0.453	0.555
Naphthalene	0.5-20	-0.038	0.071	0.157	0.213
Phenanthrene	0.5-20	-0.034	0.062	0.138	0.188
Pyrene	0.5-20	0.082	0.055	0.174	0.213

(1) This data is from the user check performed after method development. See Appendix 1 for discussion of experiments and data tables.

(2) All samples at the lowest spike level of Benzo[a]pyrene (0.5 µg) gave results < 75% and were excluded from the calculation. Range studied was 0.5-20 µg/sample for all PAHs.

X. SUMMARY

Data for most analytes derived during the method development met NIOSH criteria for precision, bias, and accuracy in all studies performed [9, 11, 12]. The method proved to be rugged for most analytes, with acenaphthylene being a notable exception due to its degradation during sampling.

A user check has been performed on this method, and the results are located in Appendix 1.

XI. REFERENCES

[1] Wood AW, Levin W, Chang RL, Yagi H, Thakker DR, Lehr RE, Jerina DM, Conney AH [1979]. Bay-Region activation of carcinogenic polycyclic hydrocarbons. In: Jones PW, Leber P, eds. Polynuclear aromatic hydrocarbons. Ann Arbor, MI: Ann Arbor Science Publishers, Inc.

[2] NIOSH [1994]. Polynuclear aromatic hydrocarbons by HPLC: Method 5506. In: Eller PM, Cassinelli ME, eds. NIOSH manual of analytical methods, 4th edition. Cincinnati, OH: Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[3] NIOSH [1994]. Polynuclear aromatic hydrocarbons by GC: Method 5515. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th edition. Cincinnati, OH: Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[4] OSHA [1983, 1986]. 2,4-Dintrotoluene and/or 2,4,6-Trinitrotoluene: Method 44 and Chlorpyrifos, DDVP, diazinon, malathion, and parathion: Method 62. Salt Lake City, UT: U.S. Department of Labor, Occupational Safety and Health Administration.

[5] NIOSH [2021]. Polynuclear aromatic hydrocarbons in air by GC-MS SIM: Method 5528. In: Andrews RA, O'Connor PF. NIOSH Manual of Analytical Methods, 5th edition. Cincinnati, OH: Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. https://www.cdc.gov/niosh/nmam/default.html

[6] DataChem Laboratories [2005]. Polynuclear aromatic hydrocarbons in air by GC-MS SIM: Method 5528 Backup Data Report. By: Hendricks RA, Reynolds JM, Perkins JB. Salt Lake City, UT: DataChem Laboratories, Inc. NIOSH contract CDC-200-2001-0800. LIMS Sequence 10313. Unpublished.

[7] SKC Inc [2005]. Eighty Four, PA. www.skcinc.com

[8] Sigma-Aldrich [1998]. St Louis, MO. https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Sigma/Product_Information_Sheet/1/xad7pis.pdf

[9] NIOSH [1995]. Guidelines for air and analytical method development and evaluation. By: Kennedy ER, Fishbach TJ, Song R, Eller PM, Shulman, SA. Cincinnati, OH: Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 95-117.

[10] Burkart JA [1986]. General procedures for limit of detection calculations in industrial hygiene chemistry laboratory. App Ind Hyg *1*(3):153-155.

[11] Bartley DL [2001]. Definition and assessment of sampling and analytical accuracy. Annals Occ Hyg. *45*:357-364.

[12] NIOSH [2012]. Components for evaluation of direct-reading monitors for gases and vapors. Cincinnati, OH: Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2012-162.

[13] Neter J, Wasserman W, Kutner MH. [1990]. Applied linear statistical models, 3rd ed. Boston, MA: Irwin.

Appendix 1. User Check

User check samples were prepared by the Quality Assurance group of the NIOSH/DART contract laboratory, BVNA (contract 200-2011-39202, sequence #11571), to evaluate NIOSH Method 5528. Six tubes at 4 spiking levels (0.5, 2, 5, and 20 µg) were prepared, for a total of twenty-four OVS-7 samples, for each of the 16 PAHs in the method. Samples for LOD/LOQ determination were also prepared and analyzed. The procedure followed by the laboratory for sample analysis was as given in the method. Results are presented in Tables 1-1 through 1-17. The LOD was 0.05 µg for 14 compounds, 0.06 µg for naphthalene, 0.08 µg for dibenzo[a,h]anthracene; LOQ was 0.17 µg for 13 compounds, 0.19 µg for naphthalene, 0.26 for dibenzo[a,h]anthracene, and 0.18 µg for benzo[a]anthracene. Only benzo[a]pyrene had a recovery below 75%, at the 0.5 µg spike level. Additionally, 7 of the PAHs recovered below 90% at the lowest spike level (0.5 µg). Therefore, it is recommended that sample volume be maximized when a low PAH level is anticipated. The correlation coefficient was 0.990 or higher for all but naphthalene (0.970). The user check was successful.

To check for humidity interference, additional experiments were performed by NIOSH/DART contract laboratory BVNA (contract 200-2011-39202, sequence #11760). Sample spikes were prepared at five different levels of 0, 10, 48, 96 and 192 µg for each PAH in the method. Each level was composed of six replicate spikes. After the OVS-7 sampling tubes were spiked at the various levels, 80% relative humidity air was drawn through them. The spiked tubes were placed on an air-sampling manifold. The flow rate of the manifold was adjusted to 1 liter per minute (LPM). After the flow rate for the individual tubes was set, each tube was connected to a Miller/Nelson atmosphere generator to produce the humid air that would be drawn through the tubes. The tubes had the humid air drawn across them for 480 minutes. After sampling was performed, the tubes were placed in freezer storage conditions. The tubes sat overnight before desorption was done. The procedure followed by the laboratory for sample analysis was as given in the method. The results for the humidity test are presented in Tables 1-18 through 1-21. For 11 of the 16 PAHs tested, results at the lowest spiking level, 10 µg/sample, were low. Therefore, when sampling an atmosphere high in humidity where the PAH level is expected to be low, be aware that results may be biased low. All other results for the humidity test were acceptable.

All samples (user check and humidity user check) were analyzed under the instrument parameters listed below:

- Instrument: Hewlett Packard Model 6890 GC/Hewlett Packard Model 5972 MS
- Column: Phenomenex ZB-5MS, 30 meter, 0.25-mm ID with a 0.25 µm film thickness (Catalog# 7GH-G010-11-GGC)
- Column Flow: Pressure program, approximately 1.0 mL/min
- Injection Temperature: 280 ºC
- Injection Volume: 1 µL
- Oven Temperature Profile:
- Initial Temperature: 100 ºC
- Initial Hold Time: 0.5 minutes
- Temperature Program Rate: 12 ºC/minute
- Temperature: 290 ºC
- Hold Time: 1.0 minutes
- Temperature Program Rate: 20 ºC/minute
- Final Temperature: 320 ºC
- Final Hold Time: 3.0 minutes
- MS Operating Parameters: SIM mode

Table 1-1. LOD/LOQ results

Compound	LOD (µg/sample)	LOQ (µg/sample)	Analytical Range (µg/sample)
Acenaphthene	0.05	0.17	0.05 to 30
Acenaphthylene	0.05	0.17	0.05 to 30
Anthracene	0.05	0.17	0.05 to 30
Benzo[a]anthracene	0.05	0.18	0.05 to 30
Benzo[a]pyrene	0.05	0.17	0.05 to 30
Benzo[b]fluoranthene	0.05	0.17	0.05 to 30
Benzo[ghi]perylene	0.05	0.17	0.05 to 30
Benzo[k]fluoranthene	0.05	0.17	0.05 to 30
Chrysene	0.05	0.17	0.05 to 30
Dibenz[a,h]anthracene	0.08	0.26	0.08 to 30
Fluoranthene	0.05	0.17	0.05 to 30
Fluorene	0.05	0.17	0.05 to 30
Indeno[1,2,3-cd]pyrene	0.05	0.17	0.05 to 30
Naphthalene	0.06	0.19	0.06 to 30
Phenanthrene	0.05	0.17	0.05 to 30
Pyrene	0.05	0.17	0.05 to 30

Table 1-2. Recovery results for Acenaphthene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Acenaphthene	19.4	20	96.8		
Acenaphthene	20.6	20	103		
Acenaphthene	20.5	20	103		
Acenaphthene	20.9	20	105		
Acenaphthene	19.7	20	98.4	Avg recovery	101
Acenaphthene	20.4	20	102	Std Dev	3.00
Acenaphthene	4.59	5	91.8		
Acenaphthene	5.24	5	105		
Acenaphthene	5.49	5	110		
Acenaphthene	5.47	5	109		
Acenaphthene	5.27	5	105	Avg recovery	103
Acenaphthene	4.76	5	95.2	Std Dev	7.51
Acenaphthene	2.28	2	114		
Acenaphthene	2.0	2	100		
Acenaphthene	1.91	2	95.5		
Acenaphthene	1.80	2	90.0		
Acenaphthene	1.98	2	99.0	Avg recovery	97.6
Acenaphthene	1.74	2	87.0	Std Dev	9.50
Acenaphthene	0.43	0.5	86.0		
Acenaphthene	0.48	0.5	96.0		
Acenaphthene	0.48	0.5	96.0		
Acenaphthene	0.49	0.5	98.0		
Acenaphthene	0.46	0.5	92.0	Avg recovery	93.7
Acenaphthene	0.47	0.5	94.0	Std Dev	4.27

Table 1-3. Recovery results for Acenaphthylene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Acenaphthylene	20.2	20	100		
Acenaphthylene	21.4	20	107		
Acenaphthylene	21.4	20	107		
Acenaphthylene	21.8	20	109		
Acenaphthylene	20.5	20	102	Avg recovery	105
Acenaphthylene	21.3	20	107	Std Dev	3.37
Acenaphthylene	4.98	5	99.6		
Acenaphthylene	5.67	5	113		
Acenaphthylene	5.98	5	120		
Acenaphthylene	5.98	5	120		
Acenaphthylene	5.70	5	114	Avg recovery	110
Acenaphthylene	4.81	5	96.2	Std Dev	10.1
Acenaphthylene	2.26	2	113		
Acenaphthylene	1.99	2	99.5		
Acenaphthylene	1.91	2	95.5		
Acenaphthylene	1.78	2	89.0		
Acenaphthylene	1.96	2	98.0	Avg recovery	96.4
Acenaphthylene	1.67	2	83.5	Std Dev	10.1
Acenaphthylene	0.41	0.5	82.0		
Acenaphthylene	0.44	0.5	88.0		
Acenaphthylene	0.44	0.5	88.0		
Acenaphthylene	0.46	0.5	92.0		
Acenaphthylene	0.48	0.5	96.0	Avg recovery	88.7
Acenaphthylene	0.43	0.5	86.0	Std Dev	4.84

Table 1-4. Recovery results for Anthracene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Anthracene	18.9	20	94.4		
Anthracene	20.7	20	103		
Anthracene	20.4	20	102		
Anthracene	20.3	20	101		
Anthracene	19.8	20	99.2	Avg recovery	100
Anthracene	20.0	20	99.8	Std Dev	3.13
Anthracene	4.60	5	92.0		
Anthracene	5.19	5	104		
Anthracene	5.48	5	110		
Anthracene	5.44	5	109		
Anthracene	5.38	5	108	Avg recovery	103
Anthracene	4.68	5	93.6	Std Dev	7.84
Anthracene	2.19	2	110		
Anthracene	1.86	2	93.0		
Anthracene	1.81	2	90.5		
Anthracene	1.70	2	85.0		
Anthracene	1.88	2	94.0	Avg recovery	92.3
Anthracene	1.63	2	81.5	Std Dev	9.72
Anthracene	0.39	0.5	78.0		
Anthracene	0.40	0.5	80.0		
Anthracene	0.39	0.5	78.0		
Anthracene	0.40	0.5	80.0		
Anthracene	0.41	0.5	82.0	Avg recovery	79.3
Anthracene	0.39	0.5	78.0	Std Dev	1.63

Table 1-5. Recovery results for Benzo[a]anthracene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Benzo[a]anthracene	19.7	20	98.6		
Benzo[a]anthracene	21.0	20	105		
Benzo[a]anthracene	21.1	20	105		
Benzo[a]anthracene	21.7	20	108		
Benzo[a]anthracene	21.1	20	105	Avg recovery	105
Benzo[a]anthracene	21.3	20	106	Std Dev	3.29
Benzo[a]anthracene	4.88	5	97.6		
Benzo[a]anthracene	5.61	5	112		
Benzo[a]anthracene	5.60	5	112		
Benzo[a]anthracene	5.78	5	116		
Benzo[a]anthracene	5.57	5	111	Avg recovery	108
Benzo[a]anthracene	4.86	5	97.2	Std Dev	8.09
Benzo[a]anthracene	2.49	2	125		
Benzo[a]anthracene	1.99	2	99.5		
Benzo[a]anthracene	1.94	2	97.0		
Benzo[a]anthracene	1.76	2	88.0		
Benzo[a]anthracene	1.86	2	93.0	Avg recovery	96.9
Benzo[a]anthracene	1.59	2	79.5	Std Dev	15.3
Benzo[a]anthracene	0.38	0.5	76.0		
Benzo[a]anthracene	0.39	0.5	78.0		
Benzo[a]anthracene	0.38	0.5	76.0		
Benzo[a]anthracene	0.38	0.5	76.0		
Benzo[a]anthracene	0.38	0.5	76.0	Avg recovery	79.3
Benzo[a]anthracene	0.47	0.5	94.0	Std Dev	7.23

Table 1-6. Recovery results for Benzo[a]pyrene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Benzo[a]pyrene	19.2	20	96.2		
Benzo[a]pyrene	20.3	20	102		
Benzo[a]pyrene	20.4	20	102		
Benzo[a]pyrene	20.9	20	104		
Benzo[a]pyrene	19.4	20	97.2	Avg recovery	100
Benzo[a]pyrene	20.2	20	101	Std Dev	3.11
Benzo[a]pyrene	4.52	5	90.4		
Benzo[a]pyrene	5.17	5	103		
Benzo[a]pyrene	5.53	5	111		
Benzo[a]pyrene	5.20	5	104		
Benzo[a]pyrene	5.29	5	106	Avg recovery	101
Benzo[a]pyrene	4.58	5	91.6	Std Dev	8.13
Benzo[a]pyrene	2.09	2	105		
Benzo[a]pyrene	1.78	2	89.0		
Benzo[a]pyrene	1.72	2	86.0		
Benzo[a]pyrene	1.51	2	75.5		
Benzo[a]pyrene	1.72	2	86.0	Avg recovery	85.9
Benzo[a]pyrene	1.49	2	74.5	Std Dev	10.9
Benzo[a]pyrene	0.33	0.5	**66.0**		
Benzo[a]pyrene	0.35	0.5	**70.0**		
Benzo[a]pyrene	0.34	0.5	**68.0**		
Benzo[a]pyrene	0.35	0.5	**70.0**		
Benzo[a]pyrene	0.33	0.5	**66.0**	Avg recovery	**69.0**
Benzo[a]pyrene	0.37	0.5	**74.0**	Std Dev	3.03

Table 1-7. Recovery results for Benzo[b]fluoranthene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Benzo[b]fluoranthene	18.5	20	92.5		
Benzo[b]fluoranthene	19.7	20	98.5		
Benzo[b]fluoranthene	19.8	20	98.9		
Benzo[b]fluoranthene	20.2	20	101		
Benzo[b]fluoranthene	19.1	20	95.7	Avg recovery	97.3
Benzo[b]fluoranthene	19.4	20	97.2	Std Dev	2.93
Benzo[b]fluoranthene	4.37	5	87.4		
Benzo[b]fluoranthene	4.98	5	99.6		
Benzo[b]fluoranthene	5.24	5	105		
Benzo[b]fluoranthene	4.94	5	98.8		
Benzo[b]fluoranthene	4.95	5	99.0	Avg recovery	96.4
Benzo[b]fluoranthene	4.43	5	88.6	Std Dev	6.86
Benzo[b]fluoranthene	2.21	2	111		
Benzo[b]fluoranthene	1.84	2	92.0		
Benzo[b]fluoranthene	1.76	2	88.0		
Benzo[b]fluoranthene	1.50	2	75.0		
Benzo[b]fluoranthene	1.72	2	86.0	Avg recovery	87.7
Benzo[b]fluoranthene	1.49	2	74.5	Std Dev	13.2
Benzo[b]fluoranthene	0.37	0.5	74.0		
Benzo[b]fluoranthene	0.40	0.5	80.0		
Benzo[b]fluoranthene	0.39	0.5	78.0		
Benzo[b]fluoranthene	0.40	0.5	80.0		
Benzo[b]fluoranthene	0.38	0.5	76.0	Avg recovery	79.3
Benzo[b]fluoranthene	0.44	0.5	88.0	Std Dev	4.84

Table 1-8. Recovery results for Benzo[ghi]perylene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Benzo[ghi]perylene	19.1	20	95.6		
Benzo[ghi]perylene	20.3	20	102		
Benzo[ghi]perylene	20.1	20	100		
Benzo[ghi]perylene	20.8	20	104		
Benzo[ghi]perylene	19.5	20	97.3	Avg recovery	99.7
Benzo[ghi]perylene	19.9	20	99.6	Std Dev	2.98
Benzo[ghi]perylene	4.23	5	84.6		
Benzo[ghi]perylene	4.88	5	97.6		
Benzo[ghi]perylene	5.35	5	107		
Benzo[ghi]perylene	4.93	5	98.6		
Benzo[ghi]perylene	5.0	5	100	Avg recovery	97.5
Benzo[ghi]perylene	4.86	5	97.2	Std Dev	7.27
Benzo[ghi]perylene	2.24	2	112		
Benzo[ghi]perylene	2.04	2	102		
Benzo[ghi]perylene	1.93	2	96.5		
Benzo[ghi]perylene	1.74	2	87.0		
Benzo[ghi]perylene	1.97	2	98.5	Avg recovery	97.5
Benzo[ghi]perylene	1.78	2	89.0	Std Dev	9.11
Benzo[ghi]perylene	0.47	0.5	94.0		
Benzo[ghi]perylene	0.50	0.5	100		
Benzo[ghi]perylene	0.50	0.5	100		
Benzo[ghi]perylene	0.51	0.5	102		
Benzo[ghi]perylene	0.48	0.5	96.0	Avg recovery	98.0
Benzo[ghi]perylene	0.48	0.5	96.0	Std Dev	3.10

Table 1-9. Recovery results for Benzo[k]fluoranthene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Benzo[k]fluoranthene	17.9	20	89.4		
Benzo[k]fluoranthene	19.1	20	95.5		
Benzo[k]fluoranthene	19.4	20	96.8		
Benzo[k]fluoranthene	19.9	20	99.3		
Benzo[k]fluoranthene	18.2	20	91.0	Avg recovery	94.6
Benzo[k]fluoranthene	19.1	20	95.5	Std Dev	3.70
Benzo[k]fluoranthene	4.32	5	86.4		
Benzo[k]fluoranthene	5.02	5	100		
Benzo[k]fluoranthene	5.51	5	110		
Benzo[k]fluoranthene	5.03	5	101		
Benzo[k]fluoranthene	5.23	5	105	Avg recovery	99.1
Benzo[k]fluoranthene	4.62	5	92.4	Std Dev	8.53
Benzo[k]fluoranthene	2.17	2	109		
Benzo[k]fluoranthene	1.95	2	97.5		
Benzo[k]fluoranthene	1.88	2	94.0		
Benzo[k]fluoranthene	1.74	2	87.0		
Benzo[k]fluoranthene	1.98	2	99.0	Avg recovery	95.8
Benzo[k]fluoranthene	1.77	2	88.5	Std Dev	7.85
Benzo[k]fluoranthene	0.45	0.5	90.0		
Benzo[k]fluoranthene	0.47	0.5	94.0		
Benzo[k]fluoranthene	0.47	0.5	94.0		
Benzo[k]fluoranthene	0.48	0.5	96.0		
Benzo[k]fluoranthene	0.47	0.5	94.0	Avg recovery	93.7
Benzo[k]fluoranthene	0.47	0.5	94.0	Std Dev	1.97

Table 1-10. Recovery results for Chrysene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Chrysene	18.4	20	91.9		
Chrysene	19.7	20	98.3		
Chrysene	19.7	20	98.7		
Chrysene	20.1	20	101.		
Chrysene	19.3	20	96.5	Avg recovery	97.4
Chrysene	19.7	20	98.7	Std Dev	3.02
Chrysene	4.46	5	89.2		
Chrysene	5.00	5	100		
Chrysene	5.34	5	107		
Chrysene	5.29	5	106		
Chrysene	5.16	5	103	Avg recovery	99.9
Chrysene	4.72	5	94.4	Std Dev	6.90
Chrysene	2.37	2	119		
Chrysene	2.08	2	104		
Chrysene	1.99	2	99.5		
Chrysene	2.05	2	103		
Chrysene	2.14	2	107	Avg recovery	105
Chrysene	1.95	2	97.5	Std Dev	7.48
Chrysene	0.52	0.5	104		
Chrysene	0.53	0.5	106		
Chrysene	0.52	0.5	104		
Chrysene	0.56	0.5	112		
Chrysene	0.53	0.5	106	Avg recovery	105
Chrysene	0.50	0.5	100	Std Dev	3.93

Table 1-11. Recovery results for Dibenz[a,h]anthracene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Dibenz[a,h]anthracene	20.0	20	99.8		
Dibenz[a,h]anthracene	21.0	20	105		
Dibenz[a,h]anthracene	21.0	20	105		
Dibenz[a,h]anthracene	21.7	20	108		
Dibenz[a,h]anthracene	20.3	20	102	Avg recovery	104
Dibenz[a,h]anthracene	20.7	20	104	Std Dev	3.05
Dibenz[a,h]anthracene	4.63	5	92.6		
Dibenz[a,h]anthracene	5.29	5	106		
Dibenz[a,h]anthracene	5.69	5	114		
Dibenz[a,h]anthracene	5.24	5	105		
Dibenz[a,h]anthracene	5.34	5	107	Avg recovery	105
Dibenz[a,h]anthracene	5.25	5	105	Std Dev	6.85
Dibenz[a,h]anthracene	2.39	2	120		
Dibenz[a,h]anthracene	2.16	2	108		
Dibenz[a,h]anthracene	2.01	2	101		
Dibenz[a,h]anthracene	1.76	2	88.0		
Dibenz[a,h]anthracene	2.03	2	102	Avg recovery	101
Dibenz[a,h]anthracene	1.79	2	89.5	Std Dev	11.8
Dibenz[a,h]anthracene	0.45	0.5	90.0		
Dibenz[a,h]anthracene	0.47	0.5	94.0		
Dibenz[a,h]anthracene	0.44	0.5	88.0		
Dibenz[a,h]anthracene	0.47	0.5	94.0		
Dibenz[a,h]anthracene	0.44	0.5	88.0	Avg recovery	90.3
Dibenz[a,h]anthracene	0.44	0.5	88.0	Std Dev	2.94

Table 1-12. Recovery results for Fluoranthene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Fluoranthene	19.2	20	96		
Fluoranthene	21.1	20	105		
Fluoranthene	20.6	20	103		
Fluoranthene	20.7	20	103		
Fluoranthene	20.2	20	101	Avg recovery	102
Fluoranthene	20.6	20	103	Std Dev	3.24
Fluoranthene	4.51	5	90.2		
Fluoranthene	5.30	5	106		
Fluoranthene	5.63	5	113		
Fluoranthene	5.40	5	108		
Fluoranthene	5.74	5	115	Avg recovery	104
Fluoranthene	4.73	5	94.6	Std Dev	9.89
Fluoranthene	2.34	2	117		
Fluoranthene	1.88	2	94.0		
Fluoranthene	1.89	2	94.5		
Fluoranthene	1.70	2	85.0		
Fluoranthene	1.87	2	93.5	Avg recovery	94.3
Fluoranthene	1.63	2	81.5	Std Dev	12.4
Fluoranthene	0.40	0.5	80.0		
Fluoranthene	0.42	0.5	84.0		
Fluoranthene	0.40	0.5	80.0		
Fluoranthene	0.42	0.5	84.0		
Fluoranthene	0.40	0.5	80.0	Avg recovery	84.0
Fluoranthene	0.48	0.5	96.0	Std Dev	6.20

Table 1-13. Recovery results for Fluorene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Fluorene	19.6	20	97.9		
Fluorene	20.9	20	104		
Fluorene	20.6	20	103		
Fluorene	21.0	20	105		
Fluorene	19.9	20	99.5	Avg recovery	102
Fluorene	20.6	20	103	Std Dev	2.87
Fluorene	4.67	5	93.4		
Fluorene	5.28	5	106		
Fluorene	5.55	5	111		
Fluorene	5.51	5	110		
Fluorene	5.27	5	105	Avg recovery	105
Fluorene	5.26	5	105	Std Dev	6.29
Fluorene	2.47	2	123.5		
Fluorene	2.16	2	108		
Fluorene	2.09	2	104.5		
Fluorene	1.99	2	99.5		
Fluorene	2.14	2	107	Avg recovery	106
Fluorene	1.84	2	92.0	Std Dev	10.5
Fluorene	0.47	0.5	94.0		
Fluorene	0.49	0.5	98.0		
Fluorene	0.49	0.5	98.0		
Fluorene	0.49	0.5	98.0		
Fluorene	0.48	0.5	96.0	Avg recovery	97.0
Fluorene	0.49	0.5	98.0	Std Dev	1.67

Table 1-14. Recovery results for Indeno[1,2,3-cd]pyrene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Indeno[1,2,3-cd]pyrene	19.7	20	98.4		
Indeno[1,2,3-cd]pyrene	20.7	20	103		
Indeno[1,2,3-cd]pyrene	20.8	20	104		
Indeno[1,2,3-cd]pyrene	21.2	20	106		
Indeno[1,2,3-cd]pyrene	20.2	20	101	Avg recovery	102
Indeno[1,2,3-cd]pyrene	20.4	20	102	Std Dev	2.69
Indeno[1,2,3-cd]pyrene	4.39	5	87.8		
Indeno[1,2,3-cd]pyrene	4.91	5	98.2		
Indeno[1,2,3-cd]pyrene	5.27	5	105		
Indeno[1,2,3-cd]pyrene	4.93	5	98.6		
Indeno[1,2,3-cd]pyrene	4.9	5	98.0	Avg recovery	97.3
Indeno[1,2,3-cd]pyrene	4.8	5	96.0	Std Dev	5.67
Indeno[1,2,3-cd]pyrene	2.2	2	110		
Indeno[1,2,3-cd]pyrene	1.98	2	99.0		
Indeno[1,2,3-cd]pyrene	1.82	2	91.0		
Indeno[1,2,3-cd]pyrene	1.49	2	74.5		
Indeno[1,2,3-cd]pyrene	1.63	2	81.5	Avg recovery	88.3
Indeno[1,2,3-cd]pyrene	1.48	2	74.0	Std Dev	14.4
Indeno[1,2,3-cd]pyrene	0.39	0.5	78.0		
Indeno[1,2,3-cd]pyrene	0.39	0.5	78.0		
Indeno[1,2,3-cd]pyrene	0.38	0.5	76.0		
Indeno[1,2,3-cd]pyrene	0.40	0.5	80.0		
Indeno[1,2,3-cd]pyrene	0.38	0.5	76.0	Avg recovery	78.3
Indeno[1,2,3-cd]pyrene	0.41	0.5	82.0	Std Dev	2.34

Table 1-15. Recovery results for Naphthalene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Naphthalene	18.6	20	93.0		
Naphthalene	20.1	20	101		
Naphthalene	20.2	20	101		
Naphthalene	20.5	20	103		
Naphthalene	19.8	20	99.2	Avg recovery	99.3
Naphthalene	20.0	20	99.9	Std Dev	3.33
Naphthalene	4.48	5	89.6		
Naphthalene	5.08	5	102		
Naphthalene	5.27	5	105		
Naphthalene	5.35	5	107		
Naphthalene	5.16	5	103	Avg recovery	99.9
Naphthalene	4.63	5	92.6	Std Dev	7.12
Naphthalene	2.28	2	114		
Naphthalene	1.99	2	99.5		
Naphthalene	1.89	2	94.5		
Naphthalene	1.70	2	85.0		
Naphthalene	1.95	2	97.5	Avg recovery	95.4
Naphthalene	1.69	2	84.5	Std Dev	10.9
Naphthalene	0.41	0.5	82.0		
Naphthalene	0.46	0.5	92.0		
Naphthalene	0.47	0.5	94.0		
Naphthalene	0.46	0.5	92.0		
Naphthalene	0.45	0.5	90.0	Avg recovery	89.7
Naphthalene	0.44	0.5	88.0	Std Dev	4.27

Table 1-16. Recovery results for Phenanthrene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Phenanthrene	18.5	20	92.3		
Phenanthrene	20.0	20	100		
Phenanthrene	19.9	20	99.7		
Phenanthrene	19.9	20	99.6		
Phenanthrene	19.5	20	97.5	Avg recovery	97.8
Phenanthrene	19.5	20	97.6	Std Dev	2.94
Phenanthrene	4.43	5	88.6		
Phenanthrene	4.99	5	99.8		
Phenanthrene	5.31	5	106		
Phenanthrene	5.21	5	104		
Phenanthrene	5.20	5	104	Avg recovery	99.3
Phenanthrene	4.65	5	93	Std Dev	7.04
Phenanthrene	2.25	2	113		
Phenanthrene	1.92	2	96.0		
Phenanthrene	1.86	2	93.0		
Phenanthrene	1.78	2	89.0		
Phenanthrene	1.99	2	99.5	Avg recovery	96.2
Phenanthrene	1.74	2	87.0	Std Dev	9.20
Phenanthrene	0.44	0.5	88.0		
Phenanthrene	0.48	0.5	96.0		
Phenanthrene	0.46	0.5	92.0		
Phenanthrene	0.48	0.5	96.0		
Phenanthrene	0.46	0.5	92.0	Avg recovery	93.0
Phenanthrene	0.47	0.5	94.0	Std Dev	3.03

Table 1-17. Recovery results for Pyrene

Analyte	Concentration (µg)	Spike (µg)	% Recovery		
Pyrene	18.1	20	90.4		
Pyrene	18.9	20	94.5		
Pyrene	19.3	20	96.6		
Pyrene	19.6	20	98.1		
Pyrene	19.0	20	95.2	Avg recovery	95.3
Pyrene	19.4	20	97.0	Std Dev	2.71
Pyrene	4.39	5	87.8		
Pyrene	4.95	5	99.0		
Pyrene	5.18	5	104		
Pyrene	5.25	5	105		
Pyrene	5.05	5	101	Avg recovery	99.2
Pyrene	4.93	5	98.6	Std Dev	6.11
Pyrene	2.46	2	123		
Pyrene	2.19	2	110		
Pyrene	2.08	2	104		
Pyrene	2.10	2	105		
Pyrene	2.20	2	110	Avg recovery	108
Pyrene	1.96	2	98.0	Std Dev	8.44
Pyrene	0.51	0.5	102		
Pyrene	0.53	0.5	106		
Pyrene	0.53	0.5	106		
Pyrene	0.53	0.5	106		
Pyrene	0.53	0.5	106	Avg recovery	104
Pyrene	0.50	0.5	100	Std Dev	2.66

Table 1-18. Humidity recovery results for 10 µg spike on tube

Analyte	Amount Spiked (µg)	Average Recovery (%)	Standard Deviation
Naphthalene	10	**74.3**	6.34
Acenaphtylene	10	**72.4**	6.94
Acenaphthene	10	**73.1**	6.74
Fluorene	10	**75.0**	7.56
Phenanthrene	10	75.4	7.26
Anthracene	10	**73.5**	6.88
Fluoranthene	10	75.5	8.27
Pyrene	10	76.0	6.99
Benz[a]anthracene	10	**72.6**	6.89
Chrysene	10	78.5	6.84
Benzo[b]fluoranthene	10	**70.4**	6.63
Benzo[k]fluoranthene	10	77.9	7.96
Benzo[a]pyrene	10	**70.5**	6.91
Indeno[1,2,3-c,d]pyrene	10	**67.8**	5.43
Dibenz[a,h]anthracene	10	**71.1**	7.04
Benzo[ghi]perylene	10	**72.6**	5.75

Table 1-19. Humidity recovery results for 48 µg spike on tube

Analyte	Amount Spiked (µg)	Average Recovery (%)	Standard Deviation
Naphthalene	48	91.2	3.73
Acenaphtylene	48	91.7	4.46
Acenaphthene	48	94.5	4.70
Fluorene	48	94.2	4.70
Phenanthrene	48	95.4	5.73
Anthracene	48	98.1	6.04
Fluoranthene	48	95.0	5.88
Pyrene	48	95.0	6.42
Benz[a]anthracene	48	95.9	5.12
Chrysene	48	95.8	6.44
Benzo[b]fluoranthene	48	100	5.88
Benzo[k]fluoranthene	48	96.8	6.70
Benzo[a]pyrene	48	90.0	6.28
Indeno[1,2,3-c,d]pyrene	48	96.7	6.74
Dibenz[a,h]anthracene	48	92.6	5.90
Benzo[ghi]perylene	48	104	5.45

Table 1-20. Humidity recovery results for 96 µg spike on tube

Analyte	Amount Spiked (µg)	Average Recovery (%)	Standard Deviation
Naphthalene	96	78.0	2.05
Acenaphthylene	96	83.4	1.77
Acenaphthene	96	81.5	1.96
Fluorene	96	82.7	1.87
Phenanthrene	96	82.5	1.75
Anthracene	96	84.0	1.56
Fluoranthene	96	86.0	1.99
Pyrene	96	82.9	1.90
Benz[a]anthracene	96	83.0	1.41
Chrysene	96	81.7	1.91
Benzo[b]fluoranthene	96	85.1	2.79
Benzo[k]fluoranthene	96	85.1	2.62
Benzo[a]pyrene	96	85.6	1.68
Indeno[1,2,3-c,d]pyrene	96	78.9	3.03
Dibenz[a,h]anthracene	96	86.1	3.06
Benzo[ghi]perylene	96	80.1	4.36

Table 1-21. Humidity recovery results for 192 µg spike on tube

Analyte	Amount Spiked (µg)	Average Recovery (%)	Standard Deviation
Naphthalene	192	79.8	2.67
Acenaphthylene	192	84.0	3.50
Acenaphthene	192	83.9	2.27
Fluorene	192	84.7	1.70
Phenanthrene	192	80.9	2.11
Anthracene	192	83.1	3.55
Fluoranthene	192	85.3	3.54
Pyrene	192	83.3	2.91
Benz[a]anthracene	192	86.0	2.72
Chrysene	192	81.7	2.22
Benzo[b]fluoranthene	192	86.6	2.18
Benzo[k]fluoranthene	192	82.7	3.00
Benzo[a]pyrene	192	87.8	2.53
Indeno[1,2,3-c,d]pyrene	192	81.2	2.29
Dibenz[a,h]anthracene	192	87.0	2.65
Benzo[ghi]perylene	192	81.3	2.06